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Plastic Films in Food Packaging

Materials, Technology, and Applications

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PLASTIC FILMS IN FOOD PACKAGING

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Preface

Almost everyone deals with foods packaged in plastic containers on a daily basis. Plastic bags and packages have proliferated around the world, including remote locations such as Himalayan peaks. There are many reasons for the inception of plastic food packaging. There are also many functions which these packages must fulfill depending on the type of food being protected.

Once upon a time, people were sustained by locally grown, seasonal food and what could be safely transported within no longer than the maximum time before spoilage. The increase in the population of the earth has long outgrown the capacity of local products to meet the needs of nearby populations. Large cities have virtually no local growth areas.

The ease of travel, efficient transportation, and information systems have exposed people from one corner of the earth to foods from vast distances away. Marketing by food suppliers and sellers has given rise to a demand for food variety. Access to an astonishing array of foods from the four corners of the world is no longer considered a luxury.

There are several requirements which food packaging must meet. The foremost function of a package is protection of food products. Packages protect food from the loss of nutrients, functional properties, color, aroma, taste, and preserve the general appearance expected by consumers. A good package should create an acceptable barrier between the food and external environment; particularly water vapor, oxygen, and microorganisms. The shelf life, the length of time that product remains in acceptable conditions for use, strongly depends on the barrier ability of a package.

The second function of the package is to transport the product in a convenient manner. Finally, a good package should provide clear information about the food to consumers and attract them to buy it. Food packaging disregarding of the material of packaging is intended to protect the food from contamination and preserve the quality of the food between manufacturing and retail sales and consumption. To be a candidate for use in food packaging applications, a plastic must possess a few attributes. They include mechanical strength to allow the package food to withstand the rigors of handling, transportation, storage, refrigeration, and consumer interactions, abrasion, and irradiation. The plastic must also have the appropriate thermal stability for thermal processing such as retort and sterilization processes. These characteristics and proper package design usually prevent concealed tampering.

The size of food markets is massive globally. Packaged foods are not only common in the developed economies but have become commonplace in the developing world. Packaged foods are increasingly available in the third-world countries of Africa, Asia, and South America. For example, the size of grocery business is over $500 billion annually in the United States, most of which is offered in packaged form.

This book brings together the key applications, technologies, machinery, and waste management practices for packaging foodstuffs using plastic films. The selections address questions related to the film grades, types of packages for different types of foods, packaging technologies, machinery, and waste management. Additionally, the book provides a review of the new technologies for packaging foodstuffs. A reader with an interest in food packaging would save substantially because the contents of this book gather the salient aspects of several recent books from which materials have been drawn.

This book contains three new chapters. Chapter 1 is an introduction to the use of plastics in food packaging. Chapter 2 covers the development of barrier films for food packaging. Chapter 16 presents a survey of numerous regulations which govern food packaging in the United States of America and the European Union. The combination of new chapters and the selected chapters from other books render this title unique among all the titles available on the subject of food packaging in the market.

I would like to offer my deepest thanks to Pamela L. Langhorn, who is a partner at the firm of Keller and Heckman in Washington, DC, for reviewing Chapter 16. Pamela is one of the foremost experts in the food packaging laws with a global purview. She made numerous corrections, suggestions, and upgrades to this chapter for which I am most grateful.

I would like to thank all the authors who have contributed to this book: C. Maier, T. Calafut, T.I. Butler, B.A. Morris, J. Breil, J.H. Han, M.L. Rooney, J. Singh, P. Singh, H.A. Hughes, E. Rudnik, and I.S. Arvanitoyannis.

Special thanks go to my friends Dr. Larry McKeen for authoring Chapter 1 and Dr. Maryam Fereydoon, the coauthor of Chapter 5.

I am indebted to Matthew Deans, the Senior Publisher of William Andrew, for his leadership and invaluable support. Thanks to Matthew's wisdom and guidance Plastics Design Library continues to grow in both the number of titles and the breadth of subject matters it offers.

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Sina Ebnesajjad
September 2012

1 Introduction to Use of Plastics in Food Packaging

L.W. McKeen

Packaging film is very thin plastic and the basic component of plastic and elastomer materials is polymer. This chapter is narrowly focused on the commercial plastic films used in packaging. Generally, films are used as barriers; they keep dirt, germs, liquids or gases on one side of the film. Nearly any plastic can be made in film form, but this chapter will discuss only those that are used for packaging on a commercial basis. By definition, flexible packaging includes bags, envelopes, pouches, sachets, and wraps made of easily yielding materials such as film, foil, or paper sheeting which, when filled and sealed, acquires pliable shape. This chapter also will not cover multilayer films which are commercially very important but covered in another chapter.

Polymeric packaging materials are used to surround a package completely, securing its contents from gases and vapors, moisture, and biological effects of the outside environment, while providing a pleasing and often decorative appearance. Water vapor and atmospheric gases if allowed to permeate in or out of a package can alter the taste, color, and nutritional content of the packaged good. The effects of gas and vapors on food are complex and comprise a major branch of food science. The following is a brief overview. Additional details in terms of typical film properties and permeation properties are available in the literature (McKeen 2011, 2012).

1.1 Background

The global flexible packaging market is very large, as is shown in Table 1.1 for 2009. The table shows that polyethylenes and polypropylenes make up the bulk of the market. The six plastic types listed in the table account for over three quarters of the total packaging films produced. The growth rate is expected to be about 4% annually until 2016. Other key market drivers and trends identified for flexible packaging include:

- A trend toward conversion to biodegradable, sustainable, and recyclable flexible packaging materials to improve the environmental footprint of packaging.
- Flexible packaging films being made thinner to reduce costs and minimize waste after use, which also drives the need for higher performing materials.
- Flexible packaging products will replace bottles and containers for a range of food and beverage products.

The following sections will look at the chemistry of various plastics used in flexible packaging films. The discussion will include chemical structures and where flexible films made of those materials are used.

1.2 Polyolefins

Polymers made from hydrocarbon monomers that contain a carbon−carbon double bond through which the polymer is made by addition polymerization are called polyolefins. An alkene, also called an olefin, is a chemical compound made of only carbon and hydrogen atoms containing at least one carbon-to-carbon double bond. The simplest alkenes, with only one double bond and no other functional groups, form a homologous series of hydrocarbons with the general formula C_nH_{2n}. The two simplest alkenes of this series are ethylene and propylene. When these are polymerized, they form polyethylene and polypropylene, which are the two of the plastics that account for the bulk of the plastic film packaging market. There are other specialty polyolefins that are made into very low-volume specialty films.

Polyolefins are made by addition polymerization (sometimes called chain-growth polymerization). A chain reaction adds new monomer units to the growing polymer molecule, one at a time through double bonds in the monomers. This is shown in Figure 1.1.

Ebnesajjad: Plastic Films in Food Packaging. DOI: http://dx.doi.org/10.1016/B978-1-4557-3112-1.00001-6

Table 1.1 Global Flexible Packaging—2009

Material	Millions of Tons (MMT)	%
Polyethylenes (PE)	4.8	32.6
Polypropylenes (PP)	4.7	32
Biaxial-orientated polyethylene terephthalate (BoPET)	0.4	3
Polyvinyl chloride (PVC)	0.3	2.1
Polyamide, nylon (PA)	0.6	3.9
Ethylene–vinyl alcohol (EVOH)	0.4	2.6
Total plastics	11.3	76.2
Paper, Aluminum foil, Cellulosics	3.5	23.8

Source: PIRA International.

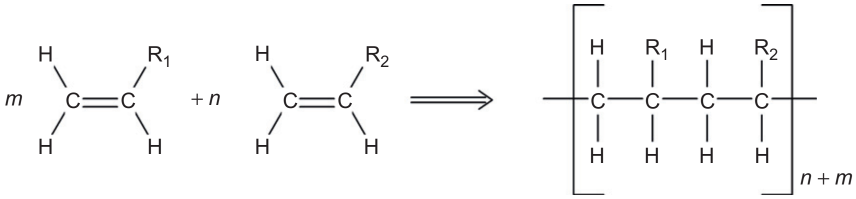


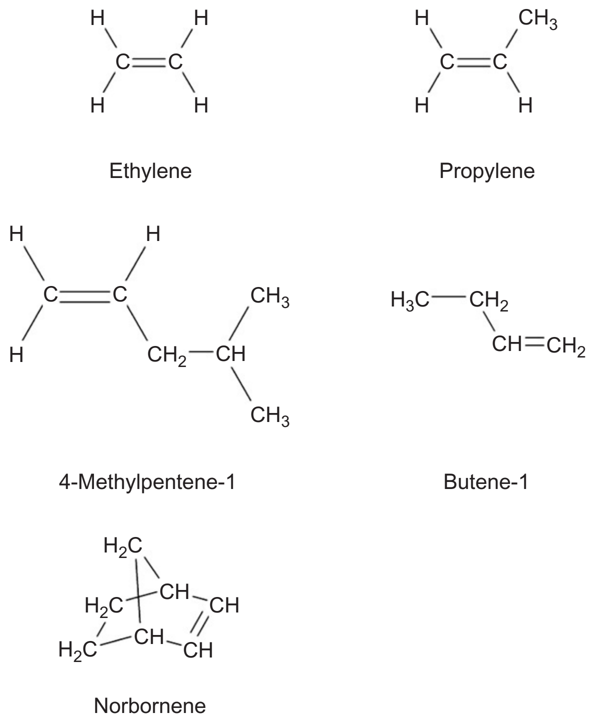
Figure 1.1 Addition polymerization.

The structures of some of the monomers used to make polyethylene, polypropylene, and the other polyolefins discussed here are shown in Figure 1.2. Structures of the polymers may be found in the appropriate sections contain the data for those materials.

1.2.1 Polyethylene

The structure of polyethylene is given in Figure 1.1 where both R_1 and R_2 are replaced by H. There are several types of polyethylene, which are classified mostly by their density. There are several ASTM standards that are used to describe polyethylene including ASTM D2103—10 Standard Specification for Polyethylene Film and Sheeting. According to ASTM D1248—12 Standard Specification for Polyethylene Plastics Extrusion Materials for Wire and Cable, the basic types or classifications of polyethylene are as follows:

- Ultra low-density polyethylene (ULDPE), polymers with densities ranging from 0.890 to 0.905 g/cm^3, contains comonomer.



Ethylene

Propylene

4-Methylpentene-1

Butene-1

Norbornene

Figure 1.2 Chemical structures of the monomers used to make the polyolefins polyethylene, and polypropylene.

- Very low-density polyethylene (VLDPE), polymers with densities ranging from 0.905 to 0.915 g/cm^3, contains comonomer.
- Linear low-density polyethylene (LLDPE), polymers with densities ranging from 0.915 to 0.935 g/cm^3, contains comonomer.
- Low-density polyethylene (LDPE), polymers with densities ranging from about 0.915 to 0.935 g/cm^3 (further specification ASTM D4635—08a Standard Specification for Polyethylene Films Made from Low-Density Polyethylene for General Use and Packaging Applications).
- Medium-density polyethylene (MDPE), polymers with densities ranging from 0.926 to 0.940 g/cm^3, may or may not contain comonomer (further specification ASTM D3981—09a Standard Specification for Polyethylene Films Made from Medium-Density Polyethylene for General Use and Packaging Applications).
- High-density polyethylene (HDPE), polymers with densities ranging from 0.940 to 0.970 g/cm^3, may or may not contain comonomer.

Figure 1.3 shows the differences in the structures graphically. The differences in the branches in terms of number and length affect the density and melting points of some of the types.

Branching affects the crystallinity. A diagram of a representation of the crystal structure of polyethylene is shown in Figure 1.4. One can imagine how branching in the polymer chain can disrupt the crystalline regions. The crystalline regions are the highly ordered areas in the shaded rectangles of Figure 1.4. A high degree of branching would reduce the size of the crystalline regions, which leads to lower crystallinity.

Film applications and uses of polyethylene include:

- ULDPE—Heavy-duty sacks, turf bags, consumer bags, packaging for cheese, meat, coffee, and detergents, silage wrap, mulch films, and extruded membranes.
- LDPE—Food packaging (bread bags, baked goods, light-duty produce bags, etc.); light- to heavy-duty bags; textile packaging (shirts, sweaters, etc.).
- LLDPE—Agricultural films, saran wrap, and bubble wrap.
- MDPE—Specialty merchandise bags; mailing envelopes; heavy-duty shipping sacks; pallet shrink films; fresh-cut produce packaging.
- HDPE—Food packaging: dairy products and bottled water, cosmetics, medical products, and household chemicals.

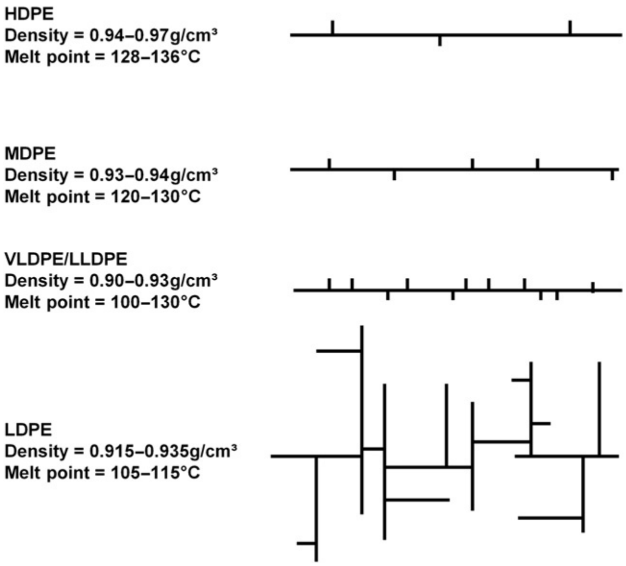


Figure 1.3 Graphical depictions of polyethylene types.

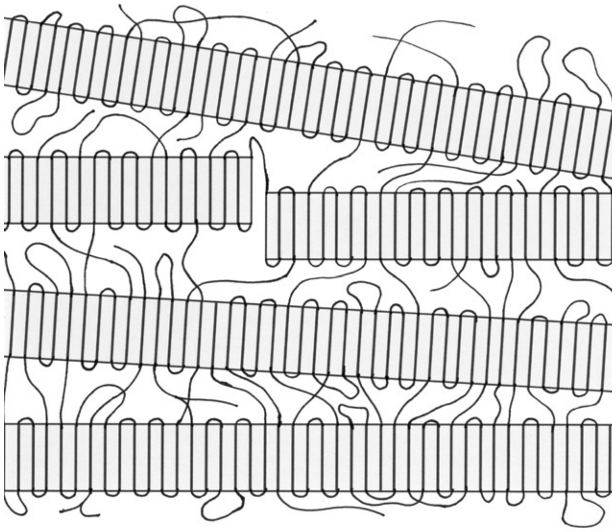


Figure 1.4 Graphical diagram of polyethylene crystal structure.

1.2.2 Polypropylene

The structure of polypropylene is given in Figure 1.1 where both R_1 and R_2 are replaced by CH_3. Polypropylene can be made in a number of ways. The way it is produced can affect its physical properties. It can also have very small amounts of comonomers, which will alter its structure and properties. The three main types of polypropylene generally available are:

- Homopolymers are made in a single reactor with propylene and a catalyst. It is the stiffest of the three propylene types and has the highest tensile strength at yield. In the natural state (no colorant added), it is translucent and has excellent see-through or contact clarity with liquids. In comparison to the other two types it has less impact resistance, especially below 0°C.
- Random copolymer (homophasic copolymer) is made in a single reactor with a small amount of ethylene ($< 5\%$) added, which disrupts the crystallinity of the polymer allowing this type to be the clearest. It is also the most flexible with the lowest tensile strength of the three. It has better room temperature impact than homopolymer but shares the same relatively poor impact resistance at low temperatures.
- Impact copolymers (heterophasic copolymer), also known as block copolymers, are made in a two reactor system, in which the homopolymer matrix is made in the first reactor and then transferred to the second reactor, where ethylene and propylene are polymerized to create ethylene propylene rubber in the form of microscopic nodules dispersed in the homopolymer matrix phase. These nodules impart impact resistance at both ambient and low temperatures to the compound. This type has intermediate stiffness and tensile strength and is quite cloudy. In general, the more ethylene monomer is added, the greater the impact resistance, with correspondingly lower stiffness and tensile strength.

ASTM Standards related to polypropylene films include:

- ASTM D2103—10 Standard Specification for Polyethylene Film and Sheeting.
- ASTM D2673—09 Standard Specification for Oriented Polypropylene Film.

Applications and uses of polypropylene include:

- Homopolymer: Thermoforming, slit film, and oriented fibers.
- Random copolymer: Food, household chemicals, beauty-aid products, clear containers, and hot-fill applications.
- Impact copolymers: film, sheet, and profiles.

1.2.3 Specialty Polyolefins

Two specialty polyolefins with packing applications are discussed in the next two sections.

Polybutene-1

Polybutene-1 (PB-1) is made from 1-butene, as shown in Figure 1.5. PB-1 resins are high-molecular-weight isotactic, semicrystalline thermoplastic polyolefins. Some products contain small amounts of comonomers, ethylene and/or propylene.

PB-1 has high flexibility and creep resistance over a wide temperature range. Applications and uses include two main fields:

- Peelable easy-to-open packaging where PB-1 is used as blend component predominantly in polyethylene to tailor peel strength and peel quality, mainly in alimentary consumer packaging and medical packaging.
- Lowering seal-initiation temperature of high-speed packaging polypropylene-based films. Blending PB-1 into polypropylene achieves heat sealing temperatures as low as 65°C, maintaining a broad sealing window and good optical film properties.

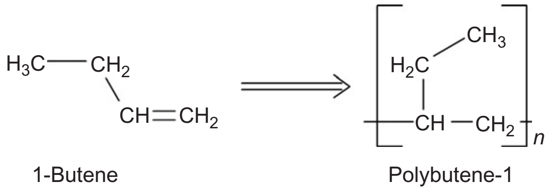


Figure 1.5 Structure of 1-butene monomer and PB-1 polymer.

4-Methylpentene-1-Based Polyolefin

4-Methylpentene-1-based polyolefin (PMP) is a lightweight, functional polymer that displays a unique combination of physical properties and characteristics due to its distinctive molecular structure, which includes a bulky side chain as shown in Figure 1.6. PMP possesses many characteristics inherent in traditional polyolefins such as excellent electrical insulating properties and strong hydrolysis resistance. Moreover, it features low dielectric, superb clarity, transparency, gas permeability, and heat and chemical resistance and release qualities.

Applications and uses include:

- Paper coatings and baking cartons,
- Release film and release paper,
- High-frequency films,
- Food packaging such as gas permeable packages for fruit and vegetables.

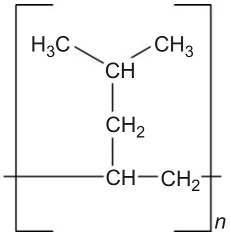


Figure 1.6 Structure of PMP.

Cyclic Olefin Copolymer

Cyclic olefin copolymer (COC) is an amorphous polyolefin made by reaction of ethylene and norbornene in varying ratios. Its structure is given in Figure 1.7. The norbornene structure in Figure 1.7 is designated "Y". The properties can be customized by changing the ratio of the monomers found in the polymer. COC is amorphous, so it is transparent. Other performance benefits include:

- Low density,
- Extremely low water absorption,
- Excellent water vapor barrier properties,
- High rigidity, strength, and hardness,
- Variable heat deflection temperature up to 170°C,
- Very good resistance to acids and alkalis.

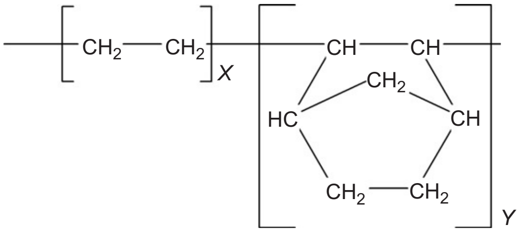


Figure 1.7 Chemical structure of COCs.

Applications and uses: COC is used as a core layer in push-through packaging, either in five-layer coextruded or three-layer laminated film structures. It is also used as flexible and rigid packaging for food and consumer items.

1.3 Polyester

Polyethylene terephthalate (PET) is the most common thermoplastic polyester packaging film and is often called just "polyester". PET exists both as an amorphous (transparent) and as a semicrystalline (opaque and white) thermoplastic material. Semicrystalline PET has good strength, ductility, stiffness, and hardness. Amorphous PET has better ductility but less stiffness and hardness. It absorbs very little water. Its structure is shown in Figure 1.8.

Applications and uses: Roasting bags, audio/video tapes, release liner, stamping foil, and label overlay.

1.3.1 Specialty Polyesters

While PET is by far the most common polyester packaging film, there are many other polyesters also offered. These specialty films are described in the following sections.

Polyethylene Napthalate

Polyethylene napthalate (PEN) is similar to PET but has better temperature resistance, strength, hydrolysis resistance, dimensional stability, and low oligomer extraction. It is particularly stable when

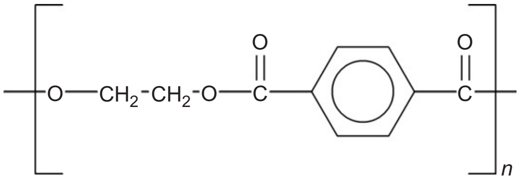


Figure 1.8 Chemical structure of PET.

exposed to sterilization processes. The structure of this polyester is shown in Figure 1.9.

Significant commercial markets have been developed for its application in textile and industrial fibers, films, and foamed articles, containers for carbonated beverages, water and other liquids, and thermoformed applications.

Liquid Crystalline Polymers

Liquid crystalline films are high-performance specialty films. Though their structures vary, they are highly aromatic as shown in Figure 1.10.

Liquid crystalline polymer (LCP) films and sheets are well suited for many medical, chemical, electronic, beverage, and food packaging applications. They are more impermeable to water vapor, oxygen, carbon dioxide, and other gases than typical barrier resins. When LCP film is biaxially oriented, it forms a high-strength material, with relatively uniform properties and low fibrillation. Also, its high-temperature capability enables it to meet the needs of thermally demanding applications, such as films for printed wiring boards.

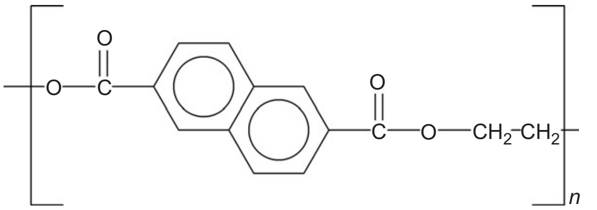


Figure 1.9 Structure of PEN.

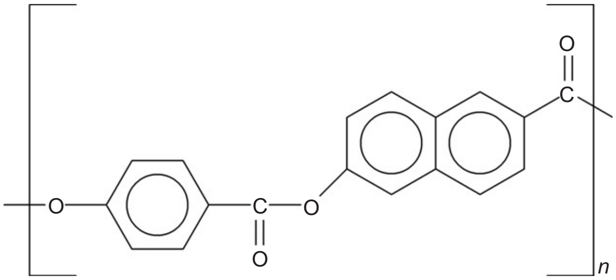


Figure 1.10 Chemical structure of Ticona Vectra® A950 LCP.

Polybutylene Terephthalate

Polybutylene terephthalate (PBT) is semicrystalline, white or off-white polyester similar in both composition and properties to PET. It has somewhat lower strength and stiffness than PET, is a little softer but has higher impact strength and similar chemical resistance. As it crystallizes more rapidly than PET, it tends to be preferred for industrial scale molding. Its structure is shown in Figure 1.11.

PBT is a dimensionally stable, sterilizable film with good optical quality, even after sterilization.

Polycarbonate

Polycarbonate (PC) is another polyester film. Its structure is shown in Figure 1.12.

PC performance properties include:

- Very impact resistant and is virtually unbreakable and remains tough at low temperatures,
- "Clear as glass" clarity,
- High heat resistance,
- Dimensional stability,
- Resistant to ultraviolet light, allowing exterior use,
- Flame retardant.

This film offers high heat resistance and superior dimensional stability and finds uses in packaging of medical devices.

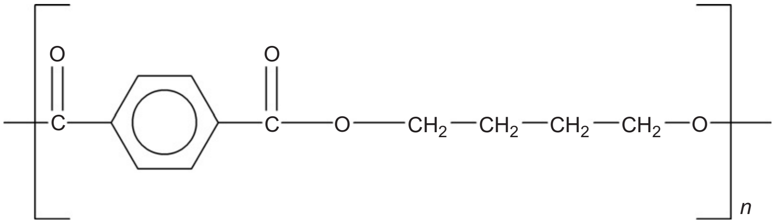


Figure 1.11 Chemical structure of PBT polyester.

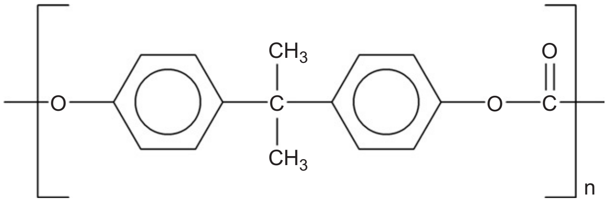


Figure 1.12 Chemical structure of PC polyester.

Polycyclohexylene-Dimethylene Terephthalate

Polycyclohexylene-dimethylene terephthalate (PCT) is high-temperature polyester that possesses the chemical resistance, processability, and dimensional stability of PET and PBT. However, the aliphatic cyclic ring shown in Figure 1.13 imparts added heat resistance. This puts it between the common polyesters and the LCP polyesters described in the previous sections.

Applications and uses include bags, rigid medical and blister packaging.

1.4 Polystyrene

Polystyrene (PS) is the simplest plastic based on styrene. Its structure is shown in Figure 1.14.

There are three general forms of PS film:

- General purpose PS,
- Oriented PS,
- High impact (HIPS).

One of the most important plastics is high impact PS or HIPS. This is a PS matrix that is imbedded with an impact modifier, which is basically a rubber-like polymer such as polybutadiene. This is shown in Figure 1.15.

Applications and uses: General Purpose—Yogurt, cream, butter, meat trays, egg cartons, fruit and vegetable trays, as well as cakes, croissants, and cookies. Medical and packaging/disposables, bakery packaging, and large and small appliances, medical and packaging/disposables, particularly where clarity is required, window envelope patches and labels. Oriented—Oriented-PS films can be printed and laminated to foams for food-service plates and trays offering improved esthetics. The films can also be used as a laminate to PS sheet for a high gloss shine for bakery and convenience food items.

1.5 Polyvinyl Chloride

Polyvinyl chloride (PVC) is a flexible or rigid material that is chemically nonreactive. Rigid PVC is easily machined, heat formed, welded, and even solvent cemented. PVC can also be machined using standard metal working tools and finished to close tolerances and finishes without great difficulty. PVC resins are normally mixed with other additives such as impact modifiers and stabilizers, providing hundreds of PVC-based materials with a variety of engineering properties.

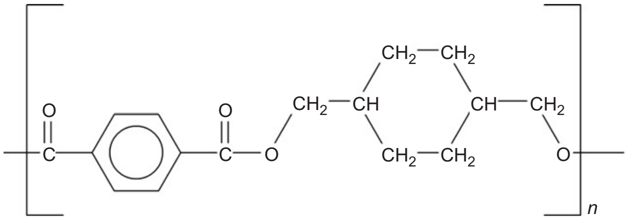


Figure 1.13 Chemical structure of PCT polyester.

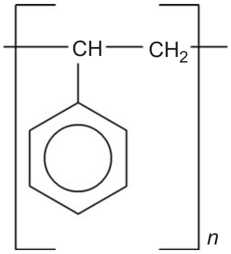


Figure 1.14 Chemical structure of PS.

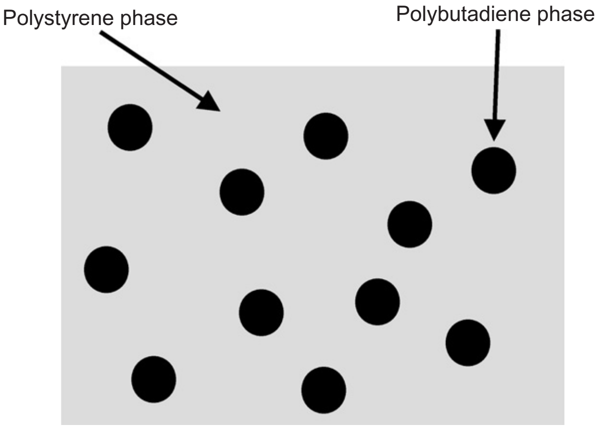


Figure 1.15 The structure of HIPS.

There are three broad classifications for rigid PVC compounds: Type I, Type II, and CPVC. Type II differs from Type I due to greater impact values but lower chemical resistance. CPVC has greater high temperature resistance. These materials are considered “unplasticized” because they are less flexible than the plasticized formulations.

Applications and uses: Packaging is a major market for PVC. Rigid grades are blown into bottles and made into sheets for thermoforming boxes and blister packs. Flexible PVC compounds are used in food packaging applications because of their strength, transparency, processability, and low raw material cost.

1.6 Polyvinylidene Chloride

Polyvinylidene chloride (PVDC) resin, the structure of which is shown in Figure 1.16, is usually a copolymer of vinylidene chloride with vinyl chloride or other monomers. PVDC is commonly known as Saran™.

Applications and uses: Monolayer films for food wrap and medical packaging, coextruded films and sheet structures as a barrier layer in medical packaging, and packaging of foods such as fresh red meats, cheese, and sausages. Coatings are often applied to prevent specific gas transmission.

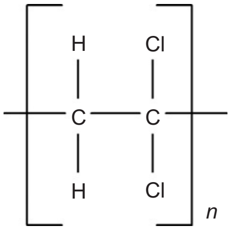


Figure 1.16 Structure of PVDC homopolymer.

1.7 Polyamide

High-molecular weight polyamides are commonly known as nylon. Polyamides are crystalline polymers typically produced by the condensation of a diacid and a diamine. There are several types, and each type is often described by a number, such as nylon 66 or polyamide 66 (PA66). The numeric suffixes refer to the number of carbon atoms present in the molecular structures of the amine and acid respectively (or a single suffix if the amine and acid groups are part of the same molecule).

The polyamide plastic materials discussed in this book and the monomers used to make them are given in Table 1.2.

The general reaction is shown in Figure 1.17.

1.7.1 Nylon 6

Nylon 6 begins as pure caprolactam which is a ring-structured molecule. This is unique in that the ring is opened and the molecule polymerizes with itself. Since caprolactam has six carbon atoms, the polyamide that is produced is called nylon 6, which is nearly the same as Nylon 66 described in Section 1.7.3. The structure of Nylon 6 is shown in Figure 1.18 with the repeating unit in the brackets.

Table 1.2 Monomers Used to Make Specific Polyamides/Nylons

Polyamide/Nylon Type	Monomers Used to Make
Nylon 6 (PA6)	Caprolactam
Nylon 11 (PA11)	Aminoundecanoic acid
Nylon 12 (PA12)	Aminolauric acid
Nylon 66 (PA66)	1,6-Hexamethylene diamine and adipic acid
Nylon 610 (PA610)	1,6-Hexamethylene diamine and sebacic acid
Nylon 612 (PA612)	1,6-Hexamethylene diamine and 1,12-dodecanedioic acid
Nylon 666 (PA6/66)	Copolymer based on nylon 6 and nylon 66
Nylon 46 (PA46)	1,4-Diaminobutane and adipic acid
Polyamide amorphous (6-3-T)	Trimethyl hexamethylene diamine and terephthalic acid
Polyphthalamide (PPA)	Any diamine and isophthalic acid and/or terephthalic acid

Some of the Nylon 6 characteristics are as follows:

- Outstanding balance of mechanical properties.
- Outstanding toughness in equilibrium moisture content.
- Outstanding chemical resistance and oil resistance.
- Outstanding long-term heat resistance (at a long-term continuous maximum temperature ranging between 80°C and 150°C).
- Offers low gasoline permeability and outstanding gas barrier properties.
- Highest rate of water absorption and highest equilibrium water content (8% or more).
- Excellent surface finish even when reinforced.
- Poor chemical resistance to strong acids and bases.

Films can be made by extrusion, extrusion coating, and blown film; polyamide films can be easily thermoformed and biaxially stretched.

Applications and uses: Multilayer packaging—food and medical, cover/base, pouch, and solid films.

1.7.2 Nylon 12

Nylon 12 has only one monomer, aminolauric acid. It has the necessary amine group on one end and the acid group on the other. It polymerizes with itself to produce the polyamide containing twelve carbons between the two nitrogen atoms of the two amide groups. Its structure is shown in Figure 1.19.

The properties of semicrystalline polyamides are determined by the concentration of amide groups in the macromolecules. Polyamide 12 has the lowest amide group concentration of all commercially available polyamides thereby substantially promoting its characteristics:

- Lowest moisture absorption (~2%),
- Good to excellent resistance against greases, oils, fuels, hydraulic fluids, various solvents, salt solutions, and other chemicals,
- Low coefficient of sliding friction,
- Lowest strength and heat resistance of any polyamide unmodified.

Applications and uses: Grilamid L 25 is used for sausage skins for precooked sausages and packaging films for deep-frozen goods.

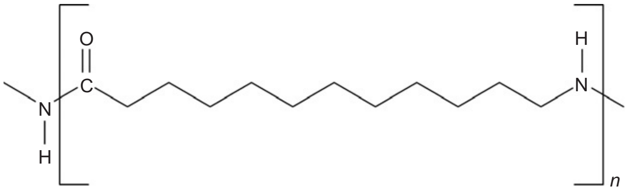


Figure 1.19 Chemical structure of nylon 12.

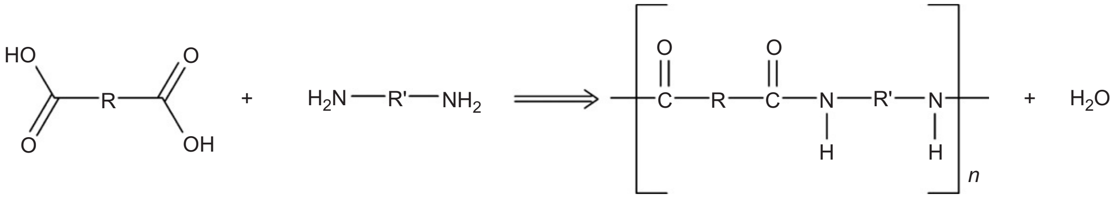


Figure 1.17 Generalized polyamide reaction.

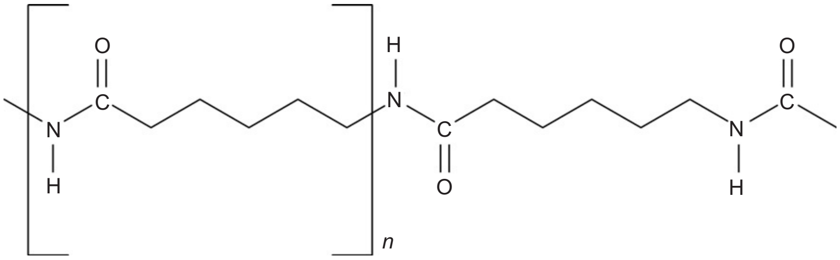


Figure 1.18 Chemical structure of nylon 6.

1.7.3 Nylon 66

The structure of Nylon 66 is shown in Figure 1.20.

Some of the Nylon 66 characteristics are as follows:

- Outstanding balance of mechanical properties.
- Outstanding toughness in equilibrium moisture content.
- Outstanding chemical resistance and oil resistance.
- Outstanding long-term heat resistance (at a long-term continuous maximum temperature ranging between 80°C and 150°C).
- Offers low gasoline permeability and outstanding gas barrier properties.
- High water absorption.
- Poor chemical resistance to strong acids and bases.

Applications and uses: Packaging meat and cheese, industrial end uses, pouch and primal bag, stiff packages, snacks, condiments, shredded cheese, and coffee. Also used in wrapping fine art, potable water, and electrical applications.

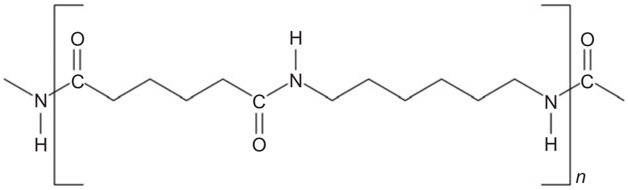


Figure 1.20 Chemical structure of nylon 66.

1.7.4 Nylon 66/610

Nylon 66/610 is a copolymer made from hexamethylenediamine, adipic acid, and sebacic acid. Its structure is represented in Figure 1.21.

Applications and uses: Flexible packaging for foodstuff and medical packaging such as IV bags.

1.7.5 Nylon 6/12

The structure of Nylon 6/12 is given in Figure 1.22.

Some of the Nylon 6/12 characteristics are as follows:

- High impact strength,
- Very good resistance to greases, oils, fuels, hydraulic fluids, water, alkalis, and saline,
- Low coefficients of sliding friction and high abrasion resistance, even when running dry,
- Heat deflection temperature (melting point nearly 40°C higher than Nylon 12),
- Tensile and flexural strength,
- Outstanding recovery at high wet strength.

Applications: Multilayer food packaging and boil in bag.

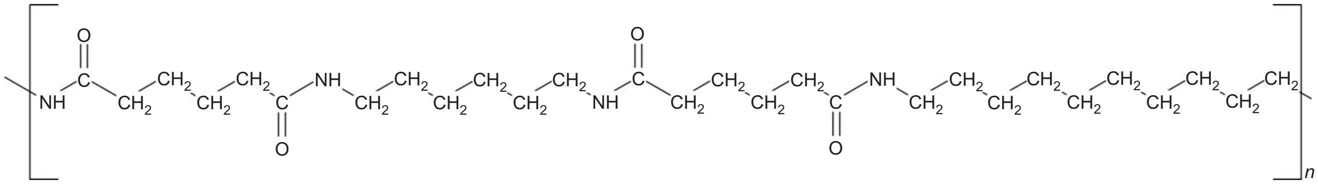


Figure 1.21 Structure of polyamide 66/610.

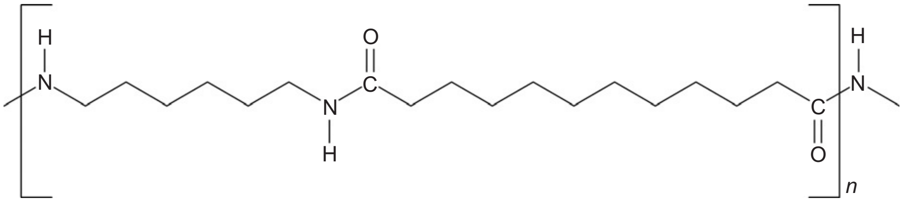


Figure 1.22 Chemical structure of nylon 6/12.

1.7.6 Polyamide 6/69 (Nylon 6/69)

This resin is specifically suited for applications requiring superior toughness and abrasion resistance. *Applications and uses*: Flexible packaging for foodstuffs, especially for packaging of ripening cheeses, shrinkable packaging of meat, cheese, sausage, and fish.

1.7.7 Amorphous Polyamides

Amorphous polyamides are designed to give no crystallinity to the polymer structure. An example is shown in Figure 1.23.

The tertiary butyl group attached to the amine molecule is bulky and disrupts this molecule's ability to crystallize. This particular amorphous polyamide is sometimes designated as Nylon 6-3-T. Amorphous polymers can have properties that differ significantly from crystalline types, one of which is optical transparency.

Some of the amorphous polyamide characteristics are as follows:

- Crystal-clear, high optical transparency,
- High mechanical stability,
- High heat deflection temperature,
- High impact strength,
- Good chemical resistance compared to other plastics,
- Good electrical properties,
- Low mold shrinkage.

Another amorphous polyamide is called Nylon 6I/6T and is a mixture of the two polyamide segments shown in Figure 1.24.

Blending even low percentages (20%) of Selar® PA (PA 6I/6T) with nylon 6, nylon 66, and polyamide copolymers will result in a product that behaves like an amorphous polymer. These blends retain all of the advantages of the Selar® PA resin with some of the mechanical property advantages of semicrystalline polyamide.

Applications and Uses: Used as a monolayer or as a component of multilayer flexible films in meat and cheese packages as well as rigid packaging. Multilayer or monolayer types are used in transparent hollow vessels (bottles), packaging films, and deep-drawn plates.

1.8 Ethylene–Vinyl Alcohol Copolymer

Ethylene–vinyl alcohol (EVOH) is a copolymer of ethylene and vinyl alcohol. Its structure is shown in Figure 1.25. These materials are highly crystalline and are produced with various levels of ethylene content.

EVOH film has many desirable properties that are summarized as follows:

- Antistatic Properties: Since EVOH resin is a highly antistatic polymer, dust is prevented from building up on the package when used as a surface layer.
- Luster and Transparency: EVOH resins produce a high gloss and low haze, resulting in outstanding clarity characteristics. The use of EVOH resin as the outer surface of a package provides excellent sparkle for improved package appearance.
- Printability: With an –OH group in its molecular chain, the EVOH resin surface can be easily printed without special treatment.
- Resistance to Oil and Organic Solvents: EVOH resins resist oils and organic solvents, making

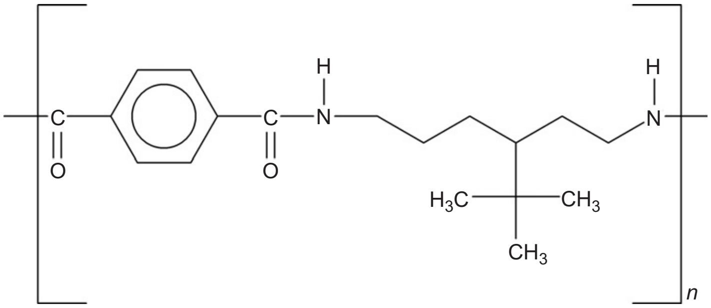


Figure 1.23 Chemical structure of amorphous polyamide, nylon 6-3-T.

them particularly suitable for packaging oily foods, edible oils, mineral oils, agricultural pesticides, and organic solvents.

- Weather Resistance: EVOH resins display excellent weatherability. Even when exposed to outdoor conditions, the polymer retains its color and does not become yellow or opaque. Mechanical property changes are minimal, demonstrating an overall high resistance to weather effects.
- Permeability: EVOH resins offer outstanding gas (oxygen, carbon dioxide, nitrogen, and helium) barrier properties, and maintain their barrier property over a wide range of humidity. The oxygen-barrier properties of EVOH vary according to the ethylene content in the polymer. Packages containing EVOH resins can effectively retain fragrances and preserve the aroma of the contents within the package. At the same time, undesirable odors are prevented from entering or leaving the package.

Film processing methods include monolayer film extrusion (blown or cast), coextruded film extrusion (blown or cast), coextrusion blow-molding, profile coextrusion, and coating.

Applications and uses: Rigid packaging for entrees, edible oils, juice, cosmetics, pharmaceuticals, heating pipe, automotive plastic fuel tanks, and packaging for condiments and toothpaste. Flexible packaging: Processed meats, bag-in-box, red meat, cereal, pesticides, and agrichemicals.

1.9 Renewable Resource and Biodegradable Polymers

This section covers those polymers that are produced from renewable resource raw materials such as corn, or that are biodegradable or compostable. This is a developing area in packaging materials and though there are a relatively limited number of polymers used commercially, they will certainly become more numerous and more common in the future.

Biodegradable plastics are made out of ingredients that can be metabolized by naturally occurring microorganisms in the environment. Some petroleum-based plastics will biodegrade eventually, but that process usually takes a very long time and contributes to global warming through the release of carbon dioxide.

Petroleum-based plastic is derived from oil, a limited resource. The plastic present in renewable raw materials biodegrades much faster and can be almost carbon neutral. Renewable plastic is derived from natural plant products such as corn, oats, wood, or other plants, which helps ensure the sustainability of the earth. Polylactic acid (PLA) is the most widely researched and used 100% biodegradable plastic packaging polymer currently, and is

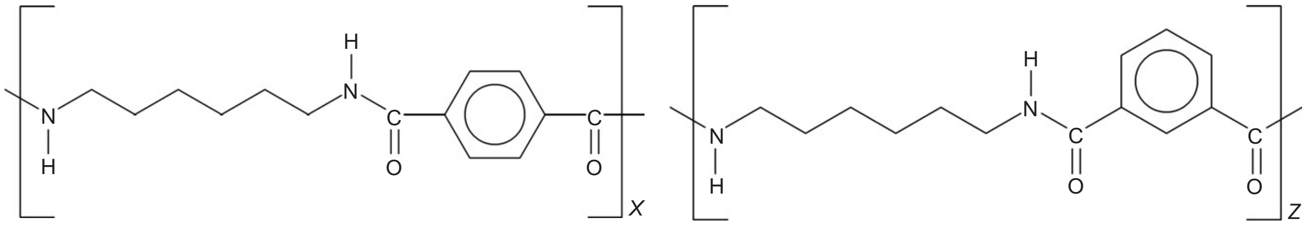


Figure 1.24 Structure of segments in polyamide 6I/6T.

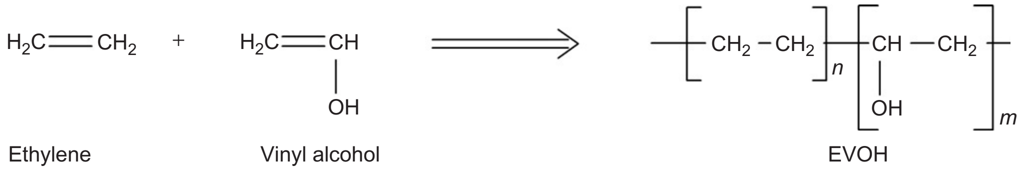


Figure 1.25 The structure of EVOH copolymer.

made entirely from corn-based cornstarch. Details on PLA are included in Section 1.9.3.

Cellophane™ is a polymeric cellulose film made from the cellulose obtained from wood, cotton, hemp, or other sources. There are several modifications made to cellulose called polysaccharides (cellulose esters) that are common including cellulose acetate, nitrocellulose, carboxymethyl cellulose (CMC), and ethyl cellulose. Details on cellophane and its derivatives are included in the sections which follow this one.

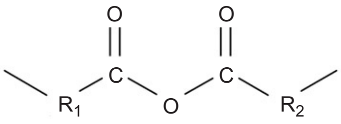
Polycaprolactone (PCL) is biodegradable polyester that is often mixed with starch. Details on PLA are included in Section 1.9.3.

Polyhydroxyalkanoates (PHAs) are naturally produced and include poly-3-hydroxybutyrate (PHB or PH3B), polyhydroxyvalerate (PHV), and polyhydroxyhexanoate (PHH); A PHA copolymer called poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is less stiff and tougher, and may be used as packaging material.

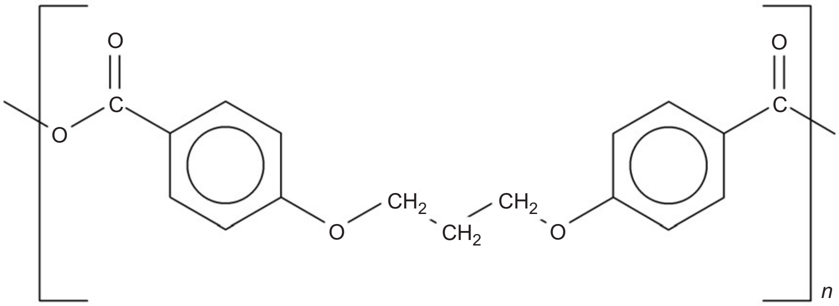
Several interesting green polymers are discussed in the next few paragraphs. These are ones for which no public permeation data have been identified.

Polyanhydrides are currently used mainly in the medical device and pharmaceutical industry (Jain et al., 2005). Figure 1.26 shows the generalized structure of an anhydride polymer and two polyanhydrides that are used to encapsulate certain drugs. Poly(bis-carboxyphenoxypropane) (pCCP) is relatively slow to degrade. Poly(sebacic anhydride) (pSA) degrades rapidly. Separately, neither of these materials can be used, but if a copolymer is made in which 20% of the structure is pCCP and 80% is pSA, the overall properties meet the needs of the drug. Polyanhydrides are now being offered for general uses.

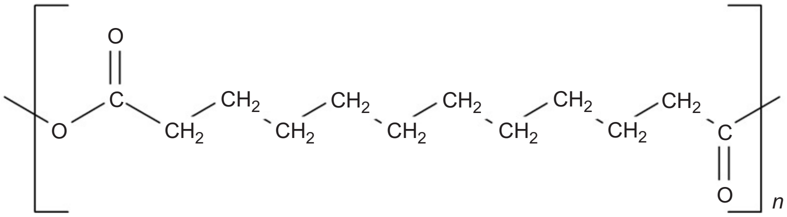
Polyglycolic acid (PGA) and its copolymers have found limited use as absorbable sutures and are being evaluated in the biomedical field, where its rapid degradation is useful. That rapid degradation has limited its use in other applications. There



General anhydride structure



pCCP



pSA

Figure 1.26 Polyanhydride chemical structures.

has been patent activity on PGA films (Kawakami et al., 1998). The structure of PGA is shown in Figure 1.27.

The following sections contain details of several of the more common biosourced/biodegradable polymers used in packaging applications.

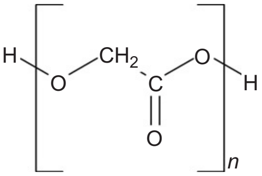


Figure 1.27 PGA chemical structures.

1.9.1 Ethyl Cellulose

Ethyl cellulose is similar in structure to cellulose and cellulose acetate but some of the hydroxyl (−OH) functional groups are replaced on the cellulose by the ethoxy group ($-O-CH_2-CH_3$). The structure of ethyl cellulose is shown in Figure 1.28.

Applications and uses: Pharmaceutical applications, cosmetics, nail polish, vitamin coatings, printing inks, specialty coatings, and food packaging.

1.9.2 Polycaprolactone

PCL is a biodegradable polyester with a low melting point of around 60°C and a glass transition temperature of about −60°C. PCL is prepared by ring opening polymerization of ε-caprolactone using a catalyst such as stannous octanoate. The structure of PCL is shown in Figure 1.29.

PCL is degraded by hydrolysis of its ester linkages under physiological conditions (such as in the human body) and has therefore received a great deal of attention for use as an implantable biomaterial. In particular it is especially interesting for the preparation of long-term implantable devices. A variety of drugs have been encapsulated within PCL beads for controlled release and targeted drug delivery. PCL is often mixed with starch to obtain a good biodegradable material at a low price.

Applications and uses: The mix of PCL and starch has been successfully used for making trash bags in Korea (Yukong Company).

1.9.3 Polylactic Acid

PLA is derived from renewable resources, such as corn starch or sugarcane. PLA polymers are considered biodegradable and compostable. PLA is a thermoplastic, high-strength, high-modulus polymer that can be made annually from renewable sources to yield articles for use in either the industrial packaging field or the biocompatible/bioabsorbable medical device market. Bacterial fermentation is used to make lactic acid, which is then converted to the lactide dimer to remove the water molecule which would otherwise limit the ability to make high-molecular weight polymer. The lactide dimer, after the water is removed, can be polymerized without producing water. This process is shown in Figure 1.30.

Applications and uses: It is being evaluated as a material for tissue engineering, loose-fill packaging, compost bags, and food packaging.

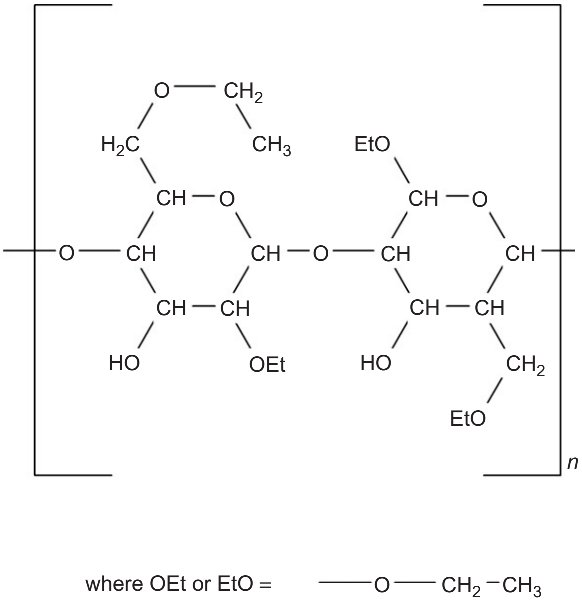


Figure 1.28 Structure of ethyl cellulose.

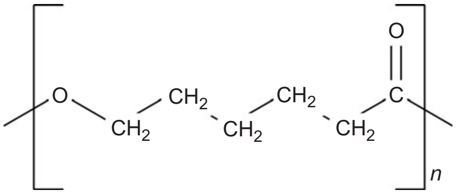


Figure 1.29 Structure of PCL.

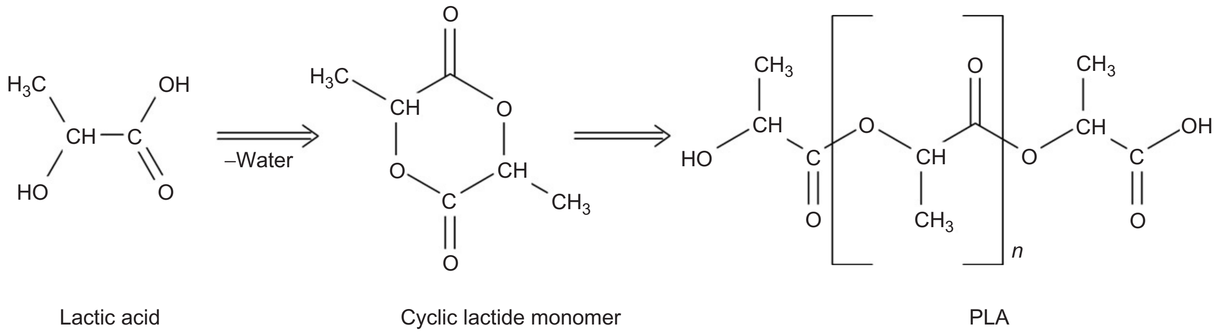


Figure 1.30 Conversion of lactic acid to PLA.

1.9.4 Poly-3-hydroxybutyrate

PHAs are naturally produced and include PHB or PH3B, PHV, and PHH. A PHA copolymer called PHBV is less stiff and tougher, and it may be used as packaging material. Chemical structures of some of these polymers are shown in Figure 1.31.

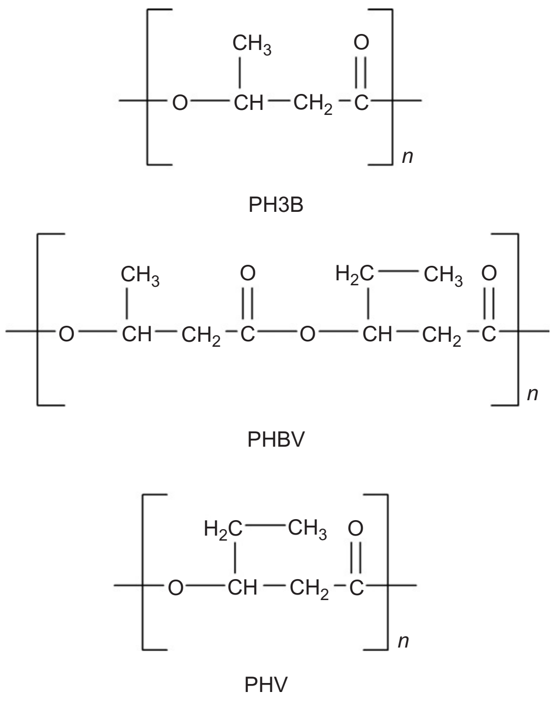


Figure 1.31 Structures of several PHAs.

1.10 Summary

Thin film packaging is an important market and even though it is mature, new technical developments are expected in the years to come.

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2 Polypropylene Films

Teresa Calafut

Polypropylene film is one of the most versatile packaging materials. It is economical due to its low density and is replacing other materials, such as polyethylene, polyvinyl chloride, polyester, and cellophane, in packaging applications. Almost 90% of plastic packaging is used in food applications; other applications include film packaging for stationery products, cigarettes, and textiles (Goddard, 1993; Graves, 1995; Shell Polypropylene Film Grade Resins Guide, 1992).

Both random copolymers and homopolymers are used in film production. Films can be unoriented, uniaxially oriented, or biaxially oriented and are defined as sheet materials that are less than 0.254 mm (10 mil) in thickness; thicker films are referred to as sheets. Resins with melt-flow indexes of ~2−8 g/10 min are generally used in films, although higher melt-flow rate resins are also used. Higher melt-flow resins are used in cast film processes (Fortilene Polypropylene Properties, Processing, and Design Manual (1981); Capshew (1997).

2.1 Unoriented Film

Unoriented polypropylene films can be produced by casting or blown film processes. Chill roll casting and tubular water quenching are commonly used. Conventional air quenching, widely used for polyethylene, produces brittle films with poor clarity in polypropylene; however, newer polypropylene resins and copolymers developed for air-quenched processes can provide economical alternatives to polyethylene. The tubular water-quench process is commonly used to produce monolayer film (Barnetson, 1996; Fortilene Polypropylene Properties, Processing, and Design Manual, 1981; Himont, 1992; Miller et al., 1991; Moore, 1996; Polymers in Contact with Food, 1991; Thompson et al., 1987).

Unoriented films have a very soft hand and are easily heat sealed. They exhibit good heat stability, low flexural moduli, excellent puncture resistance, excellent impact strength, and low moisture permeability but provide only poor barriers to gases, such as oxygen and carbon dioxide, some perfumes, and oil such as peppermint oil. Clarity of unoriented random copolymer film is moderate and is affected by processing conditions. Because its physical properties are balanced, unoriented film is easier to process on bag-making equipment than cast-oriented film, and slitting and sealing is easier in the transverse direction. Applications include packaging for shirts, hosiery, bread, and produce, used as a strength and barrier layer in disposable diapers, and used in electrical capacitors (Barnetson, 1996; Fortilene Polypropylene Properties, Processing, and Design Manual, 1981; Himont, 1992; Miller et al., 1991; Moore, 1996; Polymers in Contact with Food, 1991; Thompson et al., 1987).

2.2 Cast Film

Cast processes are usually used to produce uniaxially oriented film, oriented in the machine direction. Physical properties of the film depend on the degree of orientation, and a film is produced with different surface properties on each side. Oriented cast polypropylene film is clear and glossy, with high tensile strength. It is about three times stiffer and stronger than low-density polyethylene film. Cast film provides good moisture barrier properties and scuff resistance at low cost. Low-temperature brittleness is a problem with homopolymer polypropylene film; this can be overcome by the use of a copolymer resin (Fortilene Polypropylene Properties, Processing, and Design Manual, 1981; Graves, 1995).

A water bath is sometimes used instead of a chill or casting roll; the water bath process quenches the melt on both sides at the same time, producing a film with the same surface properties on each side. The machine direction orientation in the water bath process is somewhat different than that obtained using the casting roll, and the very rapid quenching

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lowers the crystallinity, producing a tougher film (Fortilene Polypropylene Properties, Processing, and Design Manual, 1981).

Tear initiation, by impact, puncture, or ripping, is difficult in oriented polypropylene (OPP) films; once initiated, however, the resistance to tear propagation is low. Tear strength depends on grade and process conditions and on whether the tear propagates in the machine or transverse direction. A tear strip is usually incorporated in OPP film packs to facilitate opening (Barnetson, 1996; Fortilene Polypropylene Properties, Processing, and Design Manual, 1981).

2.3 Biaxially Oriented Film

Biaxially oriented polypropylene (BOPP) film is film stretched in both machine and transverse directions, producing molecular chain orientation in two directions. BOPP film is produced by a tubular process, in which a tubular bubble is inflated, or a tenter frame process, in which a thick extruded sheet is heated to its softening point (not to the melting point) and is mechanically stretched by 300–400%. Stretching in the tenter frame process is usually 4.5:1 in the machine direction and 8.0:1 in the transverse direction, although these ratios are fully adjustable. It is a widely used process, more common than the tubular process, and a glossy, transparent film is produced. Biaxial orientation results in increased toughness, increased stiffness, enhanced clarity, improved oil and grease resistance, and enhanced barrier properties to water vapor and oxygen. Impact resistance, low-temperature impact resistance, and flexcrack resistance are substantially modified. BOPP films are used in food packaging and are replacing cellophane in applications such as snack and tobacco packaging due to favorable properties and low cost (Fortilene Polypropylene Properties, Processing, and Design Manual, 1981; Goddard, 1993).

Oriented films can be used as heat-shrinkable films in shrink-wrap applications or can be heat set to provide dimensional stability. Heat sealing is difficult in BOPP films, but can be made easier by either coating the film after processing with a heat-sealable material (such as polyvinylidene chloride) or by coextrusion with one or more copolymers before processing to produce layers of film. Copolymers used in sealing layers must have high gloss and clarity and should have low sealing temperatures to prevent distortion of the oriented polymer during sealing. Random copolymers containing 3–7% ethylene are often used as sealing layers; the

Table 2.1 Properties of OPP Films

Property	ASTM Test Method	Cast, Uniaxial Orientation	Biaxial Orientation
Area factor in 2/lb./1 mil film	–	30,400–31,300	30,600
Specific gravity (g/cm^3)	D1505	0.885–0.905	0.902–0.907
Tensile strength (psi)	D882	4500–7000	7500–40,000
Elongation (%)	D882	550–1000	352475
Tear strength (g/mil propagation)	D1922	25 MD 600 TD	3–10
Fold endurance	D2176	Very high	Excellent
24 h % water absorption	D570	0.005	0.005
Water vapor transmission rate (g/mil/100 in.^{2}/24 h at 100°F)	E96	0.7	0.25
Oxygen permeability (cm^3/100 in.^{2}/mil/24 h/atm. at 77°F)	D1434	150–240	160
Heat-sealing temperature range (°F)	–	285–400	–
Gloss (%)	–	90	95
Haze (%)	–	1–2	1–2

MD, machine direction; TD, transverse direction.

Table 2.2 Properties of Novolen Cast Film[a]

Property		Unit	Test Method	Block Copolymer	Random Copolymer		Homopolymer		
Grade				2309KX	3200 MCX	3520 LX	1125N	1127MX	1325L
Additives				None	None	Antiblock agents	Slip, antiblock agents	Slip, antiblock agents	Slip, antiblock agents
Melt flow rate		g/10 min	ISO 1133	4	8	5	11	8	5
Gloss	20°	%	DIN 67530	5	130	130	110	95	115
Haze		%	ASTM 1003	28	0.5	0.3	2.3	3.0	1.7
Tensile strength at break	Machine direction	MPa	DIN 53455	55	37	32	42	44	35
	Transverse direction	MPa	DIN 53455	36	35	30	38	40	33
Elongation at break	Machine direction	%	DIN 53455	750	730	750	680	700	750
	Transverse direction	%	DIN 53455	720	750	760	720	730	780
Dart drop impact resistance F50		g	ASTM 1709	500	450	>800	280	300	800
Modulus of elasticity in flexure	Machine direction	MPa	DIN 53121	650	480	300	700	680	370
	Transverse direction	MPa	DIN 53121	640	470	310	670	650	350
Coefficient of friction			DIN 53375	0.90	Not measurable	Not measurable	0.25	0.17	0.13

[a] *50 μm gauge; Data was obtained using film specimens prepared by internal standards. Film properties depend considerably on processing conditions. This must be taken into account when comparing these data with data obtained under different processing conditions.*

lower melting point (< 132°C; <270°F) results in a 30% increase in line speeds, and they can be recycled with no significant loss of strength or clarity. Coating or coextrusion increases the barrier properties of BOPP film, decreasing its permeability to gases. Common barrier polymers are ethylene vinyl alcohol, polyvinylidene chloride, and polyamide; five or more layers may be coextruded or laminated, or the barrier polymer can be dispersed in the matrix polymer (Fortilene Polypropylene Properties, Processing, and Design Manual, 1981; Goddard, 1993; Polymers in Contact with Food, 1991).

Some typical properties of cast, uniaxially oriented film, and BOPP films are listed in Table 2.1. Properties of films made using Novolen (BASF) homopolymers, random copolymers, and block copolymers are listed in Table 2.2 (Fortilene Polypropylene Properties, Processing, and Design Manual, 1981; Novolen Polypropylene (PP), 1992; Thompson et al., 1987).

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3 PE-Based Multilayer Film Structures

Thomas I. Butler[1] **and Barry A. Morris**[2]
[1]Blown Film Technology, LLC, Lake Jackson, TX, USA; [2]DuPont Packaging and Industrial Polymers, Wilmington, DE, USA

3.1 Introduction

Flexible packaging is used to deliver a product from the manufacturer or distributor to the retailer or ultimate consumer and protect that product during shipping, display, and storage. Multilayer flexible packaging is the combining of two or more layers into a composite web or tube that provides functional, protective, or decorative properties. The introduction of new polymers, the development of new processing equipment technology, and the emergence of new packaging applications have resulted in good growth rates in coextruded and laminated structures. Whatever the application or use, polymer materials are selected and the entire packaging structure is designed to meet the performance requirements specific to that particular application. These could include one or more of the following:

- specific performance properties,
- reduced cost,
- reduced number of processes.

The requirement for *specific performance properties* sometimes cannot be met by one polymer or even with polymer blends extruded in a monolayer film. Blending may not be desirable if the polymers are incompatible. Coextrusion with a high-strength or high-barrier polymer can allow significant down gauging while maintaining or improving key properties. Heat-seal polymers can be incorporated into a film structure to improve packaging line efficiency or speed.

Multilayer flexible packaging structures can *lower the cost* of many film structures by reducing the amounts of the expensive polymer used, increasing the less costly polymers, using recycled material, or reducing film thickness. Competitive advantages can be achieved for many film structures, ranging from the high technology barrier food packaging films to the heavy-duty shipping bag market.

Coextrusion can *reduce the number of process* operations required when several polymers are needed to obtain the desired properties (Smith, 1975). Eliminating process steps saves labor, equipment overhead, and reduces turnaround time. The more operations that can be combined into a single process means more space available for other equipment and less scrap generated with multiple process steps (Schrenk and Finch, 1981). Coextrusion can eliminate the use of solvent-based adhesives. This may provide some raw material cost savings and, with increasing regulations on solvent use and disposal, the incineration or recovery cost could be high.

The number of polymers available for extrusion have increased in recent years (Schrenk and Veazey, 1984). There are several polymers to choose from with various attributes, such as:

- high barrier
- selected permeation rate
- adhesion
- high-strength sealing
- easy opening (peelable) sealing
- low-temperature sealing
- high hot tack sealing
- high tensile strength
- high impact strength
- high tear strength
- high modulus
- high-temperature resistance
- low-temperature impact
- high clarity
- abrasion resistance
- chemical resistance

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- low taste and odor
- high cling
- low slip
- stabilized
- degradable
- antistatic
- antifog
- pigmented
- thermoformable.

This list of polymer performance attributes will continue to grow as application requirements are identified.

A critical factor in developing successful flexible packaging applications has always been a good understanding of the target application. The performance properties required by the application and economic comparisons should be evaluated against the many alternative structures. Performance requirements may include all user requirements in the chain of use. For consumers, this may mean that the packaging

- protects the product,
- identifies the product,
- is easy to open.

For retailers, the packaging may provide

- eye-catching graphics that help sell the product, and
- the proper physical form for display purposes.

For the packager, flexible packaging may need to provide

- high packaging speeds,
- low scrap rates,
- meet the functional requirements for protecting the product inside the package.

Specific performance requirements will vary greatly from one package to another, but in every case, meeting the performance requirements will help assure proper protection of the goods being packaged.

Polymer films may be manufactured by blown film or cast film extrusion or by extrusion coating a polymer onto another substrate, such as paper or aluminum foil. Blown films are made by melting and pumping polymer through an annular die (Potts, 1987). Cast films are made by melting and pumping polymer through a flat die. The extrusion coating process is similar to the cast film process except that the molten polymer is coated directly onto another material. The manufacturing process selected is governed by factors such as

- the job size,
- the packaging material to be made,
- the end-user packaging performance requirements,
- the equipment availability.

Cast film extrusion typically operates at much higher output rates than blown film, so for larger volume production, it has an advantage with high-usage single-use films such as stretch film. Blown film extrusion typically runs at a lower rate and may result in film with improved physical properties. Blown film also allows for bubble-size adjustment and thus the film width produced. This is a key advantage when many different film widths must be produced on the same machine. There are many existing coextrusion processes, ranging from two-layer to eleven-layer capability.

The coextrusion process is used to combine multiple materials into a single film (Karagiannis et al., 1987; Schrenk, 1978, 1984). Both blown films and cast films may be coextruded in three, five, seven, nine, or more layers. The combination of multiple materials in a single film is a cost-effective means of combining the performance properties of several polymers in a single film (Soutar, 1989). One example would be the coextrusion of a barrier polymer such as ethylene vinyl alcohol (EVOH) or polyvinylidene chloride (PVDC) with a sealant resin such as linear low-density polyethylene (LLDPE), ethylene vinyl acetate (EVA), or a polyolefin plastomer (POP). Coextrusion is widely used in producing high-performance packaging films, such as those used to package foods. It is also increasingly used to produce industrial films, such as stretch film.

As coextrusion technology has evolved over the past 30 years, the number of layers has increased

(Arvedson, 1984). Whereas 5−10 years ago a five-layer line was state of the art, now it is common to see seven-layer and higher lines installed (Bode, 1986; Gates, 1987, 1989). In addition to the advantages described earlier of combining different polymer materials, the extra layer capability gives the converter greater flexibility and control over its process (Gates, 1988; Wright, 1983). For example, if a five-layer line was designed to produce five layers of equal thickness, it may be a challenge to produce an unbalanced structure such as a barrier cereal liner: (60% high-density polyethylene (HDPE)/5% tie/5% EVOH/5% tie/25% EVA) (Arvedson, 1984). The line may have to be slowed down to achieve the desired HDPE thickness because of extruder output limitations. At low line speed, however, controlling the thin layer thickness can be difficult since the extruders may be oversized. Making the same structure on a seven- or nine-layer line is easier. The HDPE layer can be split into more than one layer and fed by multiple extruders, allowing for greater output and control over the process.

Another advantage of greater layer capability is the ability to split barrier layers into two or more layers (Ossmann, 1986). For example, a simple polyamide (PA) barrier film (PA/tie/LLDPE) may be split into (PA/tie/PA/tie/LLDPE). Separating the barrier layers insures barrier continuity—if a pinhole develops in one layer, the second layer still may be intact. Thin layer orientation and property nonlinearity with thickness suggest that two thin layers may have better barrier performance than a single layer of the same total thickness (DeLassus, 1985).

Polymer films may be stretched, or oriented, to impart improved properties useful for packaging applications. Oriented film is produced by a double bubble or tenter frame process. A thick film or sheet is manufactured, typically 250−1000 μm (10−40 mil), and is subsequently oriented (stretched) in a semisolid state to many times its original dimensions (Finch, 1986). The multiple step production is normally done in a continuous operation (Sacharuk, 1988). The sheet stretching or orientation may occur sequentially in the machine and transverse directions or the stretching may occur simultaneously in both directions. After orienting, the films are typically 12.5−25 μm (0.5−1.0 mil) thick. The film is typically supplied in roll form. Biaxially oriented polypropylene (BOPP) is most often manufactured by a tenter frame process. Oriented polyethylene (PE) films are usually manufactured using a double bubble process. Polyvinyl chloride (PVC) films may also be oriented. Some oriented films are cross-linked further to enhance their performance. Compared to other films, oriented films typically provide improved optical properties, higher stiffness, and increased shrinkage during packaging, which leads to improved package appearance. Coextruded barrier films may also be oriented, typically using a double bubble process. Applications include shrink bags and sausage casings.

Layer multiplication technology, developed at Dow Chemical in the 1980s (Im and Schrenk, 1988; Schrenk, 1975; Schrenk et al., 1992a,b) and used primarily for optical films (Alfey and Schenk, 1973; Pointing et al., 2009), is starting to see application in packaging structures. The concept involves forming the layers in a coextrusion feedblock, dividing them vertically and stacking the layers on top of one another, as shown in Figure 3.1. Each multiplier module results in a doubling of the number of layers. By adding several modules in series, hundreds of layers have been achieved. Improved strength and barrier properties have been claimed (Bernal-Lara et al., 2005; Kerns et al., 1999; Mueller et al., 1997; Oliver, 2009; Schirmer et al., 2010; Wang et al., 2000). For example, researchers at Case Western Reserve show an increase in oxygen barrier of polyethylene oxide (PEO) of 100 times or more when the layer dimensions reach the nanometer domain. They attribute this to changes in the crystalline structure (Wang et al., 2000). Time will tell whether this can be applied to more conventional polymers used in packaging.

While originally developed for flat die coex cast sheet or film extrusion, recently Schirmer (1998, 2002) and Dow Chemical (Dooley et al., 2011) have introduced blown film versions. Zumbrunnen of Clemson University has been promoting technology based on chaotic advection that supposedly reproducibly creates unique morphologies, including microlayers of barrier and other polymers (Zumbrunnen and Zumbrunnen, 2009). As some of the original Dow patents have now expired, equipment suppliers have begun to promote their own versions in the market.

Lamination is used to combine two or more films into a single packaging structure (Djordjevic, 1988). It allows materials that cannot be coextruded to be combined. An example would be an aluminum foil and a PE sealant film lamination. More complicated laminations may include different polymer films, paper, and foil. Laminations are usually either adhesive laminations or extrusion laminations. In adhesive laminations, the substrates are combined using an adhesive material (Djordjevic, 1989). In extrusion laminations, the substrates are adhered together using a molten polymer; often low-density polyethylene (LDPE) is used as the adhesive layer. Lamination can also protect the printing ink by placing it between layers, thus providing superior graphics for surface-printed packages. For example, glossy stand-up pouches have a reverse-printed outer layer laminated to structural and sealant materials. Laminations are also used to provide oxygen, moisture, or light barrier. The barrier functionality may be provided by foil or a barrier polymer such as EVOH or PVDC. Most high-value processed meat and cheese packages are laminations. This allows various materials to be combined into the packaging structure and for superior graphic properties when using reverse printing. Since laminations are more costly than coextruded or monolayer films, laminations are generally reserved for use in higher value applications.

Metallization is used to apply a thin coating, typically aluminum, to a polymer film. This provides improved oxygen and water barrier properties as well as forming a light barrier. The major use for metalized film is potato chip bags. Metalized films are also used for nuts and salty snacks. Metalized films may be coated to provide sealability or may be laminated to another polymer film to provide improved properties, such as seal integrity. Other coatings, whether to provide barrier properties or other functionality, may also be applied to polymer films used in flexible packaging.

3.2 Polymer Selection

Polymers are selected for the specific performance that they provide and are combined in the final package design to meet all the requirements for the specific application in which they are being used. Often, there are many different material combinations or film constructions that will meet an application's minimum performance requirements (Veazey, 1983). In these cases, the packaging structure selected may be based on considerations such as availability from multiple suppliers or ability to provide differentiation over competitive packaging. For example, a box with an inner liner or a stand-up pouch may be used, each combination providing the minimum requirements for product protection and safety. One consumer goods company may select a box and inner liner and another consumer goods company may elect to package their product in a stand-up pouch for the same product; or one manufacturer may choose to use a stand-up pouch and another manufacturer may choose to use a pillow pouch for the same product.

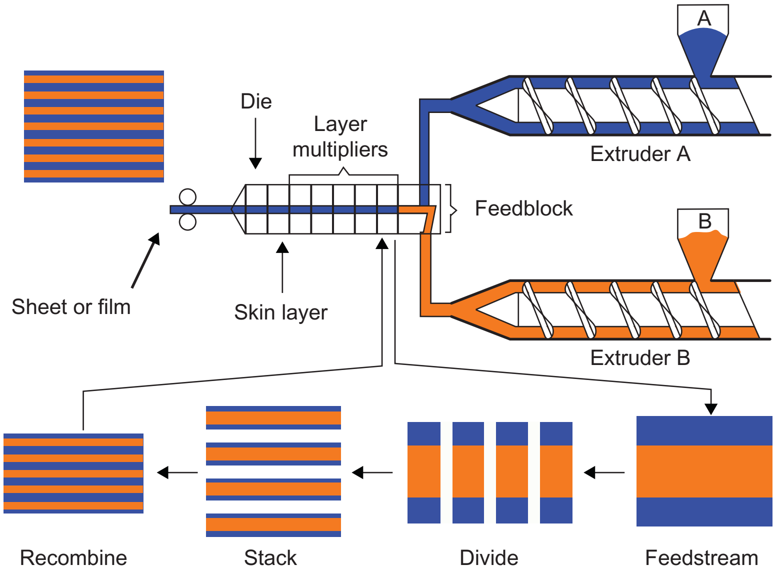


Figure 3.1 Schematic of layer multiplication technology. *Source: Taken from Dooley et al. (2011).*

Polymers are chosen for individual layers to achieve specific performance properties. For example, polymers could be selected to contribute to the film's

- tensile strength
- permeation resistance
- sealability
- adhesion
- optics
- formability
- machinability
- economics.

An individual layer could consist of virgin polymer, blends of polymers, regrind/recycled material, or high levels of additives (Daniels, 1985). Most thermoplastic polymers can be coextruded together. PE is the largest thermoplastic used in flexible packaging applications. There are many PE homopolymers and copolymers that are available for use. Some common polymers used in flexible packaging structures are included in Table 3.1.

Table 3.1 Common Polymers Used for Flexible Packaging Applications

Polymer Name	Abbreviation	Density (g/cm^3)
Ethylene acrylic acid	EAA	0.925–0.950
Ethylene carbon monoxide	ECO	0.930
Ethylene ethyl acrylate	EEA	0.925–0.950
Partially neutralized ethylene (meth)acrylic acid (ionomer)	ION	0.940–0.950
Ethylene methacrylic acid	EMAA	0.925–0.950
Ethylene methyl acrylate	EMA	0.930–0.950
Ethylene vinyl acetate	EVA	0.925–0.945
Ethylene vinyl alcohol	EVOH	1.14–1.16
Maleic anhydride grafted polyethylene	PE-g-MAH	0.91–0.940
High-density polyethylene	HDPE	0.940–0.965
High-molecular weight HDPE	HMW–HDPE	0.940–0.962
Linear low-density polyethylene	LLDPE	0.915–0.940
Low-density polyethylene	LDPE	0.915–0.925
Medium-density polyethylene	MDPE	0.925–0.940
Metallocene polyethylene	m-LLDPE	0.865–0.960
Polyolefin plastomer/elastomer	POP/POE	0.856–0.915
Enhanced polyethylene	EPE	0.900–0.925
Polyamide (nylon)	PA	1.12–1.14
Polybutylene	PB	0.909
Polycarbonate	PC	1.2
Polyethylene terephthalate	PET	1.3
Polypropylene	PP	0.89–0.902
Polystyrene	PS	1.04
Polyvinyl chloride	PVC	1.16
Polyvinylidene chloride	PVDC	1.7
Ultralow-density polyethylene	ULDPE	0.90–0.915

Some of the key performance requirements for high-performance flexible packaging include the following:

- *Barrier properties:* to keep oxygen, water, light, flavor, or grease from entering or leaving the package. Barrier properties may be characterized by measuring the oxygen and water vapor permeation through the packaging material.
- *Selective permeability:* to allow oxygen and carbon dioxide to permeate through the package at a calculated rate to extend the shelf life of fresh-cut produce. Oxygen, carbon dioxide, and water vapor permeability are frequently measured and specified.
- *Abuse resistance:* to prevent damage to the packaging material and its contents during shipping and storage. Abuse resistance may include puncture resistance, tear strength, impact strength, and modulus. Some packages require good toughness at refrigerated or freezer temperatures.
- *Sealability:* to allow packages to be made at high packaging speeds and keep the product secure by preventing the package seams from failing. Sealability may be characterized by heat-seal and hot tack strength, heat-seal and hot tack initiation temperatures, seal-through-contamination performance, caulkability, and seal integrity. Hot tack refers to the seal strength while still in the molten state. It is critically important for packages where the product drops into the package while the seal is still partly molten, but also for horizontally filled packages involving gussets where the spring-back nature of the folded film creates an opening force. Caulkability refers to the ability of the sealant material to flow, filling in gaps around folds, wrinkles, or product contaminants.
- *Machinability:* to allow the packaging films to be easily run on high-speed automatic packaging equipment. Machineability is governed largely by film modulus, film thickness, seal properties, and coefficient of friction.
- *Consumer appeal:* package appearance is an important factor driving product preference by consumers. Appeal is largely related to print quality and package gloss. Film thickness and modulus may also impact consumer appeal.

3.3 Mechanical Properties

Most published film data sheets are developed from monolayer films. A coextruded structure's mechanical strength may be estimated using the law of mixtures as shown in Eq. (3.1), i.e. the summation of the tensile strength per unit layer thickness, multiplied by its thickness, divided by the total thickness.

$$M = \frac{(t_1 \cdot M_1) + (t_2 \cdot M_2) + \sum_{i=3}^{n} t_i \cdot M_i}{t_1 + t_2 + \sum_{i=3}^{n} t_i} \tag{3.1}$$

where

M = estimate of coextruded film mechanical property,

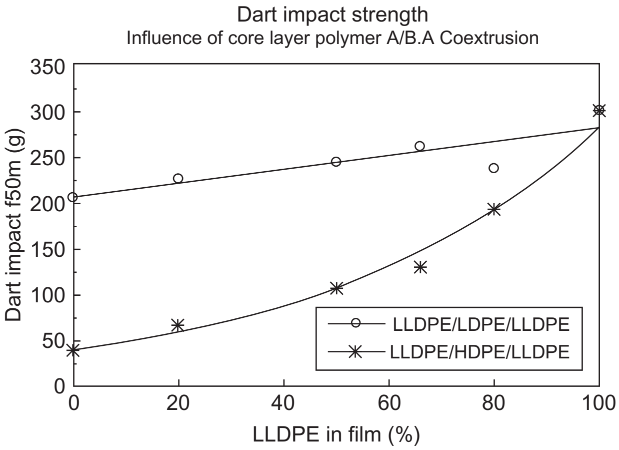
t_i = polymer layer thickness of layer i,

M_i = polymer mechanical property/unit thickness of layer i,

n = number of layers.

Determining multilayer film properties with Eq. (3.1) does not account for any interactions (positive or negative) between layers, or the influence of fabrication variables or orientation. Sometimes unfavorable interactions can lead to interlayer destruction, such as when a very ductile layer is adhered to a brittle layer, resulting in the film exhibiting the properties of the brittle layer (Hessenbruch, 1988). Figure 3.2 shows the effect of a LDPE core versus a HDPE core in a three-layer coextrusion structure (A/B/A) with increasing LLDPE polymer content in the skin layers, on dart impact.

In the first case, the dart impact strength is a linear function of LLDPE content and can be approximated by the law of mixtures. However, in the second case, dart impact strength is nonlinear and is disproportionately negatively influenced by the HDPE content. The LLDPE polymer is a highly elastic material, which allows it to absorb high levels of impact energy. The LDPE, while not as elastic as LLDPE, does not detract from the impact strength. HDPE is more brittle than the LLDPE polymer and tends to form localized stress concentration sites resulting in lower dart impact values for the film structure.



A layer 1.0MI, 0.920g/cm^3 LLDPE
B1 layer 0.7MI, 0.965g/cm^3 HDPE
B2 layer 2.0MI, 0.918g/cm^3 HDPE

Total output = LB/HR/in.
Film thickness = 1.5mil
BUR = 2.5

Figure 3.2 Influence of polymer in core layer.

Another reason that mechanical property data from monolayer film can be misleading is because some properties have a bias versus tested thickness; that is, there may not be a linear relationship between the mechanical property and film thickness. Also, the film-making process itself can impart differences between coextruded films and monolayer films. For example, the stress history may differ due to quenching differences between mono- and multilayer films, resulting in differences in orientation and properties (Morris, 1998). Therefore, the law of mixtures for coextruded films may be used for estimates, and film properties should be measured.

Film stiffness affects

- machinability on packaging equipment,
- wrinkling,
- the handling or feel of the final package, and
- in some cases, the package function (e.g. a stand-up pouch).

Multilayer film stiffness is a function of the stiffness (modulus), thickness, and position of each layer. Morris and Vansant (1997) showed that the outermost layers in a multilayer film have the greatest impact on stiffness. Like an I beam, separating stiff layers in a structure is an effective way to impart stiffness to it. Thus, using a stiff sealant layer can help build in stiffness and allow the total structure to be down gauged. Furthermore, the converting process can impact stiffness. In some cases, extrusion laminating two stiff films may build in greater stiffness than adhesive lamination, since extrusion lamination allows the layers to be separated further apart.

3.4 Barrier Properties

Flexible packaging films are used to provide barrier to gases such as the following:

- oxygen
- nitrogen
- carbon dioxide
- water vapor.

Other applications may require taste and odor resistance properties. Permeation occurs in polymer films and this mechanism allows interaction with the environment. Molecules may permeate through a package in a three-step process. First, the molecules must dissolve into the film structure. Then the molecules will diffuse through the film layers. And, finally, the molecule will desorb on the opposite side. The molecule can move either from outside the film into the package or from inside to outside. This permeation happens due to a concentration or pressure gradient and is sensitive to temperature and, for many polymers, relative humidity. The permeation rate of a material through a polymer is a function of the diffusivity at steady state times solubility in the polymer, as shown in Eq. (3.2). Diffusivity is also a function of solubility especially at the low solubility levels.

$$P = D \cdot S \tag{3.2}$$

where

P = permeability of a material through a polymer (g/s-cm),

D = diffusivity of a material through a polymer (cm^2/s),

S = solubility coefficient of a material in a polymer (g/cm^3).

Permeation rates are usually measured at steady-state conditions. The adsorption of a material can significantly influence the permeation rates, and if the adsorption mechanisms are of sufficiently long duration, this may prevent steady-state conditions from being reached during the expected shelf life of the package. Thus, in these instances, the polymer location in a film structure could influence actual permeation rates during a package's shelf life.

The gas transmission rate at steady state through a given polymer is inversely proportional to the layer thickness. The permeation coefficient through a multilayer film structure may be estimated by summing the permeation resistance of each layer, as shown in Eq. (3.3):

$$\frac{1}{P} = \frac{f_1}{P_1} + \frac{f_2}{P_2} + \cdots + \frac{f_n}{P_n} \tag{3.3}$$

where

P = coextruded film permeation coefficient,
f_n = polymer n layer thickness ratio,
P_n = polymer n permeation coefficient.

The actual transmission through a coextruded film is then calculated as shown in Eq. (3.4).

$$\mathrm{TM} = \frac{P}{t_t} \tag{3.4}$$

where

TM = transmission of film,
t_t = total thickness of coextruded film.

Table 3.2 shows a sample calculation of moisture transmission rates based on permeability factors for a three-layer film typical for a cereal liner application using Eqs (3.3) and (3.4). This apparent two-layer film is a typical cereal liner structure that is generally made on a three-layer blown film line with the HDPE layer split into two layers due to extruder size limitations.

For many high-barrier films, the overall permeability rate is controlled by the highest barrier polymer. Permeability rates are sensitive to temperature and will increase as ambient temperature increases and follow the Arrhenius equation. Some polymer's permeability rates are also a function of relative humidity and increase with increasing relative humidity. Table 3.3 lists some oxygen permeability data for various polymers ranked from the lowest to the highest measured at 1.0 mil, 23°C, and 0% relative humidity.

Table 3.4 lists the moisture transmission rate data for various polymers from the lowest permeation to the highest, measured at 1.0 mil, 100°F (37.8°C), and 90% relative humidity.

Understanding the package environment during filling, processing, distribution, and storage is required to determine the permeation needs of a multilayer flexible package. Inadequate understanding of the product barrier requirements poses a design problem in predicting shelf life from gas transmission data. Packagers must rely on extensive shelf-life testing of individual food products to evaluate barrier film performance requirements.

Taste and aroma barrier can be very important in some packaging applications. It is not possible to predict from common gas transmission data the

Table 3.2 Sample Calculation of Moisture Transmission Rate

HDPE	HDPE	EVA
0.9	0.8	0.3 mil
45%	40%	15%
P(HDPE) = 0.6 g × mil/100 in.^{2}/day		
P(EVA) = 2.0 g × mil/100 in.^{2}/day		
1/P = [(0.45/0.6) + (0.4/0.6) + (0.15/2.0)] = 1.49		
P = 0.67		
TM = 0.674/2.0 = 0.34 g/100 in.^{2}/day moisture transmission		

Basis at steady state conditions

polymer's aroma and flavor barrier to other chemicals. The chemical component's molecular size and solubility will determine the permeation rates in the polymer.

Economics is a critical concern in all flexible packaging applications. Many factors are involved in determining the value a polymer is providing. For example, when comparing the cost of two barrier polymers, the comparison should be based on an equal transmission rate and package surface areas at the target application conditions (temperature and humidity). Use Eq. (3.5) to determine the best barrier polymer value:

$$\mathrm{TR} = P \cdot \frac{A}{100} \cdot \frac{1}{t} \tag{3.5}$$

where

TR = transmission rate of a gas through film ($\mathrm{cm}^3/(\mathrm{day} \times \mathrm{atm})$),

P = permeability coefficient of a gas through polymer ($\mathrm{cm}^3 \times \mathrm{mil}/(100\ \mathrm{in}\ 2 \times \mathrm{day} \times \mathrm{atm})$),

t = thickness of polymer (mill),

A = surface area of polymer exposed to a gas ($\mathrm{in.}^2$).

Table 3.5 shows the calculations required to compare two barrier polymers. First, the equivalent thickness of each polymer that will provide the same barrier property is determined using Eq. (3.5). Then, the cost of each polymer is determined

Table 3.3 Oxygen Permeability Coefficients for Various Polymers

Oxygen Permeability Coefficients	
1. 0 mil, 73°F (23°C), 0% RH	
Polymer Type	**Oxygen Permeability Coefficient ($\mathrm{cm}^3 \times \mathrm{mil}/100\ \mathrm{in.}^2 \times \mathrm{day} \times \mathrm{atm}$)**
PVOH	0.03–0.06 (Plastics Design Library Staff, 1995)
EVOH	0.02
PVDC	0.15
PA	2.6
PET	3.5
PVC	5–20
PLA	30 (Auras et al., 2003; Cabedo et al., 2005)
PP	150
HDPE	150
EAA	200–500
EMAA	200–500
ION	200–500
PS	350
PB	385
LDPE	420
LLDPE	440
EPE	500–800
EVA	600–1000
EMA	600–1000
ULDPE	600–950
POP/POE	600–2000

based on the equivalent barrier properties. The data needed are as follows:

- the required transmission rate (TR),
- permeability coefficient (P_1 and P_2),
- package surface area (A).

The oil resistance of a polymer is influenced by its polarity and crystallinity. Polar polymers, such as PA and polyester, have good oil resistance. Among polyolefins and ethylene copolymers, polypropylene (PP) and HDPE generally have the best oil resistance due to their high crystallinity. For PE, when the density is reduced by introducing comonomers,

Table 3.4 Moisture Permeability Coefficients

Moisture Vapor Transmission Rates (MVTR): 1.0 mil, 100°F (37.8°C), 90% RH	
Polymer Type	**MVTR (g × mil/100 in.^{2} × day)**
PVDC	0.10
PP	0.7
HDPE	0.4–0.8
LLDPE	0.8–1.2
ULDPE	1.2–1.5
LDPE	1.0–1.2
PB	1.0–1.2
EVA	1.0–5.5
EAA	1.0–1.6
EMAA	1.0–1.6
ION	1.0–1.6
EMA	1.0–9.0
POP	1.3–2.0
EPE	0.9–1.2
POE	2.0–3.0
PET	2.0–3.3
PVC	0.9–5.1
EVOH	2.0–4.5
PS	7.0–10.0
PA	10.0–20.0
PLA	40 (Auras et al., 2003)

Table 3.5 Calculation of the Most Cost-Effective Barrier Polymer

Polymer	**Thickness**	**Package Cost**
1	$t_1 = P_1 \cdot \frac{A}{100} \cdot \frac{1}{TR}$	$C_{Polymer\,1} = \frac{t_1}{1000} \cdot A \cdot \rho_{Polymer\,1} \cdot \$_{Polymer\,1}$
2	$t_2 = P_2 \cdot \frac{A}{100} \cdot \frac{1}{TR}$	$C_{Polymer\,2} = \frac{t_2}{1000} \cdot A \cdot \rho_{Polymer\,2} \cdot \$_{Polymer\,2}$

t_n = *required polymer thickness (mil);* P_n = *permeability coefficient;* A = *package area (in.^{2});* ρ_n = *polymer density (lb/in^3); TR = transmission rate required to protect package contents;* C_n = *polymer cost per package;* $\$_n$ = *polymer* n *price ($/lb).*

its oil resistance decreases. An exception is ionomers, which have excellent oil and grease resistance because of their polarity. Oil penetration generally increases with increasing temperature.

3.5 Polymer Sealability

Heat sealability is a critical property for many packaging applications. Figure 3.3 shows a typical heat-seal strength as a function of seal-bar temperature. A polymer that exhibits low-temperature sealability and maintains seal integrity over a broad seal temperature, dwell time, and seal pressure can significantly increase packaging line speeds, improve efficiencies, and minimize seal failures. Such a polymer may be unacceptable, however, for packages requiring heat resistance, as in applications such as retort, boil-in-bag, or microwave cooking.

Heat-seal properties are influenced by a polymer's thermal and rheological properties as well as factors such as the following (Halle, 1989):

- seal-bar temperatures
- seal-bar pressure
- dwell time
- sealing bar configuration
- package design.

Table 3.6 shows some heat-seal data that compares the minimum seal-bar temperature required to obtain a 3.5 N/cm (2.0 lb/in.) seal strength for monolayer films at the prescribed conditions. Ethylene copolymers have low melting temperatures and are often used as sealants; generally, the higher the copolymer content, the lower the seal-initiation temperature. Stehling and Meka (1994) showed that the fusion seal-initiation temperature and the temperature for maximum seal strength of polyolefins and ethylene copolymers strongly correlate with their crystallinities. The seal interface strength is due to molecular chain interpenetration across the interface. Only after the polymer fully melts does enough penetration occur to ensure maximum seal strength. Qureshi et al. (2001) show that the molecular architecture of LLDPE plays a role: homogeneous copolymers have a more rapid seal strength increase than do heterogeneous (Zieger–Natta) polymers, presumably due to their faster diffusion rates. They estimate that, for PE to achieve its maximum seal strength, its chains must penetrate a distance on the order of its radius of gyration, a characteristic length scale of the polymer molecule in its random coiled configuration. Morris (2002) found that ionomers only require penetration of a fraction of their radius of gyration to establish maximum seal strength. He attributes this to the longer range ionic forces present in ionomers. These same forces, however, contribute to slower diffusion rates for ionomers.

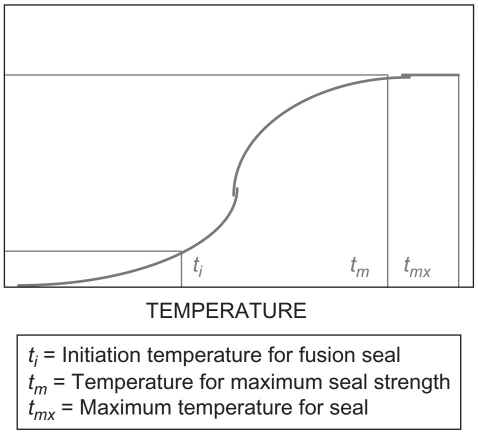


Figure 3.3 Heat-seal strength versus seal-bar temperature.

Morris also looked at the interrelationship between seal-bar temperature, dwell time, and package design on heat-seal performance (Morris, 2002). Thicker packaging structures require longer dwell times for a given seal-bar temperature to reach the same heat-seal strength as thinner structures. Nominally, this is due to heat transfer considerations; it takes longer for the heat to transfer through thicker films. Simple heat transfer modeling was not enough to account for seal performance differences. By coupling a polymer diffusion model with heat transfer analysis, Morris (2002) was able to predict packaging performance. He found that, at least for the slowly diffusing ionomers, seal strength increases at the interface after the heat-seal jaws are removed as the film slowly cools to room temperature.

Another critical sealability property is hot tack strength; the ability to maintain seal integrity while still hot and a load is applied. Hot tack is important in vertical form/fill/seal (VFFS) machines since the product weight puts a force on the bottom seal while it is still hot (Van Ness, 1983). It can also be important in horizontal form/fill/seal (HFFS) applications, particularly in gusseted areas where the films are folded. A film's dead fold or "spring-back" nature exerts an opening force that must be countered by good hot tack strength to avoid channel leakers. Hot tack derives from two competing mechanisms. The first is polymer diffusion and penetration; as in the case for heat-seal performance, strength at the interface is built by polymer interdiffusion and entanglement. The second is melt strength, which is related to polymer viscosity. Diffusion increases with increasing temperature, whereas melt strength decreases. Thus, hot tack strength versus sealing temperature typically goes through a maximum. Figure 3.4 compares hot tack for ionomer versus POP. Ionomer has a broad hot tack range and POP has a narrow hot tack range.

The maximum hot tack strength, the peak hot tack temperature, and the hot tack range can all be consequential in end use. The hot tack range versus temperature can be particularly important since it indicates how much flexibility packers may have in their packaging operation. Often, seal-bar temperatures are not well controlled or the line speed is ramped up and down during the day, which affects the seal-bar temperature. The molecular architecture and polymer chemistry play a role in the hot tack curve shape. Some POPs have very high maximum hot tack strengths near their melting points that tail off quickly at higher temperatures. Strain-induced crystallization in these homogeneous polymers has been proposed for the unusually high hot tack strength (Qureshi et al., 2001). Poor hot tack strength at elevated temperatures is due to lower melt strength. Heterogeneous LLDPE and ultralow-density polyethylene (ULDPE) tend to have broader hot tack curves. Broader yet are acid copolymers and, finally, ionomers, which have exceptionally

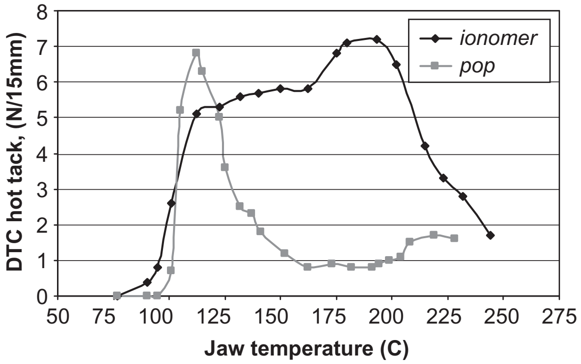


Figure 3.4 Hot tack performance. *Source: From De Garavilla (1995).*

Table 3.6 Polymer Thermal and Sealing Properties

Polymer Type	Melting Point, °C (F)	Vicat Softening Point, °C (F)	Fusion Seal Temperature[a], °C (F)
EMA (20%)	80 (176)	59 (138)	82 (189)
POP (0.902 g/cm^3)	94 (201)	80 (176)	88 (190)
EVA (12%)	90 (194)	81 (178)	91 (195)
ION	93 (200)	72 (161)	99 (210)
EAA (9% AA)	98 (208)	83 (181)	93 (200)
ULDPE (0.912 g/cm^3)	121 (250)	105 (221)	101 (215)
LDPE (0.920 g/cm^3)	110 (230)	92 (198)	107 (225)
LLDPE (0.920 g/cm^3)	122 (252)	110 (230)	118 (245)
HDPE (0.960 g/cm^3)	135 (275)	125 (257)	121 (250)
PP	168 (334)	133 (271)	149 (300)
PS	120 (248)[b]		
PVDC	160 (320)[b]		
EVOH	160 (320)		
PA	216 (420)		
PC		154 (310)	

[a] *Hot tack sealer, 50-μm (2.0-mil) film with 50-μm (2.0-mil) PET backing, 0.5-s dwell, 275-kPa (40-psi) pressure.*

[b] *Tg.*

high melt strength due to their unique ionic morphology (Morris and Chen, 2003).

Caulking or flow into cavities formed by wrinkles or gussets is sometimes required. Polymer flow is characterized by its viscosity, which is a function of temperature and shear rate. Higher sealing temperatures result in more flow and caulking. However, if the temperature is too high, the sealant may be squeezed out of the seal area, resulting in poor seal performance. Heat sealing is generally a very low shear process. The zero shear viscosity at the sealing temperature is a good starting point when comparing different polymers for their ability to caulk. Melt index, a flow measure typically used in the industry, is only a crude indicator for caulking since it does not account for a polymer's viscosity as a function of temperature and shear rate.

Seal-bar pressure is another heat-seal variable we have not discussed yet. A general guideline is to use just enough pressure to get by. Some pressure is needed to ensure the film surfaces are in intimate contact for interfacial penetration to occur. Too much pressure, however, may result in squeeze-out of the sealant from the seal area.

In some packaging applications, such as potato chip pouches, an easy opening seal is desired. There are three general methods used to control the seal strength for easy-open or peel—seal performance:

- an interfacial peel—seal mechanism where the sealant is often blended with another polymer that "contaminates" the seal strength,
- a delamination peel—seal mechanism, sometimes known as a "burst" peel where adjusting the sealant layer adhesion to the adjacent layer controls the seal strength. The opening force tears through the sealant layer and the seal fails along the sealant/adjacent layer interface,
- a cohesive failure mechanism where something is blended into the polymer to ensure the failure is within the sealant layer during opening.

3.6 Adhesive Polymers

For a coextruded structure to function during manufacture, packaging, distribution, and storage over the product life cycle, there must be sufficient adhesion between the layers. Interlayer adhesion is affected by

- the structure design,
- the individual layer properties,
- the process by which it is put together,
- the manner in which it is used (Morris, 1992).

The structure design and, in particular, the individual layers' compatibility will determine whether specialized adhesive polymers or tie layers are needed (Potts, 1987). For two polymers to bond to one another, they first must come into intimate contact. In coextrusion, this is achieved as the molten polymer streams are combined in the die or feedblock. For coatings and laminations, this requires good wetting, which is a function of viscosity, polarity, and surface tension. Once good contact is achieved, molecular segments may diffuse across the interface provided

- the molecules are compatible,
- the polymers are above their glass transition or melting temperature to allow chain segment mobility,
- there is sufficient time and temperature for diffusion to occur.

As discussed above, diffusion is the primary mechanism for heat sealing a sealant to itself. Even if conditions are not favorable for diffusion, good adhesion can be obtained as a result of chemical reaction at the interface.

Table 3.7 gives some examples of the adhesion between some typical layer combinations found in coextruded packaging films. For those cases where adhesion is poor, specialized adhesive polymers or tie resins have been developed (Guillotte and Wright, 1983). Tie resins are typically a polyolefin or ethylene copolymer matrix resin, with chemical functionality and sometimes a toughener added. The matrix resin is chosen for its compatibility with one bonded layer to take advantage of the diffusion mechanism in adhesion. In Figure 3.5, PE is being adhered to PA. In this case, the matrix resin can be PE, EVA, or other ethylene copolymer that bonds to the PE layer. Chemical functionality is incorporated into the adhesive polymer via copolymerization, grafting reaction, or alloying. Some common examples of chemical functionality are given in Table 3.8. In the example in Figure 3.5, either acid or anhydride functionality is typically chosen. The acid or anhydride groups react with the PA amine end groups to achieve good adhesion. Finally, various tie resin manufacturers often blend in proprietary modifiers, such as rubber, that impact the tie resin physical properties and its peel strength performance. The most common tie resins used today are anhydride-modified polyolefins for bonding to PA and EVOH in barrier film structures.

When selecting an appropriate tie resin, several factors come into play besides the adhesion performance. The adhesive must comply with appropriate government regulations, such as Food and Drug Administration (FDA) regulations for food packaging in the United States. It must have proper flow properties for the given converting process and sufficiently match the flow properties of adjacent layers to avoid flow instabilities during coextrusion. The tie resin may also be called upon to impart other properties, such as moisture barrier, toughness, or clarity. Selecting an appropriate tie resin matrix will often accomplish this. For example, an HDPE-based tie resin will have a lower moisture vapor transmission rate (MVTR) than one based on EVA. Finally, as with any polymer, the product quality and consistency is important for achieving good performance.

Tie resin thickness in the packaging structure can influence adhesion performance, as can coating thickness in extrusion coating (Morris, 2008a). Adhesion is most often measured by pulling the structure apart in a peel strength test. Peel strength is a function of fracture energy or energy to create new surfaces as the peel front advances. At the advancing edge, the adhesive deforms, creating an energy loss that contributes to the measured fracture energy. Increasing the adhesive thickness may increase the deformation zone, thereby increasing the fracture energy. It may also increase the energy to bend the peel arm during the peel test, although this effect is small for flexible films. In theory, the fracture energy will increase with increasing thickness until a critical value is reached where the deformation zone becomes small compared to the thickness. At this point, the fracture energy plateaus (Wu, 1982). In many flexible packaging structures, the adhesive thickness is below this critical thickness so that reducing thickness reduces the peel strength performance. There are also practical limits on how low the thickness can be for a given converting process and still ensure adhesive layer

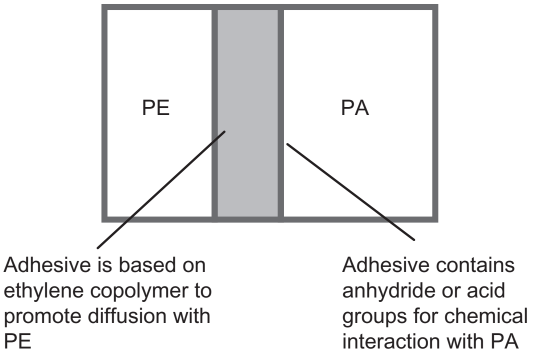


Figure 3.5 Coextrusion adhesive technology.

Table 3.7 Chart of Adhesion Between Polymers

Polymer	HDPE	PP	PS	PA	EVOH	PVDC	PC
LDPE	G	P	P	P	P	P	P
LLDPE	G	G	P	P	P	P	P
ECO	F	P	X	P	P	G	F
EVA	G	G	G	P	P	G	F
EMA	G	G	X	P	P	G	F
EAA	F	P	P	G	P	P	P
ION (Na)	P	P	P	P	P	P	P
ION (Zn)	P	P	P	G	P	P	P
PE-g-MAH	G	P	P	G	G	P	F

G = good, F = fair, P = poor, X = no data.

continuity. For most processes, 2−3 μm (0.1 mil) is the lower adhesive layer thickness limit.

How the film is fabricated can have a significant impact on adhesion. Typically, less orientation and greater contact time at higher temperatures favor adhesion. Several processing parameters are important for optimizing adhesion performance (Guillotte and Wright, 1983):

- Adhesion generally increases with increasing processing temperatures. Both diffusion and chemical interaction are favored at higher temperatures.
- Increasing melt contact time generally improves adhesion. Combination technology (feedblock or die design), the order in which layers are brought together, and die land length can affect adhesion.
- Increasing line speed generally reduces adhesion. In studying the blown film process, Morris (1996a,b) found that the peel strength of an anhydride-modified polyolefin to EVOH increased ten-fold by changing the process time, which is inversely related to line speed. He attributed this to a decrease in stress imparted during quenching. Morris (2008b,c) found similar behavior in coextrusion cast film and coextrusion coating, although the nature of the process time versus peel strength behavior suggests time for reaction may play a role. He related the differences between blown and cast film/extrusion coating back to fundamental differences in the time and temperature at which new interfacial area is created during drawing of the resin in the processes (Morris, 2008c). By scaling the process time by the characteristic relaxation time of the tie resin and the peel strength by the modulus of the tie resin, he was able to develop a single relationship that describes the effect of processing and material parameters on peel strength in both blown and cast film (Morris, 2008b).
- Orientation decreases adhesion. Increasing blow-up ratio in blown film, or increasing draw-down ratio in cast film, can reduce adhesion. Orientation processes such as double bubble processes can substantially reduce adhesion by increasing stress, reducing thickness, and creating new interfacial area (decreasing bond density).
- Thermoforming can reduce adhesion by some of the same mechanisms as orientation.

Finally, the manner in which the structure is used can impact adhesion (Morris, 1992). End-use storage conditions (temperature, RH) and the environment the package is subjected to, both physical (e.g. cook-in meats, post-packaging sterilization or pasteurization) and chemical, can alter adhesion. The product itself can contain chemical species that migrate to the interface and destroy adhesive bonds. A well-known example is the effect an acid species in orange juice and condiments has on LDPE or EAA adhesion to foil (Olafsson and Hildingsson, 1994; Olafsson et al., 1993a,b, 1995; Pieper, 1994; Schroeder et al., 1990). It is critically important to test structures under conditions that closely simulate the end use before finalizing a packaging structure.

3.7 Applications for Flexible Packaging Film Structures

Packages may be formed in-line by several techniques or may be supplied to the packer as preformed

Table 3.8 List of Commonly Used Functional Groups in Tie Resins

Functionality	Adheres to
Acid	PA, Al foil
Anhydride	PA, EVOH
VA	PVDC, PP, PET
Acrylate	Some inks, PET, PP
Epoxy	PET
Silane	Glass

pouches or bags. Packaging may be created by wrapping or shrinking a basic film around a bundle of goods. In-line packaging forming examples include VFFS, HFFS, and thermoform/fill/seal. In VFFS operations, film from a roll is guided through rollers and then shaped by a forming collar into a tube. The film moves in a vertical direction (down) over a filling tube. A vertical seal is made, forming the film into a continuous tube. As the film continues through the machine, a horizontal seal is made, perpendicular to the film machine direction, forming the bottom-end seal of the bag being formed and the top seal of the previously filled bag. The product is dropped into the partially formed bag, advanced to the seal bars, and the next bottom- and top-end seal is made. The process may operate in a step-wise or continuous manner. One example of a product normally packaged on VFFS equipment is fresh-cut produce. In HFFS operations, the film moves in a horizontal direction during the packaging step, reducing the need for high hot tack strength. One application that typically uses HFFS equipment is chunk cheese. In thermoform/fill/seal operations, a bottom web is formed, product is added, and the top web, which is normally flat, is sealed to the bottom web. Thermoform/fill/seal packaging is frequently used for bacon and processed meats. Stand-up pouches and other types of packaging may be formed in-line with the filling equipment, or may be fully or partially prefabricated prior to the filling step.

Markets for flexible packaging films have continued to grow in many applications. PE and the various copolymers account for more than 75% of the flexible packaging film. Some major market segments where coextruded film is used include the following (Keymark Associates North American Flexible Packaging Strategies, 2002):

- medical packaging
- food packaging
- heavy-duty shipping bags
- stretch wrap
- trash bags
- condiments—OPET/print/LDPE/Al/EAA/LDPE and variations
- aseptic packaging OJ—juice boxes—print/LDPE/paperboard/LDPE/Al/EMAA/LDPE and variations
- towelettes—OPET/print/LDPE/Al/ION and variations
- condoms—similar structures as towelettes
- laminates for toothpaste tubes—PE-film/(LDPE-EAA)/Al/(EAA/LDPE)/PE-film
- stand-up pouches—OPET/print/adh/m-OPP/adh/(LLDPE−HDPE−LLDPE) and variations.

3.7.1 Medical Packaging

A wide variety of structures are used in the medical packaging area (Table 3.9). The structure requirements include

- sterilization capability,
- microbial barrier,
- linear tear properties,
- puncture resistance.

Sterilization methods used for medical packaging film include ethylene oxide gas or radiation. The package is typically a forming web and a nonwoven fabric (like TYVEK®) that lets the ethylene oxide in and out of the package. Medical packaging usually does not require oxygen barrier properties, so EVOH is normally not required in medical packaging structures. Coextrusion processes are growing in this market. Blown film, cast film, and extrusion coating processes are used in producing flexible packaging structures for medical packaging applications. Films ranging from three layers to eleven layers are now available. These markets are typically small and require many years to meet the required qualifications.

The forming webs were historically three-layer EVA and ionomer films, as shown in the syringe package in Figure 3.6. Heavy gauge films were sometimes produced by combining a three-layer film to form six layers. Newer film structures have seen more layers being used and incorporating PA to replace ionomer in film structures to address economic issues.

Consumer and industrial heath care packaging includes the following:

- medical disposables
- surgical instruments—structures similar to disposables

Table 3.9 Medical Device Packaging Structures

									Layers (%)	Gauge (μm)
Three-layer structure										
EVA			ION			EVA			20|60|20	50–400
ION			EAA			EVA			30|30|40	50–400
Paper			PE			Foil			Lamination	
Five-layer structure										
LLDPE	Tie		PA		Tie		LLDPE		40|5|10|5|40	50–400
m-LLDPE	Tie		PA		Tie		m-LLDPE		40|5|10|5|40	50–400
LLDPE	Tie		PA		Tie		PA		70|5|10|5|10	50–400
LDPE	Paper		LDPE		Foil		LDPE		Lamination	
PET	Adh		LDPE		EVA		ION		Lamination	
Seven-layer structure										
LLDPE	Tie	PA	EVOH	PA	Tie		LLDPE		30|5|10|10|10|5|30	50–400
Nine-layer structure										
PE	Tie	PA	Tie	PE	Tie	PA	Tie	PE	20|5|10|5|20|5|10|5|20	50–400
LLDPE	LDPE	Tie	PA	EVOH	PA	Tie	LDPE	LLDPE	10/15/10/10/10//10/10/15/10	50–400

- resterilization packaging
- syringes and hypodermic needles
  - forming web
  - nonforming web
- sutures
- pharmaceutical
- condoms and towelettes.

Lidding stock is normally produced by extrusion coating and/or lamination processes and combines paper, polymers, and foil to form multilayer structures. Sachets for condom and towelette packaging typically use the structure OPET/print/LDPE/Al/ION and variations, with ionomers used as the sealant for its chemical flex crack resistance.

3.7.2 Food Packaging

Primal Meat Packaging (Shrink)

Packaging primal and subprimal meat requires a package that must:

- provide high shrinkage to fully collapse around irregular shapes,
- have excellent optical properties,
- shrink at low temperature to prevent product damage,
- impart good softness and elasticity,
- provide excellent oxygen, moisture, odor, and grease barrier protection,
- prevent freezer burn,
- facilitate using individual cuts by food preparers,
- help reduce purge loss,
- extend shelf life,
- offer easy disposal,
- have good machinability,
- have an oxygen transmission rate (OTR) less than 1.0 cm^3/100 in.^{2} day atm (nonfrozen only).

Figure 3.6 Multilayer film used for syringe package.

A shrinkable film used in this application is a PVDC barrier film with the sealant layer designed to provide toughness and puncture resistance. These films must be oriented to provide acceptable shrink properties using a double bubble process. Table 3.10 shows some typical film structures used in shrink film for primal and subprimal meat packaging.

Processed Meat Packaging

Processed and cook-in meat such as luncheon meat, ham, bologna and salami are packaged in barrier films that are designed to keep oxygen from entering the package. This extends shelf life and gives the retailer extended product display time. It also allows consumers to keep the product in their refrigerator, unopened, for some time after purchase. These packages are often printed with

Table 3.10 Primal and Subprimal Meat Packaging

Five-Layer Structure					Layers (%)	Gauge (μm)
ULDPE	EVA	PVDC	EVA	ULDPE	40|5|10|5|40	50–120
m-LLDPE	EVA	PVDC	EVA	m-LLDPE	40|5|10|5|40	50–120
m-LLDPE	LLDPE	Tie	EVOH	PA	30|40|10|10|10	50–120
ION	LLDPE	Tie	EVOH	PA	30|40|10|10|10	200–300
ION	EVA	LLDPE	PVDC	oriented-PA	20|30|35|5|10	50–100

Note: /PVDC/ is an adhesive lamination with PVDC.

eye-catching graphics to increase sales. These films may contain

- a barrier polymer,
- printing surface, such as polyethylene terephthalate (PET) or PA, that also provides thermal resistance during sealing and helps provide abuse resistance during distribution,
- LLDPE or ULDPE toughness layers,
- a sealant layer that could be LLDPE, a POP, or an ionomer.

The processed meat package comprises a forming film and a backing film. The forming film is thermoformed to the meat product shape. In addition, low oxygen permeability, abuse resistance, and seal integrity are critical to maintaining the proper atmosphere inside the package. Optical properties, such as high gloss and high clarity, are important on the backing film where reverse-printed PET is used to create consumer appeal. Barrier requirements for processed meats range from 0.2 to 1.0 $cm^3/100\ in.^2$ day atm for OTR and 0.2−0.5 $g/100\ in.^2$ day for water vapor transmission rates (WVTR). Table 3.11 shows some typical film structures used in processed meat packaging.

Poultry/Fish Packaging

Moisture barrier properties are more critical. The packages are normally vacuum packaged (Figure 3.7) with a good sealant polymer such as EVA, ionomer, or LLDPE (Table 3.12).

Cereal Box Liners

Cereal box liners (Figure 3.8) also require good moisture barrier properties to provide good taste and freshness protection. HDPE polymers are typically used to provide a moisture barrier. Sealant polymers such as EVA, ionomer, POP, or blends are used for low-temperature seals, form-fill-seal packaging, and easy opening seals. Certain products have additional requirements, such as puncture resistance to keep the product from poking through the packaging film, and flavor and aroma barrier for highly flavored cereals. Heat-seal-initiation temperatures of 90°C and below are commonly required. MVTRs less than or equal to 0.1 $g/100\ in.^2$ day atm are often required. Packages requiring aroma or taste barrier properties will contain either PA or EVOH polymers. (Table 3.13).

Snack Food Packaging

Potato chips are often packaged in structures that contain metalized films (Table 3.14). Polymer film metallization provides an oxygen barrier, moisture barrier, and light barrier. The light barrier is to protect the potato chips from ultraviolet radiation that initializes an oxidation mechanism. Seal strength must be optimized to provide a secure package that can be easily opened by the consumer. Seal integrity and consumer appeal are also critical.

Salty Snack Packaging

Salty snacks are frequently high in fat content and may require a package that provides an oxygen barrier in order to prevent the fat in the food from going rancid. They may also require grease resistance to keep the package from leaving an oily spot. Salty snacks may be packaged in barrier films containing foil, a metalized polymer film, or a barrier polymer such as EVOH or PVDC and are gas flushed with nitrogen to maintain a low oxygen concentration inside the package (Table 3.15).

Bakery

Moisture barrier is normally the critical property in bakery applications. Polymers used for moisture barrier include LDPE, LLDPE, HDPE, or PP. Typically, EVA polymers are used for sealability and optics. Applications, such as the cake mix pouch, will require aroma, taste, and moisture barrier properties. PA is used for taste and aroma barrier. In bread bags, the LLDPE polymer's toughness allows down gauging, while LDPE allows good optics and printability (Table 3.16).

Cheese Packaging

Most cheese sold in the United States is prepackaged in flexible packaging. The cheese packaging includes

- individually wrapped slices (IWS) of processed cheese,
- chunk cheese,
- shredded cheese.

Table 3.11 Processed Meat Packaging Film Structures

Product Structure	**Layers (%)**	**Gauge (μm)**
Ground beef		
LLDPE/Tie/PA	(75/5/20)	150–200
LLDPE/Tie/EVOH/PA	(75/5/10/10)	150–200
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	40–150
Barrier overwrap		
m-LLDPE/LLDPE/Tie/EVOH	(30/40/10/10/10)	150–200
m-LLDPE/LDPE/LDPE/Tie/PA/EVOH/PA	(20/15/15/10/15/10/15)	150–200
Chub films		
LLDPE/PVDC//PA	(75//5//20)	150–200
Foodservice portion: steaks/chops/roasts		
Forming web		
LLDPE/Tie/EVOH/PA	(75/5/5/15)	150–200
ION/Tie/EVOH/PA	(75/5/5/15)	150–200
LLDPE/Tie/PA	(75/5/20)	150–200
ION/PA	(80/20)	150–200
ION/EVA//PVDC/PA	(60/10//5/25)	150–200
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	150–200
Nonforming web		
LLDPE/Tie/EVOH/PA	(70/10/10/10)	50–80
ION/Tie/EVOH/PA	(70/10/10/10)	50–80
LLDPE//PVDC//o-PET	(85//5//10)	50–80
ION//PVDC//o-PET	(85//5//10)	50–80
ION/Tie/PA	(80/10/10)	50–80
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	50–80
Skin packaging forming web		
ION/Tie/EVOH//Tie/EVA	(35/10/10//10/35)	150–250
Skin packaging nonforming web		
ION/Tie/EVOH//Tie/EVA	(35/10/10//10/35)	50–80
Luncheon meat		
Forming web		
LLDPE/Tie/EVOH/PA	(75/5/5/15)	150–200
ION/Tie/EVOH/PA	(75/5/5/15)	150–200
m-LLDPE/Tie/EVOH/PA	(75/5/5/15)	150–200
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	150–200
Nonforming web		
LLDPE/EVA/PVDC//o-PET	(60/10/5//25)	50–100
m-LLDPE/Tie/EVOH//o-PET	(60/10/5//25)	50–100

(*Continued*)

Table 3.11 (Continued)

Product Structure	**Layers (%)**	**Gauge (μm)**
ION/Tie/EVOH//o-PET	(60/10/5//25)	50–100
LLDPE/Tie/EVOH/PA	(60/10/5/25)	50–100
LLDPE//PVDC//o-PA	(60/10//5//25)	50–100
LLDPE/Tie/PA/EVOH/PA	(60/10/10/10/10)	50–100
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	50–100
Frankfurters		
Forming web		
LLDPE/Tie/EVOH/PA	(75/5/5/15)	150–200
m-LLDPE/EVOH/PA	(75/5/5/15)	150–200
ION/EVOH/PA	(75/5/5/15)	150–200
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	150–200
ION/Tie/PA/EVOH/PA/Tie/PA	(15/20/10/5/10/25/15)	150–200
LLDPE/Tie/PA/EVOH/PA/Tie/PA	(20/15/10/5/10/25/15)	150–200
ION/Tie/PA/EVOH/PA/Tie/PP	(15/20/10/5/10/25/15)	150–200
Nonforming web		
LLDPE-EVA//PVDC//o-PA	(60/25//5//10)	50–100
m-LLDPE/Tie/EVOH/o-PET	(60/15/10/15)	50–100
ION//PVDC//o-PET	(85//5//10)	50–100
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	50–100
ION/PE/o-PET	(25/50/25)	50–100
ION/Tie/EVOH/Tie/PE/o-PET	(15/10/10/10/40/15)	50–100
Sausage		
Forming web		
LLDPE/LDPE/Tie/EVOH/PA/Tie/EVA	(30/5/10/10/10/5/30)	150–200
m-LLDPE/Tie/EVOH/PA	(75/5/5/15)	150–200
ION/Tie/EVOH/PA	(75/5/5/15)	150–200
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	150–200
ION/Tie/PA/EVOH/PA/Tie/PA	(15/20/10/5/10/25/15)	150–200
LLDPE/Tie/PA/EVOH/PA/Tie/PA	(20/15/10/5/10/25/15)	150–200
ION/Tie/PA/EVOH/PA/Tie/PP	(15/20/10/5/10/25/15)	150–200
LLDPE/Tie/EVOH//o-PET	(60/15/10//15)	50–100
m-LLDPE/Tie/EVOH/PA	(60/15/10/15)	50–100
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	50–100
Shrink bags		
EVA/EVOH/EVA	(48/5/47)	50–80
EVA/PVDC/EVA	(48/5/47)	50–80

(*Continued*)

Table 3.11 (Continued)

Product Structure	Layers (%)	Gauge (μm)
Ham		
Forming web		
LLDPE/Tie/EVOH/PA	(60/15/10/15)	150–200
ION/Tie/EVOH/PA	(60/15/10/15)	150–200
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	50–100
Nonforming web		
LLDPE//PVDC//PA	(70//5//25)	50–80
ION//PVDC//PA	(70//5//25)	50–80
LLDPE//PVDC//o-PET	(70//5//25)	50–80
ION//PVDC//o-PET	(70//5//25)	50–80
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	50–100
Shrink bags		
EVA/EVOH/EVA	(48/5/47)	50–80
EVA/PVDC/EVA	(48/5/47)	50–80
m-LLDPE/Tie/EVOH/Tie/m-LLDPE	(30/10/10/10/30)	50–80
Bacon		
ION/Tie/EVOH/PA	(50/10/10/30)	50–100
ION/PE/PA	(15/50/35)	50–100
ION/Tie/PA/EVOH/PA/Tie/PA	(20/20/10/5/10/20/15)	50–100
Deli meats		
Shrink bags		
EVA/EVOH/EVA	(48/5/47)	50–80
EVA/PVDC/EVA	(48/5/47)	50–80
m-LLDPE/Tie/EVOH/Tie/m-LLDPE	(30/10/10/10/30)	50–80
Forming web		
LLDPE/Tie/EVOH/PA	(80/5/5/10)	200–250
ION/Tie/EVOH/PA	(80/5/5/10)	200–250
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	50–100
Nonforming web		
LLDPE//Tie/PA/EVOH/EVA	(40//10/10/20/30)	50–80
ION/Tie/EVOH/PA	(60/15/10/15)	50–80
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	(25/10/10/10/10/10/25)	50–100
Casings		
LLDPE//o-PA	(70//30)	50–80
LLDPE//o-PA//PVDC	(70//20//10)	50–80

Both chunk cheese and shredded cheese require substantial oxygen barrier to prevent mold growth and spoilage. EVOH, PVDC, or PVOH (poly vinyl alcohol) may provide the oxygen barrier. While EVOH is generally coextruded into the film structure, PVDC or PVOH may be coated on a film via a coating process. Cheese packaging also requires excellent seal integrity and abuse resistance to prevent the controlled atmosphere inside the package from being lost. Cheese packages are often laminations made with reverse-printed outer webs containing PET or PA for superior graphical presentation. They may also be extrusion coated structures where the sealant layer has been extrusion coated onto the outer layer. Sealant layers may consist of EVA, an ionomer, or a POP. Low heat seal-initiation temperature (90°C or below) and good seal-through-contamination performance are required. Processed cheese typically requires films with an OTR of 0.6–1.0 $\mathrm{cm}^3/100\ \mathrm{in.}^2$ day atm and WVTR of 1.0 g/100 $\mathrm{in.}^2$ day (Table 3.17).

An acrylic, PVOH-coated, OPP film is also used in cheese packaging in both extrusion and adhesive laminations. It is an ExxonMobil product called Bicor AOH. Acrylic is coated on one side and PVOH on the other side.

Milk Pouches

LLDPE or LDPE/LLDPE blends provide the sealant in both milk powder and liquid pouches (Table 3.18). If oxygen barrier is required for long shelf life, then PA could be used.

Frozen Food

Frozen foods (Figure 3.9) are packaged in a variety of packaging types. Examples of frozen foods packaged in flexible packaging include

- frozen fruits,
- vegetables,
- French fries,
- individually quick frozen chicken breasts.

Many frozen foods are packaged in surface-printed PE films. Some higher value-added items are packaged in laminations, which may be shaped into stand-up pouches. Most frozen food bags are made on standard VFFS machinery.

Key requirements for frozen food packaging are

- low-temperature toughness,
- modulus,
- high hot tack strength,
- high-seal strength.

Figure 3.7 Poultry packaging.

Figure 3.8 Cereal boxes.

Table 3.12 Poultry/Fish Packaging

Seven-Layer Structure	Layers (%)	Gauge (μm)
LLDPE/Tie/PA/EVOH/PA/Tie/LLDPE	25|10|10|10|10|10|25	40–150
LLDPE/Tie/PA/EVOH/PA/Tie/Ion	25|10|10|10|10|10|25	40–150

Some packages are clear and require good clarity, while others are pigmented and require good gloss. LLDPE, ULDPE, EVA, and POP resins are all commonly used in creating frozen food packaging. Stiffness must be adequate for high-speed packaging, and packaging films must have tear and puncture strength high enough to prevent package damage during transportation and storage

Table 3.13 Cereal Packaging

Market Structure	**Layers (%)**			**Gauge (μm)**
Bag-in-box				
HDPE/HDPE/EVA	45	|45	|10	40–60
HDPE/HDPE/ION	45	|45	|10	40–60
Bag-in-box (peelable seal)				
HDPE/HDPE/EVA + ION	45	|45	|10	40–60
Bag-in-box (barrier bag)				
HDPE/Tie/EVOH/Tie/EVA	60	|10|10|10	|10	40–60
HDPE/Tie/PA/Tie/EVA	60	|10|10|10	|10	40–60

Table 3.14 Snack Food Packaging Films

Structure	**Layers (%)**			**Gauge (μm)**
Potato chips (OTR 2.0, MVTR 0.02)				
o-PP//met o-PP	50	||	50	20–60
o-PP//LDPE//met o-PP	25||	50	||25	20–60
EVA/HDPE//met o-PP	15|	70	||15	40–80
Tortilla and corn chips (OTR <2.0, MVTR <0.35)				
o-PP//LDPE//o-PP	25||	50	||25	20–60
o-PP//PVDC//o-PP	50	//p/5||	45	20–60
Pretzels (OTR <2.0, MVTR <0.5)				
o-PP//LDPE//o-PET	25||	50	||25	30–80
o-PP//LDPE//o-PP	25||	50	||25	30–80
o-PP//PVDC//o-PP	45	||5||	50	30–60
Meat snacks				
LDPE//PVDC//o-PET	45	||5||	50	30–60
LLDPE/Tie/EVOH/PA	60	|10|10|10|10		40–80

p, primer.

Table 3.15 Snack Nuts Packaging

Structure	**Layers (%)**	**Gauge (μm)**
o-PP//LDPE//o-PP	20||60||20	40–60
o-PP//LDPE//Foil//LDPE	10||20||5||65	40–60

(Table 3.19). Stand-up pouches and self-venting (microwave) technologies are also used for frozen food packaging these days.

Fresh-Cut Produce

Key performance requirements for fresh-cut produce packaging include proper oxygen and carbon dioxide permeability, seal integrity, machinability, and consumer appeal. Consumer appeal includes both feel and appearance. Feel is generally determined by film thickness and modulus while appearance is governed by print quality and film optical properties, such as clarity, haze, and gloss. In order to extend the shelf life of the produce being packaged, films must provide the proper oxygen

Table 3.16 Bakery Packaging

<table>
<tr><th>Structure</th><th>Layers (%)</th><th>Gauge (μm)</th></tr>
<tr><td>cPP/PP/cPP</td><td>10|80|10</td><td>30–60</td></tr>
<tr><td>EVA/PP</td><td>20|80</td><td>30–60</td></tr>
<tr><td>HDPE/EAA/PA/EAA</td><td>70|10|10|10</td><td>30–70</td></tr>
<tr><td>LLDPE/PP/LLDPE</td><td>10|80|10</td><td>30–60</td></tr>
<tr><td>LLDPE/Tie/PA/EVOH/PA</td><td>30|10|20|10|20</td><td>100–160</td></tr>
</table>

Table 3.17 Cheese Packaging

<table>
<tr><th>Structure</th><th colspan="2">Layers (%)</th><th>Gauge (μm)</th></tr>
<tr><td colspan="4">Natural chuck cheese pouches</td></tr>
<tr><td>LLDPE/Tie/EVOH//o-PET</td><td>75</td><td>|10||15</td><td>40–60</td></tr>
<tr><td>LLDPE//PVDC//o-PP</td><td>75</td><td>|10||15</td><td>50–60</td></tr>
<tr><td>LLDPE//PVDC//o-PET</td><td>75</td><td>|10||15</td><td>45–50</td></tr>
<tr><td>EVA//PVDC</td><td>95</td><td>||5</td><td>50–60</td></tr>
<tr><td>LLDPE//PVDC//o-PA</td><td>75</td><td>|10||15</td><td>45–50</td></tr>
<tr><td colspan="4">Vacuum bags for aging</td></tr>
<tr><td>EVA//PVDC//o-PA</td><td>85</td><td>||5||10</td><td>40–100</td></tr>
<tr><td>LLDPE/Tie/PA</td><td>80</td><td>|10|10</td><td>40–100</td></tr>
<tr><td>EVA/Tie/PA</td><td>80</td><td>|10|10</td><td>40–100</td></tr>
<tr><td colspan="4">Shredded cheese</td></tr>
<tr><td>PVDC//PA//LDPE</td><td>5||20||</td><td>75</td><td>80–100</td></tr>
<tr><td>PVDC//PET//LDPE</td><td>5||20||</td><td>75</td><td>80–100</td></tr>
<tr><td>PA/EVOH/Tie/LDPE</td><td>10|10|10|</td><td>70</td><td>80–100</td></tr>
<tr><td colspan="4">Processed cheese slices</td></tr>
<tr><td>o-PP//EVA</td><td>50||</td><td>50</td><td>20</td></tr>
<tr><td>PP/EVA</td><td>20|</td><td>80</td><td>35–40</td></tr>
</table>

Table 3.18 Milk Packaging

<table>
<tr><th>Structure</th><th>Layers (%)</th><th>Gauge (μm)</th></tr>
<tr><td>LLDPE/Tie/PA/Tie/LLDPE</td><td>35|10|10|10|35</td><td>40–70</td></tr>
<tr><td>HDPE/(LDPE + LLDPE)</td><td>40|60</td><td>40–80</td></tr>
</table>

permeability that is matched to the packed produce respiration rate. Cut produce respires after harvesting, consuming oxygen and giving off carbon dioxide. By controlling the permeation of gases through the package, the environment inside the package is controlled, respiration is slowed, and shelf life is extended. The bags must have complete seal integrity in order to prevent the unplanned transfer of gases between the bags and the environment. Bags may contain PP, LLDPE, ULDPE, EVA, or POP. OTR requirements vary widely depending on the produce being packaged, but common items range from about 100 $\text{cm}^3/100\ \text{in.}^2$ day atm for Caesar salad mixes, 150–200 $\text{cm}^3/100\ \text{in.}^2$ day atm for iceberg salad mixes, and 200–350 $\text{cm}^3/100\ \text{in.}^2$ day atm for specialty salad mixes such as baby greens and exotic lettuces. Perforation may be used to obtain high transmission rates for some applications.

Retortable Pouches

A growing flexible packaging is in the replacement of metal cans with retortable pouches. These pouches are typically laminations containing biaxially oriented PA for toughness, foil for oxygen barrier, and a PP sealant film. These pouches may contain items like tuna, pet food, and soup. The food items are held at elevated temperature after packaging, so the packages must remain intact at elevated temperatures. In addition to temperature resistance, toughness, seal strength, and barrier properties are critically important.

Figure 3.9 Frozen food packaging.

Edible Oil Packaging

The packaging of cooking oil uses PA to provide oxygen barrier properties. Ethylene acrylic acid is typically used as the sealant layer. The seal type determines the PA layer location (Table 3.20).

Bag-in-Box

Coextruded films containing oxygen barrier polymers are replacing some metalizing laminates where flex crack resistance is required. LLDPE or EVA polymers are used as sealants (Table 3.21).

Stretch Wrap

Stretch film, or stretch/cling film, is used to unitize goods for transportation. A thin film is stretched, either by machine or by hand, and wrapped around packages to hold the goods together. The film clings to itself and to the pallet, securing the load. In its most common form, stretch/cling film is applied to a stacked pallet using a power pre-stretch pallet wrapper in an automated operation (Figure 3.10). In this operation, the film is stretched, between 100% and 300%, by rollers turning at different speeds and is then applied to a loaded pallet that sits atop a moving turntable. Machine wrap film is typically supplied on rolls that are 20- or 30-in. (51- or 76-cm) wide. Hand wrap film is supplied on smaller rolls. Stretch/cling films may be manufactured by either a cast film or blown film process. Most stretch/cling films are

Table 3.19 Frozen Food Packaging

Structure	Layers (%)			Gauge (μm)
EVA/LLDPE/EVA	15|	70	|15	40–80
PET//Tie//LDPE/ION	15||5||	40|	40	40–80
m-LLDPE/LLDPE/m-LLDPE	15|	70	|15	40–80
HDPE/MDPE/EVA	15|	70	|15	40–80

coextruded structures containing three to seven layers. Most cast film lines are now being installed with five-layer capability, and blown film coextruded films are typically three layers. LLDPE is the primary component of most stretch films. For specialized applications, coextrusions containing minor PP, EVA, POP, m-LLDPE, EPE, or ULDPE layers may be employed (Table 3.22). For most stretch film structures, a resin with good inherent cling is used on either one or both surface layers. A tackifier, such as poly-isobutylene, can also be added to the structure to provide the desired cling force. Stretch film is used to unitize entire or partial pallets stacked with products such as resin bags, fertilizer bags, consumer goods, and food products during distribution. Most stretch film is removed by the retailer prior to displaying the packaged items for sale. Stretch films must have the following:

- good cling
- stretchability
- load retention
- puncture resistance.

Heavy-Duty Bags (Shipping Bags)

Heavy-duty shipping sacks are used to transport items such as the following:

- resin
- salt
- pet food
- fertilizer
- chemicals
- topsoil
- bark mulch
- compressed bales of fiberglass insulation.

When filled they weigh 40 pounds (18 kg) or more. Heavy-duty shipping sacks may be supplied as preformed bags or as roll stock, which is formed into bags in a continuous VFFS operation. Special machinery is required to form heavy-duty shipping sacks on VFFS machinery in a high-speed continuous operation. These bags need moderate coefficient of friction (COF) because they must easily pass through the packaging equipment, but stacked bags must not slide off each other. Bags filled with

Figure 3.10 Rotary pallet stretch cling wrapper.

Table 3.20 Edible Oil Packaging

Structure	Layers (%)	Gauge (μm)
PA/Tie/EAA	10|15|75	50–150
EAA/Tie/PA/Tie/EAA	30|10|10|10|35	50–150
EAA/PA/EAA	40|20|40	50–150

Table 3.21 Bag-in-Box

Structure	Layers (%)	Gauge (μm)
LLDPE/Tie/PA/Tie/LLDPE	35|10|10|10|35	40–80
EVA/Tie/PA/Tie/EVA	35|10|10|10|35	40–80
LLDPE/Tie/EVOH/Tie/LLDPE	35|10|10|10|35	40–80

hot products, such as salt, must also withstand the filling temperatures without excessive stretching or dimpling. Film toughness and creep resistance are also important in many heavy-duty shipping sack applications. LLDPE has allowed significant gauge reduction. LDPE is used to reduce creep and improve processability. HDPE and PP are used for stiffness and higher end-use temperature resistance. EVA polymers are used for low-temperature sealability in form-fill-seal applications (Table 3.23).

Trash Bags

LLDPE introduction is accelerated using coextrusion in trash (or refuse) bags (Table 3.24). Down gauging and using recycled material allows for improved economics and addresses environmental concerns. High-molecular weight HDPE polymers are also finding increased usage due to further down-gauging opportunities. This is the largest coextruded film market segment.

Grocery Sacks (Merchandize Bags)

High-molecular weight HDPE coextruded with LLDPE provides improved sealability with good down-gauging potential (Table 3.25). This film is typically made on high-stalk HDPE blown film coextrusion lines.

High-Clarity Shrink Film (Oriented)

Oriented, high-clarity shrink film is used to protect and display high-value consumer goods. It is distinguished from regular shrink film by its superior clarity and appearance as well as increased shrinkage properties and higher stiffness. Goods are packaged by wrapping the film loosely around the goods, sealing the film to make a completely enclosed bag, and then shrinking the film in a shrink tunnel or oven. Small holes may be poked in the film before wrapping to allow air to escape while the film is shrinking. As in industrial shrink film, heat causes the polymer molecules to relax, causing the film to return to its original unoriented size and shrink tightly around the packaged goods. Since the polymer molecules in oriented shrink film are much more highly oriented, greater shrinkage may be obtained. Boxed software and stationery products are often wrapped with high-clarity shrink film. Ice-cream cartons and other food products are also wrapped in high-clarity shrink film. Optical properties, seal properties, shrinkage, and holding force are key requirements for oriented

Table 3.22 Stretch Cling Pallet Wrap

Structure	**Layers (%)**			**Gauge (μm)**
Stretch cling film				
EVA/ULDPE/LLDPE	10|	80	|10	15–30
ULDPE/LLDPE/ULDPE	10|	80	|10	15–30
ULDPE/LLDPE/m-LLDPE/LLDPE/ULDPE	10|25|30|25|10			15–30
One-side cling film				
m-LLDPE/LLDPE/LMDPE	10|	80	|10	15–30
EMA/LLDPE/PP	10|	80	|10	15–30
POP/LLDPE/PP	10|	80	|10	15–30
ULDPE/LLDPE/LLDPE/e-LLDPE/PP	10|20|30|30|10			10–30

Table 3.23 Heavy-Duty Bags

Structure	**Layers (%)**	**Gauge (μm)**
LLDPE/EPE/LLDPE + LDPE	20|60|20	100–200
EPE/PP/EPE	20|60|20	100–200

shrink film. These structures are normally biaxially oriented films of LLDPE and PP (Table 3.26).

3.8 Summary

It is critical for the flexible packaging film producers to understand their market. Even within a given market segment, there are usually several film structures that are used. The film producers must evaluate the alternative film structures to determine the best fit for the market identified and for their production capabilities. Market trends should be analyzed to determine strategy. The market studies will dictate which coextrusion/lamination equipment design will be optimum. Economic evaluation of each market should include the cost incurred in scrap recycle (or disposal). The average production run size and the polymer changes will determine the off-spec film produced. A new consideration for today's marketplace may also include some thoughts into after-use disposal of the multilayer film. The design and testing of multilayer film, particularly in the barrier films, will require more manpower and overhead costs than typical monolayer film.

The markets identified for multilayer flexible packaging should value higher performance properties and high-value films. In addition to performance properties, some markets may have other barriers to entry such as qualification cost, experience in the market, or lack of business relationships. These considerations must be evaluated. The multilayer coextrusion line design requires knowledge of the specific structures and polymers to be produced. It is recommended that mutual discussions with the equipment supplier and polymer suppliers be made to insure that proper consideration is given to all critical aspects.

New applications continue to be developed for multilayer films, and film structures continue to evolve as new market drivers come into play. The structures highlighted in this chapter are intended only as examples and may not represent where packaging is headed in the future. For example, sustainability has recently garnered attention in the marketplace. For packaging, this may mean a number of things, such as down gauging to reduce the carbon footprint or the use of new biosourced or biodegradable polymers. No matter what the market driver, the principles developed in this chapter remain true. Combining high-performance polymers and low-cost polymers will expand market opportunities. Understanding how to combine easily the properties of new polymers and knowledge of the market needs and trends will lead to development of more coextrusion applications.

Table 3.27 gives a list of conversion factors.

Table 3.24 Trash Bag Coextrusion Structures

Structure	Layers (%)	Gauge (μm)
LLDPE/LLDPE	50|50	15–70
LLDPE/RECYCLE/LLDPE	33|34|33	15–70
LLDPE/HMW–HDPE/LLDPE	10|80|10	15–25

Table 3.25 Grocery Bags

Structure	Layers (%)	Gauge (μm)
LLDPE/HMW–HDPE/LLDPE	10|80|10	12–20

Table 3.26 High-Clarity Shrink Film

Structure	Layers (%)	Gauge (μm)
PP/LLDPE/PP	25|50|25	15–25

Table 3.27 Conversion Factors

Property	To Convert from:	To:	Multiply by:
Density	g/cm^3	lb/ft^3	62.43
Pressure	lb/in.^{2}	MPa	0.00689
Output	lb/h	kg/h	0.45359
Output	lb/h	g/s	0.125997
Length	in.	mm	25.4
Specific output	lb/h/in.-c	kg/h/mm-c	0.017858
Specific output	lb/h/in.-c	kg/h/mm-d	0.05622
Viscosity	poise	Pa-s	0.1
Viscosity	poise	lb-s/in.^{2}	1.45E-05
Stress	lb/in.^{2}	kPa	6.8947
Stress	lb/in.^{2}	dynes/cm^2	68947
MVTR	g × mil/100 in.^{2}/day	g × mm/m^2/day	0.394
Permeability	cm^3 × mil/100 in.^{2}/day/atm	cm^3 × mm/mm^2/s/atm	4.56E-12
Permeability	cm^3 × mil/100 in.^{2}/day/atm	cm^3 × mil/m^2/day/atm	15.5
Weight	lb	kg	0.4536
Peel or seal strength	lb/in.	g/in.	454
Peel or seal strength	g/in.	N/15 mm	0.0058

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4 Biaxially Oriented Films for Packaging Applications

Jürgen Breil
Brückner Maschinenbeau GmbH & Co. KG/Germany

4.1 Introduction

Oriented plastic films for packaging applications are industrially produced in large quantities. As such, the majority are biaxially oriented, which means that stretching is applied in both directions in order to improve the film characteristics in the machine direction as well as in the transverse direction (Briston and Katan, 1989). These characteristics ideally meet the demands on modern flexible packaging. As illustrated in Figure 4.1, flexible packaging has to fulfill a protective function and allow product design in line with economic and, increasingly, environmental aspects. The required packaging product protection is attained by the excellent barrier properties against gases (water vapor, oxygen, and others) as well as good quality seals. The required product appearance is attained by high-gloss and transparent thin packaging film as well as by excellent printability. The requirements for sought-after economic packaging are met by good material utilization and the fulfillment of the demand for high-speed packaging lines. Environmental aspects, which play an ever-increasing role, can be satisfied by utilizing environmentally friendly materials (such as polyolefin), as well as the optimum raw material yield, thus ensuring maximum packaging effect with minimum material cost.

The extent to which biaxial orientation improves properties is shown in Figure 4.2 using biaxially oriented polypropylene (BOPP) in comparison to nonoriented cast polypropylene (CPP) as an example. Along with a significant increase in the mechanical properties (Young's modulus, tensile strength), a considerable improvement in the optical (haze, gloss) as well as the barrier properties can be observed. The overall improved barrier properties attained are due to the orientation of the molecule chains which, for a nonoriented polymer, are random, whereas in the stretching process, a clear molecule-chain orientation occurs. As such, biaxial orientation of plastic films represents a refinement process which is applicable for almost all plastics. Semicrystalline plastics in particular, such as polypropylene (PP) and polyester, also have their crystallinity augmented by the stretching process, which considerably improves the mechanical strength.

A similar improvement in properties as a result of the biaxial orientation process is also observed for many other polymers (polyethylene terephthalate (PET), polyamide (PA), polystyrene (PS), etc.). The exceptional mechanical properties in combination with the barrier and optical properties and comparably low raw material costs have led to the fact that BOPP, biaxially oriented polyethylene terephthalate (BOPET), and biaxially oriented polyamide (BOPA) films account for the largest and most significant share among stretched films, which have a large share in packaging applications.

4.2 Orienting Technologies

In orienting technologies, one can, in general, differentiate between the orientation draw direction and the related stretching process. The existing stretching processes (longitudinal and transverse stretching, sequential-biaxial stretching, and simultaneous-biaxial stretching) do not depict competitive, but rather supplementary, features used to attain specific film characteristics. As such, the required stretching equipment varies depending on the process. Stretching in the machine direction is normally done by means of a machine direction orienter (MDO) via rolls with increasing speeds. Typical products are, for example, tear strips or PP adhesive tapes. For all transverse-oriented films, the stretching process takes place by means of a transverse direction orienter (TDO), where the film is fixed on both ends and, upon passing through an oven at various temperatures, is stretched in a transverse direction. Typical examples of transverse stretched film types are shrink sleeves, where shrinkage merely occurs in the transverse direction. Biaxial

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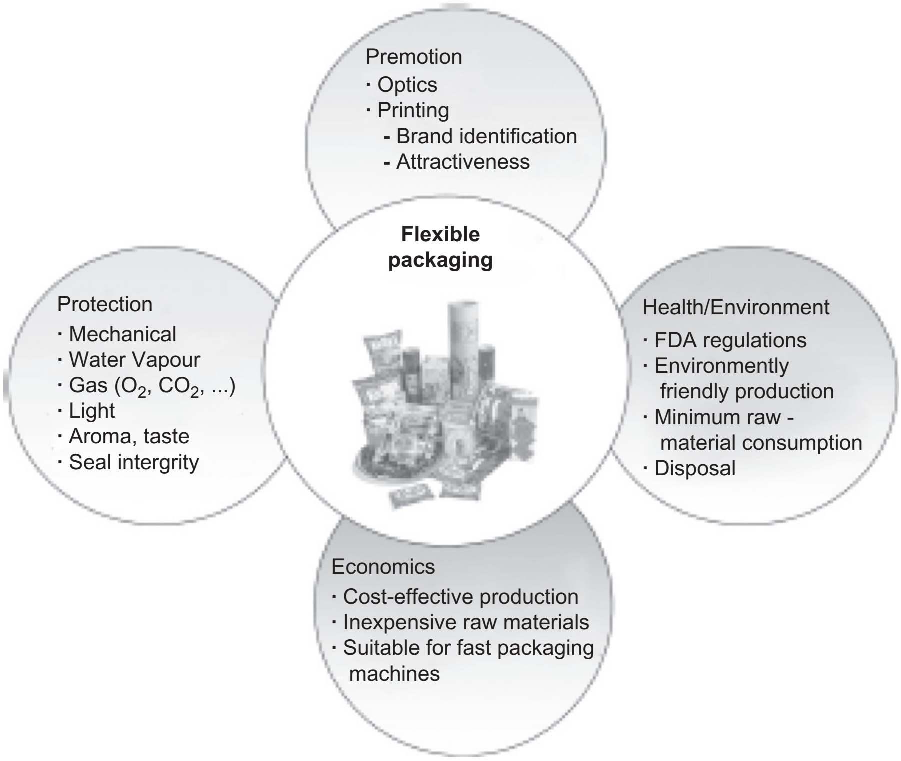


Figure 4.1 Flexible packaging requirements for protection, promotion, health/environment and economics.

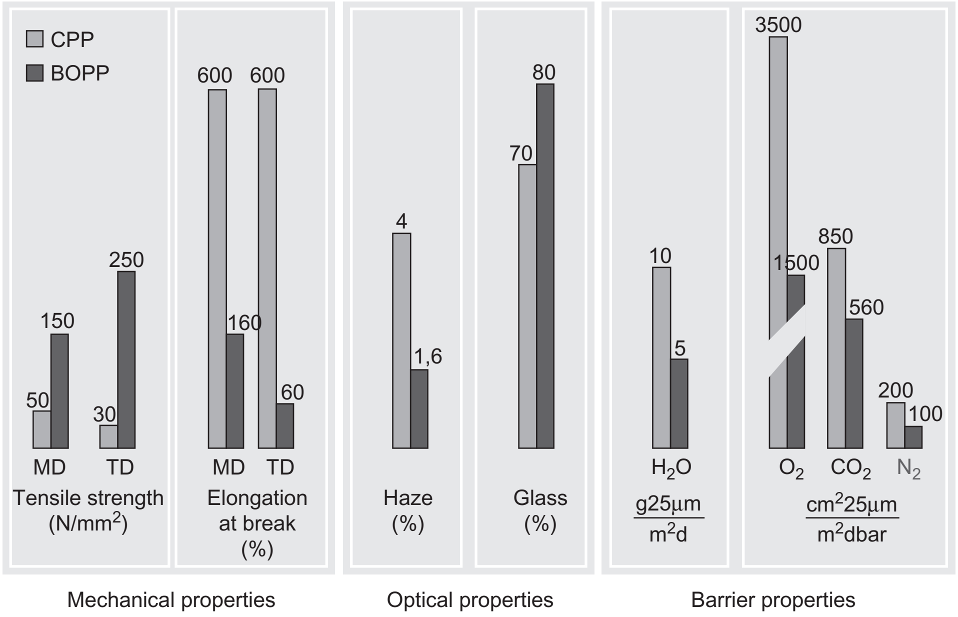


Figure 4.2 Property improvement for biaxially stretched PP (BOPP) versus cast PP (CPP).

orientation, in the machine and transverse directions, can be done either sequentially or simultaneously. In the sequential process, an MDO and a tenter frame are utilized successively (Hansen et al., 1989; Tobita et al., 1999). This process has the widest prevalence for all stretched film types. All types of packaging films, tapes, labels, and industrial films are manufactured with this process. Simultaneous orientation is possible with the tenter and the blown process (Figure 4.3). The blown process is a so-called double- or triple-bubble technology where, initially, a tube is extruded, then rapidly cooled, and then heated to the stretching

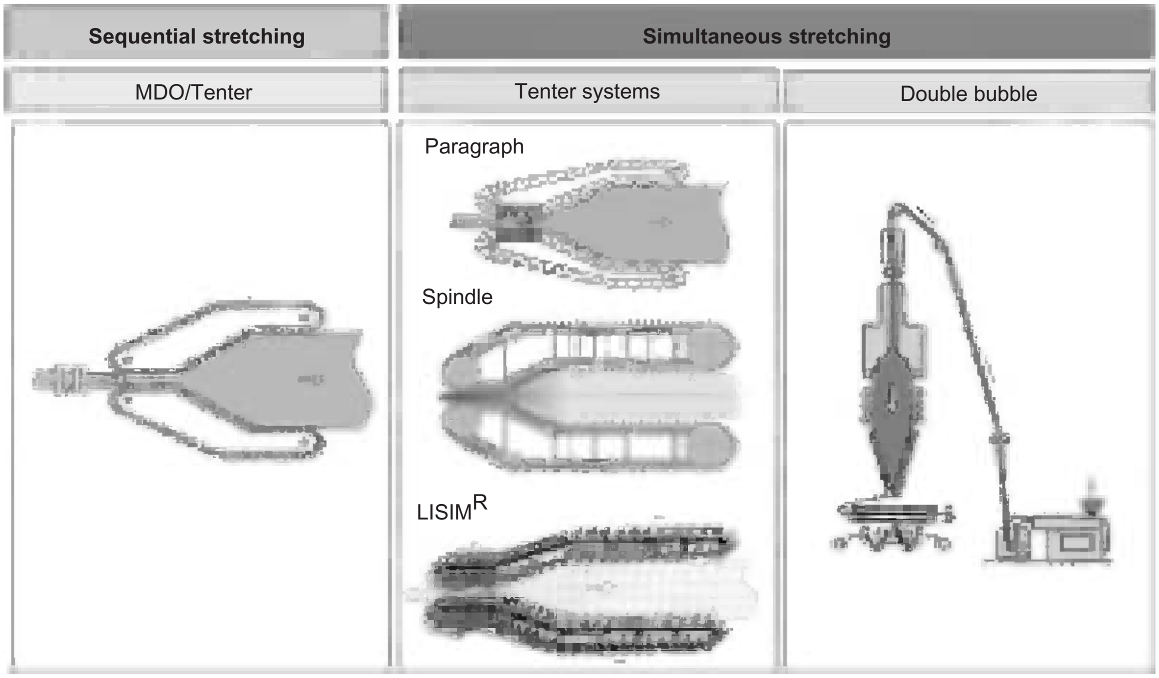


Figure 4.3 Biaxial orientation technologies.

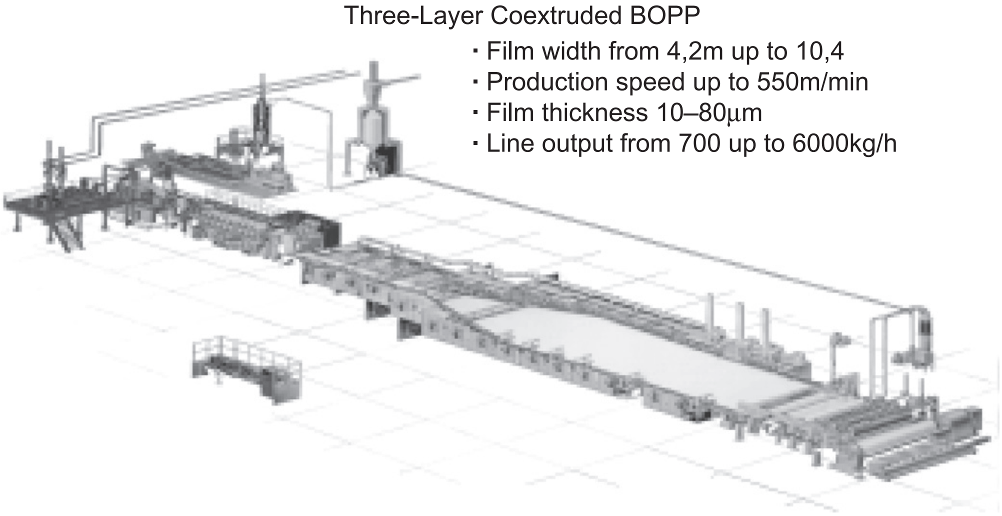


Figure 4.4 Sequential-biaxial stretching line.

temperature. A synchronous increase of the draw-off speed and bubble expansion by internal pressure results in the required simultaneous orientation process.

Sequential stretching first in the machine direction and then in the transverse direction utilizing an MDO and a TDO is the most prevalent process in use today. Figure 4.4 is a cut-away view of a three-layer coextruded BOPP line that shows the main extruder, two coextruders, die and casting station, MDO, TDO, gauging station, treatment, and full width winder. Figure 4.5 shows a finished

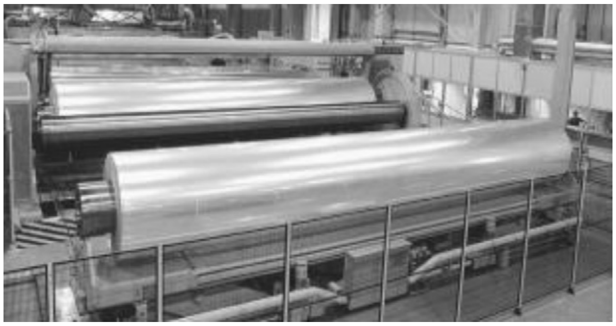


Figure 4.5 Finished 10 m BOPP mill roll.

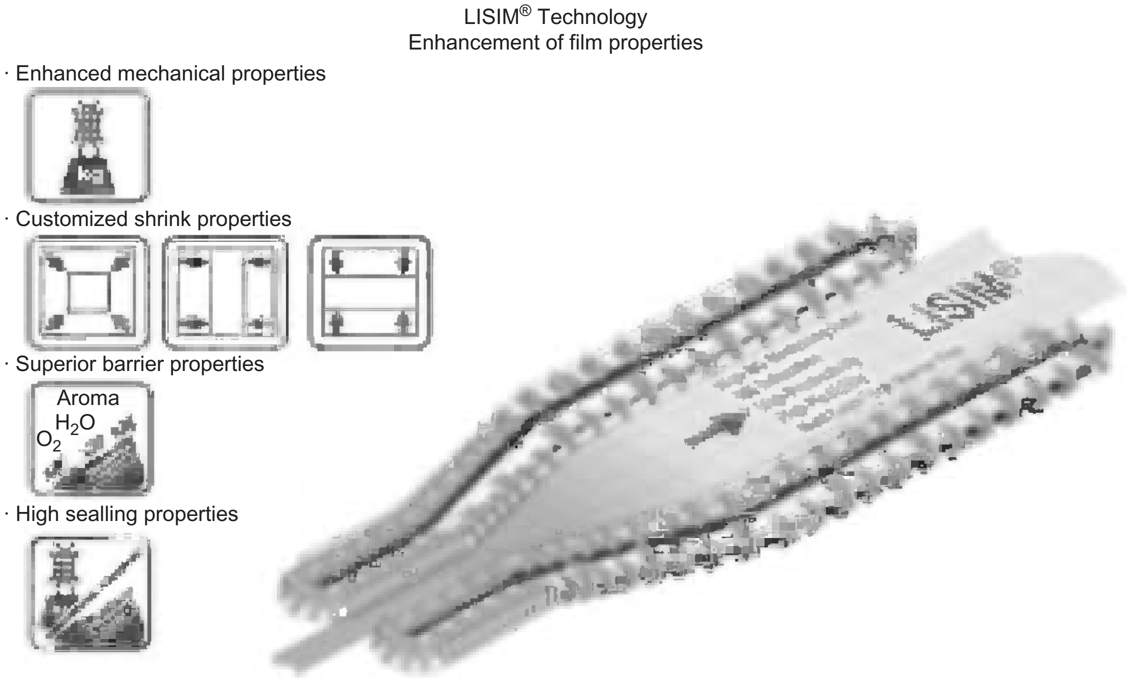


Figure 4.6 Enhanced film property possibilities with LISIM®.

10,4 m mill roll after being removed from the winder. Today, the state of the art for BOPP lines features:

- working width 10,4 m,
- speed 530 m/min,
- output capacity 6000 kg/h.

The trend to even higher output capacities will continue in the future.

Simultaneous orienting (LISIM® technology; Breil, 2002) represents an alternative to the prevalent sequential orientation and offers the following advantages (Figure 4.6):

- Improved film properties (shrinkage, mechanical, barrier, sealing, etc.),
- High productivity in comparison to mechanical simultaneous systems (speed, width).

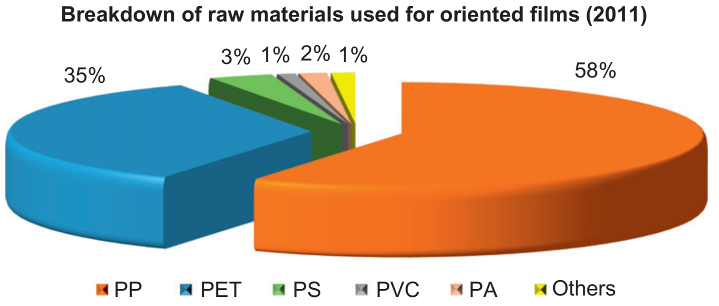
LISIM® technology is available and proven in production scale for BOPP, BOPET, and BOPA.

4.3 Oriented Film Types—Applications

In addition to the orientation technology outlined previously, the film products and their applications will now be explained further. In most cases, oriented films for packaging applications are further processed. The most significant converting processes are vacuum coating (metallizing, SiO_x, AlO_x), offline coating (acrylic, polyvinylidene chloride, polyvinyl alcohol, etc.), lamination with other oriented films, polyethylene (PE) sealing layers and printing (front printing, reverse printing). Such downstream processing will not be discussed in this chapter. Considering the market for oriented films in general, the various raw materials used can be distinguished. Figure 4.7 shows a breakdown of oriented films manufactured worldwide. A comparison of the properties of the most common biaxially oriented film types, BOPP, BOPET, and BOPA, is given in Table 4.1. The given thickness refers to the most common film types. The various film types mainly differ with regard to their mechanical, thermal and barrier characteristics and these determine the particular application. Also, other properties, like thermal resistance or electrical properties, differentiate the film types and predestine them for specific applications.

4.3.1 BOPP Films

With a worldwide consumption of over 6 million tons, BOPP films constitute by far the largest share in biaxially oriented film. Its applications are very



Worldwide production capacity

Raw material	PP	PET	PS	PVC	PA	Others	Total
x1000tpa	10.250	6.150	603	170	267	230	17.670

Figure 4.7 Production capacity for biaxially oriented film.

Table 4.1 Film Properties of Common Biaxially Oriented Films

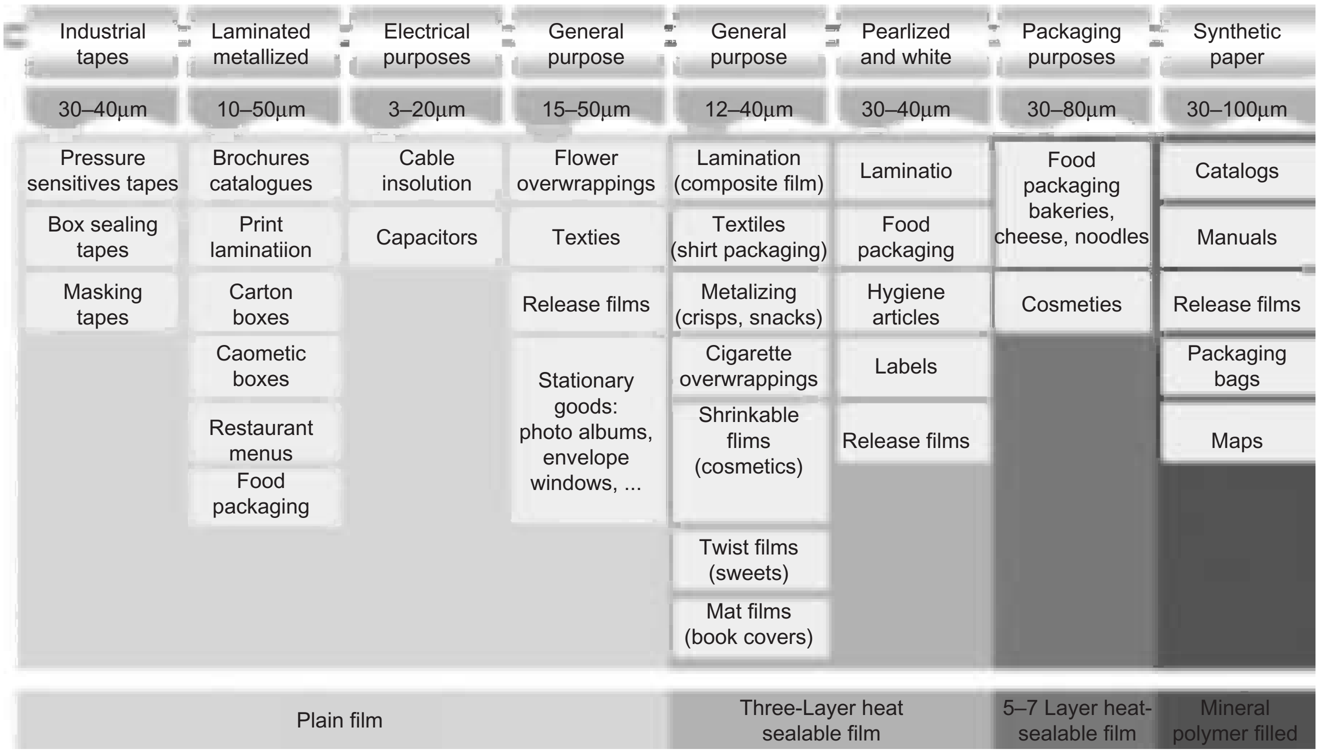
Mechanical Properties		**Unit**	**20 μm BOPP**	**12 μm BOPET**	**15 μm BOPA**
Tensile strength	MD	N/mm^2	140	230	250
E-Modulus	TD	N/mm^2	280	260	280
	MD	N/mm^2	2000	4400	3500
	TD	N/mm^2	3500	5200	3800
Elongation	MD	%	220	110	110
	TD	%	70	90	100
Impact strength		kg/cm	5	5	15
Tear propagation		g	3.5	3.5	7.5
Thermal shrinkage		%	5% at 135°C	2% at 190°C	2% at 160°C
Density		g/cm^3	0.91	1.393	1.16
Yield		m^2/kg	55	59	58
OTR		cm^3/m^2/d	1600	90	40
WVTR		g/m^2/d	6.0	8.5	270–300
Surface tension		dyn	40	50–55	50–55

diverse and can basically be split into packaging applications, not only in the food sector but also in the nonfood sector. Figure 4.8 shows a few of these applications which play an important role in everyday life. A classification of such applications can be made in terms of the thickness range and the number of layers. The thinnest films are required for electrical applications, such as capacitor film, with a thickness of at least 2,7 μm. The thickest films are used within the synthetic paper sector, up to 180 μm. As shown, films with a thickness range between 15 and 35 μm are widely applied in various packaging applications (Figure 4.9).

Coextruded films containing three, five or seven layers are available, where three-layer coextruded film has the largest share. The core layer of PP homopolymer is coextruded with the outer PP copolymer layers (Figure 4.10). The outer layers have a lower melting point thus ensuring that the sealing process necessary for packaging applications can take place at temperatures that do not deform the main layer. The surface layers essentially serve to define:

- the sliding characteristics—friction value, surface roughness,

Figure 4.8 Examples for BOPP film applications.



Industrial tapes	Laminated metallized	Electrical purposes	General purpose	General purpose	Pearlized and white	Packaging purposes	Synthetic paper
30–40µm	10–50µm	3–20µm	15–50µm	12–40µm	30–40µm	30–80µm	30–100µm
Pressure sensitives tapes	Brochures catalogues	Cable insolution	Flower overwrappings	Lamination (composite film)	Laminatio	Food packaging bakeries, cheese, noodles	Catalogs
Box sealing tapes	Print laminatiion	Capacitors	Texties	Textiles (shirt packaging)	Food packaging		Manuals
Masking tapes	Carton boxes		Release films	Metalizing (crisps, snacks)	Hygiene articles	Cosmeties	Release films
	Caometic boxes		Stationary goods: photo albums, envelope windows, ...	Cigarette overwrappings	Labels		Packaging bags
	Restaurant menus			Shrinkable flims (cosmetics)	Release films		Maps
	Food packaging			Twist films (sweets)			
				Mat films (book covers)			
Plain film				Three-Layer heat sealable film		5–7 Layer heat-sealable film	Mineral polymer filled

Figure 4.9 Overview of BOPP film applications.

- sealing properties,
- surface treatment for printing coating adhesion and metallizing properties,
- hot tack,
- antistatic,
- optical properties (haze, gloss),
- whiteness,
- stiffness,
- barrier properties.

For some applications, five-layer films and, in certain cases, even seven-layer films are used (Wellenhofer 1979). The advantages of five-layer technology are, on the one hand, improved characteristics, such as better optical, gloss, transparent, opaque properties, as well as cost advantages;

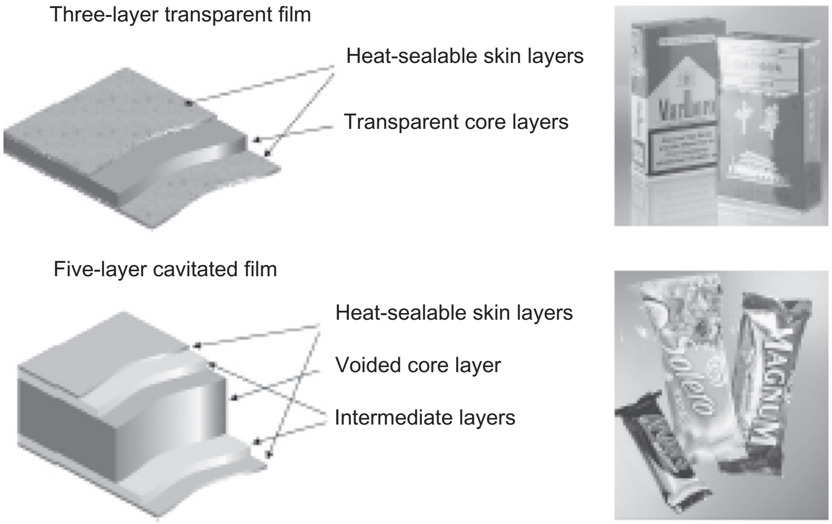


Figure 4.10 Typical BOPP film structures.

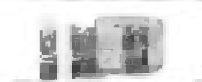
Film type category	Thickness (µm)	Examples for end-use application
Wrap-around labels	35–50	White voided film, both sides high gloss, one side treated 
Wrap-around labels	35	White voided metallized film, High-gloss surfaces, very high yield 
Food packaging	35	White voided metallized film, heat sealable, high protection against light (ice cream) 
Food packaging	30–50	White voided film, both sides heat sealable, high protection against light 
Business cards, maps, bags	40–80	Synthetic paper 
Paper lamination	15–40	Matt film 

Figure 4.11 Five-layer film applications for BOPP.

expensive additives are predominantly added in the thinner intermediate layers. Five-layer film structures allow for more flexibility by implementing intermediate layers between the main layers and skin layers. The following benefits can be obtained:

- Use of special masterbatches for the main, intermediate, and skin layers to change optical properties:
  - a high-opacity film, for example, white opaque films,
  - provide high-gloss or matte surfaces.
- More cost-effective structures without impairing the optical film quality by using higher levels of recycled material and reducing the amount of additives,
- Increase the seal properties by adding low-sealing copolymer onto a comparatively thick PP copolymer layer as an intermediate layer.

An overview of five-layer applications is given in Figure 4.11.

As one example, Figure 4.12 shows the structure, advantages, applications, and seal strength

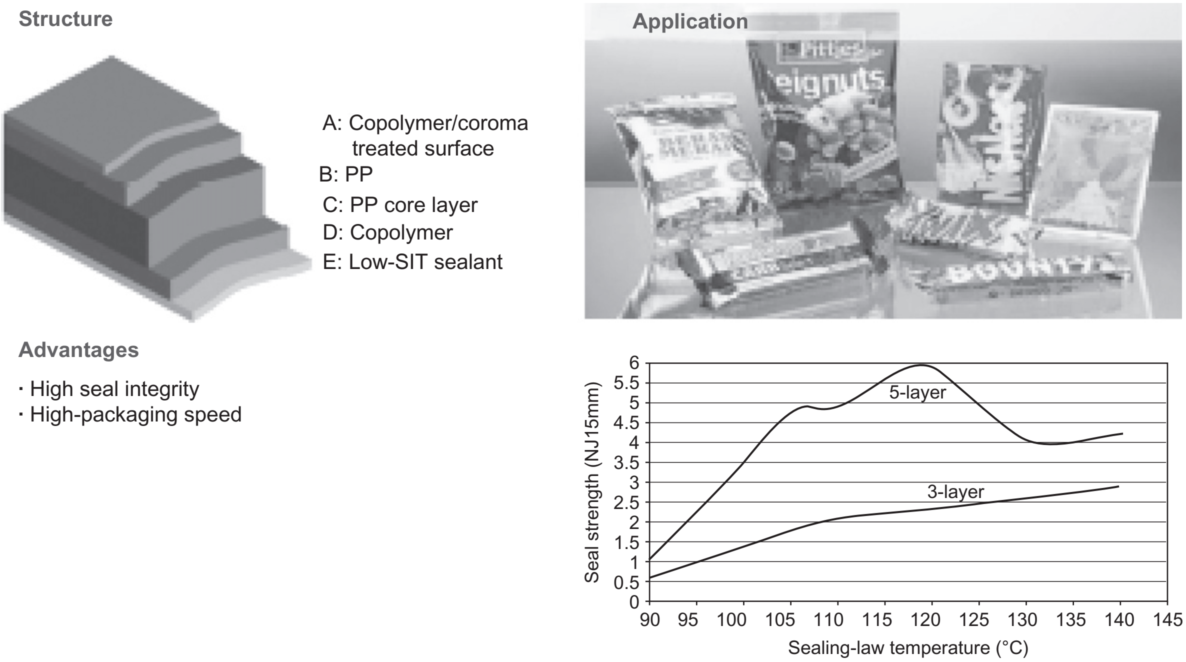


Figure 4.12 Five-layer low-SIT BOPP film structure.

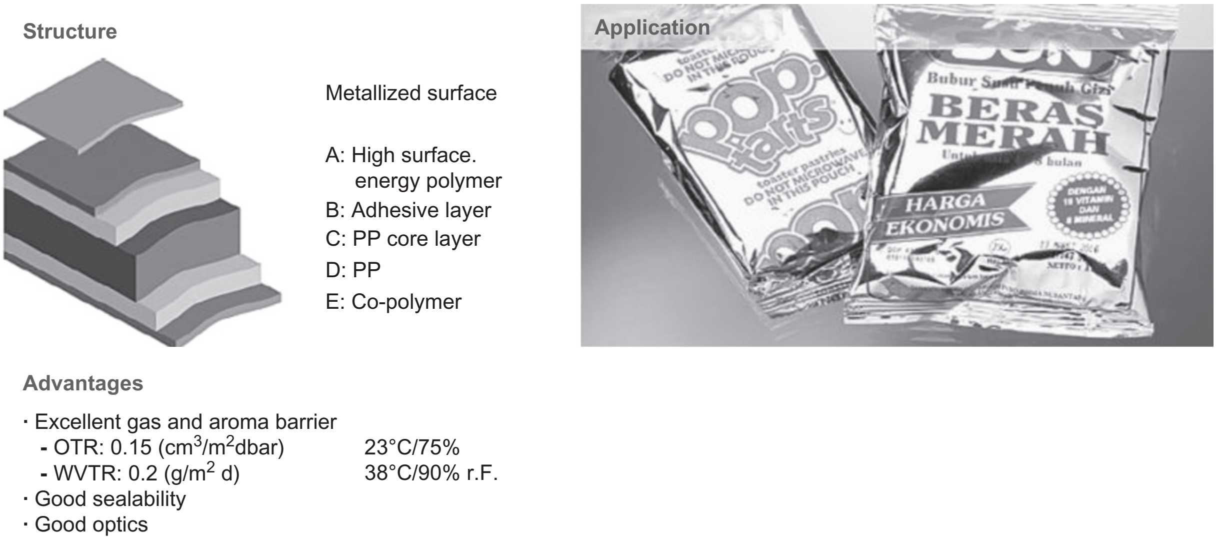
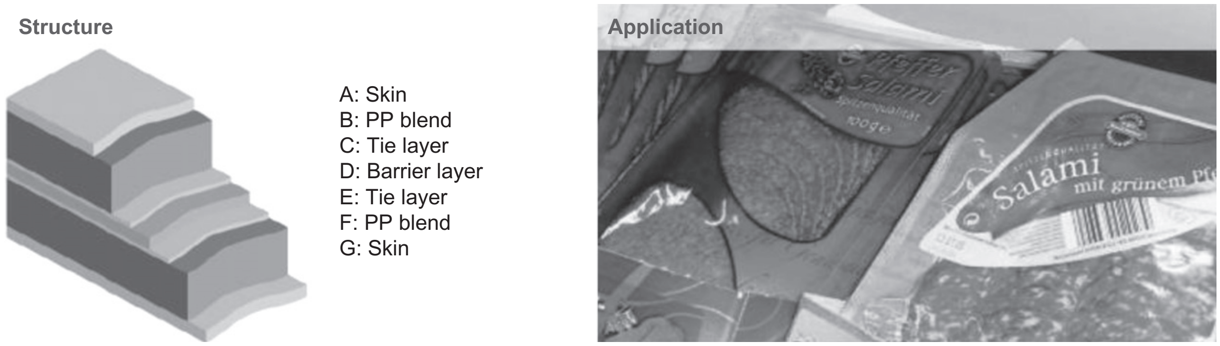


Figure 4.13 Five-layer metallized UHB BOPP film structure and advantages.

versus sealing-jaw temperature for a five-layer low-seal-initiation temperature (SIT) BOPP film. A very high-seal strength and sealed seam rigidity is achieved with this structure. This characteristic is vitally important for many packaging applications, since both the film and the sealed seam quality provide the necessary product protection.

Another example of the diversity of five-layer structures is given in Figure 4.13 which represents an ultra-high-barrier (UHB) metallized film. In this particular product design, the first surface is a polymer with a high surface energy (PA, ethylene vinyl alcohol (EVOH), and others). This polymer requires a tie or adhesive layer to bond to the PP main layer. The fourth layer is also PP and is covered with a heat-sealable copolymer skin. The metallized properties of this structure, compared to PP homopolymer or PP copolymer surfaces, show a much better adhesion strength and metallized surface uniformity. The combination of the barrier



Advantages

- Superior oxygen barrier <2cm^3/m^{2}bar
- Excellent optics
- Low-temperature sealing properties

Figure 4.14 Seven-layer transparent barrier film.

properties of the skin layer and metallization results in 300 times better oxygen-barrier values than obtained by standard metallized BOPP films. The UHB metallized film example shows that, when suitable barrier materials are combined, the overall barrier characteristics (OTR and WVTR) can be substantially enhanced. Metallized film also provides a light barrier and UV protection.

There is also a demand for transparent barrier films which is being satisfied by clear barrier coatings, but this is also possible to realize by coextrusion, i.e. with seven-layer structures. Seven-layer technology is particularly suitable for such films, since it is possible to attain the required barrier values without metallizing. In this case, a barrier material preferentially EVOH is applied in the middle of the main layer imbedded between the tie layers. Furthermore, such symmetrical film layer configuration has the advantage that the occurrence of curling becomes less likely. A typical seven-layer configuration is shown in Figure 4.14. Such seven-layer structures with the application of various polymers, such as PP and EVOH, can be manufactured with sequential and with simultaneous orientation technology. However, upon selection of the types of raw material to be used, one has to bear in mind the divergence of the various process requirements for the particular stretching process. The available types of EVOH resin show a distinct correlation between the ethylene content and the stretchability on the one hand and, on the other hand, with the barrier values. Generally, it can be said that a higher ethylene content implicates a less-complicated orientation process, permits higher stretching ratios, and, furthermore, the implementation of the sequential orientation process. For the simultaneous orientation process, however, it is possible to stretch all types of EVOH with an ethylene content of 24−47%. Although the barrier properties of the EVOH types are increased, in view of the orientation process, it is still the case that EVOH with a high ethylene content has considerably poorer barrier properties. This is illustrated in Figure 4.15 showing an evaluation of the oxygen barrier in various EVOH types and orientation with area-stretching ratio of almost 50. It can therefore be concluded that the use of EVOH types with an ethylene content of not more than 33% is particularly beneficial, since a good oxygen barrier of less than 2 cm^3/m^2/d bar can be attained with thin layers of 2 μm thickness. This value can easily compete with other high-barrier film types, which are off-line coated. The examples of multilayer BOPP films demonstrate the wide variability of structures achievable by implementing coextrusion technology. This also applies to other film types such as BOPET and BOPA. There is a strong trend to enhance the barrier properties further with a minimum of packaging material, so there is no doubt that coextruded oriented films will continue with stable growth rates.

BOPP films are widespread, not only in transparent applications but also as white opaque film types which are mainly used for packaging and labeling. Inorganic additives (e.g., calcium carbonate) are implemented in the polymer matrix (Jabarin, 1993). These particles lead to an initial flaking/separation from the polymer matrix during machine

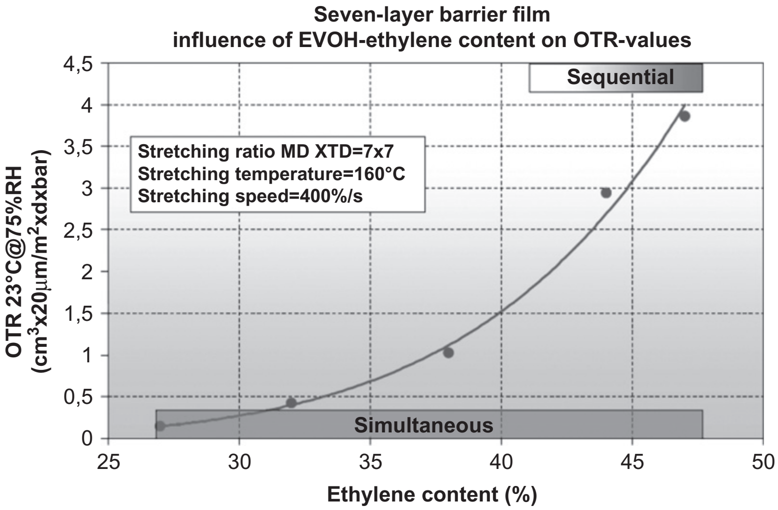


Figure 4.15 Evaluation of the oxygen barrier with the use of various EVOH types.

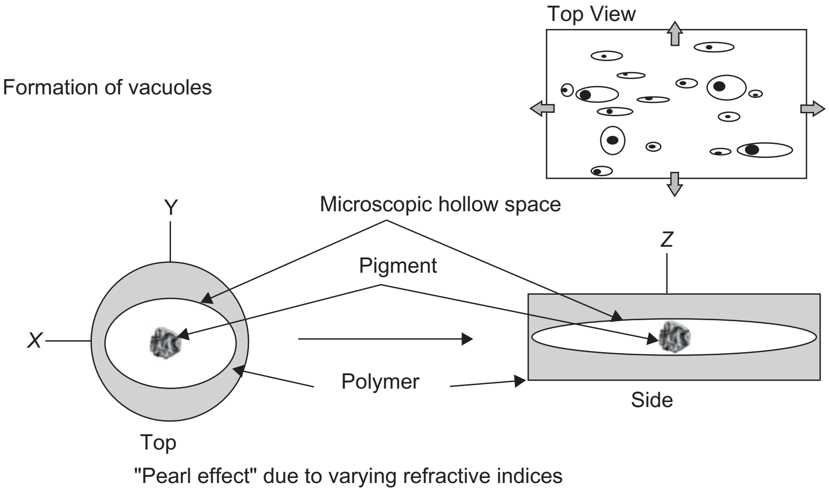


Figure 4.16 Cavitated BOPP film mechanism.

direction orientation, so that, during consequential transverse direction orientation, small cavities occur (Figure 4.16). These so-called vacuoles cause the light to be refracted in varying ways such that the required pearl effect arises. At the same time, the density reduction increases the yield proportionally. Both aspects are mainly used for confectionary, chocolate bars, ice cream, etc. Synthetic paper takes a special role among cavitated BOPP films. The effect of vacuole formation during orientation is also made use of, where a larger density range of 0.6–0.9 g/cm^3 can be produced. Applications for synthetic paper are extremely wide-ranging and cover a large thickness range (Table 4.2). Three-layer and five-layer films are coextruded where the surface is optimized in order to attain good printability. Figure 4.17 shows a 100 μm synthetic paper cross section showing the calcium carbonate particles, the cavities, and the nondensity-reduced skin layers. Synthetic paper is frequently coated in further processing in order to attain a better absorption and a quicker drying of the printing inks.

4.3.2 BOPET Films

BOPET films, with a consumption of approximately 2 million tons per year, are the second most common oriented film, following BOPP. In the past, BOPP films dominated in packaging applications and BOPET films dominated in technical applications.

Table 4.2 Thickness Range for Synthetic Paper

Thickness (μm)	Recommended Applications
50–180	Pressure sensitive, cut and stack, and wrap-around labels; release liners, posters, and ink-jet printing base
75–100	Pressure sensitive, wrap-around and in-mold labels
75–200	Cut and stack and wrap-around labels, posters, maps, shopping bags, business cards, calendars, and banners
75–250	Labels, books, posters, and calendars
75–400	Maps, posters, tags, cards, charts, menus, phone cards, calendars, and banners
130–700	Carriers, files, and folders
250–1000	Cards, tags, book covers, folders, charts, and maps

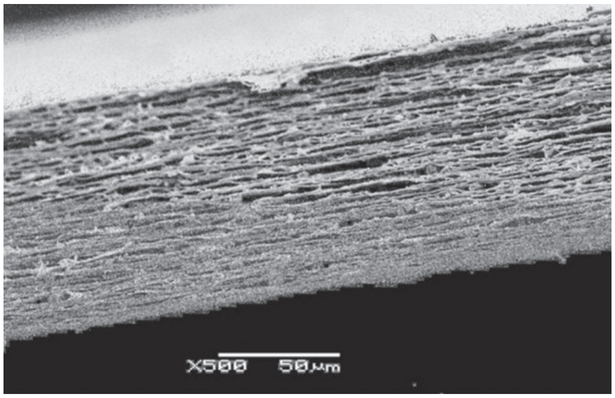

Three-layer coextruded, thickness 100μm

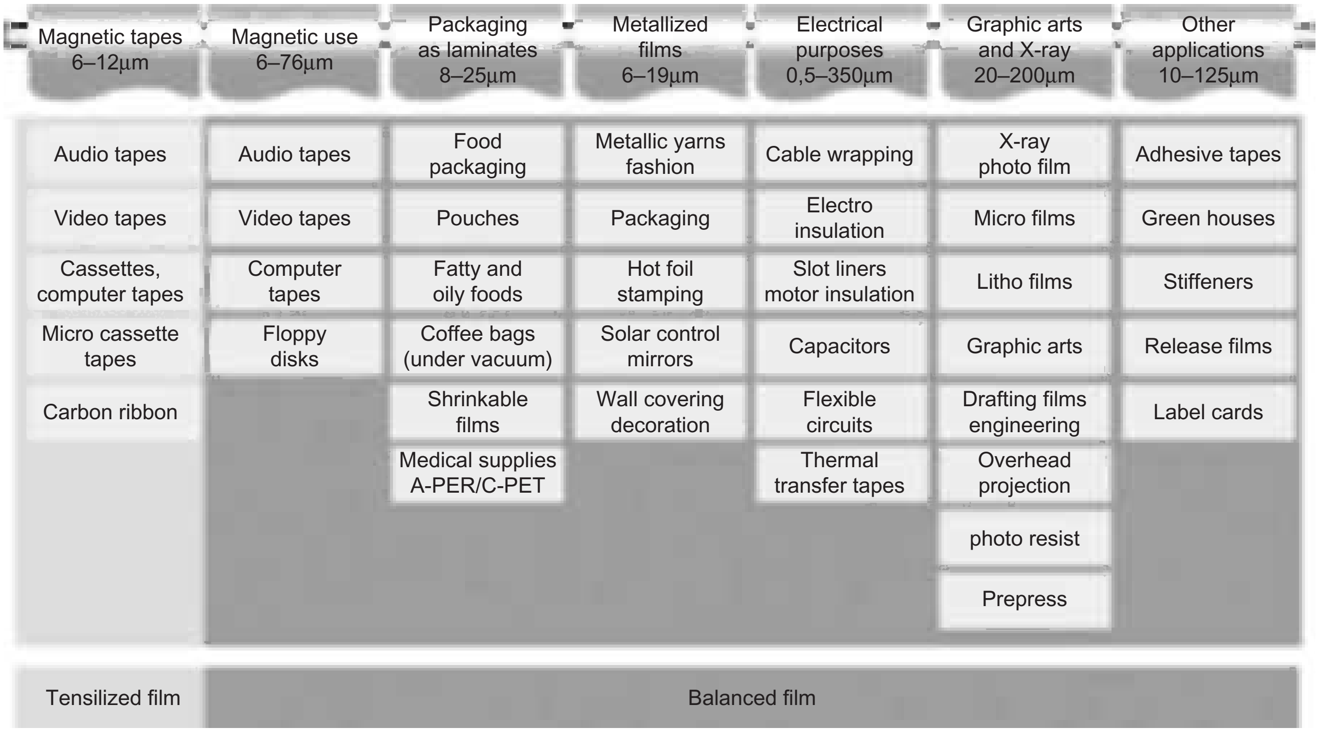
Figure 4.17 Cross section of 100 μm BOPP synthetic paper.

Biaxially oriented polyester film, with its high rigid properties, was ideal as a carrier film for magnetic tapes, floppy disks, and capacitors. Since this magnetic recording medium has been replaced by optical data media, this application has nearly disappeared in a short time. At the same time, however, an increase in the prevalence of BOPET films in the packaging industry has taken place, resulting in a worldwide growth of 4–5%.

The basic characteristics are:

- high mechanical strength,
- good temperature and chemical resistance,
- dimensional stability over a broad temperature range,
- adjustable friction coefficient,
- excellent optical clarity,
- good printability.

These characteristics reflect the specific beneficial features for the various applications accordingly (Figure 4.18). Variants ensue from the different stretching processes, recipes, coextrusion, and coating processes. In the sequential stretching process, the longitudinal–transverse (MD/TD) process is dominant (Tsunashima et al., 1999). However, the transverse–longitudinal (TD/MD) and longitudinal–transverse–longitudinal (MD/TD/MD) processes are also applied. For the MD/TD/MD process, higher stiffness values in machine direction can be achieved. The simultaneous stretching process is applied to very thin films, for example, for capacitor films, and contact-free stretching technology is also used for thicker film with high-quality optical uses. In view of the good stiffness values and sliding properties in the packaging sector, the benefits, such as excellent machinability plus good printability and optical appearance, are applied. With coextrusion, sealable or matte surfaces can be attained (Figure 4.19). Furthermore, a frequently applied advantage of coextrusion technology is the application of inorganic additives in the thin outer layers, in order to adjust the required friction coefficient without having a negative influence on the transparency. In-line coating processes are also widespread which ensure optimum printing ink adhesion. A common downstream processing phase of BOPET film is metallizing, which is mainly used to improve the barrier properties, but also to attain an attractive visual appearance. For numerous food wrappings, the barrier properties, in terms of oxygen and aroma, are particularly vital criteria to ensure that the required minimum shelf life is attained. With metallizing, an oxygen permeation value of $<1\ \mathrm{cm^3/m^2/d\ bar}$ can be reached (Figure 4.20).



Magnetic tapes 6–12µm	Magnetic use 6–76µm	Packaging as laminates 8–25µm	Metallized films 6–19µm	Electrical purposes 0,5–350µm	Graphic arts and X-ray 20–200µm	Other applications 10–125µm
Audio tapes	Audio tapes	Food packaging	Metallic yarns fashion	Cable wrapping	X-ray photo film	Adhesive tapes
Video tapes	Video tapes	Pouches	Packaging	Electro insulation	Micro films	Green houses
Cassettes, computer tapes	Computer tapes	Fatty and oily foods	Hot foil stamping	Slot liners motor insulation	Litho films	Stiffeners
Micro cassette tapes	Floppy disks	Coffee bags (under vacuum)	Solar control mirrors	Capacitors	Graphic arts	Release films
Carbon ribbon		Shrinkable films	Wall covering decoration	Flexible circuits	Drafting films engineering	Label cards
		Medical supplies A-PER/C-PET		Thermal transfer tapes	Overhead projection	
					photo resist	
					Prepress	
Tensilized film	Balanced film					

Figure 4.18 BOPET film applications.

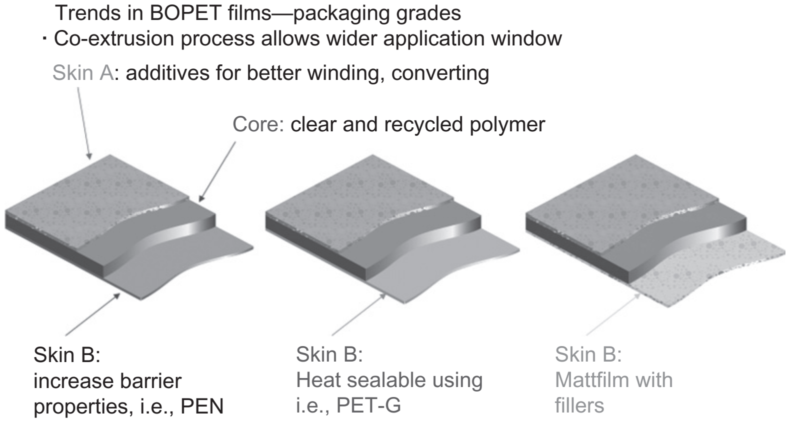


Figure 4.19 Coextruded structures in BOPET.

Biaxially oriented polyester packaging films are frequently laminated with BOPP, PE film, aluminum foil, or other packaging material. A typical laminate structure is shown in Figure 4.21 as an example coffee wrapping. The polyester film is reverse-side printed and laminated with aluminum foil as a barrier layer and polyethylene film as a sealing layer. Good transparency, high gloss, and the print quality are thus reflected in the image appearance.

4.3.3 BOPA Films

With a worldwide consumption of 250,000 tons per annum, BOPA films represent a small specialty segment, predominantly used in the packaging sector (Goetz, 2005). In view of the excellent puncture resistance along with good oxygen and aroma barriers, BOPA is primarily used for flexible wrappings for sausages, cheese, fish, and liquid contents (Figure 4.22). Thickness is normally in the range of 12–25 µm with a dominant fraction of 15 µm.

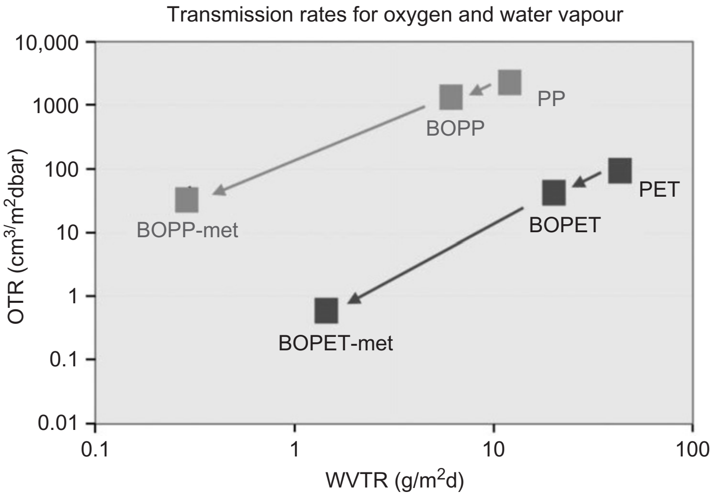
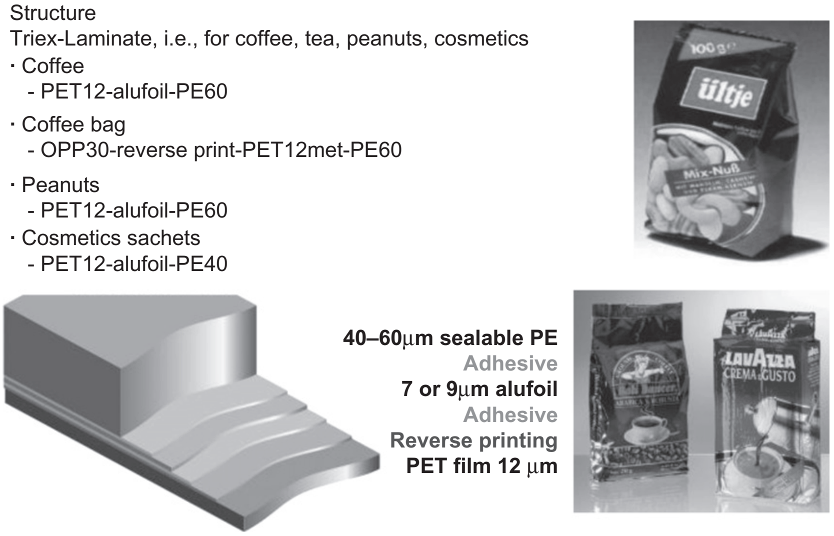


Figure 4.20 Comparison of transmission rates for PP and PET.



Structure
Triex-Laminate, i.e., for coffee, tea, peanuts, cosmetics
- Coffee
  - PET12-alufoil-PE60
- Coffee bag
  - OPP30-reverse print-PET12met-PE60
- Peanuts
  - PET12-alufoil-PE60
- Cosmetics sachets
  - PET12-alufoil-PE40

Figure 4.21 Typical packaging lamination structures with BOPET film.

Typical applications
- Frozen foods
- Cooked foods
- Pickled vegetables
- Agricultural products
- Aquatic products
- Medical products
- Designer balloons

Figure 4.22 Typical applications of BOPA film.

Special applications, such as gas-filled balloons, are primarily made from metallized thin BOPA film (10−12 μm).

In principle, all the above-mentioned stretching processes are suitable for manufacturing BOPA films, so that sequential, simultaneous and double-bubble lines are used. Sequential stretching lines with longitudinal−transverse process and a working width of 4−5 m are widely abundant.

For packaging applications, BOPA films are laminated with other films, mainly PE, in order to ensure sealability in bag manufacture. Typical laminate structures are shown in Figure 4.23.

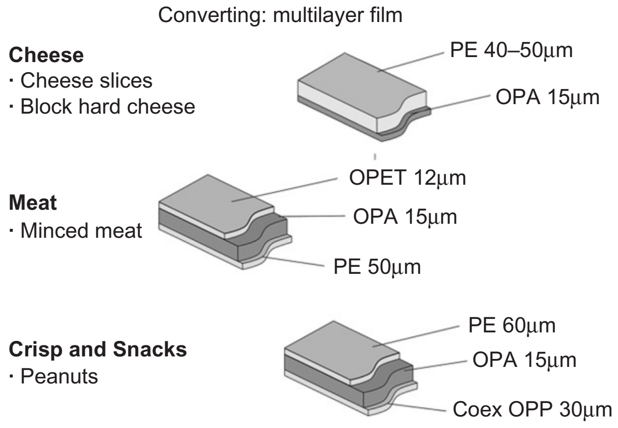


Figure 4.23 Typical packaging lamination structures with BOPA film.

4.3.4 Biaxially Oriented Polystyrene Films

The worldwide market demand for biaxially oriented polystyrene (BOPS) film amounts to approximately 600,000 tons per annum and is basically split into two market segments (Nentwig, 1994). Thinner 30−150 μm films are suited for applications such as envelope windows and separating film for photo albums, and thicker 150−800 μm films are mainly cover applications such as deep-draw vacuum packaging film (Figures 4.22, 4.24, and 4.25). Thinner film types very often require a matte surface, and deep-draw applications require high transparency and luster. In addition, a good deep-draw performance has to be ensured and can be adjusted via the stretching parameters.

BOPS films are produced exclusively by the sequential process (longitudinal−transverse). In order to make the cast sheet, a roll stack is used to ensure that the thick film has optimum surface quality.

4.3.5 Other Biaxially Oriented Films

Besides the oriented films previously discussed (BOPP, BOPET, BOPA, and BOPS), various other specialty film types need to be mentioned.

Biaxially oriented polyethylene (BOPE) films are solely in use as shrink film applications, where there are many different products varying in layer structure, recipe, and process parameters. In principle, each

Figure 4.24 Examples of BOPS film applications.

application has its own tailored shrink values, shrink forces, strengths, and barriers. Barrier properties preferably are attained by coextrusion with EVOH. For the production of BOPE shrink films, the double-bubble process is almost solely used.

Oriented films from renewable resins represent another quite new film type on the market at present and are biodegradable. Polylactide (PLA) is the major resin used since it has attractive properties and is already available in large quantities. The raw material is primarily corn. PLA film can be monoaxially and biaxially oriented and yields an attractive property spectrum (Figure 4.26). In particular, the excellent visual appearance has made it an interesting alternative for packaging. Furthermore, the deadfold characteristics should be noted which are a prerequisite for twist wrap. Compared with other packaging films, the water vapor barrier, however, is considerably inferior, although to some extent this can be compensated for by metallizing or SiO_x coating. Further uses ensue in view of the permeability for water vapor

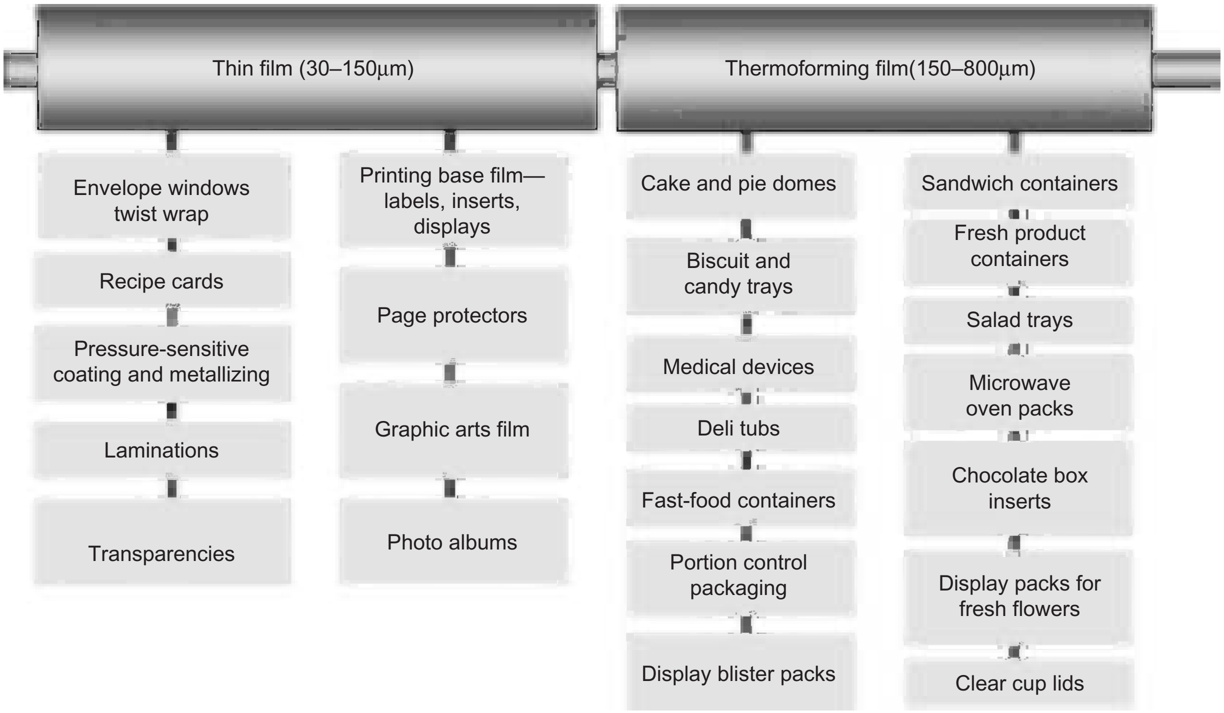


Figure 4.25 BOPS film applications.

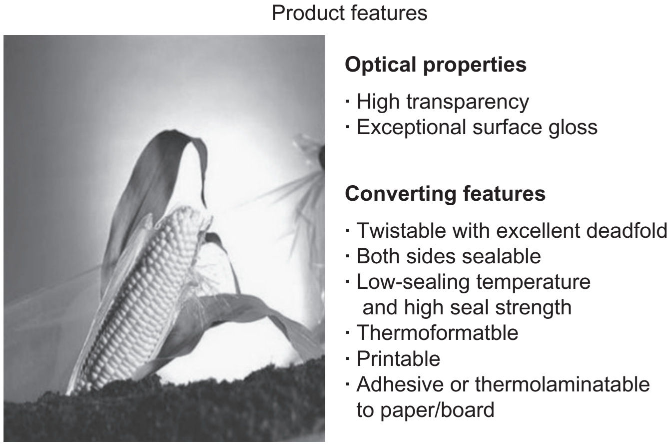
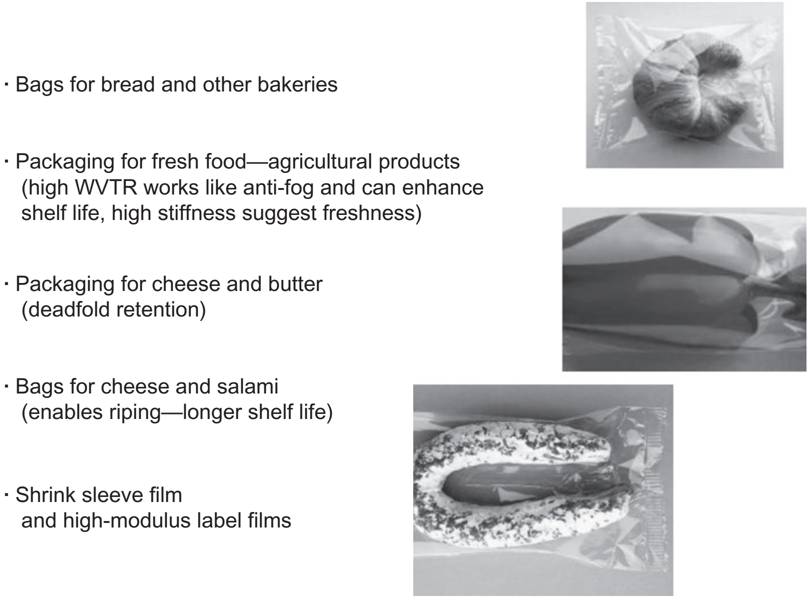


Figure 4.26 Product features for biodegradable polymers (PLA).



- Bags for bread and other bakeries
- Packaging for fresh food—agricultural products (high WVTR works like anti-fog and can enhance shelf life, high stiffness suggest freshness)
- Packaging for cheese and butter (deadfold retention)
- Bags for cheese and salami (enables riping—longer shelf life)
- Shrink sleeve film and high-modulus label films

Figure 4.27 PLA film applications.

Figure 4.28 Shrink film applications.

and, thus, such a characteristic is most suited for bread and vegetable packaging (Figure 4.27).

4.3.6 Film Oriented in Transverse Direction

A relatively large and strongly growing market segment is represented by films oriented in the transverse direction. These are used solely as shrink films where it is necessary that the films only shrink in the transverse direction and machine direction shrink is not required. Such films are, to a large extent, used as sleeves and this anisotropic shrink behavior is required in order that the container-contours appear clearly, and the desired print is attained (Figure 4.28).

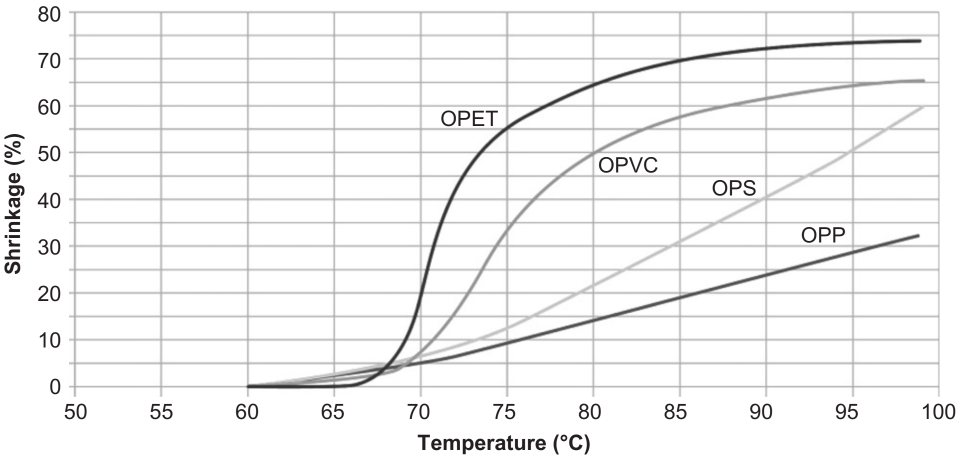


Figure 4.29 TD shrinkage versus temperature for four shrink films.

Shrink values of up to 80% in the transverse direction can be attained, whereas full body sleeves can also be attained for containers with strong contours. Polyvinyl chloride, PS, PET-G, and PP materials are used where, in terms of shrinkage, the different characteristics of these materials become apparent (Figure 4.29).

4.4 Trends for Oriented Films

Basically, oriented films are most suitable for meeting the trends in the packaging sector set by politics, society, and the industry. Packaging regulations, compel the industry to give consideration not only to the material and manufacturing costs but also to the disposal costs and in future perhaps to the CO_2 footprint. This induces one to use minimum packaging material to achieve maximum protection with packaging. These goals can only be reached with high-strength materials to reduce thickness while meeting the protection and barrier functions, plus operational properties that ensure high-speed packaging. With sophisticated orienting processes (e.g., simultaneous stretching technology), a significant increase of strength and barrier can be attained for all plastics. Furthermore, future potential in terms of packaging can be further developed, for example, by the substitution of aluminum foil with transparent or metallized high-barrier stretched film. Another large potential lies within the integration of many-function layers in the production process of oriented films, so that complex processing steps can be waived (Breil and Lund, 2008). For example, it was proven in pilot line scale that all functions of a complex triplex laminate could be attained by a coextruded stretched film manufactured in one process step. In view of limited crude oil resources, coupled with ever-increasing oil prices, plastics manufactured from crude oil bases are also subject to price increases. This, accordingly, gives a boost for alternative materials and thus the possibility of cost-efficient production on an industrial scale. The production of suitable stretchable films for packaging applications from such alternative raw materials is evident in the PLA example. One can predict that much research and development will be performed within this sector in the near future.

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5 Development of High-Barrier Film for Food Packaging

***Maryam Fereydoon*[1] *and Sina Ebnesajjad*[2]**

[1]École Polytechnique de Montréal, Montreal, Quebec, Canada; [2]President, FluoroConsultants Group, LLC

The first and most important function of package is the protection of food products. Packages protect food from the loss of nutrients, functional properties, color, aroma, taste, and preserve the general appearance expected by consumers. A good package should create an acceptable barrier between the food and external environment, particularly with respect to water vapor, oxygen, and microorganisms. The shelf life, the length of time that product remains in an acceptable condition for use, strongly depends on barrier capability of a package. The second function of the package is to transport the product in a convenient manner. Finally a good package should provide clear information about the food to consumers and attract them to buy it. Food packaging, regardless of its material, is intended to protect the food from contamination and preserve the quality of the food from manufacturing to retail sales and consumption. For use in packaging applications, a polymer needs some attributes such as mechanical strength to allow the packaged food to withstand the rigors of handling, transportation, storage, refrigeration and consumer handling, abrasion, and irradiation. Food packaging also needs appropriate thermal stability for thermal processing such as retort and sterilization process. The focus of this chapter is on the barrier properties aimed at the preservation of the quality of food.

5.1 Introduction

The barrier property of a polymer refers to its ability to transfer a permeant through it. When a polymer is exposed to a permeant having different concentrations on its two sides, the permeant passes through the polymer by net effect from the high-concentration to the low-concentration side in three steps: sorption to polymer, diffusion, and desorption from polymer (Figure 5.1).

Under steady-state conditions, the permeability coefficient is defined as "*the rate at which a quantity of permeant passes through a unit surface area of polymer in unit time having unit thickness with a unit pressure difference across the sample*" (Selke, 1997). The number of permeant molecules that penetrate into a package depends on the characteristics of the polymer, the characteristics of the penetrating molecules, their interaction and cross-effects, the temperature, and the permeant concentration inside and surrounding the package. However, the gas transport coefficients vary according to the nature of the polymer (chemical structure), polymer properties such as the degree of crystallinity, and in some cases the thermal and mechanical histories of plastic films. Orientation also has a major influence on the barrier properties and mechanical performances of both semicrystalline and amorphous polymers. According to this fact, it is possible to improve the barrier properties of the polymers by inducing the orientation of the polymer molecules during the process or post-processing of the films. Oriented films are significantly stronger than unoriented ones.

Actually, monolayer films are not able to bring all the properties required for the food packaging. In addition, single-layer films are generally quite permeable to a variety of gases. Barrier films are usually multilayer films that have been designed to be impervious to gas migration. Multilayer films are widely used for food packaging applications and can be produced by thermal lamination, coating, or coextrusion technologies. Combining different polymers in order to design a multilayer film structure with excellent barrier property to gas (usually water vapor and oxygen) and high mechanical and optical performance without significant cost increase is the main challenge in food packaging industries.

Over the past decades, plastic packaging materials have been optimized to match product-specific

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sensitivities and minimize environmental impacts. Therefore, packaging materials are sometimes very complex. In the area of packaging, particularly food packaging, multiple layer films have been developed by incorporating one or more layers of the same polymer or different types of polymers blended or coextruded together to provide good transparency, excellent mechanical performance such as tensile and impact strengths, gas barrier properties, moisture barrier property, optical properties, and thermal and dimensional stability. Application examples include packaging for meat, potato chips, cheese, snack foods, and pharmaceuticals.

Interest in the use of intelligent and active packaging systems for food packaging has increased recently. The most common food quality defects caused by microorganisms are associated with water vapor and oxygen entry into the packaged food. Loss of moisture and flavor that are transferred out of some foods also results in a loss of quality. Active packaging refers to the incorporation of certain additives into packaging systems (whether slack within the pack, attached to the inside of packaging materials, or incorporated within the packaging materials themselves) with the purpose of improving the shelf life and quality of food. Active packaging systems include oxygen scavengers, moisture control agents, and antimicrobial packaging technologies. Intelligent packaging systems are those that monitor the condition of packaged foods to give information regarding the quality of the packaged food during transport and storage. In some cases such as fresh food packaging, intelligent packaging is carried out to avoid contamination, delay spoilage, and permit some enzymatic activity to improve tenderness and decrease weight loss. In cooked, cured, packaged food products, factors such as percentage residual oxygen, oxygen transmission rate (OTR) of the packaging material, storage temperature, light intensity, and product composition are critical factors affecting quality, stability and ultimately consumer acceptance. Exposure to light in combination with even low levels of oxygen in food packages may facilitate microbial growth, thereby causing a significant reduction in the shelf life of foods. Although oxygen-sensitive foods can be packaged accordingly using vacuum packaging, such techniques do not always facilitate complete removal of oxygen. Oxygen that is transferred through the packaging film or is trapped within the product cannot be removed by these techniques. Oxygen scavengers and oxygen absorbing systems improve product quality and shelf life by absorbing the residual oxygen after the packing.

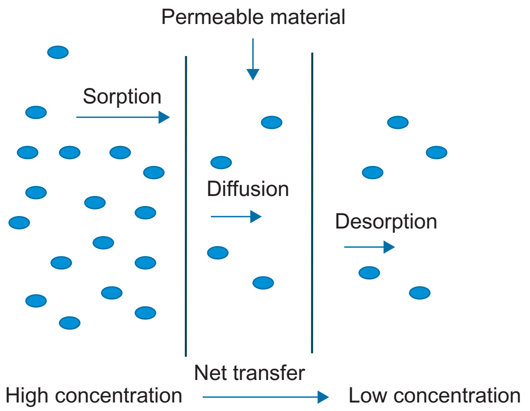

Figure 5.1 Permeation of a substance through a plastic packaging material (Selke, 1997).

The function of carbon dioxide in a packaging environment is to reduce microbial growth. Therefore, a carbon dioxide-generating system can be viewed as a technique complimentary to oxygen scavenging. In some cases, releasing of carbon dioxide by simultaneously consuming oxygen is desirable. In such cases, systems are based on either ferrous carbonate or a mixture of ascorbic acid and sodium bicarbonate.

Intelligent packaging, defined as systems that check the condition of packaged foods to give information about the quality of the packaged food during transport and storage, is another category of packaging of interest recently. Intelligent packaging concepts involve the use of sensors and indicators that consist of a receptor and a transducer. The receptor receives the physical or chemical information and transforms it into a form of energy. The information can be measured by the transducer. The transducer is a device capable of transforming the energy carrying the physical or chemical information about the product into a useful analytical signal that can be monitored.

5.2 Background

Generally, categories of packaging are classified according to the function of the package, including its barrier properties, strength, ability to withstand abuse during filling and shipping, sealability, optical and clarity properties, and so on. The material used to structure design the package is classified according to the package function. For example, from the point of view of barrier function of the package, there are two categories of films. The first category is the films that are used as barriers; they keep liquid or gasses on one side of the film. The second category consists of films that are used as membranes that allow certain materials to pass through the membrane but block others. Barrier film applications include packaging, coating, gloves, containers, hoses, and tubing. Generally, packaging materials may be classified into three categories: flexible, semirigid, and rigid.

- Flexible materials' applications may include wraps, lidding, pouches, or bags, and its films are of a thickness equal to or less than 0.127 mm (5 mil).
- Semirigid materials are thicker than 0.127 mm. They are usually formed as sheets.
- Rigid materials' applications may include trays, boxes, or crates, and are composed of thick films or rigid polymers. Beverage packaging mostly is in the rigid category, which covers a broad range of applications.

To design a flexible film structure of a multilayer to meet packaging requirements, particularly for food packaging applications, materials are selected according to the package function and cost consideration, and cost to the environment is another main consideration in package design.

At the same time, the package must be cost-effective. Costs include the cost of materials and packing waste as well as costs to the environment. Finally, the package structure must satisfy the consumers' desire in the aspects of sustainability, safety, and legislation. However, the performance of a package should be determined by the market potential for any particular product.

Most food packages have multilayer constructions to achieve the desired functional requirements of the package in a cost-effective manner. Generally speaking, in any multilayer structure several layers are seen. The outer layer of a multilayer structure consists of an abuse-resistant layer. The purpose of using such a layer in the design of a package is to protect or preserve its contents from damage due to external forces. The polymers that are typically used as the abuse layer are polypropylene (PP), high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), polyamide (PA), and polyethylene terephthalate (PET). The sealant layer of the multilayer structure provides a hermetic seal to protect the product. Copolymers consisting of ethylene are often used as sealants because of their low melting points. However, the polymers with low temperature heat sealants, such as low-density polyethylene (LDPE), ethylene vinyl acetate (EVA), LLDPE, metallocene polyethylene (mPE) plastomers, acid copolymers, and ionomers, are used as the seal layer. The selection of the best sealant for a given application depends on what the sealant needs to contribute to the overall performance of the package. These features may include seal initiation temperature, hot tack over a wide temperature range, caulkability, clarity, puncture resistance, stiffness, tensile strength, and compatibility with adhesive layers. In the core layer, the polymers with low gas permeability are used, such as aliphatic polyamide 6, aromatic polyamide MXD6, ethylene vinyl alcohol (EVOH), or polyvinylidene chloride (PVDC). Special tie resins or adhesive layers are used to combine the outer layers, skin layers, and core layers via coextrusion or lamination. Table 5.1 shows OTR of a number of plastic films that are well known in the market as good oxygen barriers. The data indicate orders of magnitude differences among the oxygen barrier properties of different plastic films.

In the design of a multilayer structure, the selection of material for each layer is done according to the preferred functional requirements of the package. Many food products need to be protected against the gain or loss of moisture. Materials such as coated cellophane, polyethylene (PE), PP, polyvinylidene chloride (PVC), and polyester films are excellent barriers to water vapor and are used to obstruct the transmission of water vapor through the film. These materials are often used on the outside (and inside) layers of multilayer films. It should be noted, however, that even the most impermeable of these films has a measurable permeability.

Other products such as fresh vegetables need to breathe; so to avoid condensation of water, materials such as polyolefin plastomers and certain grades of cellophane are used for these applications. The

Table 5.1 High Oxygen Barrier Polymers (Giles and Bain, 2000)

Material	Oxygen Permeability ($cm^3 \cdot mm/m^2$/day atm, 0% RH)	Oxygen Permeability ($cm^3 \cdot mm/m^2$/day atm, 100% RH)
LCP	0.003	0.003
PVDC	0.004	0.004
EVOH	0.003	0.25
MXD6	0.09	0.1
PA6	0.5	1.3
PET	1.5	1.5
PEN	0.3	0.3

rate of water vapor transmission (WVT) will depend upon the vapor pressure gradient across the film. Dry contents in a humid environment would absorb moisture, wet contents in a dry environment would lose moisture, and if the relative humidity (RH) inside and outside the package are equal, there will be no transmission even through the most permeable of films.

Oxygen, carbon dioxide, and nitrogen within a package often must be controlled. If oxygen is allowed into a package, it may speed up the degradation of organic materials by initiating or accelerating the decay process. Uncontrolled, this will promote staleness and loss of nutritive value. In the case of fresh meat, a high rate of oxygen transmission is required to maintain its bright red color. To meet this special requirement, special grades of cellophane, PEs, and nitriles have been developed to provide the low WVT needed to avoid drying the meat while providing high oxygen transmission to maintain the color.

This phenomenon of high transmission of oxygen combined with low transmission of water seems paradoxical but is very critical to these specialized needs. The reverse characteristics apply to PA and other films that have a relatively high permeability to water vapor but a low permeability to oxygen, nitrogen, and carbon dioxide. Other films have high (or low) transmission rates for all gases as well as for water vapor.

The oxygen barrier property of some films is strongly affected somehow by the water vapor. In order to prevent the moisture effect, the barrier layer would be sandwiched between two layers that have high water vapor barrier properties (Poisson et al., 2008; Thellen et al., 2009). The interaction of water with a polymer depends on the polarity of its functional groups which influences the mechanism of diffusion in macromolecular compounds. Table 5.2 shows the water transmission rate of a number of plastic films. The data indicate orders of magnitude differences in the moisture barrier properties of different plastic films. For example, the water vapor transmission rate (WVTR) of polycarbonate (PC) is greater than that of polyvinylidene chloride (PVC).

5.3 Improvement of Barrier Properties of Films

Developing high-barrier films has been the main challenge for film suppliers. Surface modification, crystallization and orientation, blending, and incorporation of nanoparticles as an impermeable phase have been suggested by researchers for the improvement of barrier properties.

Typically, it is difficult to obtain all the desirable barrier properties from a single film layer. Polymer suppliers and the plastic film manufacturers have long recognized the need for multilayered, laminated, coextruded, coated, and metalized films to meet the varied requirements of food packaging. High-barrier packaging can comprise several different layers and various types of resins, which provide advanced properties for such things as extended shelf life and the ability to let in certain gases to change product coloring.

Surface modification is one method for improving barrier properties. Transparent silicon oxide (SiO_x) coating on polymers such as PET, PP, PA, polyethylene naphthalate (PEN), and polyvinyl alcohol (PVA) films have been greatly investigated by researchers (Giles and Bain, 2000). Many

Table 5.2 Water Vapor Transmission Rate of Plastic Films

Material	Water Vapor Transmission Rate, g (25 μm)/m^2/day
Polycarbonate	170.5
Biaxially oriented polyamide 6	158.1
Biaxially oriented PET	131.8
Rubber-modified acrylonitrile copolymer	94.6
Amorphous PA	50
Rigid polyvinyl chloride	46.5
PET	20.2
Ethylene vinyl alcohol	21.7–124
Biaxially oriented PET	18.6
LDPE	17.7
PP	10.7
BOPP	5.9
HDPE	5.9
Saran® PVDC polyvinylidene chloride	0.93–3.4

researchers are interested in surface modification through SiO_x coating for food packaging, medical devices, and beverage packaging applications because of its transparency, water resistance, recyclability, retortability, microwave use, and excellent barrier properties. Two techniques have been used for SiO_x coating: physical vapor deposition (PVD) and plasma-enhanced chemical vapor deposition (PECVD). PECVD was preferable because it can be used to deposit materials at low temperatures, with excellent coverage at a higher deposition rate, creating better adhesion and less brittle failure than films produced by PVD (Giles and Bain, 2000). From the industrial point of view, PVDC, well known as a high-barrier polymer, is coated on the surface of polymer films in order to improve the oxygen barrier property. In Table 5.3, the OTRs of a number of plastic films that are PA6/PVDC and PP/PVDC coated are compared. The data indicate orders of magnitude differences in the oxygen barrier properties of different plastic films compared to the films coated with PVDC. For example, the oxygen permeation of oriented PP is comparable with PP-coated PVDC.

Another surface modification technology that has been used for the improvement of barrier properties in film packaging is carbon deposition by plasma technique. Diamond-like carbon (DLC) deposition on polymers, especially PET, by the PECD (plasma electrochemical deposition) technique has been widely used to dramatically improve gas barrier properties in food packaging. The main disadvantage of this method is that high-barrier films are not transparent (Abbas et al., 2005; Hasebe et al., 2007; Shirakura et al., 2006). Another technology in surface modification is the deposition of inorganic–organic materials formulated through sol–gel chemistry as coating layers on polymers. It has been shown that high density cross-linking epoxy-amine cross-linked[1] silicon sol–gel created excellent barrier protection coating (Vreugdenhil et al., 2008). Metalized film under very high vacuum at high temperatures is the other technique to improve barrier properties of the film. This technique has the capability to improve barrier properties of films such as PET, PP, LDPE, PC, and biaxially oriented PA. The main disadvantage of this method is that it affects opacity. Epoxy-amine coating is the technique that some companies have used to improve barrier properties; Graham Packaging and Crown Cork & Seal used this coating technique in PET bottles and used have Bairocade in PET bottles for packaging beer.

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[1] The three cross-linkers used are diethylenetriamine (DETA), ethylenediamine (EDA), and *N*-aminoethylpiperazine (AEP).

In fact, surface modification methods are expensive and not appropriate for food packaging industries. Furthermore, crack formation at the surface during stretching of the coated products causes barrier properties to deteriorate.

Blending is a way to produce barrier materials by bringing desired properties of different polymers together. Blending is a less costly technology than coextrusion or coinjection. However, blends are difficult to recycle. In the blending technique, barrier properties are strongly influenced by the morphology of the product. The main challenge in blending is to have a favorable morphology at a reasonable cost. Some of the blends that have been developed for barrier applications in the packaging field are EVOH in PP (Faisant et al., 1998), EVOH in PA (De Petris et al., 1998), PA in PP (Citterio et al., 1999), PA in PET (Hu et al., 2004), or PEN in PET (Wu et al., 2006).

Inclusion of nanoparticles is an effective and practical method of improving barrier properties of polymeric materials. Adding any kind of impermeable fillers improves the barrier properties of materials. Using nanoscale filler particles with a high surface area to thickness aspect ratio, in order to reduce the cost combined with good process ability, has received much more attention recently (Alexandre et al., 2006; Dennis et al., 2001; Filippone et al., 2010; Fornes and Paul, 2004; Liu et al., 2003; Okada et al., 1988; Tianxi et al., 2003). Dispersion of nanosized particles within the polymer matrix has been widely used in the past few years in order to reduce oxygen permeability. Among nanofillers, clay minerals have been used in a variety of polymers to reduce oxygen permeability. The improvement in barrier properties is based on the tortuosity (Figure 5.2), in which the permeant must travel a longer diffusive path in the presence of clay fillers in the polymer matrix (Aleperstein et al., 2005; Artzi et al., 2004, 2005; Bharadwaj, 2001; Chang et al., 2001; Cussler et al., 1988; Krook et al., 2002, 2005).

It is well known that the strength and stiffness of films increase and permeability decreases as their density goes up. For example, biaxially oriented polypropylene (BOPP) film has become one of the most popular high-growth films in the world market. The oxygen transmission of BOPP was shown to be modifiable by vapor deposition of melamine, which formed a transparent uniform layer on polymeric films. The vapor-deposited melamine molecules underwent a large number of cooperative

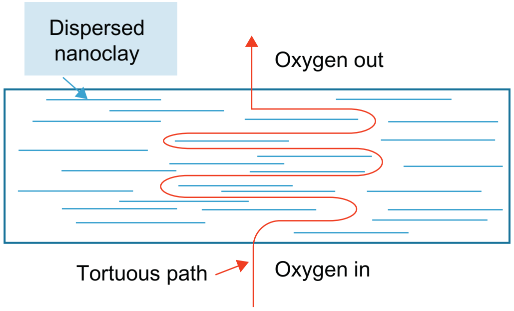


Figure 5.2 Schematic showing silicate layers effect on permeation by increasing tortuosity path.

Table 5.3 High Oxygen Barrier Films (Giles and Bain, 2000)

Film (20 μm at 20°C)	Oxygen Permeability ($cm^3 \cdot m^2$/day atm, 0% RH)	Oxygen Permeability ($cm^3 \cdot m^2$/day atm, 85% RH)
EVOH 32% ethylene	0.13	1.5
EVOH 44% ethylene	1.3	3.3
MXD6	3	3.6
PA6/PVDC coated	7	7
PP/PVDC coated	11	11
OPA6 (oriented polyamide [PA] 6)	25	65
OPET (oriented polyethylene terephthalate)	60	60
OPP (oriented polypropylene)	2000	2000

hydrogen bond interactions leading to a coherent layer consisting of an infinite network (Lazić et al., 2010). Metallization as a means of reducing moisture permeation through films such as PET is quite well known. Metallization of 13 micron polyester reduces the WVTR by two orders of magnitude (Cumberbatch, 1995).

When deciding which barrier film is correct for your application, the following factors must be considered (Barrier Films, 2012):

1. What kind of microclimate do you wish to maintain? Most films control moisture well, but oxygen transmission varies.
2. For how long do you wish to maintain the microclimate? There is no reason to use the most effective film if you need to only maintain a controlled atmosphere for a few days, but long-term storage demands better barrier properties.
3. How will you maintain the microclimate? An active system is more forgiving than one based on absorbents.
4. Do you wish to make visual inspections of the enclosed objects? Films vary in clarity and color, and some are opaque.
5. Will a difference in material costs matter? While materials are usually the least expensive part of a project, cost savings could be substantial in a large project.

5.4 Review of Permeation

Permeation or the barrier property of a plastic refers to its abilities of transferring something through it. When a polymer is exposed to a permeant with different concentration on two sides, the permeant passes through the polymer by net effect from high-concentration to low-concentration side in three steps: sorption to polymer, diffusion, and desorption from polymer. It is a significant consideration in the selection of a plastic material, because permeation follows a solution-diffusion mechanism. The gas absorbs at the entering face and dissolves at the high-pressure side of the material, diffuses through the polymer phase, and desorbs or evaporates at the low-pressure side (Figure 5.3).

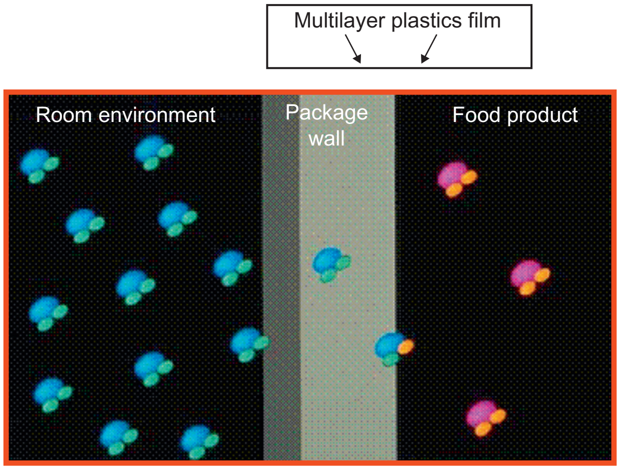


Figure 5.3 Mechanism of permeation of water vapor.

In its simplest form, permeation can be expressed as a product of the solubility and diffusion coefficients of the permeant in the polymer. Permeation of a gas can be calculated from Eq. (5.1). This equation is derived from Fick's first law of mass transfer. Permeation concerns the movement of a species through the molecules of another species, e.g., a gas through a polymer. It does not take into account transport of material through cracks, voids, and general physical flaws in the structure of the second species such as the polymer. Both phenomena result in the migration of chemicals through the structure. This means that after an appropriate plastic material has been selected to meet the permeation requirements of a process, the equipment must be fabricated carefully to avoid flaws in the polymer structure.

$$P = D \cdot S \tag{5.1}$$

where P (cm^3/s cm atm) is the permeability of the gas, D (cm^3/s) is the diffusion coefficient, and S (cm^3/cm^3 atm) is the solubility coefficient.

Several factors affect the permeation rate in a semicrystalline polymer. Temperature increase raises the permeation rate nearly exponentially (Figure 5.4). Solubility of the liquid permeants increases in the polymer at higher temperatures while gas solubility decreases. At above the glass transition temperature, the segmental mobility of the polymer chains increases, thus creating larger "holes" for the passage of permeant molecules. The permeation rate follows the Arrhenius equation (Eq. (5.2)), albeit with some limitations.

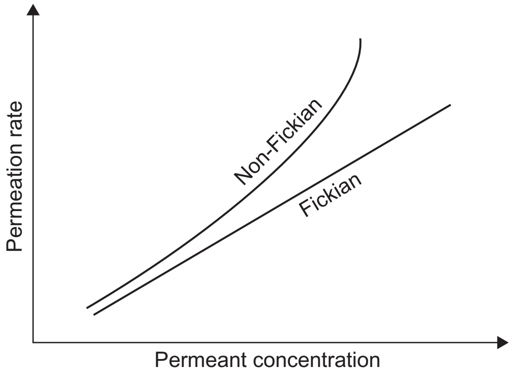


Figure 5.4 Fickian and non-Fickian permeation behaviors.

$$P = P_0 \cdot e^{(-E_a/RT)} \tag{5.2}$$

Permeation rate of gases increases at higher partial pressures. For liquids, permeation rates rise with an increase in the concentration of the permeant. Unless the permeant species are highly soluble in the polymer, the permeation rate increases linearly with pressure, concentration, and the area of permeation. Significant errors can occur when testing at elevated temperatures close to the glass transition temperature (T_g) of the plastic film (Figure 5.5). Table 5.4 provides data for permeation rate constant (P_0) and activation energy (E_a) of several polymers used in packaging Figure 5.6.

The permeation rate decreases sharply at higher film thickness, as illustrated in Figure 5.7, for WVT through a typical hydrophobic plastic film. While the permeation rate is high at a low thickness and decreases near exponentially with increase in the thickness, after a critical thickness is reached, the effect of thickness is diminished and the permeation rate reaches a plateau. At lower thicknesses, the effect of surface structure begins to play a significant role in the permeation. A more oriented (ordered) surface will inhibit permeation. In general, other factors such as the chemical and physical characteristics of the polymer affect the permeation rate significantly. Chemical affinity of the polymer for the permeant, intermolecular forces such as van der Waals and hydrogen bonding forces, degree of crystallinity, and degree of cross-linking are the influential variables.

In summary, it can be seen clearly that film thickness of the package, polymer type, and ambient conditions of the use/storage environment influence the transfer of gases and vapor into and out of the food package.

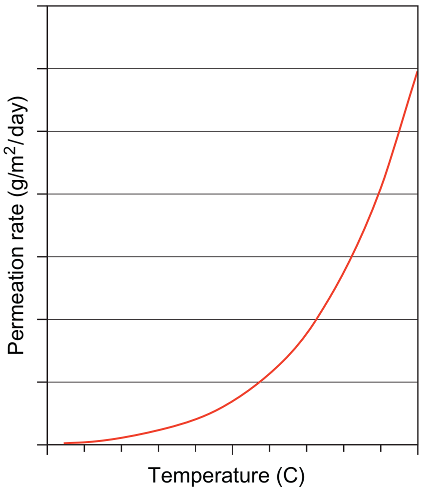


Figure 5.5 Effect of temperature on permeation rate through a plastic film.

5.5 Multilayer Flexible Packaging Structures

Layer-multiplying coextrusion represents an advanced polymer processing technique for combining two or more polymers in a layered configuration with controlled structure. It is a continuous processing technique capable of producing films economically. Coextrusion is an industrial process used to produce sheets and films that are suitable for food packaging. In this process, two or more polymers are extruded simultaneously from individual extruders. The melted polymers are delivered from extruders to a feedblock to be shaped and combined. Then, the melt flow is directed to the die to spread, become thin, and distribute uniformly to form the coextruded film. The main problem in coextrusion is to simultaneously process polymers of different rheological properties, which may cause problems such as interfacial instability and encapsulation that significantly affect the quality of the product (Wanger, 2010).

Multilayer film structures that provide high-barrier levels to oxygen, water vapor, aromas/flavors, and/or UV light for food applications usually contain a combination of *barrier*, *bulk*, and *sealant* films. Structures that use aluminum foils as a barrier or graphic substrate are usually excluded from this group. The thickness of the entire structure is usually less than 0.25 mm (0.010 in.), including the printed layer, bulk, barrier, tie, and sealant layers.

Table 5.4 Permeation Constant and Activation Energy for Polymer Films and Permeants (Selke, 1997)

Polymer	Permeant	T (°C)	$P \times 10^{14}$ ($cm^3\ cm\ cm^{-2}\ s^{-1}\ Pa^{-1}$)	E_a ($kJ\ mol^{-1}$)
HDPE				
0.964 density	Oxygen	25	3.023	35.1
	Carbon dioxide	25	2.70	30.2
	Water vapor	25	90	–
LDPE				
0.914 density	Oxygen	25	21.6	42.6
	Carbon dioxide	25	94.5	38.9
	Water vapor	25	675	33.4
PA6	Oxygen	30	0.285	43.5
	Carbon dioxide	20	0.66	40.6
	Water vapor	25	1,328	–
PET				
Crystalline	Oxygen	25	0.263	32.3
	Carbon dioxide	25	1.275	18.4
	Water vapor	25	975.	2.9
Amorphous	Oxygen	25	0.443	37.6
	Carbon dioxide	25	2.25	27.6
PVC				
	Oxygen	25	0.340	55.6
	Carbon dioxide	25	1.178	56.9
	Water vapor	25	2,060	22.9
PVDC				
	Oxygen	30	0.040	66.5
	Carbon dioxide	30	0.225	51.4
	Water vapor	25	3.75	46.0
PVOH (polyvinyl alcohol)				
	Oxygen	25	0.067	–
	Carbon dioxide	25	0.090	–

($cm^3\ cm/cm^2\ s\ Pa) \times (2.224 \times 10^{15}) = cm^3\ mil/100\ in.^2/24\ h\ atm$.

A single layer capable of working as a barrier film is very rare. The true value is created when the barrier film is a component that enables the effective performance of the final packaging film. Lists of polymers used to manufacture common barrier, bulk, tie layer, or sealant films have been provided in the following paragraphs (Wanger, 2010). The specific action of each barrier material has been described. Different subtypes of the bulk layer plastics, such as PE, which are used to construct multilayer structures, have been listed.

Barrier layers
1. EVOH copolymer
   Oxygen barrier, flavor/aroma barrier
2. Polyamide (PA6)
   Oxygen barrier, aroma barrier, and some oil barrier

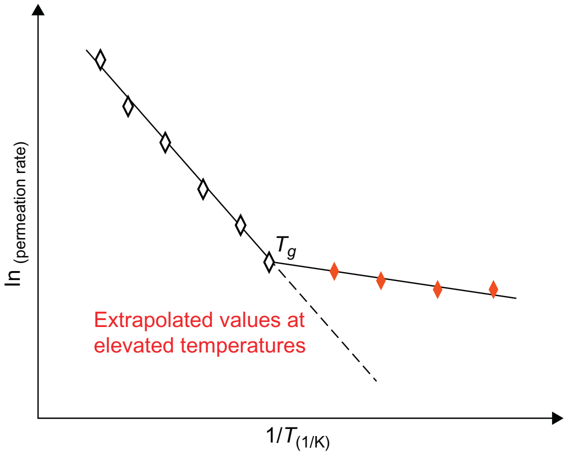


Figure 5.6 Arrhenius plot of permeation rate (McKeen, 2012).

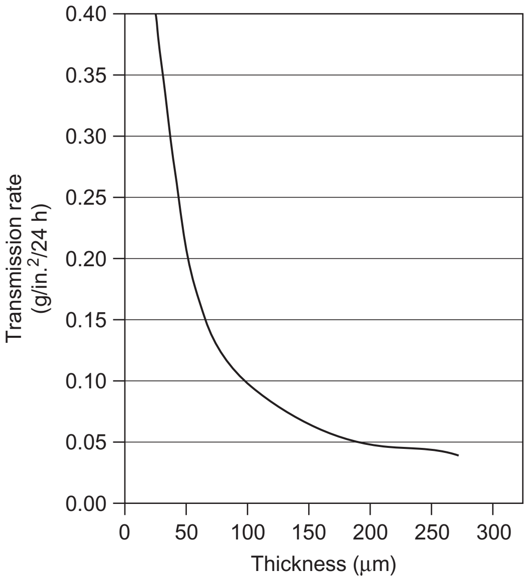


Figure 5.7 Effect of thickness of WVTR through a hydrophobic plastic film.

3. Semicrystalline PAs (polyamide MXD6)
   Gas (O_2, CO_2) barrier, aroma barrier
4. Polyesters (PET)
   Moisture barrier, some flavor/aroma barrier, and some chemical barrier
5. Poly vinylidene chloride (PVDC)
   Moisture, oxygen, flavor, aroma, and some chemical barrier
6. PEN
7. HDPE
   Moisture barrier
8. PP
   Moisture barrier
9. Ionomer
   Oil barrier and chemical barrier for some agents
10. Liquid crystal polymer (LCP)

Bulk layer

1. PE
   High density (HD), linear low density (LLD), low density (LD), very low density (VLD)
2. PP
   HoPP (homopolymer PP), CoPP (ethylene-propylene copolymer), Ter-PP (ethylene-propylene-butene terpolymer)
3. Acrylates
   Ethyl methyl acrylate (EMA)
   Ethylene butyl acrylate (EBA)
   Ethylene ethyl acrylate (EEA)
   Poly(methyl methacrylate) (PMMA)
   Ethylene/methylmethacrylate (EMMA)
4. EVA: low, medium, and high VA content
5. Polystyrene (PS), high impact PS (HIPS), general purpose PS (GPPS)

Sealant (also adhesive or tie) layer

1. Ionomers of acid copolymers
2. Acid copolymer EAA (ethylene acrylic acid) or EMAA (ethylene methacrylic acid)
3. VLDPE (very low-density polyethylene)
4. EVA or EMA (ethyl methacrylate) blends with LLDPE
5. CoPP/Ter-PP, EVA, EMA, LLDPE, mLLDPE (metallocene Linear Low Density Polyethylene)
6. LDPE or PP

A multilayer film is generally constructed by coextrusion, coating, lamination, or metallization of a substrate. Food barrier structures often include components such as polyvinylidene chloride coating, which acts both as a barrier and a sealant/tie layer, ethyl vinyl alcohol copolymer film (tie layer), PA, metalized films, or additives such as aluminum and silicon oxides.

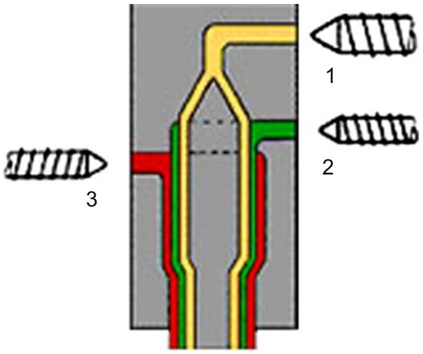
The main manufacturing technology to produce multilayer flexible packaging films is coextrusion (Figure 5.4), which is used in the following processes:

1. Film blowing,
2. Film casting (<10 mil or <0.25 mm),
3. Extrusion coating and laminating.

Coextruding polymers is no simple matter. In the food industry, they have their compatibility issues, and in the polymer processing industry, the complexity is taken to a higher level (Wanger, 2010). The benefits of combining materials by coextrusion, however, far outweigh the challenges associated with such an endeavor. Coextrusion provides solutions to meet product functionality. A variety of film properties must be taken into consideration when designing a food packaging film. Some of those properties relate to the surface characteristics, while others pertain to the entire thickness/body of the film. Surface characteristics typically include coefficient of friction (COF), gloss, haze (surface induced), and sealability, as well as surface tension and chemical receptivity, which are important for materials to be printed. The important characteristics of the bulk layer include tensile properties, elongation, internally induced haze, transparency, color, impact strength, and a variety of other parameters.

Figure 5.8 is a flow diagram of a coextrusion feedblock where three extruders are employed to produce a three-layer asymmetrical structure. This particular design has a barrier on the outside with a tie layer to provide adhesion to the bulk layer resin Figures 5.8 and 5.9.

In coextrusion process, viscosity dependence of polymer on extrusion temperature and shear-thinning behavior of non-Newtonian polymers must be carefully considered; otherwise serious problems will occur during the film processing that will significantly affect the quality of the product. It should be considered that the polymer that is used as thin skin layer in a coextruded multilayer film tolerates higher shear rate than the polymer used in the core layer.



three-layered coextrusion with barrier
layer outside body layer
1 Main extruder
2 Satellite extruder (Adhesive)
3 Satellite extruder (Barrier layer)

Figure 5.8 Flow diagram of a coextrusion feedblock using three extruders to produce a three-layer asymmetrical structure (Wanger, 2010).

Coextrusion layer instability is called "melt disturbance" and is related to the flow of the layer polymers with different rheological properties in the die and also to other processing conditions. Interfacial instability is an unsteady-state process condition in which the interface position between two neighbor layers changes. Interface distortion causes uniformity in the thickness of layers. Interfacial instability in a multilayer film significantly affects the clarity of the film. As the level of instability increases, the interface can begin to become wavy (Ganpule and Khomami, 1999). By increasing the instability at interface, the waves are propagated and the surface becomes deformed. The layer instability is known as zig-zag, arrow heads, fish scales, or chevron, depending on its severity. Generally, interfacial instability in a coextrusion system creates differences in elasticity between resins based on storage modulus (G'). So for inhabitation of interfacial instability, selection of polymers for different layers and also the selection of processing conditions should be done such that the elasticity ratio approaches one (Khomami and Ranjbaran, 1997).

Interfacial instability is determined by the following factors:

- Layer thickness,
- Viscosity ratio,
- Elasticity ratio,
- Interfacial tension.

Interfacial instability can be eliminated by (Wanger, 2010):

- lowering the shear stress by lowering extrusion rate,
- increasing the melt or die temperature,
- increasing the die gap (reducing the stress),
- lowering the polymer viscosity in skin layer by resin replacement,
- increasing the skin layer thickness,
- selecting optimum processing conditions,
- changing the choice of polymeric material.

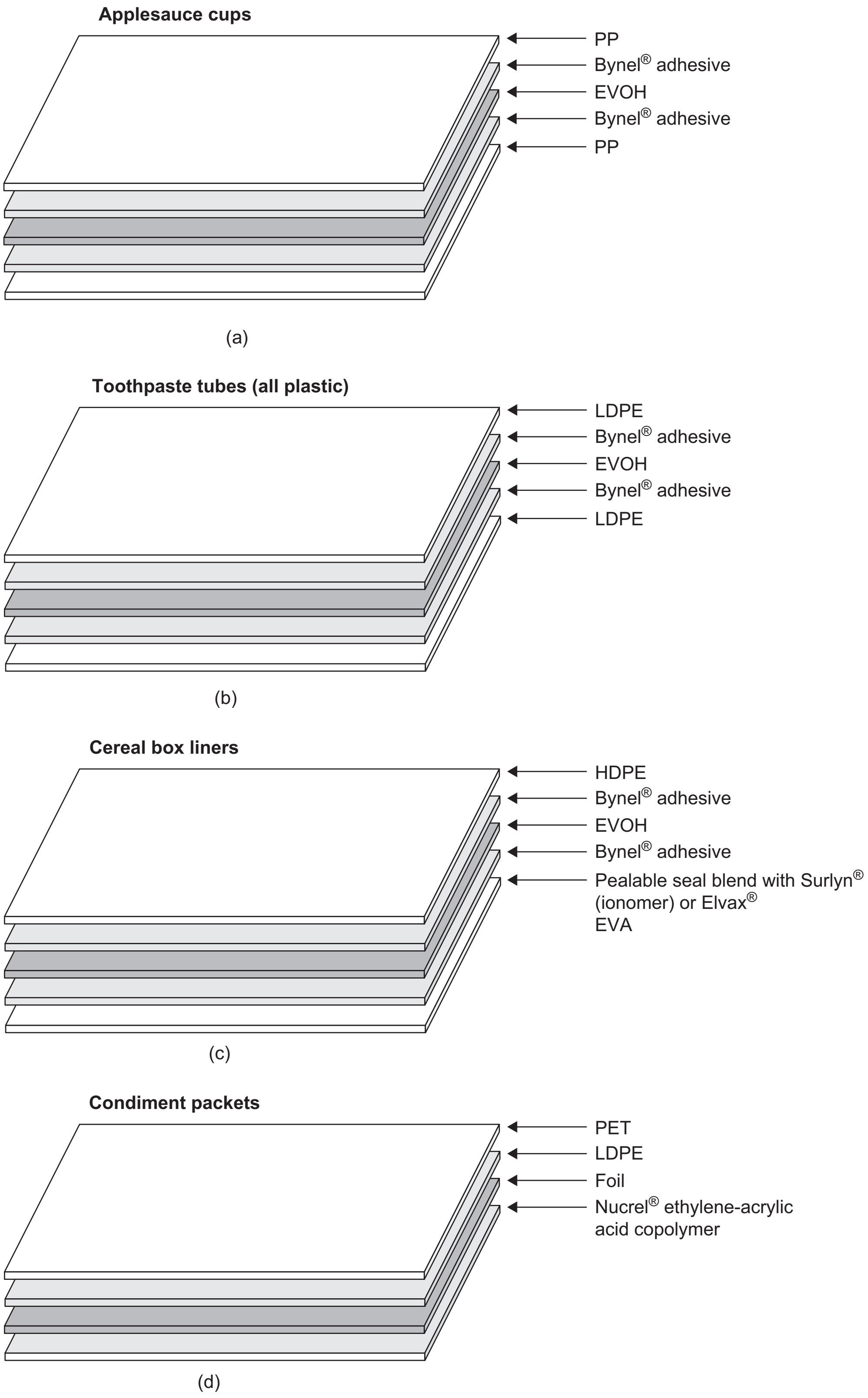
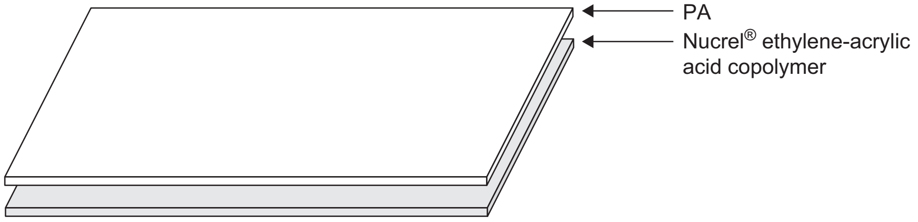


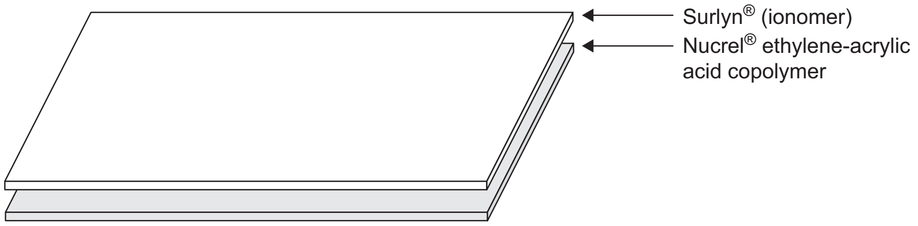
Figure 5.9 Examples of the structures of multilayered packaging film. Materials made by DuPont were selected as examples to assist the reader in finding additional information. [McKeen, L.W., 2012. Permeability Properties of Plastics and Elastomers. Elsevier, Oxford.]

Cook-in poultry or ham



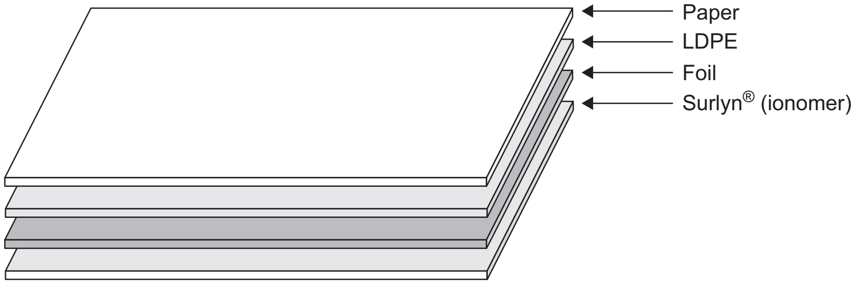
(e)

Frozen seafood



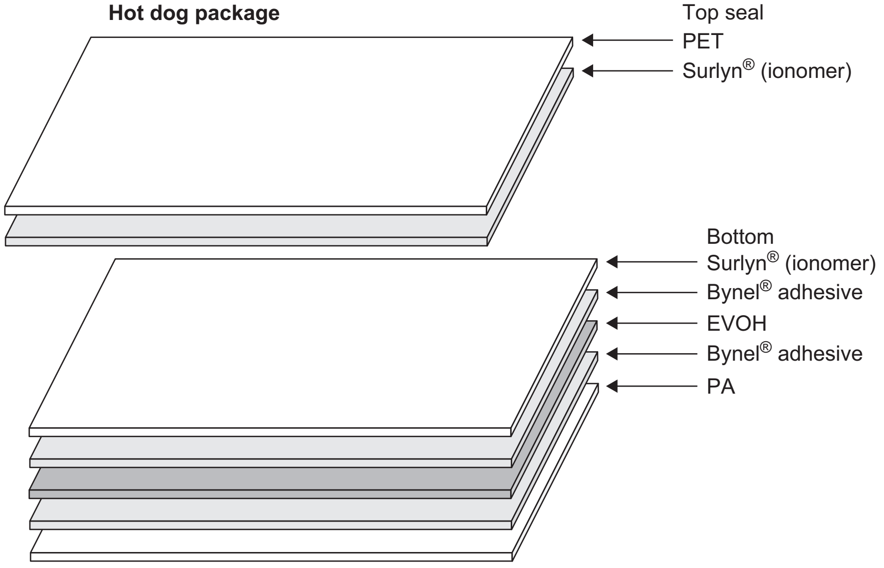
(f)

Granola bars



(g)

Hot dog package



(h)

Figure 5.9 (Continued)

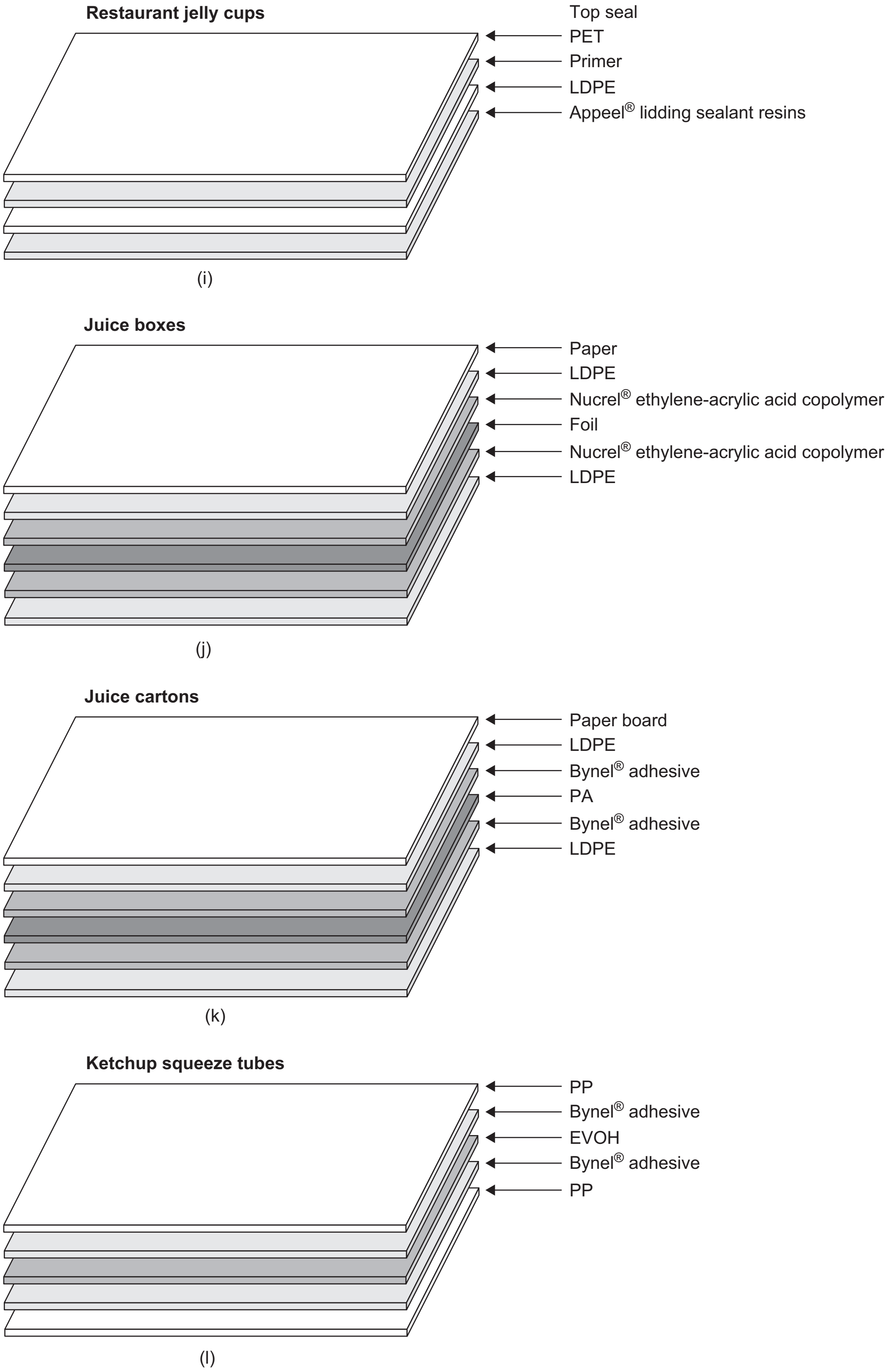


Figure 5.9 (Continued)

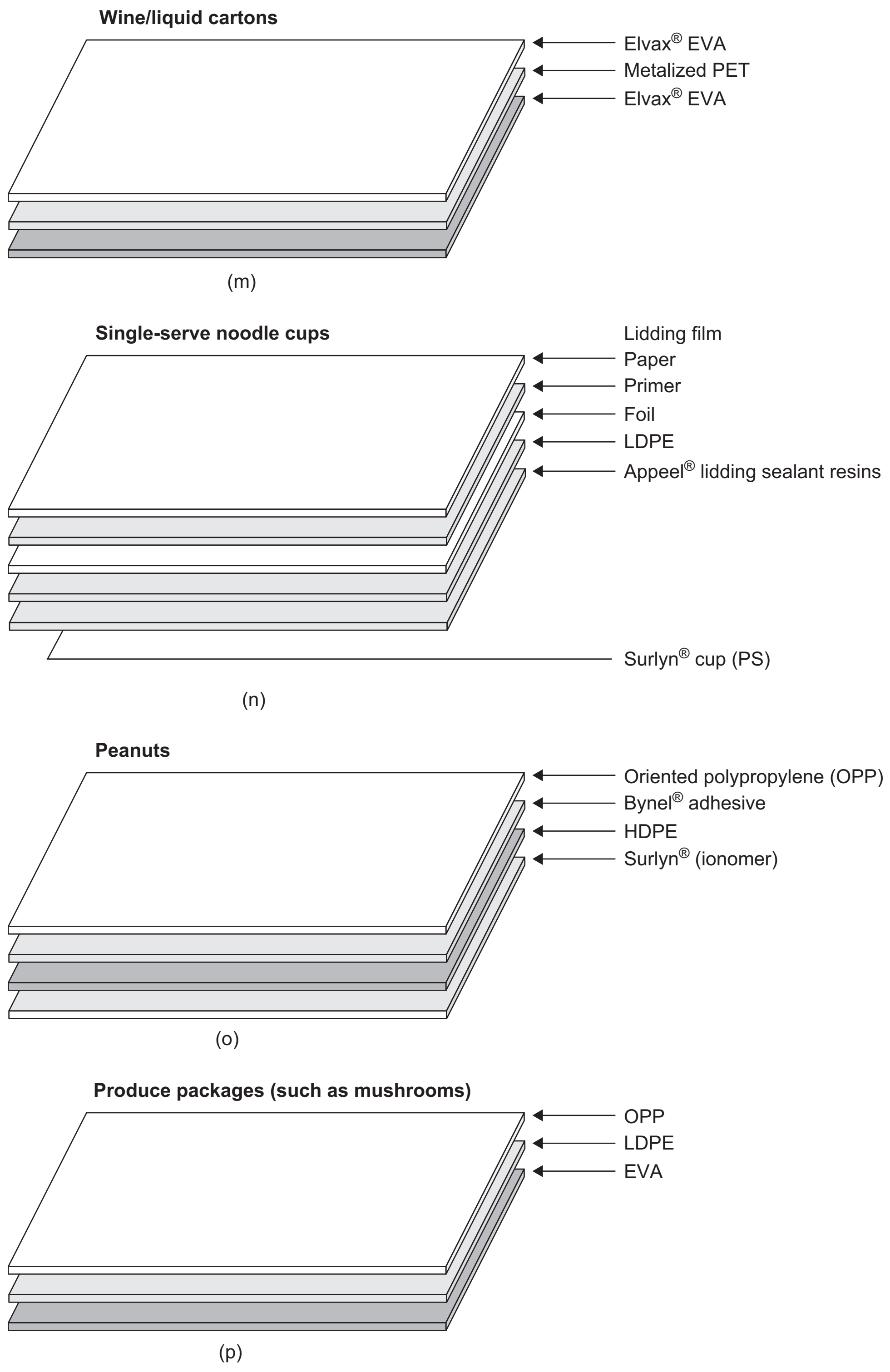


Figure 5.9 (Continued)

So for reducing the interfacial instabilities in a coextrusion process, optimization of processing conditions, proper design of die, control of process, and polymer selection for matching rheology seem to be necessary.

Another significant problem in coextrusion process is encapsulation. In the feedblock channel, there is the shear profile. Respectively, there is a viscosity distribution across the channel. Viscosity of the individual layers decreases from center to wall channel because the shear rate is high near the wall and the viscosity of flows at the center of the channel is low as a result of shear rate dropping to zero. Therefore, when we stack polymers in a layered coextrusion flow, we should ensure that the viscosity of the individual layers decreases as the flow channel wall is approached. If this is not done, the layers will attempt to rearrange themselves to place the lowest viscosity layer on the outside of flow against the wall where the shear rate is highest, to lower the shear stress in the system. These flow problems, where the viscosities are not properly stacked, lead to layer rearrangement or encapsulation. Encapsulation is mainly caused when the viscosity ratio at neighbor layers is high. It is strongly dependent on viscosity ratio and thickness of less viscous fluid. If the viscosity and thickness of less viscous fluid are increased, the encapsulation rate is increased.

5.6 Measurement of Barrier Properties of Films

A number of standard methods are available to measure the permeation of oxygen, water vapor, and carbon dioxide through plastic films. These methods are issued by standards organizations such as American Society for Testing Materials (ASTM International) and International Standards Organization (ISO). Table 5.5 gives a listing of some of the common permeation and transmission measurement methods.

5.6.1 Oxygen Test Methods

ASTM D3985 OTR

The OTR is an important determinant of the packaging protection provided by barrier materials. It is not the sole determinant, and additional tests, based on experience, must be used to correlate packaging performance with OTR. It is suitable as a common method of testing, provided that the same sampling procedures, standardization procedures, test conditions, and acceptance criteria are followed.

This test method provides a procedure for the determination of the steady-state rate of transmission of oxygen gas through plastics in the form of film, sheeting, laminates, coextrusions, or plastic-coated papers or fabrics. It provides for the determination of (1) oxygen gas transmission rate (O_2GTR), (2) the permeance of the film to oxygen gas (PO_2), and (3) oxygen permeability coefficient ($P'O_2$) in the case of homogeneous materials.

ASTM F1307: Standard Test Method for OTR through Dry Packages Using a Coulometric Sensor

This test method covers a procedure for the determination of the steady-state rate of transmission of oxygen gas into packages. More specifically, the method is applicable to packages that in normal use will enclose a dry environment.

ASTM F1927 Standard

O_2GTR at a given temperature and percentage relative humidity (%RH) are important determinants of the packaging protection afforded by barrier materials. It is not the only determinant, and additional tests, based on experience, must be used to correlate packaging performance with O_2GTR. It is suitable as a common method of testing, provided that the same sampling procedures, standardization procedures, test conditions, and acceptance criteria are followed.

This test method gives a procedure for the determination of the rate of transmission of oxygen gas, at steady state and at a given temperature and %RH level, through film, sheeting, laminates, coextrusions, or plastic-coated papers or fabrics. This test method extends the common practice in dealing with zero humidity or, at best, an assumed humidity. Humidity plays an important role in the O_2GTR of many materials. This test method provides for the determination of O_2GTR, the permeability of the film to oxygen gas (PO_2), the permeation

Table 5.5 Test Methods for Measurement of Barrier Properties of Plastic Films

Method Designation	Title	What Is Measured?
Oxygen		
ASTM D3985	Method for determination of oxygen transmission rate	Measurement of O_2 transmission through films, sheets, laminates, etc.
ASTM F1307	Method for determination of oxygen transmission rate through dry packages using a Coulometric sensor	Measurement of steady-state rate of transmission of oxygen gas into packages
ASTM F1927	Method for determination of O_2GTR, permeability, and permeance at controlled relative humidity through barrier materials using a coulometric detector	Determination of the rate of transmission of O_2 gas, at steady state, at a given temperature, and %RH level, through film, sheeting, laminates, etc.
JIS K 7126	Method for determining the gas transmission rate of any plastic material in the form of film, sheeting, laminate, etc.	Determination of the gas transmission rate of any plastic material in the form of film, sheeting, laminate, etc.
DIN-53380 Part 3	Testing of plastics—Determination of gas transmissions rate	Oxygen-specific carrier gas method for testing of plastic films and plastics moldings
ISO−14663-2	Determination of steady-state rate of transmission of oxygen	Determination of steady-state rate of transmission of oxygen gas through ethylene/vinyl alcohol copolymer in the form of film
Water vapor		
ASTM F1249	Test method for determination of O_2GTR, permeability, and permeance at controlled RH through barrier materials using a coulometric detector	Obtain reliable values for the water vapor transmission rate (WVTR) of plastic film and sheeting. The WVTR is an important property of packaging materials and can be directly related to shelf life and packaged product stability
ASTM D6701	Test method for determining WVTRs through nonwoven and plastic barriers (withdrawn)	Covers a procedure for determining the rate of water vapor transmission (WVT) ranging between 500 and 100,000 g/m^2/day through nonwoven and plastic barrier materials. The method is applicable to films, barriers consisting of single or multilayer synthetic or natural polymers, nonwoven fabric, and nonwoven fabrics coated with films up to 3 mm (0.1 in.) in thickness
ASTM E 398	Test method for determination of O_2GTR, permeability, and permeance at controlled RH through barrier materials using a Coulometric detector	Covers a procedure for determining the rate of WVT ranging between 500 and 100,000 g/m^2/day through nonwoven and plastic barrier materials. The method is applicable to films, barriers consisting of single or multilayer

(*Continued*)

Table 5.5 (Continued)

Method Designation	Title	What Is Measured?
		synthetic or natural polymers, nonwoven fabric, and nonwoven fabrics coated with films up to 3 mm (0.1 in.) in thickness
JIS K-7129	Plastics—film and sheeting—determination of WVTR by instrumental method	Specifies an instrumental method for determining the WVTR of plastic film, plastic sheeting, and multilayer structures including plastics that have smooth surfaces without any embossed portions, using a humidity detection sensor method, infrared detection sensor method, and gas chromatographic sensor method
ISO−15106-2	Plastics—film and sheeting—determination of WVTR—Part 2: infrared detection sensor method	Specifies an instrumental method for determining the WVTR of plastic film, plastic sheeting, and multilayer structures including plastics, using an infrared detection sensor. The method provides rapid measurement over a wide range of WVTRs.
TAPPI T-557	WVTR through plastic film and sheeting using a modulated infrared sensor	Covers a procedure for determining the rate of WVT through flexible barrier materials. The method is applicable to sheets and films up to 2.54 mm (0.1 in.) in thickness, consisting of single or multilayer synthetic or natural polymers and foils, including coated materials. It provides for the determination of (1) WVTR, (2) the permeance of the film to water vapor, and (3) for homogeneous materials, water vapor permeability coefficient
Carbon dioxide		
ASTM F2476	Method for the determination of CO_2TR through barrier materials using an infrared detector	Determination of the steady-state rate of transmission of carbon dioxide gas through plastics in the form of film, sheeting, laminates, coextrusions, or plastic-coated papers or fabrics. It provides for the determination of (1) CO_2TR, (2) the permeation of the film to carbon dioxide gas (PCO_2), and (3) carbon dioxide permeability coefficient ($P''CO_2$) in the case of homogeneous materials.
DIN-53380 Part 4	Testing of plastics—determination of gas transmissions rate	Testing of plastics: carbon dioxide−specific infrared absorption method for testing of plastic films and plastic moldings

coefficient of the film to its thickness (PO_2), and the oxygen permeability coefficient (PO_2) in the case of homogeneous materials at given temperature and %RH level(s).

JIS K 7126

Japanese Industrial Standards (JIS) are developed by the JIS Committee. The letter K stands for chemical engineering—related standards. JIS K 7126 specifies a method for determining the gas transmission rate of any plastic material in the form of film, sheeting, laminate, coextruded material, or flexible plastic-coated material under a differential pressure.

DIN-53380 Part 3: Testing of Plastics—Determination of Gas Transmissions Rate

This is an oxygen-specific carrier gas method for the testing of plastic films and plastic moldings.

ISO-14663-2: Determination of Steady-State Rate of Transmission of Oxygen Gas through Ethylene/Vinyl Alcohol Copolymer in the Form of Film Using a Coulometric Sensor and Is Standardized by the ISO-14663-2:1999

The O_2GTR is usually expressed in cubic centimeters (at 0°C under standard atmospheric pressure) per m^2 per 24 h under a pressure difference of 1 atm ($cm^3/m^2/24$ h atm).

5.6.2 Water Vapor Test Methods

ASTM F1249: Standard Test Method for WVTR through Plastic Film and Sheeting Using a Modulated Infrared Sensor

The purpose of this test method is to obtain reliable values for the WVTR of plastic film and sheeting. WVTR is an important property of packaging materials and can be directly related to shelf life and packaged product stability.

Data from this test method is suitable as a referee method of testing, provided that the purchaser and seller have agreed on sampling procedures, standardization procedures, test conditions, and acceptance criteria.

This test method gives a procedure for determining the rate of WVT through flexible barrier materials. The method is applicable to sheets and films up to 3 mm (0.1 in.) in thickness and consisting of single or multilayer synthetic or natural polymers and foils, including coated materials. It provides for the determination of (1) WVTR, (2) the permeance of the film to water vapor, and (3) for homogeneous materials, water vapor permeability coefficient.

ASTM D6701: Standard Test Method for Determining WVTRs through Nonwoven and Plastic Barriers (Withdrawn)

This test method covers a procedure for determining the rate of WVT, ranging from 500 to 100,000 g/m^2/day, through nonwoven and plastic barrier materials. The method is applicable to films, barriers consisting of single or multilayer synthetic or natural polymers, nonwoven fabric, and nonwoven fabrics coated with films up to 3 mm (0.1 in.) in thickness. This test method provides for the determination of (1) WVTR and (2) the permeation to water vapor.

ASTM E 398: Standard Test Method for WVTR of Sheet Materials Using Dynamic RH Measurement

The WVTR, under known and carefully controlled conditions, may be used to evaluate the vapor barrier qualities of a sheet. Direct correlation of values obtained under different conditions of test temperature and RH will be valid provided the barrier material under test does not undergo changes in solid state (such as a crystalline transition or melting point) at or between the conditions of test.

This test method covers dynamic evaluation of the rate of transfer of water vapor through a flexible barrier material and allows conversion to the generally recognized units of WVT, as obtained by various other test methods including the gravimetric method described in Test Methods E 96/E 96M.

This test method is limited to flexible barrier sheet materials composed of either completely hydrophobic materials or combinations of hydrophobic and hydrophilic materials having at least one surface that is hydrophobic.

The minimum test value obtained by this test method is limited by the leakage of water vapor past the clamping seals of the test instrument. A reasonable value may be approximately 0.01 g/24 h m^2 for any WVTR method, including the desiccant procedure of Test Methods E 96/E 96M at 37.8°C and 90% RH. This limit can be checked for each instrument with an impervious specimen such as aluminum foil. Calibration procedures can compensate for the leakage rate if so stated.

This test method is not suitable for referee testing but is suitable for control testing and material comparison. Several other ASTM test methods are available to test a similar property. This test method is unique in that it closely duplicates typical product storage where a transfer of moisture from a package into the environment is allowed to proceed without constantly sweeping the environmental side with dry gas. Methods with constantly swept dry sides include Test Methods F1249, F372, and F1770.

JIS K-7129: Plastics—Film and Sheeting—Determination of WVTR—Instrumental Method

This standard specifies an instrumental method for determining the WVTR of plastic film, plastic sheeting, and multilayer structures including plastics that have smooth surfaces without any embossed portions using a humidity detection sensor method, infrared detection sensor method, and gas chromatographic sensor method.

ISO-15106-2: Plastics—Film and Sheeting—Determination of WVTR—Part 2: Infrared Detection Sensor Method

ISO-15106-2 method specifies an instrumental method for determining the WVTR of plastic film, plastic sheeting, and multilayer structures including plastics using an infrared detection sensor. The method provides rapid measurement over a wide range of WVTRs.

TAPPI T-557: WVTR through Plastic Film and Sheeting using a Modulated Infrared Sensor

This test method is a procedure for determining the rate of WVT through flexible barrier materials. The method is applicable to sheets and films up to 2.54 mm (0.1 in.) in thickness and consisting of single or multilayer synthetic or natural polymers and foils, including coated materials. It provides for the determination of (1) WVTR, (2) the permeance of the film to water vapor, and (3) for homogeneous materials, water vapor permeability coefficient.

5.6.3 Carbon Dioxide Test Methods

ASTM F2476: Test Method for the Determination of Carbon Dioxide Gas Transmission Rate (CO_2TR) through Barrier Materials Using an Infrared Detector

CO_2TR is an important determinant of the packaging protection afforded by barrier materials. It is not, however, the only determinant, and additional tests, based on experience, must be used to correlate packaging performance with CO_2TR. It is suitable as a referee method of testing, provided that purchaser and seller have agreed on sampling procedures, standardization procedures, test conditions, and acceptance criteria.

This method covers a procedure for the determination of the steady-state rate of transmission of carbon dioxide gas through plastics in the form of film, sheeting, laminates, coextrusions, or plastic-coated papers or fabrics. It provides for the determination of (1) CO_2TR, (2) the permeation of the film to carbon dioxide gas (PCO_2), and (3) carbon dioxide permeability coefficient ($P''CO_2$) in the case of homogeneous materials.

DIN-53380 Part 4: Testing of Plastics—Determination of Gas Transmissions Rate

Testing of plastics: Carbon dioxide−specific infrared absorption method for testing of plastic films and plastic moldings.

Designing a multilayer film for coextrusion requires consideration of a variety of factors including:

1. Physical properties such as tensile, elongation, flexure, stiffness, hardness, toughness, puncture, COF, sealability, and peelability.

2. Barrier properties to agents such as oxygen, moisture, oil, chemical, aroma/fragrance, and carbon dioxide.
3. Additives such as colorants, mineral fillers, surface friction modifier, property modifiers, melt fracture inhibitors, and scavengers.

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6 Applications of Polypropylene Films

Teresa Calafut

Polypropylene is used in components of automobiles and large and small appliances, packaging films and containers, medical devices, and textiles. A good balance of properties, which can be tailored to a wide range of fabrication methods and applications, and its low cost make it useful in many different industries.

6.1 Automotive Applications

Polypropylene is used throughout the automobile—in interiors, exteriors, and under the hood. It is used in the automobile industry more than any other single polymer, and its usage is increasing. In the Opel Astra, 68% of the thermoplastic components are composed of polypropylene, compared to 10% polyamide, 6% acrylonitrile butadiene styrene (ABS), 4% polyethylene, and 12% of other thermoplastics. In Ford models, use of polypropylene has increased from an average of 5.5 kg (12.1 lb) in 1980, to 8.0 kg (17.6 lb) in 1985, to 17.0 kg (37.4) in 1990 (Dufton, 1992; Williams, 1992).

Mineral- and glass-reinforced polypropylenes, polypropylene homopolymers and copolymers, thermoplastic vulcanizates, and polypropylene foams are used in applications ranging from structural components and energy-absorbing media to interior trim, carpeting, and fluid containers. The wide use and versatility of polypropylene in automotive applications facilitates mechanical recycling, since less material separation is required, and the resin maintains good mechanical properties after reprocessing (Libert and Rosenthal, 1992; Royle, 1992).

6.1.1 Exterior Automotive Applications

Automobile bumpers are commonly made using polypropylene. Plastic bumper systems generally consist of an inner beam, an energy-absorbent core, and a fascia. Elastomer-modified, ultraviolet (UV)-stabilized polypropylenes, reinforced or unreinforced, and foamed grades are usually used in bumpers. Elastomer-modified grades in fascia provide a balance of toughness and rigidity in order to meet current regulations. Bumper fascia must have good rigidity and maximum impact resistance, even at low temperatures (Figures 6.1 and 6.2) (Inform—Hostalen PP, 1996; Libert and Rosenthal, 1992; Williams, 1992).

Stampable glass mat-reinforced (GMT) polypropylene homopolymer can be used in bumper beams, depending on the application. GMT is composed of continuous, unidirectional glass fibers that can be arranged in a particular direction to meet demanding performance requirements. In the Jaguar saloon, the bumper beam is used mainly as a carrier for the cosmetic cover; replacement of steel by GMT, appropriate for this application, can result in 30−40% weight savings and ~40% reduction in tooling costs, and the cost of corrosion prevention is eliminated (Inform—Hostalen PP, 1996; Libert and Rosenthal, 1992; Williams, 1992).

Modern bumpers are integrated into the car body, painted the color of the car, and adjusted to fit the contours of the load-bearing structure. Primers are necessary to promote adhesion of the paint to the bumper surface, and a surface treatment such as flame treatment may be required (Inform—Hostalen PP, 1996; Libert and Rosenthal, 1992; Williams, 1992).

Automobile manufacturers that use polypropylene bumpers include Ford (Orion, Escort), Peugeot (405), Volvo, Opel, and BMW. Polypropylene/EPDM (ethylene propylene diene monomer) blends used in the Opel Omega provide impact resistance (at temperatures as low as −30°C (−22 °F)), UV resistance, high dimensional accuracy, high-quality surface finish, and excellent weathering and chemical resistance properties. The bumpers are lightweight and easily painted, and special grades are available that result in low shrinkage, necessary when painted and unpainted bumpers are produced

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from the same injection mold. Resins have low thermal expansion (expansion coefficient of $50-80 \times 10^{-5}\ \mathrm{K}^{-1}$) in order to accommodate the small gaps ("zero-gap" concept) between the bumper and body parts present in modern automotive design. A polypropylene bumper is shown in Figure 6.3 (Future—The Hoechst Magazine, 1992; Inform—Automotive Industry, 1995; Inform—Hostalen PP, 1996).

Expanded polypropylene (EPP) foam is used in the bumper core on the 1997 Buick Park Avenue (Figure 6.4a). EPP is more resilient and is 30% lighter than other cushioning materials with the

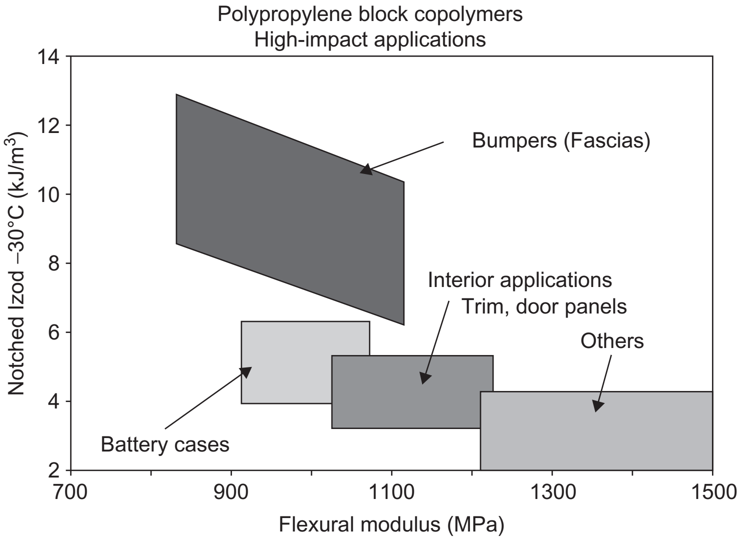

Figure 6.1 Rigidity and impact strength necessary for high-impact automotive applications. Bumper fascia requires good rigidity and maximum impact resistance; good rigidity and high-impact resistance are necessary for battery cases. In interior applications, trim, door panels, and lower interior parts require rigidity and good impact resistance; rigid block copolymers are usually used. Dashboards, commonly made from blends of polypropylene/EPDM/talc, require rigidity, high heat-deflection temperatures, and good impact resistance for sun-exposed parts. Parts in the upper half of the car interior, usually made from homopolymer or block copolymer and talc, require high rigidity (>3000 MPa; 435,110 psi) (*Libert and Rosenthal, 1992*).

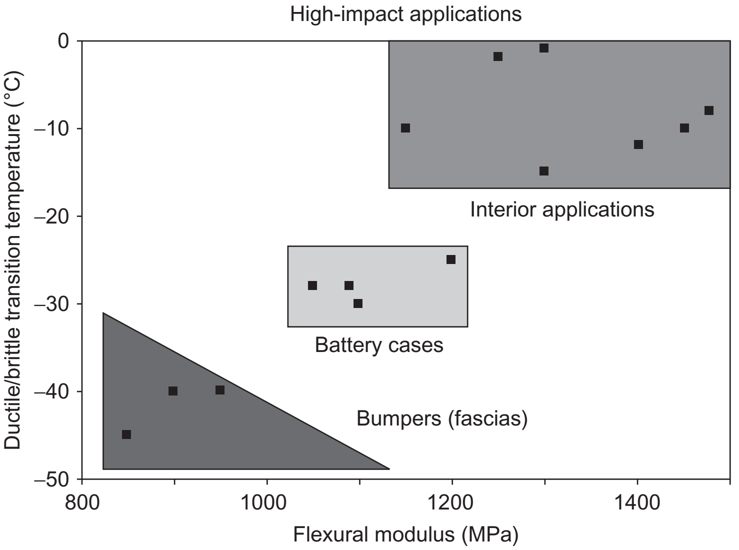

Figure 6.2 Impact resistance of automobile applications at low temperatures. Exterior bumper fascias require maximum impact resistance at low temperatures. A high level of impact strength is required for battery cases; for interior applications, low-temperature impact resistance is not as critical (*Libert and Rosenthal, 1992*).

Figure 6.3 A bumper made from talc-reinforced, elastomer-modified polypropylene (*Hostacom, Hoechst*) (*Inform—Hostalen PP, 1996*).

same performance properties. Due to a high ratio of impact strength to density, thinner walls can be used on the bumper cores, resulting in greater styling flexibility. Other uses of EPP foam in automotive applications are shown in Figure 6.4b (Neopolen).

Other exterior automotive applications include mirror housings, side protective strips, underbody trim, hubcaps, bumper brackets, spoilers, windscreens, air inlet grilles for bumpers, radiator grilles, and wheel arch linings. In the Opel Astra, polypropylene is used in the front and rear bumpers, spoilers, tailgate linings, and sill trim for the boot. The 1997 Mercury Mountaineer uses a "gouge-resistant" grade of enhanced or high-crystallinity polypropylene (Mytex) in the side body panels, replacing thermoplastic polyurethane elastomer (TPU)

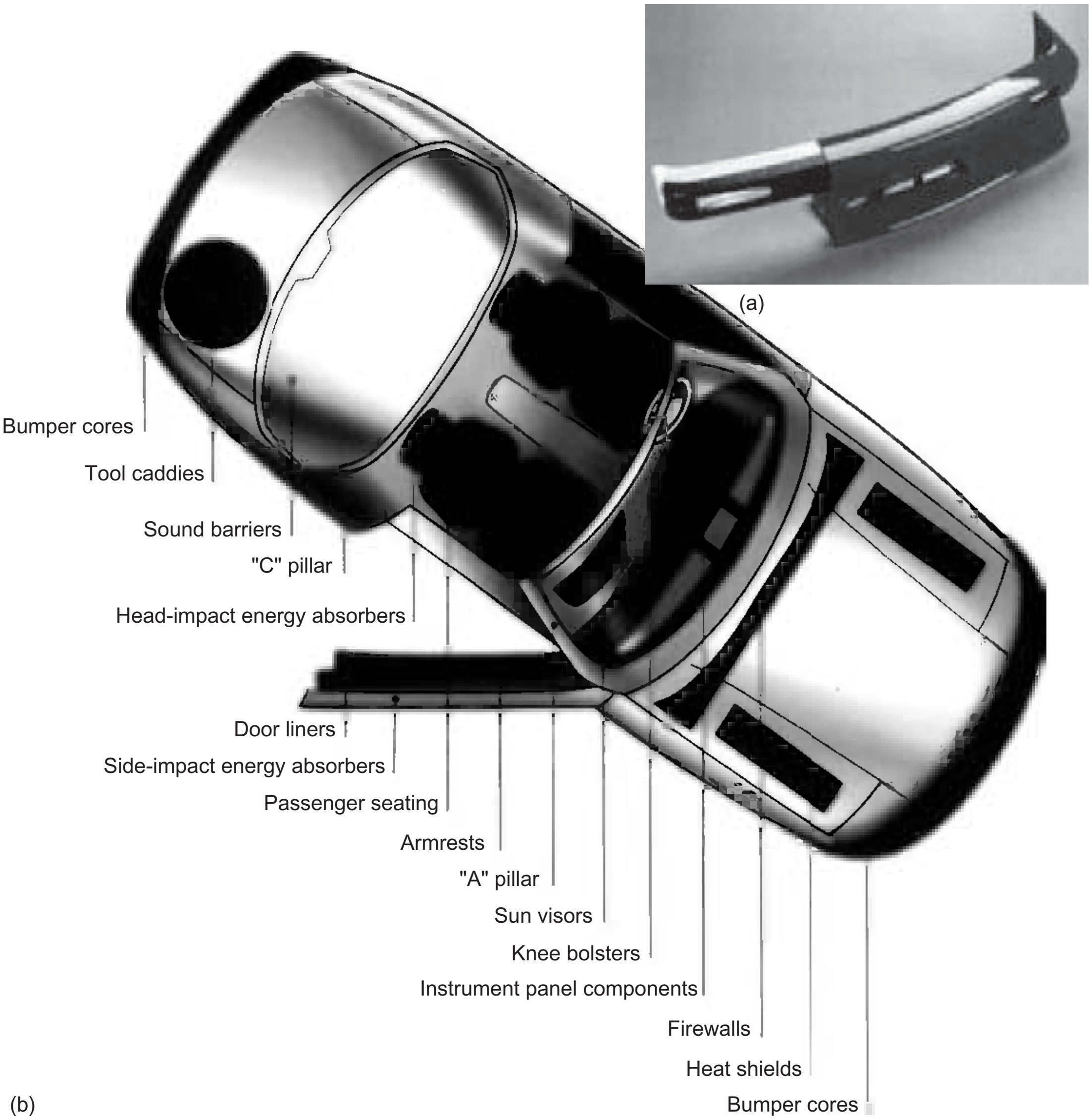

Figure 6.4 Automotive applications for EPP foam (EPP, BASF). (a) A bumper for the Buick Park Avenue and (b) interior and exterior automotive uses of EPP foam (*Neopolen*).

Figure 6.5 The side rubbing or protector strip on the Audi A4, produced from a polypropylene mineral-reinforced thermoplastic elastomer (*Hostacom, Hoechst*). The strip is painted to match the color of the car, and no metal insert is used (*Inform—Automotive Industry, 1995*).

(Dufton, 1992; Future—The Hoechst Magazine, 1992; Inform—Automotive Industry, 1995).

The Opel Omega uses a recyclable polypropylene/EPDM thermoplastic elastomer for the side protective strip, which protects the doors from damage. The easy-flowing material is bonded to a galvanized steel profile and fixed to the car with double-sided adhesive tape. The resin has a low coefficient of thermal expansion and excellent weathering resistance. The Audi A4 uses a mineral-reinforced thermoplastic elastomer, with no metal insert, for the side rubbing strip (Figure 6.5). The painted strip is fixed to the car with adhesive tape (Dufton, 1992; Future—The Hoechst Magazine, 1992; Inform—Automotive Industry, 1995).

Polypropylene rearview mirror housings are used in the Renault Clio and Twingo and the Peugeot 106. Rearview mirror housings require materials with adequate mechanical strength, even at low temperatures, resistance to cleaning agents and UV radiation, and the ability to withstand high winds and vibration (Future—The Hoechst Magazine, 1992).

6.1.2 Interior Automotive Applications

Although the performance requirements of interior trim components are less demanding than exterior applications, interior automotive components must also comply with esthetic and safety requirements. Environmental aging tests subject the interior component to temperature extremes of −40°C (−40°F) to 75°C (167°F) for components below waist level and up to 105°C (221°F) for components in sunlight (above waist level), in addition to UV exposure and humidity, cracking, crazing, color changes, or other effects should not be apparent after testing. Other tests include color fastness, abrasion resistance, fluid resistance, and flammability. Components within a specific radius of the driver cannot break into pieces with sharp, jagged surfaces on impact, and the component should be esthetically pleasing, with no rattles or squeaks during operation (Williams, 1992).

Interior automotive applications generally use a talc-filled, impact-modified grade of polypropylene. Applications of polypropylene include doorpost cladding and pockets, air ducts, heater/air-conditioning unit casings, armatures for fascia panels and center consoles, and carpeting. Polypropylene is used for fascia panels on the Ford Fiesta and Escort and the Opel Vectra and has been used in instrument panels, consoles, quarter panels, and pillars in Chrysler, Ford, and GM vehicles since the early 1990s (Barnetson, 1997; Williams, 1992).

Polypropylene provides a good price-to-performance ratio, weight reduction, recyclability, improved acoustic damping compared to other polymers such as ABS, and reduced windscreen fogging. Windscreen fogging is generally due to migration of volatile components from the polymer resin. The low stiffness of polypropylene makes thicker, bulkier moldings necessary, so that direct replacement of other plastics is not possible without expensive tool and design modifications (Barnetson, 1997; Czerski, 1992; Williams, 1992).

Talc-filled polypropylenes generally have poor scratch resistance; however, coated grades are available that do not exhibit the usual white marks after flexing or scuffing. Marking occurs when mechanical damage to the surface disturbs the resin's surface layer, resulting in changes in light reflection and exposure of talc particles; whitening and increases in gloss occur in the affected area. Whitening is most noticeable on dark moldings or finely textured surfaces; colors exhibit increased gloss (Barnetson, 1997; Czerski, 1992; Williams, 1992).

Volkswagen uses 20% talc-reinforced polypropylene for the pillar trim of the Polo (Figure 6.6). The material displays good flowability and retains toughness even at low temperatures. In the Opel Omega, the textile surface of the A pillar is produced by backmolding the textile trim with mineral-reinforced polypropylene. Scratch-resistant grades are used in the central console of the Volvo S40/V40 (polypropylene/EPDM), in the dashboard carrier and facing and the glove box lid of the

Mercedes Benz Sprinter (reinforced polypropylene), and in the tailgate trim material on the Audi A4 (block copolymer) (Future—The Hoechst Magazine, 1992; Inform—Automotive Industry, 1995; Inform—Hostalen PP, 1996).

Other applications include fascia in the Opel Corsa and Tigra (Figure 6.7); tailgate and side trim, hand grips, doorpost trim, and the center console on the Opel Astra; and speaker housings in the Ford Mondeo and Fiesta (40% mineral-reinforced). The housing for the warning, control, and indicator lights for the Ford Mondeo is made from a white-colored grade of polypropylene due to good light-absorbing properties that shield the lights from each other. Polypropylene is being used to replace ABS, polyamide (PA), and polycarbonate (PC) due to its recyclability, rigidity, low warpage, and flowability (Dufton, 1992; Future—The Hoechst Magazine, 1992; Inform—Hostalen PP, 1996).

Figure 6.6 Pillar trim of the Volkswagon Polo, made with 20% talc-reinforced polypropylene (*Hostacom, Hoechst*) (*Future—The Hoechst Magazine, 1992*).

Figure 6.7 Fascia on the Opel Corsa, made from 40% mineral-reinforced polypropylene (*Hostacom, Hoechst*) (*Inform—Automotive Industry, 1995*).

In the BMW 3 series, polypropylene is used in door handles (Figure 6.8), door pockets, trim and parcel shelves. The resin provides a balanced rigidity/toughness ratio, good scratch resistance, low thermal expansion, sound-deadening properties, and recyclability. In Volvo trucks, polypropylene is used in the three-part center console with storage trays, A and B pillar trim, and door tread. Truck materials must withstand much harsher conditions than those in cars, due to vehicle vibrations and increased driver use. The polypropylene components, designed for hard wear, deaden sound, and vibrations, are UV resistant and have a touch-friendly finish (Inform—Automotive Industry, 1995).

Cross-linked, foamed blends of polypropylene and polyethylene sheetstock are widely used in Japan as padding in car interiors in door trim panels, inserts, instrument panels, glove box doors, roof liners, pillars, and seatbacks. Polypropylene contributes durability, high thermal stability, and mechanical stiffness, while polyethylene provides elongation, ductility, and softness. The blends, which are foamed after cross-linking, may provide a substitute for polyvinyl chloride (PVC) foams (Smock, 1997).

Figure 6.8 Polypropylene door handles on the BMW 3 series (*Hostacom, Hoechst*) (*Inform—Automotive Industry, 1995*).

Dashboards made entirely of polypropylene are being developed. Currently, most dashboards are a three-layer structure consisting of a glass-filled polypropylene beam, a polyurethane foam core, and a PVC skin cover. An example of an all-polypropylene dashboard includes a beam of talc-reinforced homopolymer or copolymer, a core of EPP (BASF), and a rubber-modified block copolymer skin cover. Ferro is developing a foamable polypropylene with a small amount of metallocene polypropylene (mPP) added for a softer feel and more flexIbility and heat resistance in the dashboard core (Barnetson, 1997; Czerski, 1992).

6.1.3 Under-the-Hood Automotive Applications

The most severe environment in the automobile is the engine compartment; temperatures can range from −40°C (−40°F) to 140°C (280°F), and parts are exposed to vibrations and to chemical attack by lubricants and fuels. Heat resistance has become even more important in recent years due to the tendency of engine compartments to become more enclosed, causing higher temperatures (Dufton, 1992; Inform—Automotive Industry, 1995).

The largest amount of polypropylene in under-the-hood applications is used for battery cases. Polymer properties required for battery cases include good rigidity and a high level of impact resistance, especially at low temperatures (Figures 6.1 and 6.2). Other applications include fluid reservoirs (water, antifreeze, brake fluid, etc.), headlamp housings, air ducts, fans and brackets, fan wheels, air filter housings, charcoal canisters, radiator frames, steering rod covers, cable ducts, timing chain covers, heater housings, and central electric housings. GMT materials are used in semistructural applications such as battery trays, engine shields, and support panels for radiator and fan housings; polypropylene, PBT, or PC/PBT is used as the thermoplastic material, depending on the heat resistance required for the component (Dufton, 1992; Libert and Rosenthal, 1992; The Hostalen PP, 1996).

In the Mercedes Benz E class, reinforced polypropylene is used in the radiator frame, the air intake grille, the radiator tank cover, the housing of the central electrical components, the lid of the cooling water compensation reservoir, the heating and ventilation housings, and the headlight housings. Headlight housings are generally made from talc- and glass fiber-reinforced grades and have high dimensional stability, good heat resistance and low-temperature stability, good processability, and good chemical resistance. Due to their toughness, the housings can be installed by snapfitting, making dismantling and recycling easier (Inform—Automotive Industry, 1995; Inform—Hostalen PP, 1996).

Heater housings for the Mercedes C class are made of 40% mineral-reinforced polypropylene. Use of this material has reduced fogging and eliminated the unpleasant odor that entered new car interiors along with the heated air. The housing is dimensionally and heat stable and reduces transmission of structural-borne sound (Inform—Automotive Industry, 1995).

Polypropylene used in ventilation grilles exhibits good weathering resistance, and the grilles retain their visual appearance even after several years. The polypropylene spoiler on the Peugeot 406 remains UV resistant and dimensionally stable under severe heat; in addition, the good flowability of the resin makes production easier. The Opel Astra uses polypropylene in air cleaner housings, air ducts, coolant, washer, brake fluid reservoirs, battery casings, and fan mounts. Two-part polypropylene structural ducts in the 1997 Ford Flareside truck replaced ABS, resulting in lower cost and improved sound-deadening properties. The ducts can be hot plate welded. Several under-the-hood applications of polypropylene are shown in Figure 6.9 (Barnetson, 1997; Dufton, 1992; Inform—Hostalen PP, 1996).

6.2 Medical Applications

Polypropylene is used in a variety of medical applications—medical devices; drug delivery systems; nonwoven fabrics; packaging for medical devices, solutions, and drugs; and other applications. It is used in disposable and prefilled syringes, sample cups, diagnostic cuvettes, centrifuge tubes, parenteral kit parts, needle shields, connectors, surgical trays, infectious waste containers and bags, drapes, clamps, spine support boards, and blow-molded containers. Other uses include contact lens molding cups, needle disposal containers, phlebotomy needle holders, infant feeding tubes, medication spoons, analytical test strips, and blood oxygenator membranes. Syndiotactic polypropylene is frequently preferred for applications such as blood bags and sterile garments. It is more transparent than isotactic

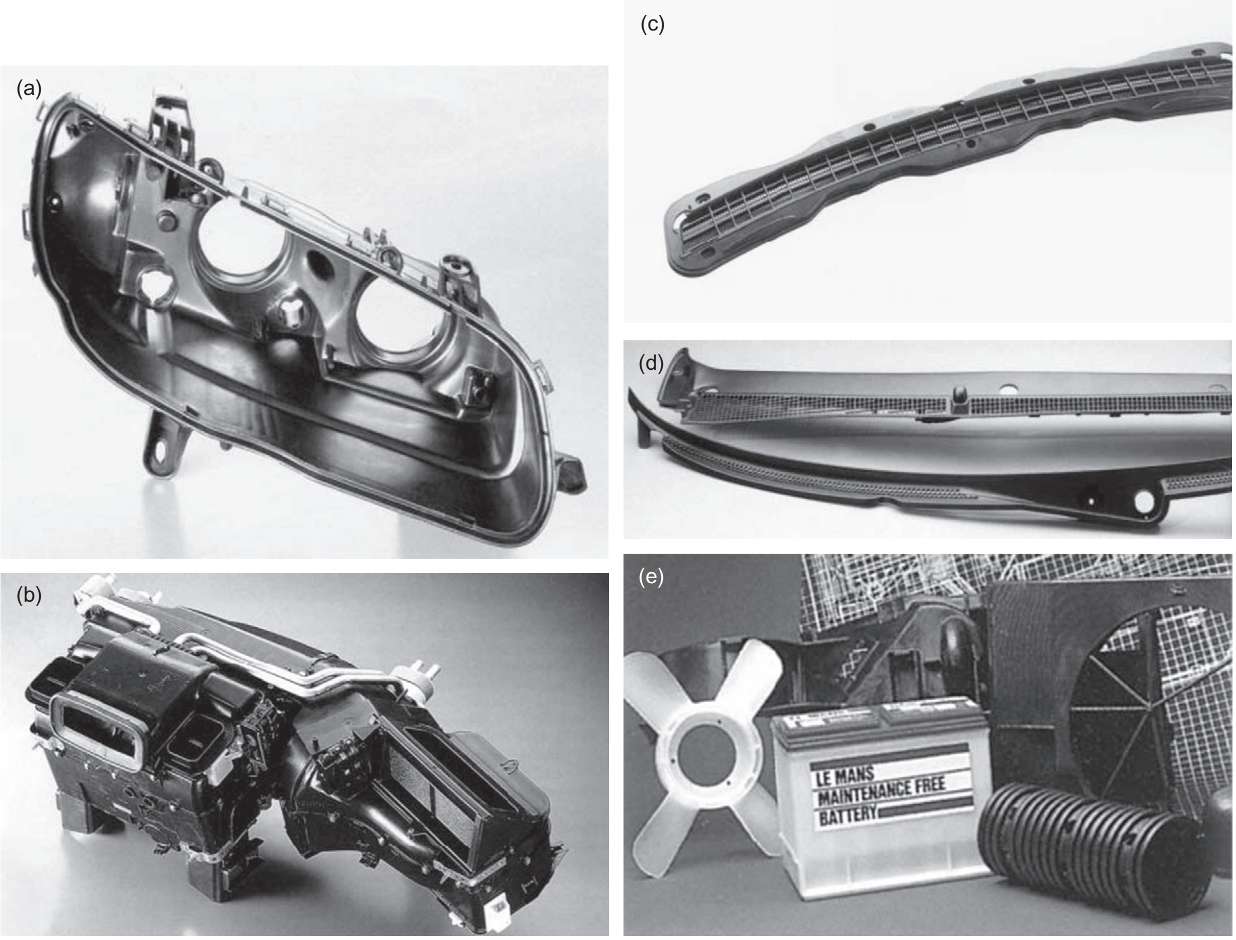

Figure 6.9 Under-the-hood applications of polypropylene ((a)–(d) made from Hostacom from Hoechst and (e) from Amoco). (a) Headlight housing, (b) heater housing, (c) ventilation grid, (d) draft deflector, and (e) battery case, fan (*Amoco Polypropylene Homopolymers, 1992; Inform—Hostalen PP, 1996*).

polypropylene and is more resistant to gamma sterilization (Ewen, 1997; Performance Polyolefins, 1991; Portnoy, 1994a; Precision Woven Screening Media, 1997).

Tamper-resistant/evident closures can be inexpensively injection molded from polypropylene, and waste containers and bags extruded from polypropylene can be sterilized. Clamps, connectors, and closures for solution bottles can be made by injection molding using the "living hinge" property of polypropylene. Living hinges can be flexed over a million times before failure for a description of living hinges in polypropylene) (Performance Polyolefins, 1991; Portnoy, 1994a; Precision Woven Screening Media, 1997).

Polypropylene is also used in health-care-related applications such as packaging for health and beauty aids, cosmetics, and nutritional products. It is estimated that over 150 million pounds of polypropylene is used per year in medical devices, with the largest fraction (over 70 million pounds per year) used for disposable hypodermic syringes and other small parts. Polypropylene thermoplastic elastomers and thermoplastic vulcanizates are gaining in popularity for medical applications as replacements for rubber and urethane in applications such as wound dressings, drainage bags, and gloves. Cost reduction, in addition to allergic reactions to latex proteins and biocompatibility concerns about the use of natural rubber, has led to increased use of these materials (Boschert, 1997; Performance Polyolefins, 1991; Portnoy, 1994a,b; Precision Woven Screening Media, 1997).

Useful properties for medical applications include an excellent resistance to solvents and autoclave heat, good tensile strength and stiffness, a long flex life, a high heat distortion temperature, and a low density and moisture vapor transmission rate (MVTR). Polypropylene is easily processed into complex shapes and is generally nontoxic, chemically inert, and tolerant to sterilization. The low to moderate level of additives used for stabilization do not usually interfere with medical use. Polypropylene waste forms noncorrosive incineration products, and the material is easier to recycle than many other polymers. Most polypropylene grades easily pass USP Class VI and Tripartite testing protocols (From Rexene Technology, 1987; Performance Polyolefins, 1991; Portnoy, 1994a).

The use of polypropylene in medical products is cost-effective. Chemical inertness results in a longer shelf life, and handling costs and costs per unit volume are reduced due to polypropylene's lightweight. The cost-effectiveness of polypropylene has led to its substitution for other materials such as glass and other plastics, a trend that is expected to continue with the current emphasis on cost containment in health care (Precision Woven Screening Media, 1997; Performance Polyolefins, 1991; Portnoy, 1994b).

Several medical applications of polypropylene are shown in Figure 6.10.

6.3 Appliances

Appliance applications of polypropylene include ductwork for dryers, door liners for dishwashers, wash racks and lids for clothes washers, hand mixers, and hair dryers. Mineral-filled polypropylene is used in refrigerator liners, replacing ABS (DeBoest, 1988).

6.3.1 Small Appliances

The use of polypropylene in small appliances is growing, as producers strive to lower production costs; the use of polypropylene is growing faster than any other resin. In kitchen appliances, polypropylene is being substituted for engineering plastics such as ABS, PC, and polyamide. Although ABS, an amorphous polymer, provides better scratch resistance and a higher surface finish than homopolymer polypropylene (65–80% Gardner gloss scale compared to 95% for ABS), resins like ABS or polyamide are 13–20% more dense, resulting in increased resin cost. In Japan, filled grades are substituted for ABS in rice cookers and are also being used in coffee makers and large thermos flasks. Processors use barium sulfate fillers to obtain surface finishes similar to those obtained with ABS. Other useful properties for small appliances include abrasion resistance and resistance to fruit juices, bleach, and cleaning liquids; in addition, high-flow grades allow easier coloring and processing of unique shapes than metal (Colvin, 1996; O'Neill, 1996).

Glass-reinforced polypropylene is used in the base of the Bosch-Siemens hand mixer. High rigidity, toughness, and heat resistance enable the resin to withstand the severe loads encountered in uses such as kneading dough. The use of polypropylene has resulted in lower material costs compared to polyamide, the original material used in the mixer (Hostacom, 1993).

The excellent stress cracking resistance of polypropylene makes it useful in commercial hair dryers, which undergo many heating and cooling cycles per day. Polypropylene in the Wella M36 Sensortronic drying hood provides dimensional stability and accuracy, even at high temperatures, and allows snapfit hooks and cable cleats to be integrally molded into the chassis, eliminating additional assembly operations. The resin used (Hoechst Hostacom) is flame retardant, with a UL–94 V–0 rating (Hostacom, 1993).

Polypropylene is used in various models of the Rowenta steam irons. In the Dolphino, natural color, stabilized polypropylene replaced PC. Although changing materials usually requires changing molds, no major mold changes were necessary—only adjustments that took 2 days to complete. The tank was molded with in-line coloring using a 2% masterbatch. In the Surfline DE41, the upper and lower housing parts and the tank base are made from 10% mineral-reinforced polypropylene; advantages include lightweight, heat resistance, and a balanced rigidity/toughness ratio. The surface finish is not affected by long-term exposure to steam, and snap-fits can be molded in, allowing for lower cost assembly and easier servicing (Colvin, 1996; Hostacom, 1993).

The Rowenta deep fat fryer uses a high-gloss, temperature- and scratch-resistant grade of polypropylene. Improved processing and a reduction in the

Figure 6.10 Various medical applications of polypropylene. (a) Centrifuge tubes, (b) connectors, (c) syringes and drug containers, (d) trays, syringes, connectors, and woven fabrics, and (e) containers and IV supplies (*Amoco Polypropylene Homopolymers, 1992; Boschert, 1997; From Rexene Technology, 1987; Mitsui Sekka; Performance Polyolefins, 1991*).

number of different plastics used in the part resulted in high cost savings (Barnetson, 1997).

In the juice centrifuge of the multifunctional MK3 kitchen appliance from Bosch-Siemens Hausgeräte, 10% mineral-reinforced polypropylene withstands very high mechanical stress due to the high-speed centrifuge (2400 rpm). The easy-flowing, hard and rigid grade can withstand the centrifugal force over the long term and can be injection molded in a filigree part with 2304 openings (Figure 6.11) (Future—The Hoechst Magazine, 1992).

The pump housing and the flange between the motor and housing in the BADU "90" swimming pool pump are made from 30% glass-reinforced polypropylene. Material damage due to heat from the pump is eliminated because of the high heat-deflection temperature (HDT/B of 155°C; 311°F); other useful properties are chemical resistance, rigidity, toughness, and dimensional stability. The pump is thick walled but lightweight, due to the low density of polypropylene (Hostacom, 1993).

Several applications of polypropylene in small appliances are shown in Figure 6.11.

6.3.2 Large Appliances

Use of polypropylene in large appliances is increasing, due to its low cost and the enhanced properties of newer grades. Polypropylene is competing with thermosets, metals, and other thermoplastics such as styrenics. The weight of polypropylene used in washing machines was estimated as 22 lb/unit in 1995; use is expected to rise to 44 lb/unit in 2000 as it replaces engineering polymers (O'Neill, 1996).

Polypropylene is used in washing machine drums (typically 30% glass-reinforced, 40% talc-filled, and homopolymer). Unfilled polypropylene is used in drums for top-loading machines at spin speeds of ~600 rpm; a glass-reinforced grade is now used in a front-loading drum with a spin speed of 1200 rpm, replacing metal. In 1995, General Electric began using an injection-molded glass-reinforced polypropylene drum to eliminate the need for metal stamping. Other applications include pump housings; 90% of all West European washing machines have plastic pump housings, with a 60:40 ratio between talc-filled and glass-reinforced grades. Talc-filled bases are used for washing machines, washer-dryers, and dishwashers, primarily for cost reduction; however, the use of polypropylene also eliminates corrosion and allows structures and supports to be built in for functional integration (Barnetson, 1997; O'Neill, 1996).

Substitution of polypropylene for established resins such as ABS requires changes in processing, including minimizing the length of the parting line due to the higher flow rate of polypropylene compared to ABS, and the necessity of designing reinforcements such as ribs into housings to compensate for the lower structural strength. Newer grades designed for large appliances have increased stiffness, higher temperature and deformation resistance, and improved surface hardness, and they are easier to process. The sound-deadening properties of polypropylene compared to metal are useful when appliances in smaller dwellings are placed in the kitchen instead of the basement or laundry room, and the recyclability of polypropylene aids in meeting consumer demands for recyclable components and in adhering to environmental regulations (O'Neill, 1996).

Whirlpool uses polypropylene reinforced with 30% chemically coupled glass fibers for a washing machine drum; the spin speed of the machine is 1200 rpm. The geometry of the drum was optimized using a CAD study that simulated the deformation of the washing machine drum at high spin speeds, in order to offset high-speed stresses. To improve the connection between the motor and the container, belt pre-tensioning was used to compensate for material creep. Use of polypropylene led to a lower cost production process, better integration of functions, and a water- and energy-saving part design (Future—The Hoechst Magazine, 1992).

A 40% mineral-reinforced grade is used in the dispenser dish of a Miele washing machine. The most important requirement of a dispenser dish is detergent resistance; a second requirement is the ability to withstand a reasonable amount of stress due to vibrations of the motor. The rigidity of polypropylene and its excellent chemical resistance make it useful for this application, and the dish design, with three compartments, allows for water penetration throughout the dish and for efficient detergent removal (Future—The Hoechst Magazine, 1992).

Polypropylene (30% mineral-reinforced) is used in the inner door of a Bosch-Siemens Hausgeräte

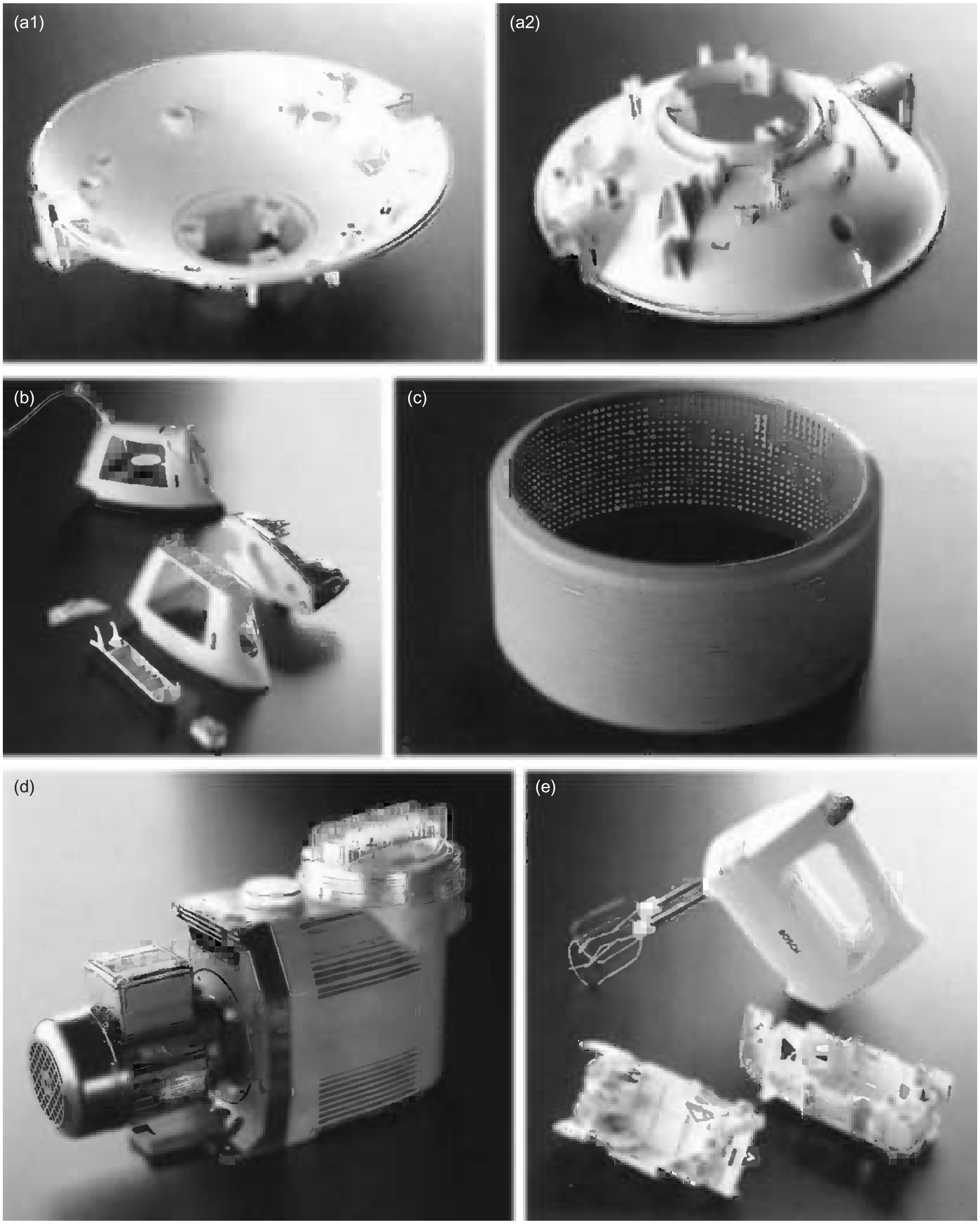

Figure 6.11 Applications of polypropylene in small appliances ((a)–(e) made of Hostacom from Hoechst and (f) from Amoco). (a) Parts for a commercial hair dryer, (b) steam iron, body is made from polypropylene, (c) juice centrifuge, (d) swimming pool pump, (e) hand mixer, and (f) coffee maker (*Amoco Polypropylene Homopolymers, 1992; Future—The Hoechst Magazine, 1992; Hostacom, 1993*).

Figure 6.11 (Continued)

GmbH tumbler dryer that has the largest loading porthole of all tumble dryers on the market. The inner door with integral fluff filter holder ensures perfect closure of the porthole opening and serves as a carrier for the outer door. The good rigidity, high dimensional accuracy, and high HDT/B (of >120°C; >240°F) of polypropylene ensure tight door closure and reliable dryer operation. High gloss provides a pleasant appearance, and very good flow properties are useful for large parts (Hostacom, 1993).

Several applications of polypropylene in large appliances are shown in Figure 6.12.

6.4 Textiles and Nonwovens

Polypropylene fibers are used in carpeting, automobile interiors, apparel, geotextiles, and nonwoven applications. Polypropylene is versatile, colorfast, chemically resistant, economical, lightweight, and environmentally friendly. It has good insulating properties and a soft textile feel, and fibers are insensitive to moisture and dirt. Use of polypropylene in textiles has grown since the mid-1970s; textile applications now account for 25% of the total polypropylene market in western Europe, comprising 20% of western Europe's synthetic fiber production.

6.4.1 Floor Coverings and Home Furnishings

Polypropylene floor coverings are used in homes, offices, and automobiles. Polypropylene fibers are also used in upholstery fabric, wall coverings, and bedding. Polypropylene is economical—its low density provides more fiber per pound of polymer—and durable, able to withstand years of traffic with no change in appearance. Due to its low weight compared to other fibers, carpets can be produced with more volume but with the same surface weight. Floor coverings are stain resistant, colorfast, static resistant, and nonallergenic—polypropylene is not affected by moisture, mold, or mildew and does not support fungi or bacteria (Polyolefin: Because It Works).

6.4.2 Automotive

Needle-punched polypropylene carpeting has been developed for automotive use. It is lightfast and aging resistant and is used in floor coverings, rear parcel shelves, and in the boot. The use of polypropylene in automotive textiles, in addition to the diversity of other automotive applications of polypropylene, aids in the goal of achieving a single-material system for easy recycling (Inform—Hostalen PP, 1995).

6.4.3 Apparel

The wicking action of polypropylene makes it useful in clothing for outdoor sports, such as hiking, skiing, biking, and swimming. Polypropylene does not absorb moisture, so polypropylene clothing worn next to the skin does not get wet from perspiration; the moisture passes through the material into the air or to an outer absorbent material, such as cotton. Clothing also dries faster. The low density of polypropylene makes it lightweight (the only fiber lighter than water) and useful in swimwear, biking shorts, and other apparel. Gases, such as oxygen, pass through the material; this "breathability" ensures that the wearer remains cool and comfortable, even in warm weather (Polyolefin: Because It Works).

Polypropylene apparel resists fading, odors, stains, mold, mildew, and bacteria. It is easy to care for; it is colorfast, even in chlorinated environments, and light and dark colors can be

Figure 6.12 Polypropylene applications in large appliances. (a) Inner door of a washing machine, (b) washing machine drum, (c) dispenser unit for a washing machine, (d) washing machine pump, and (e) dispenser unit for dishwashers. All are made of Hostacom from Hoechst (*Future—The Hoechst Magazine, 1992*).

washed together. Most apparel can be dried in home dryers at low temperatures (Polyolefin: Because It Works).

6.4.4 Industrial Applications and Geotextiles

Polypropylene is used in filters and filaments, as cordage for rope, fish netting, and other applications. Cordage is lighter than water, so nautical ropes float, and the strength-to-weight ratio is up to 10 times that of steel. The nonwettable fibers are useful in oil-absorbing booms, soaking up oil, fuel, hazardous wastes, inks, and solvents. Other uses are in woven packing bags (Big Bags), strapping tape, binder twine, tarpaulins, artificial grass, tow ropes for motor vehicles, and brushes (Elber, 1993; Inform—Hostalen PP, 1995; Polyolefin: Because It Works).

Filtration products are used in the medical, electronics, chemical, mining, and food processing industries. They are used in biotechnology and medical research for cell separation, tissue cultures, fluids filtration, water purification, drug preparation, and blood treatment. Filters are used in clothes dryers, power tools, coffee machines, and water filters. The woven mesh structure filters out water, oil, fuel, lint, debris, food, and other impurities. Filters are available that meet Food and Drug Administration (FDA) requirements for food contact applications (CFR Title 21) and can be obtained in a variety of forms—bags, tubes, pouches (Polyolefin: Because It Works; Precision Woven Screening Media, 1997).

Geotextiles can be woven or nonwoven. They are used in building and construction sites and in landfills. In concrete and asphalt paving installations, geotextiles reduce crack formation and increase pavement strength and durability. At construction and landscaping sites, they stabilize soil against erosion, prevent sediment runoff, and promote rapid revegetation. Open-mesh fences reduce wind, sand, and snow damage; provide crowd control at concerts and sporting events; and protect hazardous work sites and utility areas. All geotextiles have high tear strength; other properties can be tailored to the particular application by the choice of grade and processing parameters (Inform—Hostalen PP, 1995; Polyolefin: Because It Works).

6.4.5 Nonwovens

Nonwoven fabrics are used in sanitary products, surgical garments, geotextiles, and other applications. In sanitary products—disposable diapers, feminine hygiene products, and adult incontinence aids—a soft nonwoven cover stock maintains dryness and comfort. Fibers have high tear strength, even when wet, and moisture is transported through the material. Disposable surgical nonwovens, including shoe covers, gowns, caps, and bedding, are economical and ensure proper sanitation. Nonwoven bouffant caps, wipes, and cleaning pads are used in restaurants and food service areas to keep food preparation areas free of contamination. Other uses include carpet backing, mattress pads, cushions, vacuum cleaner bags, overnight courier envelopes, and automotive car covers.

Protective garments prevent contamination of sensitive appliances in ultraclean rooms by workers. Agricultural nonwovens provide air, light, and water permeability to seeds and plants and protect against cold, bad weather, and insect pests. As a result, early sowing is possible, and plants grow well, with a high yield (Future—The Hoechst Magazine, 1992; Inform—Hostalen PP, 1995; Polyolefin: Because It Works).

Several applications of textiles and nonwoven fabrics are shown in Figure 6.13.

6.5 Packaging

Packaging is used to contain, protect, and identify the products within the package. Packaging protects the product from mechanical damage and biological attack and informs the customer about such topics as the product's size, ingredients, and instructions for use. It provides convenience throughout the life of the product—during shipping, retail, and final use—and can help preserve freshness of food products that are likely to spoil.

The most important application for plastic packaging is in food packaging (Barnetson, 1996, 1997; Goddard, 1993; Polymers in Contact with Food, 1991).

6.5.1 Plastics Versus Other Packaging Materials

Common packaging materials include wood, glass, metal, paper, and plastic. Advantages of plastics as packaging materials include easy processing,

Figure 6.13 Polypropylene applications in textiles and nonwoven fabrics. (a) Rope, (b) outdoor apparel, (c) geotextiles, (d) and (e) woven filters, (f) disposable diapers, (g) packing bags (Big Bag), (h) surgical garments, and (i) automotive upholstery and automotive interior cladding part with trim (*Amoco Polypropylene Homopolymers, 1992; Inform—Hostalen PP, 1995; Polyolefin: Because It Works; Precision Woven Screening Media, 1997*).

low cost, and lower weight due to a lower density than other packaging materials. Plastic packages can be optimized for a particular application, and they are more impact resistant than glass, which breaks when dropped and requires more careful handling. Plastics have a lower volume occupancy than glass; for the same strength as plastic, glass packaging requires a higher volume and weight. For example, a plastic drink bottle with a wall thickness of <1 mm (0.04 in.) is equivalent in strength to a glass bottle with a wall thickness of 2–3 mm (0.08–0.1 in.) (Barnetson, 1996).

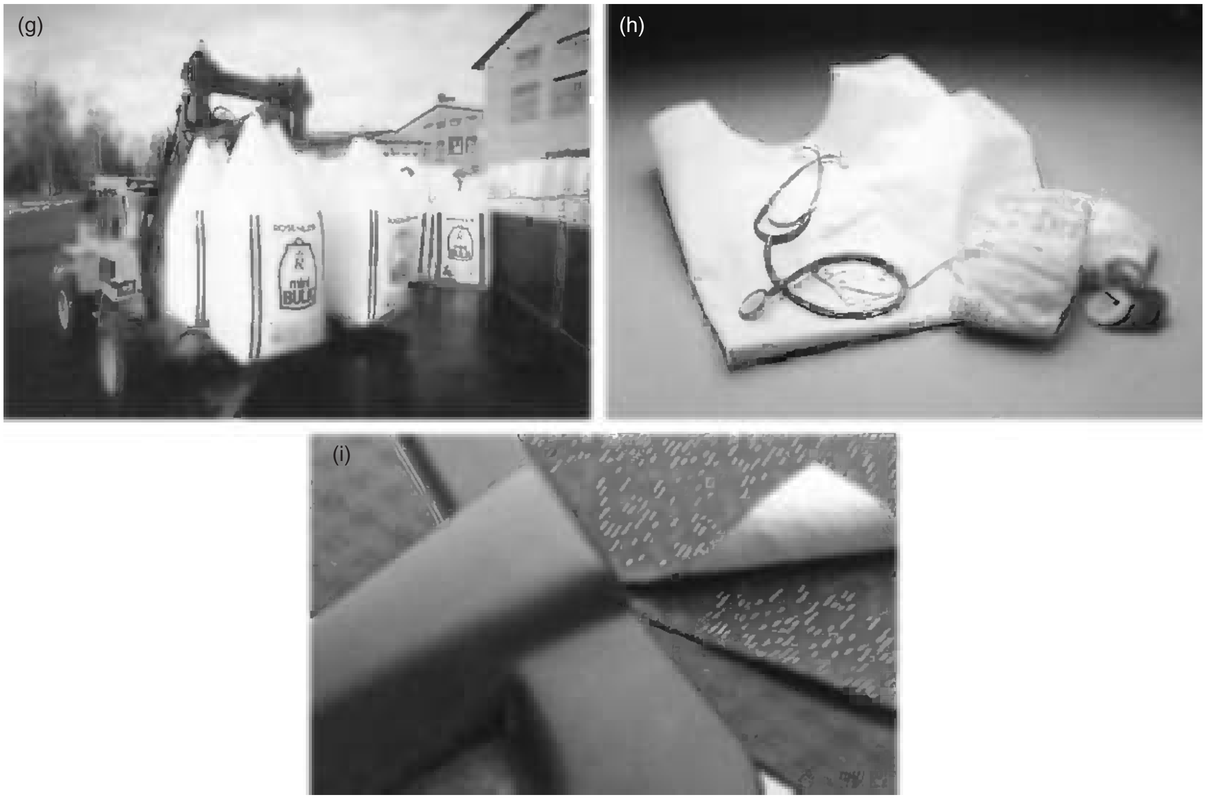

Figure 6.13 (Continued)

Disadvantages of plastics include environmental stress cracking, poor stacking strength compared to other packaging materials, and problems with sterilization when used in medical applications. Due to their similar molecular structure, polyolefins such as polypropylene can absorb paraffins and solvents, which can cause deformation. Unlike glass and metals, plastics do not provide a complete barrier to gases and moisture. However, new techniques such as lamination or coextrusion, or a combination of plastics with other packaging materials (paper, aluminum foil), can provide good product protection (Barnetson, 1996).

6.5.2 Use of Polypropylene in Packaging

One-third of all polypropylene applications is in packaging. Polypropylene is used in packaging biscuits, crisps, sweets, bread, pasta, dairy products, convenience foods, dried fruits, snacks, syringes, and medicine bottles. Polypropylene films are used in flexible packaging, for shirts, hosiery, bread, and produce, and in shrink-wrap applications for toys, games, hardware, frozen foods, and cigarette wrap. Use of polypropylene in packaging is growing, especially in blow-molded containers, sheet, profile and film extrusion, and injection-molded packaging. New grades with high stiffness, high clarity, and good elastomeric properties have enabled polypropylene to replace both plastic and nonplastic packaging materials. The trend in packaging toward thinner walls, lighter weight, and greater stiffness (in order to conserve resources) fits well with polypropylene's balanced combination of properties: toughness, stiffness, hardness, excellent chemical resistance, and low density (Bailey and Brauer, 1994; Barnetson, 1997).

Some estimates indicate that up to two-thirds of polypropylene's growth is due to replacement of other thermoplastics. Polypropylene has replaced the more expensive polystyrene in many food packaging applications due to a lower cost and properties such as toughness, resistance to stress cracking, and favorable organoleptic properties. It is being considered as a substitute for PETP (polyethylene terephthalate polyester) in applications such as dairy containers and peanut butter jars due to the increased clarity of new resins, and oriented, coextruded films are used as a replacement for cellophane in the snack food industry (Barnetson, 1997; Polymers in Contact with Food, 1991).

Polypropylene is preferred over polyethylene terephthalate (PET) for use in hot-filled products such as juice drinks due to its resistance to high temperatures (heat distortion temperature at 66 psi of 99–127°C (210–260°F) compared to 38–129°C (100–264°F) for PET). Although its oxygen barrier properties are poor, polypropylene provides five times the moisture vapor transmission (MVT) performance of PET and at least ten times the MVT of polystyrene, making it useful in packaging dry foods and moisture-sensitive products such as coated analgesics and vitamins. The use of polypropylene packaging in these applications extends shelf life and can eliminate the necessity of adding dessicants to the container to prevent moisture accumulation (Milliken Chemical, 1996).

6.5.3 High-Crystallinity and High-Melt-Strength Grades

High-melt-strength grades of polypropylene allow it to be processed on high-speed, wide-web (up to 142-cm, 56-in.-wide sheet) packaging equipment commonly used in the food industry. Conventional low-melt-strength polypropylene cannot be processed on wide-web equipment due to a tendency to sag during sheet extrusion. Low-melt strength also causes a rapid wall thinning, so that thicker walls are necessary to account for nonuniform wall thicknesses. Heterophasic copolymers, such as polypropylene polymerized with ethylene– propylene rubber, are also used on wide-web equipment and are commonly used in such melt-phase thermoformed products as microwaveable food packaging due to low odor and taste transmission properties (Bailey and Brauer, 1994; Himont, 1992).

Highly crystalline grades are used in producing highly rigid film (film for labels), very thin-walled flexible packaging (twist film, stand bags), and thermoformed articles. They are used in disposable packaging for microwave foods due to improved heat resistance and low creep (Barnetson, 1997).

6.5.4 Clarified Polypropylene

Polypropylene random copolymers have moderate clarity, although the clarity of polyolefins is generally sensitive to processing conditions. The addition of clarifying agents to random copolymers provides see-through clarity to polypropylene packaging, important in many packaging applications such as rigid containers. Combined with the other favorable properties of polypropylene (heat distortion temperature, stiffness, impact strength, cost, recyclability, etc.), clarified resins compare favorably to other materials used in rigid packaging, such as PET, styrene acrylonitrile (SAN), polystyrene, and PVC. Clarified polypropylene is clearer than high-density polyethylene (HDPE) and has superior organoleptic properties and heat resistance—it can be hot-filled at temperatures up to 100°C (212°F) compared to 91°C (196°F) for HDPE (Milliken Chemical, 1996; Polymers in Contact with Food, 1991).

Clarified polypropylene sheet is used in thermoformed cups for Brisa purified water as a replacement for the more costly polystyrene. The 8-oz. foil-sealed cups are equal in clarity to polystyrene and provide an 8-week shelf life, compared to 3–4 weeks for polystyrene. The polypropylene cups are resistant to ozone and have better organoleptic properties. They are more rigid and tougher than polystyrene cups, and are ozone resistant. They can be easily crushed after use without breaking into a number of shards (Milliken Chemical, 1996).

6.5.5 Metallocene Polypropylene

The development of metallocene catalysts has resulted in improved properties for packaging applications, including greater puncture resistance, higher impact strength, greater low-temperature impact strength, and better organoleptic and optical properties than Ziegler–Natta polypropylene. Metallocene resins for packaging applications also have good flow resistance, high stiffness, high transparency, and high heat resistance. High gas permeation rates of metallocene resins make them useful in packaging vegetables, which continue to respire after packing (Barnetson, 1996, 1997).

The enhanced clarity of mPP makes it useful in thin-walled, transparent-molded packaging such as frozen food packaging. Transparency of one grade of mPP homopolymer (M Novolen NX 50081, BASF AG) in supplier trial runs was 93%, compared to 47% for high-crystallinity polypropylene and 89% for new clarified, nucleated resins. Random copolymer mPP was even more transparent (95% transparency) and was only slightly lower than that of PET (100% transparency). Trials of mPPs with melt flow rates from 4 to 120 indicate that nucleators, used to increase the crystallinity, stiffness, and clarity of conventional polypropylene, also benefit mPP (Metallocene Grades, 1997).

The high melt flow rate of mPP reduces cycle times when molding thin-walled containers while still providing toughness and stiffness. Cycle time of a 60 MFR (melt flow rate) mPP was 10% faster than a nucleated grade, with comparable clarity and gloss. Cycle times of 60 MFR mPP and a high-crystallinity grade were equal, but the mPP provided significantly higher clarity and gloss (Metallocene Grades, 1997).

New free-flowing mPP grades for injection molding are suitable in applications such as tubs for dairy products, ice cream, cosmetics containers and for thin-walled nonfood packaging and high-volume transport containers and crates (Barnetson, 1996, 1997).

6.5.6 Rigid Packaging

Polypropylene is widely used for rigid packaging, such as margarine tubs, yogurt containers, trays, milk jugs, and bottles. Thermoformed polypropylene margarine tubs have replaced most PS and PVC tubs. Random copolymers are frequently used in products such as food storage containers due to their excellent clarity and good balance of impact strength and stiffness. In thin-walled parts, such as injection-molded delicatessen containers or yogurt cups with a length-to-thickness ratio of up to 400:1, use of polypropylene copolymers with high melt flow rates (35 g/10 min) can reduce container weights by 30% over containers produced with other materials. Containers are tough, rigid, and recyclable. They provide a moisture barrier and top-load strength, and the low-temperature resistance protects the product at refrigerator temperatures (Barnetson, 1997; Future—The Hoechst Magazine, 1992; Milliken Chemical, 1996; Oertel, 1996; Polymers in Contact with Food, 1991; Thompson et al., 1987).

Polyethylene is the material most used in rigid packaging; however, due to its lower flexural modulus compared to polypropylene, it requires a greater wall thickness in thin-walled containers. Polypropylene is used in screw-on caps and closures, due to the resin's stiffness, resistance to stress cracking, and living hinge properties, and it is used in tamper-evident closures for medicines, liquor, and food products. Polypropylene is replacing HDPE in applications such as crates and paint containers (Barnetson, 1997; Future—The Hoechst Magazine, 1992; Milliken Chemical, 1996; Oertel, 1996; Polymers in Contact with Food, 1991; Thompson et al., 1987).

Biaxially oriented, clear polypropylene bottles and jars produced by a single-stage injection blow-molding process may compete with PET containers as a substitute for glass containers. Oriented polypropylene is one-third less expensive than PET, even when allowing for extra wall thicknesses to compensate for higher flexibility. It performs better in hot-fill applications and has good water barrier properties; however, polypropylene is a poor barrier to gases, and methods to coat the material with a better barrier polymer such as polyvinylidene chloride or ethylene vinyl alcohol (EVOH) are currently under development. Possible applications for these containers include pasteurized products, pickles, sauces, creams, instant coffee, and powdered milk (Roberts, 1989).

Polypropylene is suitable for containers used in microwave cooking, as long as the food product does not have a high fat content and the container is designated as "microwave use only". In these cases, the moisture in the food ensures that the food temperature does not exceed 100°C (212°F), which is near the hot-fill temperature limit of polypropylene. Blends of materials are used in containers designed for dual oven use. For example, a blend of polypropylene, molded pulp, fillers, and additives can withstand temperatures from −40°C (−40°F) to 200°C (392°F), similar to CPET. The containers have a pearlescent finish and lack the wrinkled corners common on paperboard trays. Many microwaveable products contain several layers of different materials for shelf-stable packaging (see Section 6.5.8). Shelf-stable products may be stored at ambient temperatures and do not require refrigeration (Polymers in Contact with Food, 1991; Roberts, 1989).

Examples of polypropylene in rigid packaging include a coffee cream jug (Figure 6.14) made of a single material for easy recycling. The design incorporates a tear-off ring that can be pulled with the lid strip. The high-impact strength and low-temperature resistance of polypropylene provides product

Figure 6.14 Applications of polypropylene in rigid packaging. (a) A VCR case with a living hinge, (b) drug packaging, (c) blow-molded container for household cleaner (Pro-fax, Himont), (d) container for purified water, similar in clarity to PET, (e) candy containers, (f) dairy containers (Amoco), (g) packaging for compact discs, (h) clear color packaging for household products, (i) Brisa single-serve bottled water containers, (j) a coffee cream jug made of a single material for easy recycling (Hostalen, Hoechst), and (k) ketchup bottles (Advancing Resin and Equipment Technology, 1995; Amoco Polypropylene Homopolymers, 1992; Future—The Hoechst Magazine, 1992; Milliken Chemical, 1996).

Figure 6.14 (Continued)

protection during transport, on the supermarket shelf, and in the refrigerator. A high-clarity polypropylene is used as the container for Pledge Household Cleaner (Figure 6.14), due to its combination of clarity, impact strength, and economy. The bottle, with a linerless polypropylene closure, is produced using a single material for easier recycling (Future—The Hoechst Magazine, 1992; Himont, 1992).

Recent environmental regulations concerning the use of packaging material has led to increased use of polypropylene in rigid packaging. To reduce the amount of packaging that ends up in landfills, many US states require that packaging materials be reduced in weight, have 25% post-consumer recycled content, or be recycled at a particular rate. Polypropylene is more easily recycled than other resins and can be recycled in small amounts (~10%) as a component of the HDPE waste stream. Also, its low density reduces the weight of the package (Milliken Chemical, 1996; Oertel, 1996).

6.5.7 Film

Polypropylene is used in flexible packaging in applications such as shrink-wrap films, snack food packaging, textile bags, and cigarette packaging.

Figure 6.14 (Continued)

Oriented polypropylene is the second most dominant material used in packaging, surpassed only by polyethylene, and the use of polypropylene in films is increasing.

Although three types of materials are used in flexible packaging—paper, thin gauge aluminum, and plastics—plastic films are more in demand than both of the other materials combined (Graves, 1995).

Biaxially oriented polypropylene (BOPP) film is used in packaging for biscuits, crisps, baked goods, sweets, bread, pasta; in cigarette wrap, shrink wrap, and shrink labels; in lamination of books and magazines; in office stationery films; in industrial laminates and supports for adhesive tapes; and in films for metallization used in applications such as gift wrapping and snack food packaging. It is commonly used for packaging products that must be protected against moisture absorption or loss. Coextruded OPP films are used in the snack food industry as a replacement for cellophane (Polymers in Contact with Food, 1991; Polypropylene, 1993).

Opaque, coextruded, oriented polypropylene film (pearlized or cavitated) is formed from coextrusion of three layers; the outer layers are homopolymers or copolymers, and the middle layer is a homopolymer containing small particles. The particles are usually calcium carbonate, although polyamides or polyesters are also used. Copolymers are preferred for the outer layers due to good cold seal adhesion, good heat sealability, and ease of conversion. During the orientation process, voids are formed within the core layer, which lowers the density to 0.62–0.72 g/cm^3 (from 0.91 g/cm^3 for uncavitated OPP). The voids also cause light to be scattered, resulting in an opaque film useful for packaging fat-containing products such as chocolate and high-fat biscuits. With cavitated film, the high-fat foods do not create the appearance of an oily deposit on the outside of the product when they come in contact with the packaging (Polymers in Contact with Food, 1991).

Polypropylene film provides excellent UV resistance and transparency, and additives can be used to increase performance properties. It can be printed, laminated, and metallized and is easy to handle on automatic packaging machines. Several applications of polypropylene packaging are shown in Figure 6.15 (Polymers in Contact with Food, 1991).

6.5.8 Barrier Packaging

Different materials vary in their ability to limit passage of gases, liquids, and solids. Metals and glass (without any pinholes) are impermeable to everything, while paper is permeable to almost everything. Due to their nonpolar molecular structure, polyolefins have a very low water permeability but are readily permeable to gases such as oxygen and carbon dioxide and to hydrocarbons (Barnetson, 1996).

Barrier materials are coatings or multilayer combinations of plastics designed to reduce water and gas diffusion into and/or out of the rigid or flexible package. Barriers to oxygen are necessary to preserve food freshness; oxygen can cause a chemical change in the product and rancidity in fat products. Water vapor can change the physical appearance of a product by either caking a dry material (i.e. flour) or by causing it to become soggy. Carbon dioxide does not cause food spoilage and is used to protect some foods against spoilage. Barriers to other gases such as nitrogen are used in modified atmosphere packaging (MAP) to extend the shelf life of fresh foods without the use of preservatives. The use of barrier packaging methods has reduced food spoilage to 2–3%, compared to 30–50% in Third World countries where packaging techniques are less developed (Barnetson, 1996; Polymers in Contact with Food, 1991; Roberts, 1989).

Polyvinylidene chloride, polyamide, and EVOH are commonly used as barrier polymers in coatings and coextrusions. A typical multilayer structure consists of two layers of polypropylene separated by a layer of EVOH, with adhesive layers (tie layers) to hold the polypropylene and EVOH layers together. The plastic ketchup bottle is composed of this multilayer structure, with polypropylene for rigidity and water vapor resistance and EVOH for oxygen resistance. "Lamipac" trays, made of a six-layer structure based on polypropylene/PVC/polypropylene, are used in General Foods' "Today's Choice" ready-meals and "Sheba" cat food. The "Lamipac" containers are closed by a vacuum heat seal process and are shelf stable (shelf life of up to 24 months), retortable, and microwaveable. "Top Shelf" entrees from Hormel are vacuum packed in a four-layer polypropylene tray using PVC as the barrier layer; product shelf life is up to 18 months. The easy-open lid is also a multilayer structure (Oertel, 1996; Polymers in Contact with Food, 1991; Roberts, 1989).

MAP is used for fresh products such as meat, fish, pasta, poultry, salads, and vegetables, in order to satisfy an increasing demand for fresh, additive- and preservative-free foods. In these packages, the composition of the natural air atmosphere inside the container is replaced by a gaseous mixture. The gases used depend on the product but generally include nitrogen (an inert gas used to replace oxygen) and carbon dioxide (to retard the growth of mold and aerobic bacteria). High barrier materials, such as a laminate of PVC rigid foil and polyethylene film, are generally used for the container; however, laminated materials such as PVC–coated oriented polypropylene are used in the lids of thermoformed MAP trays (Polymers in Contact with Food, 1991; Roberts, 1989).

6.6 Consumer Products

Polypropylene is used in other applications such as housewares, recreational equipment, toys, office equipment, and lawn furniture. In housewares, polypropylene is used in large and small containers

Figure 6.15 Applications of polypropylene films in packaging. (a) Snack food packaging using metallized film (Amoco), (b) snack food packaging using clear film (Amoco), (c) floral packaging (Escorene, Exxon), and (d) apparel packaging (Escorene, Exxon) (Amoco Polypropylene Homopolymers, 1992; Polypropylene, 1993).

for food and other uses (Figure 6.16). Random block copolymers, which combine a random copolymer matrix with a dispersed rubber phase, and improved random copolymers provide high clarity and low-temperature impact strength, important in housewares used in freezer storage. New, high-flow grades of random and impact copolymers allow the molding of oversized, high-performance housewares such as the deep, 33-gallon (125 l) ToteLocker and 50-gallon (190 l) RoughTote by Rubbermaid, the under-the-bed and hangable closet clothing bins by Sterlite, and the 10-quart (9 l) "fresh-food keepers" by Culver (Leaversuch, 1996; Thompson et al., 1987).

Figure 6.16 Polypropylene applications in housewares. (a) Stackable laundry baskets (Rubbermaid), (b) 33-gallon ToteLocker (Rubbermaid), (c) clear food containers, and (d) various household products (Amoco Polypropylene Homopolymers, 1992; Leaversuch, 1996).

Polypropylene's low density makes it useful in recreational items such as bicycle helmets, ice coolers, surfboards, and flotation devices, and its toughness is useful in luggage and lawn mower parts. Polypropylene is used as a substitute for ABS in "hard", injection-molded luggage, although most "hard" luggage (66%) is still made from ABS. New grades of enhanced polypropylene are being used in lawn furniture, providing higher stiffness and warp resistance and lighter weight than the commonly used 20% and 40% talc-filled grades. High-impact polypropylene is used in the deck, cowling cover, and discharge chute of a new cordless lawn mower (Figure 6.17). Polypropylene (UV stabilized, 20% calcium-filled) provides durability and safety in the mower deck, and a proprietary grade in the cowling cover and discharge chute provides good long-term weathering resistance and a high-gloss Class A finish (Barnetson, 1997; High-Impact PP, 1997; Neopolen).

Wheels on the Ryobi self-propelled, battery-operated lawn mower are made from a long glass-fiber-reinforced, chemically coupled polypropylene composite. The material provides strength, chemical resistance, lubricity, and moisture resistance. High strength is required in the two front

Figure 6.17 A cordless lawn mower. The mower deck, cowling cover, and discharge chute are made from high-impact polypropylene (Ferro Corp.) (High-Impact PP, 1997).

drive wheels, where final gear reduction takes place through molded-in gear teeth (Figure 6.18), and the fertilizers and pesticides sprayed on the lawn require that the wheels be resistant to chemical attack. The low moisture absorption of polypropylene provides good dimensional stability for the gear teeth, even when the mower is run in damp grass and stored outside. Also, the natural lubricity of the material allows the gears to run in a dry state, eliminating the need for grease, which would collect dirt and cause greater wear. Other materials considered were mineral-filled polypropylene, which lacked the required strength, and PC, which was not as chemically resistant (Verton, 1995).

6.7 Building and Construction

In the building and construction industries, polypropylene is used in walls and partitions, as insulation for power cables and telephone wires, and in pipes. Pipe applications include underfloor heating, hot and cold water, sanitary engineering, and pipe fittings (Figure 6.19) (Future—The Hoechst Magazine, 1992; Oertel, 1996; Techniques, 1986; Vestolen P, 1995).

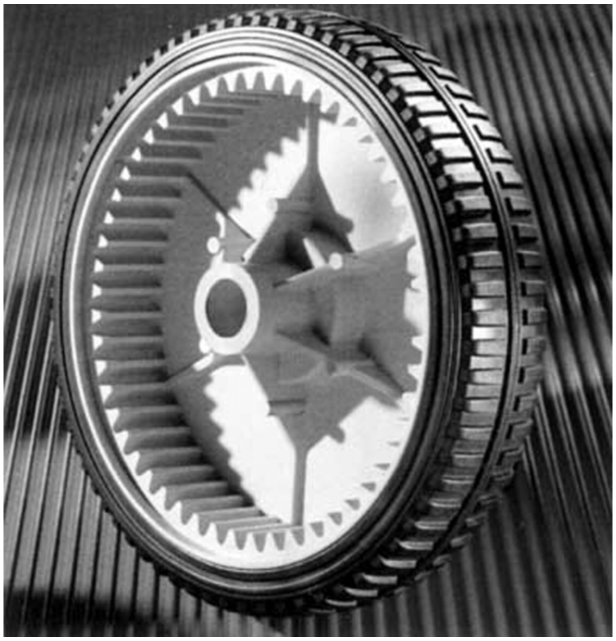

Figure 6.18 Drive wheel on the Ryobi self-propelled, battery-operated lawn mower, made from a long glass-reinforced, chemically coupled polypropylene composite (Verton MFX, LNP Engineering Plastics). Gear teeth are molded into the wheel (Verton Structural Composites, 1996).

Polypropylene pipes have a long service life, good impact strength, and good chemical resistance. They are nontoxic, with a neutral taste and odor, and are easily welded. Pipes provide long-term pressure resistance, and heat stabilized pipes can withstand high service temperatures. Pipes do not corrode and do not attract lime deposits. Polypropylene block copolymer was used as the material for pressurized pipes by Hoffman-LaRoche AG to carry waste water from chemical production to a treatment plant, a distance of 3.6 km (2.2 mi). Two pipelines for alternating operation were laid in an underground tunnel large enough to walk through. The material had to withstand pH values of from 1.5 to 15, an operating pressure of 2.3 bar (33.3 psi), and temperatures up to 35°C (95°F); the block copolymer exhibited better creep strength at higher temperatures than other pipe materials and performed better in heat aging tests (Borealis Press Release, 1995; Future—The Hoechst Magazine, 1992; Vestolen P, 1995).

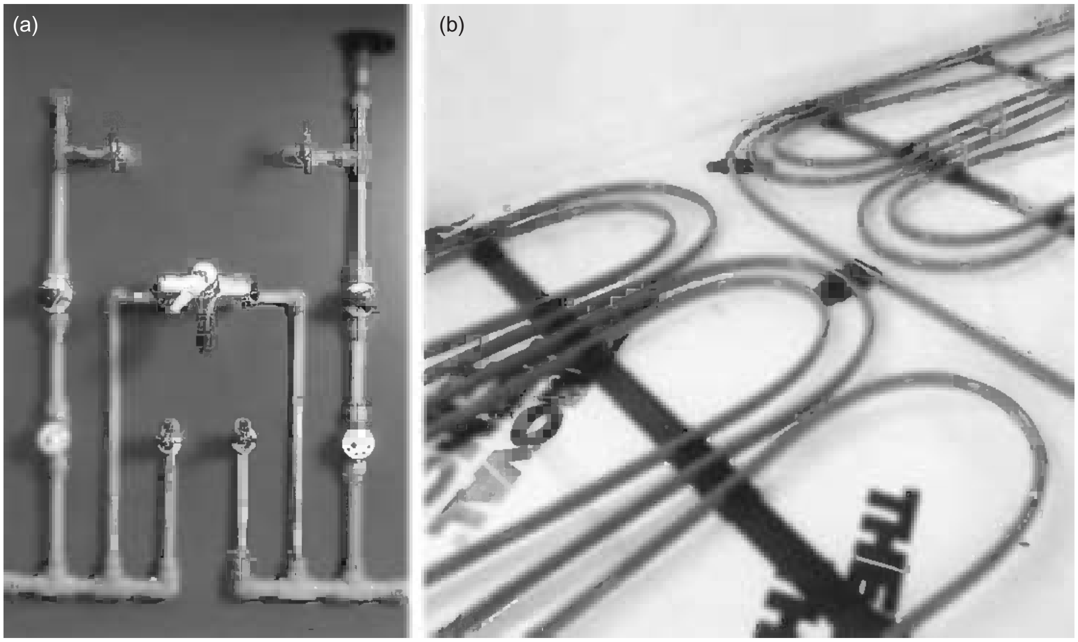

Figure 6.19 Pipe applications of polypropylene. (a) Hot and cold water pipes (Vestolen PP, Vestolen GMBH) and (b) underfloor heating pipes (Vestolen PP, Vestolen GMBH) (Hostalen, Hoechst) (Future—The Hoechst Magazine 1992; Vestolen P, 1995).

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7 Emerging Technologies in Food Packaging: Overview

Jung H. Han
PepsiCo Corporate Research, PepsiCo Inc., Plano, TX, USA

7.1 Introduction

Food packaging is a process to establish a package for food. Package in US Federal Food, Drug and Cosmetics Act is defined as "An act for preventing the manufacture, sale, or transportation of adulterated or misbranded or poisonous deleterious foods, drugs, medicines, and liquors, and for regulating traffic therein, and for other purposes" (Title 21, Chapter 9, Subchapter II, Section 321b). Packaging is one of the most important processes to maintain the quality of food products during storage, transportation, and end use (Kelsey, 1985). It prevents quality deterioration, and facilitates distribution and marketing efficiencies. The basic functions of packaging are protection, containment, information, and convenience (Kelsey, 1985). A good package can not only preserve food quality but also significantly contribute to a business profit. Beyond the functions of preservation, packaging also has secondary functions—such as selling and sales promotion. However, the main function of food packaging is to achieve preservation and the safe delivery of food products until consumption. During distribution, the quality of the food product can deteriorate biologically and chemically as well as physically. Therefore, food packaging contributes to extending the shelf life and maintaining the original quality and the safety of the food products.

Yokoyama (1985) suggested the conditions necessary to produce appropriate packaging, which are mass production, reasonable and efficient packaging material, suitable structure and form, convenience, and consideration of disposal. Therefore, according to these conditions, packaging designing and development requires not only an industrial design capability, creativity, and marketing tools but also advanced knowledge of engineering and environmental science. Preservation, convenience, and the other basic functions of packaging are certainly important, but its disposal should be treated as an important parameter in packaging development.

Food industry uses a lot of packaging materials, and thus even a small reduction in the consumption of materials for each package would result in a significant cost and material reduction, and may improve solid waste problems. Various new packaging technologies have attempted to reduce the volume and/or weight of materials in efforts to minimize resources and costs. Several trends in the food packaging evolution have been remarkable (Testin and Vergano, 1990), including source reduction, design improvement for convenience and handling, and environmental concerns regarding packaging materials and processes. Food packaging has evolved from simple preservation methods to convenience, point-of-purchase marketing, material reduction, safety, tamper-proofing, and environmental issues (Stilwell et al., 1991). Since the World Trade Center tragedy in 2001, food technologists have focused their attention on revising packaging systems and package designs to increase food safety and security. The level of concern regarding the use of food and water supplies as the possibility of bioterrorism has increased (Nestle, 2003). Therefore, many applications of active packaging will be commercially developed for the security and safety enhancement of food products.

Although food packaging has evolved in its various functions, every package still has to meet the basic functions. Food packaging reduces food waste and spoilage during distribution and decreases the cost of preservation facilities. It extends the shelf life of foods and provides safe foods to consumers. A good package has to maintain the safety and quality of foods as well as being convenient, allowing sales promotion, and addressing environmental issues.

The quality of the packaged food is directly related to the food and packaging material attributes. Most food products deteriorate in quality

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due to mass transfer phenomena. These phenomena can occur between the food product and the atmospheric environment, between the food and the packaging materials, or among the heterogeneous ingredients in the food product itself (Krochta, 1997). Therefore, mass transfer studies of the migration of package components and food ingredients; of the absorption and desorption of volatile ingredients, flavors, and moisture; of gas permeation; and of the reaction kinetics of oxidation and ingredient degradation are essential for food packaging system designs.

7.2 Innovations in Food Processing and Packaging

Year after year, technology becomes better. Most developments in the field of food technology have been oriented toward improving food processing and products more conveniently, more efficiently, at less cost, and with higher quality and safety levels. Traditional thermal processes have offered innovative developments in the food processing industry; these include commercial sterilization, quality preservation, shelf-life extension, and safety enhancement. Extended shelf-stable products manufactured by retorting or aseptic processing are available in any grocery store and do not require refrigeration. These types of products are very convenient at any place or time and are easy to handle, therefore benefiting producers, processors, distributors, retailers, and consumers. The major function of extended shelf-stable food packaging is to construct a protective barrier against the invasion of microorganisms.

Beyond this simple barrier function, there has been more research and development introducing new purposes for food packaging systems. Among these, significant new functional packaging systems which have been successfully commercialized are active packaging, modified atmosphere packaging (MAP), and edible films/coatings.

The development of new packaging functionalities has been possible because of technological advances in food processing, packaging material science, and machinery. Among the many new technologies, the development in processing and packaging machinery is notable, leading to higher standards of regulation, hygiene, health, and safety. New software and part installations in unit operations have been introduced, and high-speed automation has been achieved by using new servomotors, subsystem parts, and software technologies such as the machine vision system (Tucker, 2003). The processing and packaging equipment has new functions that feature increased safety, quality, and productivity, and therefore it seems that the development of new packaging functions may go hand in hand with the development of new processes, materials, and equipments. Packages may have new purposes if new functional packaging materials and/or materials containing functional inserts/parts are used. Developing new packaging technologies implies not only new material development but also new packaging design systems. Yam and Lee (2012) listed some socioeconomic reasons that drive packaging innovations, such as consumer lifestyle, value of products, profits, safety/biosecurity, regulations, and environmental concerns.

7.3 Food Packaging Technologies

7.3.1 Extra Active Functions of Packaging Systems

Active packaging has been defined differently by many researchers. Among them Robertson (2006) defined it as "packaging in which subsidiary constituents have been deliberately included in or on either the packaging material or the package headspace to enhance the performance of the packaging system". Many new "extra" functions have been introduced in active packaging technologies, including oxygen-scavenging and intelligent functions, antimicrobial activity, atmosphere control, edibility, biodegradability, etc. Food packaging performs beyond its conventional protective barrier function. The new active packaging systems increase product security, safety, protection, convenience, and information delivery. Active packaging systems extend the shelf life of food products by maintaining their quality longer, increase their safety by securing foods from pathogens and bioterrorism, and enhance the convenience of food processing, distribution, retailing, and consumption.

There are many applications of active packaging technologies, several of which have been commercialized and are used in the food industry; these include oxygen-scavenging, carbon dioxide−absorbing, moisture-scavenging (desiccation), and antimicrobial systems. Most researchers report that the shelf life of packaged foods has been extended by using these active packaging systems, but the combinations of multiple active packaging technologies have been suggested to improve the quality and safety of foods, and present a future trend in promising new research and development project (Cooksey, 2010). Oxygen-scavenging systems have been commercialized in the form of a sachet that removes oxygen from within packages. An oxygen-free environment can prevent food oxidation and rancidity, and the growth of aerobic bacteria and molds. Carbon dioxide-scavenging packaging systems can prevent packages from inflating due to the carbon dioxide formed after the packaging process—for example, packaged coffee beans may produce carbon dioxide during storage as a result of nonenzymatic browning reactions. Fermented products such as pickles, sauces, kimchi (lactic acid fermented vegetables), and some dairy products can produce carbon dioxide after the packaging process. Carbon dioxide-scavenging systems are also quite useful for products that require fermentation and undergo aging processes after they have been packed. Moisture-scavenging systems have been used for a very long time for packaging dried foods, moisture-sensitive foods, pharmaceuticals, and electronic devices; in these systems, desiccant materials are included in the package in the form of a sachet. Recently, the sachets have contained humectants as well as desiccants to control the humidity inside the package more specifically. Moisture-scavenging systems that are based on desiccation are evolving to control the moisture by maintaining a specific relative humidity inside the package by absorbing or releasing moisture.

Antimicrobial packaging applications are directly related to an improved level of food microbial safety and bioterrorism as well as to extended shelf life by preventing the growth of spoilage and/or pathogenic microorganisms. The growth of spoilage microorganisms shortens the food's shelf life, while the growth of pathogenic microorganisms endangers public health. Antimicrobial packaging systems consist of packaging materials, in-package atmospheres, and packaged foods, and is designed to kill or inhibit the microorganisms that cause food-borne illnesses (Han, 2000, 2003a,b).

Intelligent packaging has been categorized both as a part of active packaging and as a separate entity, depending on different viewpoints. It contains intelligent functions that have been studied to enhance convenience for food manufacturing and distribution and, increasingly, to improve food security and safety verification (Rodrigues and Han, 2003).

7.3.2 Modified Atmosphere Packaging

MAP is traditionally used to preserve the freshness of fresh produce, meats, and fish by controlling their biochemical metabolism, such as respiration or fermentation. Nitrogen flushing, vacuum packaging, and carbon dioxide injection have been used commercially for many years. However, current research and development has introduced new modified atmosphere technologies such as inert gas (e.g. argon) flushing for fruits and vegetables, SO_2 or ClO_2 gas releasing for fruits, carbon monoxide injection for red meats, and high oxygen flushing for red meats. For a MAP system to work effectively, optimal packaging material with proper gas permeability properties must be selected. The use of MAP systems is attractive to the food industry because there is a fast-growing market for fresh-cut processed fruits and vegetables, nonfrozen chilled meats/fish/poultry, ready-to-eat meals, and semiprocessed bulk foods.

MAP dramatically extends the shelf life of packaged food products, and in some cases food does not require any further treatments or any special care during distribution. However, in most cases, extending shelf life and maintaining quality require a multiple hurdle technology system—for example, temperature control in addition to MAP is generally essential to maintain the quality of packaged foods. The hurdle technology concept is therefore important for MAP applications, since the modified atmosphere provides an unnatural gas environment that can create unexpected and serious microbial problems such as the growth of anaerobic bacteria and the production of microbial toxins. Therefore, the inclusion of a temperature control system is very important for quality preservation and microbial control together with the maximum effectiveness of MAP.

7.3.3 Edible Films and Coatings

The use of edible films and coatings is an application of active food packaging, since the edibility and biodegradability of the films are functions beyond those of conventional packaging (Han, 2002). Edible films and coatings are useful materials produced mainly from edible biopolymers and food-grade additives. Most biopolymers are naturally existing polymers, including proteins, polysaccharides (carbohydrates and gums), and lipids (Gennadios et al., 1997). Plasticizers and other additives are included with the film-forming biopolymers in order to modify the film's physical properties or to create extra functionalities.

Edible films and coatings enhance the quality of food products by protecting them from natural deterioration processes. The application of edible films and coatings is an easy way to improve the physical strength of the food products, reduce particle clustering, and enhance the visual and tactile features of food product surfaces (Cuq et al., 1995). They can also protect food products from oxidation, moisture absorption/desorption, microbial growth, and other chemical reactions. The most common functions of edible films and coatings are that they are barriers against oils, gas, or vapors, and that they are carriers of active substances such as antioxidants, antimicrobials, colors, and flavors (Guilbert and Gontard, 1995; Krochta and De Mulder-Johnston, 1997). Thus edible films and coatings enhance the quality of food products, which results in an extended shelf life and improved safety.

7.4 New Food Processing Technologies

Besides the traditional heat processes for food preservation, many other new thermal and nonthermal treatment technologies have been developed recently. These include irradiation, high-pressure processes, pulsed electric fields, UV treatments, antimicrobial packaging, etc. Some of these processes have been commercially approved by regulatory agencies. These new technologies generally require new packaging materials and new package design in order to achieve optimum processing efficiency—for example, packages that undergo an irradiation process are required to be resistant to high energy to prevent polymer degradation, those that undergo UV treatments of packaged foods require UV light transmittable packaging materials, and retortable pouches should resist pressure changes and maintain seal strength. Since these new technologies each possess unique process characteristics, packaging materials should be selected with these characteristics in mind.

These new packaging materials and/or systems not only need to work technically but they should also be examined scientifically to ensure their safety and lack of toxicity, and be approved by regulatory agencies. In some cases, countries may require new regulations and legislation for the use of these new processing and packaging technologies. The globalization of the food industry enforces international standards and compliance with multiple regulations. New technologies should also be examined for their effect on product quality and public health, and the results of these tests should be disclosed to the public, government agencies, processors, and consumer groups. However, some criteria (such as threshold levels, allowable limits, and generally acceptable levels) are decided politically, as are rulings on how to practice and review the policy. Scientific intervention is limited, but it is important that scientific research results and suggestions be sought and respected during political decision making. Consumers buy and decide what they want. It is also very important to develop new packaging innovations that consumers want, choose, and adapt their life style to accept the benefits (Spencer and Junkus, 2007).

7.5 Future Trends in Food Packaging

A continuing trend in food packaging technology is the research and development of new materials that possess very high-barrier properties. High-barrier materials can reduce the total amount of packaging materials required, since they are made of thin or lightweight materials with high-barrier properties. The use of high-barrier packaging materials reduces the costs in material handling, distribution/transportation, and waste reduction.

Convenience is also a "hot" trend in food packaging development. Convenience at the manufacturing, distribution, transportation, sales, marketing, consumption, and waste disposal level is very important and competitive. Convenience parameters may be related to productivity, processibility, warehousing, traceability, display qualities, tamper resistance, easy opening, and cooking preparation.

A third important trend is safety, which is related to public health and to security against bioterrorism. It is particularly important because of the increase in the consumption of ready-to-eat products, minimally processed foods, and precut fruits and vegetables. Food-borne illnesses and malicious alteration of foods must be eliminated from the food chain.

Another significant issue in food packaging is that it should be natural and environmentally friendly. The substitution of artificial chemical ingredients in foods and in packaging materials with natural ingredients is always attractive to consumers. Many ingredients have been substituted with natural components or naturally degradable materials. This trend will also continue in food packaging system design areas. To design environmentally friendly packaging systems that are more natural requires, for example, the partial replacement of synthetic packaging materials with biodegradable or edible materials, a consequent decrease in the use of total amount of materials, and an increase in the amount of recyclable and reusable (refillable) materials.

Food science and packaging technologies are linked to engineering developments and consumer studies. Consumers tend to continuously want new materials with new functions. New food packaging systems are therefore related to the development of food processing technology, lifestyle changes, and political decision-making processes as well as scientific confirmation.

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8 Introduction to Active Food Packaging Technologies

Michael L. Rooney
Formerly Food Science Australia, CSIRO

8.1 Introduction

The field of active packaging has been the subject of substantial research and development for only the past two decades. It remains largely at that stage of development at the time of writing. The term "active packaging" was first applied by Labuza (1987) and may be defined as packaging that performs some desired function other than merely providing a barrier to the external environment (Hotchkiss, 1994; Rooney, 1995a). Active packaging should not be confused with "intelligent packaging", which informs or communicates with the consumer regarding the present properties of the food, or records aspects of its history.

There are also more expansive definitions in use to elaborate the effects achieved by packaging, but there is the potential for blurring the distinctions between activity and intelligence. A more helpful approach is to use the term "active and intelligent packaging", as used in the literature that resulted from the Actipack Project funded by the European Commission (de Jong, 2003).

The scope of active packaging research and development was consolidated by Rooney (1995a), and its development has been described and evaluated (Brody et al., 2001; Gontard, 2000). Several reviews have discussed the field from differing points of view (Labuza and Breene, 1989; Meroni, 2001; Rooney, 2000).

Traditionally, packaging is desired to assist in the maintenance of the quality of the food at the level achieved at the final stage of its processing. In practice, the quality decreases in packaged storage because, in part, the combination of packaging process and packaging material availability does not exactly match the specific requirements of each food or beverage. Packaging has normally been expected to be inert toward the packaged product, but the potential for packaging to contribute to the quality retention and the convenience of packaged goods was not utilized.

The processes by which food quality is lost often involve interaction with substances taken up from their environment. This may mean a loss or gain of water, ethylene, or oxygen, and contamination with microorganisms. There are also some substances that build up in the packaged food on storage, including the containment and cooking odors resulting from the oxidation of fats and oils. Some of these compounds are normally lost when foods are cooked shortly before serving. The utility of foods can be enhanced significantly if the package contributes to the processes of heating or cooling. These effects are summarized in Tables 8.1 and 8.2.

The principles upon which packaging acts are not limited to any one scientific discipline. Chemical reactions have been used to remove atmospheric gases such as oxygen, carbon dioxide, and ethylene. Water is merely absorbed by substances with high affinity, such as silica gel, dehydrated lime, or polyol humectants. Volatile organic compounds are largely adsorbed by porous solids such as zeolites. In some cases, the strong adsorption of ethylene onto inorganic solids has been used to retain the vapor in equilibrium with the surrounding environment. Self-heating packages normally involve exothermic or endothermic chemical reactions in a second compartment of the package.

Active packaging is normally designed to address one property or requirement of the food or beverage. The property normally chosen is that most critical as the first limiter of quality or shelf life. To this extent, active packaging is provided to fine-tune the properties of the packaging to meet the requirements of the food. This is not different from the normal aim of the packaging technologist to match the requirements of the food with the properties of the packaging.

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Table 8.1 Mechanisms of Food Quality Loss

Quality Attribute	Result of Presence	Packaging Activity
Mold	Microbial spoilage	Antimicrobial surface
		Antimicrobial release
		Oxygen scavenging
Oxidation	Rancidity	Oxygen scavenging
		Odor absorption
		Antioxidant release
	Color change	Oxygen scavenging
	Nutrient loss	Oxygen scavenging
Food chemistry	Odor/flavor formation	Absorption
Water movement	Texture change	Dessication
	Microbial spoilage	Humidity buffering
		Absorption of condensate
Senescence (produce)	Premature ripening	Ethylene scavenging
		1-MCP release
		Atmosphere modification

Table 8.2 Convenience Attributes

Effect	Opportunity	Activity
Heating	Convenience meals	Microwave susceptors
	Vending machines	Self-heating cans and cups
	Military rations	
Cooling	Vending machines	Self-cooling cans and cups
	Summer outdoor events	
Gas generation	Gasification of beer	Widgets

8.2 Drivers for Choice of Active Packaging

The decision to consider active packaging for a food or beverage is commonly based on factors typically involved in any package selection. These considerations include economic advantage, process engineering limitations, convenience in use, environmental impacts, and secondary effects resulting from some other change in the processing or packaging. The latter effects may result from new product introduction due to lifestyle changes or the availability of technologies that remove a limitation formerly experienced. Some of the constraints on optimizing the processing, packaging, and distribution of foods and beverages are shown in Figure 8.1.

8.2.1 Economic Advantage

The optimal passive packaging solution for a particular product sometimes results in an initial quality or shelf life that is at a level below that considered desirable. The packaging may be coupled with a packaging process that introduces costs in terms of line-speed limitation or use of additional processes. Packages of oxygen-sensitive foods can require evacuation followed by inert-gas flushing and evacuation a second time. Introduction of an

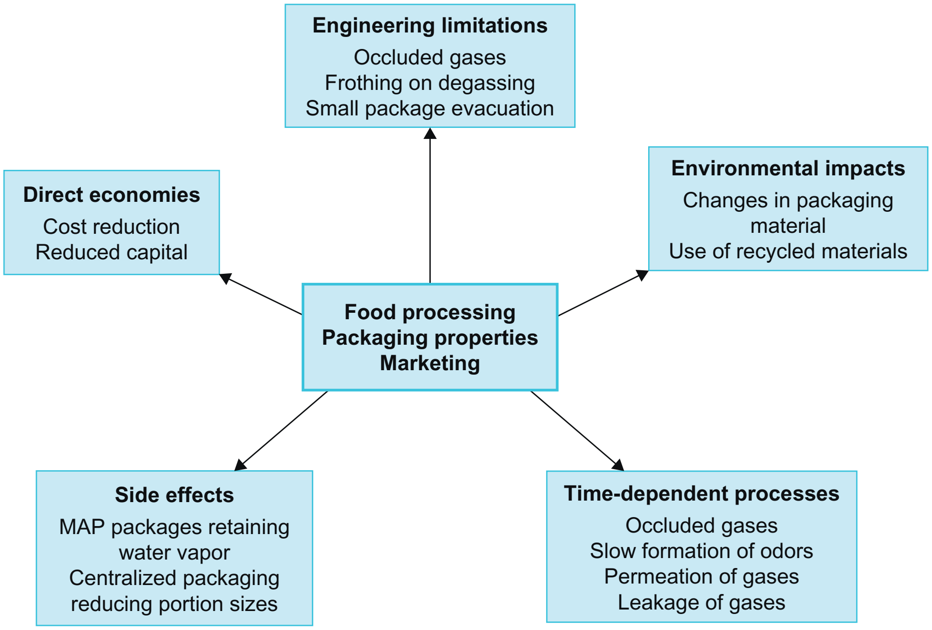

Figure 8.1 Current constraints on food processing, packaging, and marketing.

oxygen scavenger provides the opportunity for removal of two or more of these steps. The general case has been considered by Rooney (1995b).

Removal of the bitter principle, limonin, from orange juice can be achieved by means of a batch adsorption step during processing, but use of an active packaging material may achieve an acceptable effect (Chandler and Johnson, 1973; Chandler et al., 1968). Naringin is a bitter principle in grapefruit juice, and it has been shown that large concentrations of this compound can be removed from the juice by contact with an active packaging material (Soares and Hotchkiss, 1998). Such an approach allows the potential for the time taken to distribute the product to be used to advantage. This may result in avoidance of capital for equipment to remove the naringin in-line.

8.2.2 Process Engineering Limitations

Oxygen dissolved in beverages can be removed by vacuum treatments or nitrogen flushing. These processes do not always fit well with existing processing equipment due to frothing, so removal of oxygen by means of active packaging is an attractive option. Similar considerations apply to the flushing of small sachets containing low-density powders that are readily made airborne, thus interfering with sealing of the package. An additional characteristic of powders, when spray dried, is the occlusion of air within food particles. The release of this gas occurs slowly and is not achieved by means of evacuation on the processing line (King, 1955). The gas may be desorbed by equilibration with nitrogen over a period of days, but this is readily achieved by means of active packaging rather than by employing nitrogen-flushed holding tanks within the production line.

8.2.3 Time-Dependent Processes

The slow release of gases occluded in food products may also be viewed as a time-dependent process best addressed by the package during storage and distribution. Two forms of active packaging have been used to address the particular case of release of carbon dioxide from roasted coffee beans. The incorporation of one-way valves into flexible, gas-flushed coffee packs applies a physical remedy, whereas inclusion of a sachet containing absorbents for both carbon dioxide and oxygen has been utilized for cans (Russo, 1986).

There are other time-dependent chemical processes that are readily addressed by the use of active packaging. These include the scavenging of traces of aldehydes formed during the oxidation of fats and oils in foods, which give the product a rancid odor long before any nutritional damage has been done (Brodie and Visioli, 1994). Other odorous compounds are also formed in foods during storage, and the range of commercial active packaging approaches has been reviewed (Brody et al., 2001; Rooney, 1995a). It is important to avoid odor removal if this could remove indicators of microbial growth in foods.

Besides processes occurring in foods during storage, there is also a time-dependent impact of the permeability of some packaging materials to atmospheric gases. Oxygen and water vapor are of most concern, and substantial research has been directed to the development of plastics with an enhanced barrier to oxygen (Rooney, 1995a). The greatest development resources have been applied to reducing the oxygen transmission rate of PET bottles, especially for use with beer and fruit juices. The related problem of oxygen leaking under beer closures has been addressed by oxygen-scavenging closure liners (Teumac, 1995).

8.2.4 Secondary Effects

Although marketing considerations are a recognized driver leading to technical changes in the packaging of foods, changes in processing methods commonly lead to changed requirements for the packaging. The beer industry has sought to introduce PET bottles in place of some or all glass bottles for several years (Anonymous, 2000). The flavor of beer is seriously degraded by atmospheric oxidation of some components (Teumac, 1995). PET has an oxygen permeability that is six times too high to provide the required shelf life, so its barrier needs to be increased. The most economic PET-based approach at present appears to be to include an oxygen scavenger in the middle of three layers in a multilayer bottle structure. An added advantage of such a structure is the scavenging of oxygen dissolved in the PET, which is capable of diffusing into the beer. Bottles containing an active barrier can also, to some extent, scavenge some of the oxygen dissolved in the beer. Thus, the introduction of the PET bottle has resulted in oxygen removal from the beer—something not achievable by use of glass.

Possibly a more important side effect is found when fresh produce is sealed in polyolefin bags, either as carton liners or as retail packs, both of which help generate modified atmospheres. The seal allows the permeability of the plastic to regulate the concentrations of oxygen and carbon dioxide involved in the respiration of the produce (Kader et al., 1989; Varoquaux, 2000). Concurrently, the free movement of transpired water vapor is substantially reduced compared with that found in an unsealed bag. Consequently the relative humidity rises and there may be condensation of some of this water due to cycling in the cold chain. There is therefore a need for this condensate to be kept away from the produce, for example, by means of superabsorbent pads or, possibly, by inclusion of a humidity buffer in the bag to raise the dew point (Louis and de Leiris, 1991).

Centralized processing of foods can result in changes in the surface-to-volume ratio of foods, as evidenced by cut salads, diced fruit, and single cuts of steak. When each of these is packaged, there are challenges for the package engineer that are different from those posed by the unprocessed product. Removal of fruit skin introduces more concerns about microbial growth, and so there are opportunities for edible coatings containing approved antimicrobials to be used to advantage. Similar considerations may apply to sliced meat.

8.2.5 Environmental Impacts

The application of the “three Rs” (reduce, recycle, or reuse) to food package selection introduces the opportunity to question whether the food’s requirements are being met by passive packaging alone. The desire to replace glass packaging with PET is driven in part by a requirement to reduce weight during distribution and to reduce the incidence of broken glass. Although PET cannot match all of the desirable properties of glass, some of its properties relevant to specific packaging uses can be upgraded by active packaging. The barrier to oxygen is being raised by several companies using oxygen scavengers within the bottle walls (Anonymous, 2000). Such scavengers bring the added benefit of removing oxygen dissolved in the PET, which is capable of diffusion into the packaged beverage over time.

The introduction of recycled PET has the potential to introduce odors into lightly flavored liquids, and there is potential for development of taint absorbers for use in such packaging.

8.2.6 Enhanced Convenience

Consumption of convenience foods, both within and outside the home, has resulted in the development of a range of easy-to-use packages, such as “clamshells”, pizza boxes, and lidded disposable cups. Temperature retention in such foods and beverages has proved not to be easy, since the insulation characteristics of such conventional passive packaging appear to be at its economic limit. The perceived need for active packaging in temperature control is found in the event market, for military use, and for vending machine sales. Self-heating cups and cans and self-cooling cans are examples of developments designed to overcome this limitation.

The use of microwave susceptors in packaging for pastries and crisp convenience products seems to be limited to few products other than microwave popcorn. This form of active packaging appeared to have substantial potential when introduced.

8.3 Forms of Active Packaging

The choice of the form to be taken by the active packaging is made on the basis of three broad considerations. Most important is the requirement of the food, followed by the packaging format, and the requirements of the active agent.

The demands of the food can be visualized by considering the potential application of gas exchange in a retail pack of ground beef. Removal of oxygen or addition of carbon dioxide may be the chosen method of reducing spoilage by aerobic microorganisms.

This application appears too demanding, as air pockets remain within the product. However, products like shredded cheese or fresh pasta, which are packaged in low-oxygen/high-carbon dioxide atmospheres, would be more amenable to successful atmospheric modification involving package activity. In this case, the removal of oxygen could be achieved either by including oxygen-absorbing sachets in the package or by chemically active plastic packaging.

The relative rates of food degradation and gas exchange between the food and its environment determine whether or not turbulent mixing is necessary. If turbulence is needed, it can be provided only with evacuation or gas flushing, as occurs during pack filling. In other cases, the lower energy exchange generated by active packaging occurs only in response to a concentration gradient. This approach is particularly suitable where the kinetics of packaging activity are favorable when compared with those of mold growth, oxidation, and accumulation of odors.

The decision as to whether the source of activity should be localized or spread throughout the packaging material may be limited by the form of the package as well as the requirement of the food/beverage. Commercial active packaging for gas atmosphere modification is available as a variety of inserts, and in some cases is incorporated into the package structure.

8.3.1 *Localized Effects*

Inserts such as sachets, cards, and self-adhesive labels are used to achieve a range of atmospheric-modification effects. The range available commercially in the early days of active packaging has been tabulated and discussed by Abe (1990). Since that time, the nature of the inserts has changed in terms of both their content and materials of construction. This has been a significant advance, particularly where finely powdered ingredients have been replaced with the equivalent substances incorporated into plastic strips.

Rigid packs that are sealed with a lid or similar closure offer the opportunity for incorporation of activity into either the body of the pack or the closure. A variety of closure liners have been developed for the market, commencing with oxygen-scavenging closure liners for use on beer bottles (Teumac, 1995). The use of closure liners as the carrier allows both the container and the basic closure to be unchanged despite the introduction of the active function.

8.3.2 *Whole-Package Activity*

Increasingly, research and development attention has moved from localized effects to the achievement of whole-package activity. This is driven by the needs of beverages in particular and to gain specific benefits with some foods. Beverages sensitive to oxygen are largely packaged in glass. The recent trend toward replacement of glass with polyester in bottles and jars has necessitated an increase in the barrier of the latter to oxygen (and carbon dioxide in the case of beer). The oxygen-barrier enhancement may be achieved by oxygen scavenging within the bottle wall (Brody et al., 2001).

Both beverages and foods may benefit from active packaging that is antimicrobial. Unless the antimicrobial agent is volatile, it is necessary for the packaged product to contact the package surface. The latter may be active because of its antimicrobial surface chemistry or due to migration of an agent onto the contact layer of the food or beverage (Han, 2000).

Migration of an active agent from a package onto a food can occur by diffusion from one phase to the other. In the case of solid or semisolid foods, intimate contact may require evacuation (or package collapse due to gas absorption, as occurs with cheeses). If the active agent is required to act on the surface of the food, migration into the latter will impose some conditions of relative diffusivities from the packaging and into the food. This will also apply to pastes and other high-viscosity liquids. In the case of beverages, some agitation of the package contents may be required to achieve the intended effect sufficiently and rapidly. The reverse requirements apply when a migrating species is removed from the food/beverage, although diffusion to the package surface may well be the faster process.

Meroni (2001) has proposed that the functionality of packaging be categorized in order that all involved can understand the level of packaging design required. She defines a *basic level* of active packaging as one that has little or no intelligence added. An *intermediate level* may, for instance, include sensors that might determine the heating time the package with a susceptor might require in a microwave oven. The *superior level* of complexity might involve more combinations of effects, such as releasing color and flavor into the product. Developments in nomenclature of this kind will probably be necessary since such concepts are finding their way into definitions of active packaging, such as in Brody et al. (2001).

8.3.3 Edible Coatings

When an edible coating contributes to the packaging of a food, the coating performs first as a food component. However, because it is normally made from one or more food constituents, it may need protection against microbial activity. Hence if a mobile antimicrobial agent is incorporated therein, the coating can serve several additional functions. These include providing some self-preservation, helping to reduce the microbial load on the food surface, and providing an outer surface with antimicrobial properties. The latter is potentially important when used with finger foods such as hors d'oeuvres.

The requirements of foods that involve edible coatings can be very complex, so the active contribution provided by the additive may not be a major consideration in the formulation of the coating.

8.4 History of Active Packaging

The recognition of active packaging as a generic approach is a relatively new occurrence, as evidenced by the earliest reviews bringing together the concepts, even if using different descriptors—such as “smart” (Anonymous, 2000; Labuza and Breene, 1989; Sacharow, 1988). The field has been developing largely as a series of niche markets, owing to the current approach of the package converting and resin industries of viewing it in terms of a series of market opportunities. The user industries, typified by the food industry, have presented these opportunities in isolation, and this situation may continue for some years. The approach of considering a range of packaging options (both passive and active) as a whole is not yet common practice.

Many of the developments have been logical consequences of earlier commercial products or of noncommercial research publications. There are, however, some concepts that appear to have established new lines of investigation or commercial development. Any choice of this type is necessarily subjective, but some of these are shown in Table 8.3, and the discussion that follows indicates their significance.

8.4.1 Active Packaging for Processed Foods and Beverages

Oxygen Scavenging

The earliest approaches to the removal of oxygen from canned milk powder involved the use of oxidizable metal powders (Tallgren, 1938). A system with some control over the commencement of oxygen uptake was introduced by Kuhn et al. (1970), who used palladium catalyst attached to the inside of the can lids to catalyze the oxidation of hydrogen gas mixed with the nitrogen flush in the canning of milk powder. The process was incorporated into foil laminate pouches by the American National

Table 8.3 Some Seminal Technology Adaptations in Active Packaging

Technology	Significance	References
Pd catalysis of hydrogen oxidation	Triggering of oxygen scavenging	King (1955)
Ethylene oxidation by permanganate	Reactive removal of ethylene in produce packs	Scott et al. (1970)
Singlet oxygen reactions in plastics	Light as a trigger in oxygen scavenging	Rooney and Holland (1979)
Side-chain crystallizable polymers	Gas permeability adjustment with temperature in cold chain	Stewart et al. (1994)

Can Company (Warmbier and Wolf, 1976). This work represented the beginning of the research activity that led to the introduction of flexible oxygen-scavenging packs in 1996 by BP Amoco Chemicals and the Cryovac Division of Sealed Air Corporation. Since that time, refinement of the chemistry used has continued at a steady pace.

Concurrent research designed to meet the needs of the beer industry for trapping oxygen diffusing under closures resulted in a range of polymeric closure-liner modifications. These involved several chemistries, but those used most successfully incorporate sulfites, iron powder, and ascorbic acid (Teumac, 1995).

The approach of including oxidizable compounds in porous sachets was concurrently conducted in Japan, resulting in the introduction of Ageless® by Mitsubishi Gas Chemical Co. in 1977 (Smith et al., 1995). Recent developments of these porous sachets have led to a variety of self-adhesive labels and cards for insertion into food packages (Sakakibara, 2000).

Parallel developments for the polyester industry have resulted in a range of approaches to oxygen scavenging by polymeric and low-molecular-weight compounds within polyester bottle walls (Anonymous, 2000). The first approach was the oxidation of MXD-6 polyamide by the permeating oxygen in the presence of a transition metal catalyst (Cochran et al., 1991). These developments include multilayer systems as well as blends with PET in monolayer bottles.

Carbon Dioxide Scavenging or Release

Carbon dioxide serves as an antimicrobial gas in modified atmosphere packaging (MAP), but it can be undesirable when present in excess—as in natural cheeses, coffee, or kimchi. Approaches to its removal have continued to involve the incorporation of lime into sachets, or of one-way valves, as in retail coffee packs (Abe, 1990; Gaglio, 1986). In contrast, release of the gas has been achieved by use of sodium bicarbonate and food acids in sachets. When the combined antimicrobial effects of oxygen scavenging and carbon dioxide release are required, both effects can be achieved if ferrous carbonate is used as the active ingredient.

Removal of Odors and Flavors

The development of unpleasant flavors as a consequence of food processing can be the result of thermal degradation of components, such as proteins, or of reactions such as the Maillard reaction. Oxidation of fats and oils is also accelerated at processing temperatures. Besides these reactions, there can be a slow generation of unpleasant flavors when fruit components are disturbed from their structural components in the fruit. The bitter principle, limonin, builds up in orange juice after pasteurization and renders juice from some cultivars undrinkable. Chandler and Johnson (1979) showed that substantial quantities of limonin could be removed by acetylated paper, following earlier work involving cellulose acetate gel beads (Chandler et al., 1968).

The concept of odor removal using chemical affinity was further developed by Brodie and Visioli (1994), who used the reaction of aldehydes with amino polymers. The approach of focusing on more specific reactions has been taken a step further by Soares and Hotchkiss (1998), who showed that the naringin content of grapefruit juice could be reduced to acceptable levels by using naringinase immobilized within cellulose triacetate film. This increasing use of specific effects highlights the aim of active packaging to achieve a specific effect without necessarily impacting on other properties of packaging.

Active Packaging for Produce

MAP of produce has been practiced to varying degrees for several decades, following the successful controlled atmosphere storage of pome fruits. Although some contribution to modification of the package atmosphere by choice of the permeability of the package is regularly achieved, research toward better atmospheres has been conducted for at least two decades. The use of hydration of patches over holes in the packaging was the initial approach, and this was followed by the development of Intellipack® by the Landec Corporation (Stewart et al., 1994). The latter material has a sharp change in gas permeability at specific selected temperatures, allowing compensation for temperature changes during distribution.

Besides the respirational gases, the movement of water transpired by produce in a lined carton or a retail pouch is also a cause of quality loss or at least buildup of fog on the plastic. Antifog coatings were introduced and are still used. Proposals for the removal of water vapor by a form of humidity buffering initially involved porous bags of sodium chloride (Shirazi and Cameron, 1992). This was followed by the introduction of thin pouches containing humectants such as glycols and carbohydrates (Labuza and Breene, 1989). At present, humidity is still largely uncontrolled in wholesale packs for produce. This topic provides a challenge, particularly for desiccant manufacturers, to minimize losses due to buildup of condensate on fruits during distribution.

The aging of produce and flowers can be delayed by the use of MAP but accelerated by exposure to ethylene. This plant hormone is generated endogenously, especially when a particular item has been injured or is at an advanced stage of ripening. The ethylene generated by one fruit can also trigger the senescence of many others, and so packages require an ethylene-scavenging capability rather than just a high permeability that reduces buildup of the gas generated within the pack but dissipates it elsewhere. Early developments involved incorporating inorganic adsorbents into plastic liner bags, but subsequent research involved sachets of porous solids containing potassium permanganate. Recent research by Chamara et al. (2000) demonstrated that the shelf life of Kolikuttu bananas could be extended from 24 days to 54 days at 14°C and 94% relative humidity by incorporation of a potassium permanganate scavenger into polyethylene bags of the fruit. Ripening after storage in this way was found not to differ from that found in the absence of the scavenger. Research from the same laboratories showed that a similar effect could be achieved with Pollock avocados (Chamara et al., 2002). The latter are used commercially, but recent advances have included a metal complex and cyclic compounds that react with ethylene. The latter are tetrazenes, which react very rapidly and quantitatively, with a concurrent change in color (Holland, 1992).

The condensation of water in produce packs noted above has also been found to inhibit the ethylene-adsorbing capacity of a natural zeolite, molecular sieve 5A, and activated carbon (Yamashita, 2000). The condensation of water was found to lead to the release of ethylene already adsorbed. An alternative approach found useful was to utilize palladized carbon, a common catalyst used in organic chemistry. This allowed storage of broccoli for a week at 10°C, whereas the product was unsaleable after this time when no ethylene scavenger was used.

More recently, 1-methylcyclopropene (1-MCP) vapor has been found to inhibit the hormonal effect of ethylene on the senescence of produce. Inserts that release 1-MCP into packages have become available commercially and have some regulatory approval for produce application in the United States.

Active Packaging for Fresh Meat

Packaged unprocessed meats are supplied in several forms, including fresh retail cuts, MAP cuts, and chilled vacuum-packed primals. These packages often exhibit ambient, increased, and decreased levels of oxygen, respectively. The MAP and vacuum-packaged cuts feature raised carbon dioxide levels. The major chemical route to quality loss involves the formation of brown metmyoglobin at oxygen levels that are approximately between 0.1% and 2.0%. Inclusion of oxygen-scavenging sachets that also have the capacity to release some carbon dioxide enables further enhancement of the maintenance of ideal packaging conditions. Earlier forms of active packaging involved the inclusion of a bicarbonate and an organic acid in pads that absorb weep from cut meat. More recent oxygen scavenging has involved the addition of water to sachets to trigger more rapid oxygen scavenging because the metmyoglobin formation is rapid and irreversible in retail packs. Oxygen-scavenging plastics have the potential to contribute substantially to the removal of oxygen originating from occlusion and permeation of the film material.

The quality of fresh meat is also limited by the growth of slime-forming bacteria, and recent research aimed at providing packaging films that release organic acids offers potential for reducing this effect. Films that release lactic acid are particularly attractive, as this acid is normally present in the meat and can be effective when applied at the cut surface.

8.5 Impact on Packaging Materials and Processes

Creation of activity in packaging materials frequently involves the introduction of additional components into otherwise inactive materials, typically plastics. Besides the intended effect, there may be unintended consequences that must be addressed in order to bring the package to market. These additional considerations impact on material properties and the manner in which they must be used either in order to achieve their desired effect or to be processable in the expected manner.

8.5.1 Material Properties

Active components may form homogeneous mixtures with the existing plastic or may occur in a separate phase. The range of options available has been described in detail (Rooney, 2000). Some active polymers may be used as polyblends whereas low-molecular-weight additives may dissolve in the base polymer. Components that must be used as powders may interfere with the optical properties of the plastic as well as its propensity for tearing. Some hard particles can lead to reduced sharpness of slitter blades and possibly increase the wear in extruder barrels.

Chemical effects may impact on material properties where the activity involves substantial chemical change to the active polymer. Such chemical changes may lead to changed compatibility or degradation (or cross-linking) of the host polymer if the activity involves free-radical reaction mechanisms.

When silicone oxygen-scavenging films based on singlet oxygen reactions were being developed in the author's laboratory, exudation of an insoluble oxidation product was observed within a few hours when an otherwise soluble substrate was oxidized. Such an occurrence is particularly noticeable in silicones that are often poor solvents for organic compounds. In some forms of active packaging, sustained migration of substances in or out of a packaging plastic is necessary to achieve the desired effect. Such systems include, for instance, the release of antimicrobials, flavors, or antioxidants, and uptake of water vapor, oxygen, ethylene, or taints (Floros et al., 1997). The polymer required to support these effects may therefore differ from that used in a plastic with an otherwise similar passive role. The latter roles include that of a heat-seal or barrier layer in a pouch, or a closure liner in bottles. Restrictions imposed by the diffusion of selected species in polymers normally result in the active layer being as close as practicable to the food.

Premature Activity

Some active components are unaffected by the presence of air in the distribution environment. Such components include ethylene absorbers, odor absorbers, and the like. However, when the air contacts a packaging material containing a compound reactive with oxygen or water vapor, there is the opportunity for premature commencement of activity, resulting in a lower effectiveness when the package is used. For this reason, the concept of activation (or triggering) has been the subject of much patenting. Oxygen-scavenging plastics are now commonly triggered by exposure to ultraviolet (UV) light (Ching et al., 1994; Rooney and Holland, 1979; Speer et al., 1993). Active systems consisting of sachets containing desiccants or reduced iron powder are normally kept free from air in barrier laminate pouches, as they become active when exposed to the relevant air components.

8.5.2 Process Adaptation

Active packaging may require some level of adaptation at the stages of plastic extrusion, package fabrication, or when the pack is filled and sealed. If the chemistry causing activity is inhibited by the presence of antioxidants, it may be necessary to control their addition to a greater extent during extrusion. Some additives would be unstable at extrusion temperatures (200–370°C), and so it is likely that they will be applied to the packaging as internal coatings. It has been reported recently that a flavor additive manufacturer in the United States, ScentSational, has developed encapsulated food aromas in a form that does not degrade under normal plastics extrusion conditions (Ver-Bruggen, 2003a).

It is more likely that adaptation will be required in the package converting or shortly before filling. This occurs with the insertion of sachets or the application of self-adhesive labels to lidding film for thermoformed trays. Triggering of oxygen-scavenging systems by means of brief exposure to UV light may occur at the film stage, with empty packs as with PET bottles, or after package filling. Various irradiation systems have been described in patents (Ching et al., 1994; Rooney, 1993; Speer et al., 1993).

8.6 Active Packaging and the Distribution Chain

The direct effects of active packaging systems discussed above can be used to differing extents by the participants in the food and beverage distribution chain. The wide range of technologies, either available or in the process of development, will deliver benefits that depend upon both the aim of the participant and the drivers that participant sees in the particular business. This distribution of desired outputs and the prospects for active packaging inputs are shown diagrammatically in Figure 8.2.

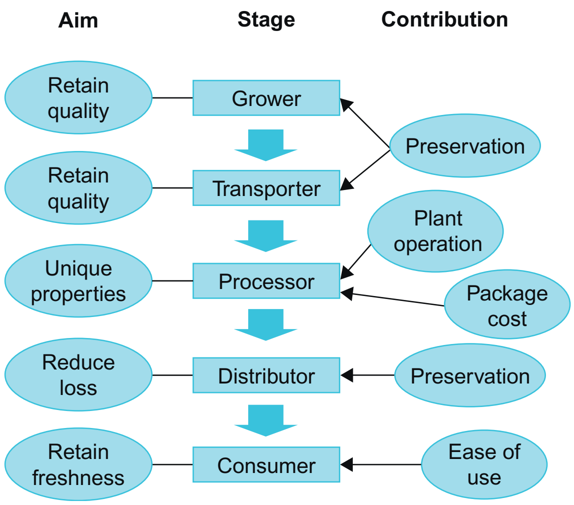

Figure 8.2 The distribution chain: targets and opportunities for active packaging.

The food chain may be followed from the grower to the consumer. The grower and distributor need primarily to retain harvested quality until the product reaches (for instance) the processor. Optimum quality retention may be achieved by the selection of packaging with some activity, such as humidity buffering or ethylene scavenging. Processors need to differentiate their products from those made by others from the same raw materials, and so will be expecting contribution from simplification of plant operations—such as by eliminating juice debittering operations and replacing this with active packaging. Cost savings on packaging operations, such as reduced vacuum use, and packaging material cost would be other inputs.

The potential for benefits to be generated along the distribution chain can be visualized using the topics in Figure 8.2 or from other considerations. Space limitations prevent showing the possible benefits, such as being able to market a difficult fish-oil product because of the oxygen scavenging possible with redesigned packaging. Another benefit not shown is the possibility of better conformity with regulations, as with removal of aluminum foil from aseptic brick packs and replacement with a barrier plastic with an enhanced barrier due to oxygen scavenging.

8.7 Regulatory Environment

Integration of active and passive technologies will be assisted when the actions of regulators have been clearly understood by potential petitioners. The European Commission took a step in this direction by funding the Actipack Project (de Jong, 2003). This project involved the coordinated work of six research institutes and three commercial enterprises in evaluating existing active technologies and classifying them in terms of their regulatory features. The migration of ingredients from some active packaging materials was investigated, and results for two iron-based oxygen absorbers have been reported (Lopez-Cervantes et al., 2003). The outcome of the research project was a series of proposals forming a new Framework Directive to replace 89/109/EEC (Ver-Bruggen, 2003b). These amendments, if implemented, will provide clear mechanisms for introduction of further commercial developments in the field. Consideration of these proposed amendments is not expected before late 2004 (Ver-Bruggen, 2003a).

Several packaging technologies based on active concepts have been approved by the US Food and Drug Administration (FDA) without change to the normal Premarket Notification process. Brody et al. (2001) have noted the benefit of the earlier FDA approval of sandwiching postconsumer PET recyclate between virgin PET in their later approval of some oxygen-scavenging compositions. Some zeolites containing silver ions have been approved for use in plastics packaging for food in Japan and, by the FDA, in the United States. The requirements of the EPA must be considered in the United States, and the position of antimicrobial compositions may be less clear there at present. Additives to packaging plastics may have implications for the environment when the package is returned to the earth via landfill or incineration, so regulations of the EPAs are a consideration in formulating packaging.

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9 Oxygen-Scavenging Packaging

Michael L. Rooney
Formerly Food Science Australia, CSIRO

9.1 Introduction

Traditionally, oxygen-sensitive foods and beverages have been packaged in such a way as to minimize their exposure to oxygen. This oxygen may be in the package at the time of sealing, or may enter the pack by permeation or leakage over the storage life. The first source of oxygen has frequently been addressed by the use of evacuation and inert-gas flushing, while the ingress has been minimized by optimal sealing and the use of high-barrier packaging materials. The approaches used to solve both oxygen problems are now recognized as providing only partial solutions, leaving options for improvements in food quality, production and distribution economics, reduction in environmental impacts, and increased convenience of use.

The impact of oxygen on food quality, and ultimately shelf life, is dependent not only upon the quantity of oxygen available for chemical oxidation or support of growth of organisms but also upon the rate of the reactions which consume the oxygen. This, in turn, will be influenced by the solubility of the gas in the medium provided by the food or beverage. The oxidation of fat in, for example, potato chips has been shown to be highly dependent upon water activity, with a minimum rate at a_w 0.3−0.4, and the increase in reaction rate above this value is interpreted in terms of the formation of an aqueous multilayer on the food with consequent dissolution of oxygen and enhancement of the oxidation (Taoukis et al., 1988). Much of the trade literature on oxygen-scavenging packaging presents a focus on the quantity of oxygen in a package without consideration of the widely different rates at which food quality can be degraded.

The quantity of oxygen which must be taken up by a food to limit its shelf life to 1 year has been estimated for a range of foods (Koros, 1990). The quantities lie in a range of a few parts per million to a few hundred parts per million based on the weight of the food. Removal of oxygen to these small amounts by conventional means is not generally achievable if the food or beverage has components that react rapidly. Beer is one of the most studied beverages, and it has been found that an uptake of around 1 ppm (or a little more) results in the beer reaching its shelf life. A conventional bottle closed with a crown seal allows an uptake or around 750 ppb of oxygen over 3 months and 2000 ppb over 8 months (Teumac, 1995).

9.2 Reviews

The various aspects of oxygen-scavenging packaging systems have been reviewed as part of general reviews of active packaging, but most of the reviews of the subject itself are found in the proceedings of conferences (Brody et al., 2001; Kline, 1999). This field is commercially the most developed in active packaging, but most of the papers at conferences still consist of presentations by developers or vendors of systems. There is still a lack of detailed investigation of the comparative performance of the systems on offer to the food industry. Brody et al. (2001) have described most of the commercial plastics-based systems and have given examples of their potential use. Smith et al. (1995) have dealt in depth with the applications of oxygen-absorber sachets, but there have been substantial developments in the area of adhesive oxygen-absorber "labels" since that time.

9.3 History

The development of oxygen-scavenging systems has followed two lines, depending upon whether the oxidizable substance was designed to be a part of the package or to be inserted into it with the food. The insert approach includes self-adhesive

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labels, adhesive devices, or free sachets included with the food. Modification of packaging materials to confer oxygen-scavenging capability includes monolayer and multilayer materials and reactive closure liners for bottles and jars.

9.3.1 Package Inserts

Oxidation of Metals

Brody et al. (2001) refer to early attempts to scavenge oxygen using ferrous sulfate in the 1920s. An early patent was authored by Tallgren (1938), who proposed the use of iron, zinc, or manganese to remove oxygen from canned foods. This approach was developed further, but research focused on the use of iron powder in sachets of porous material. Since the oxidation of iron is not inherently rapid, the approach of adding accelerators or adsorbents became popular. Addition of sodium carbonate was patented by Buchner (1968), and the use of alkali metal halides was patented by the Mitsubishi Gas Chemical Company in 1977, leading to the range of Ageless™ sachets, cards, labels, and closure liners. The development of these concepts into commercial products was accompanied by a progressive movement of the innovation from Europe to Japan, in which the bulk of the current market is found. Dainelli (2003) reported that around 12 billion oxygen-absorber units were sold in Japan in 1999, versus 300,000 in the European Union.

Iron-based compositions in the form of self-adhesive labels are manufactured by Multisorb Technologies under the trade names FreshMax™ and FreshCard™ in the United States of America. These adjuncts are applied to the inner wall or lidding film of packages as part of the filling operation. This allows placement of the absorber in a preselected position, such as behind the print on the lidding film in packs of smoked and sliced meats in the United Kingdom. Thus the esthetic property of the system is enhanced while retaining the functionality. An added benefit is that the absorber is prevented from moving to a position where its access to the headspace would be inhibited by intimate contact with a piece of food.

Other Oxidation Reactions

Patents for the oxidation of sulfites began appearing as early as 1965, when Bloch proposed the use of bisulfite salts in cloth or paper bags for insertion into cans. This patent was assigned to the US government. He saw the need for prevention of oxidation of dehydrated products in particular, and noted the capability of a variety of sulfite forms to be useful in the presence of an acid such as lactic acid. The reactions required the presence of water and this could be added, even though some might be available as water of crystallization in one or more of the salts. It is clear that the use of oxidase enzymes was already being discussed, and Bloch noted the reactivity of bisulfites at refrigerator temperatures when enzymes were inefficient. It is interesting to note that he recognized the need for intimate mixing of the bisulfite with an activator such as an iron salt, particularly in the presence of a porous support such as carbon or silica gel. Another useful feature was his recommendation of the inclusion of a carbonate salt to release carbon dioxide to maintain pressure in flexible packs as the oxygen is removed. Most of these considerations are emphasized in the more recent literature of oxygen absorbers. Perhaps, most important was his recognition that the relative rates of bisulfite oxidation and food degradation might be different.

The reaction of sodium metabisulfite in the presence of lime was patented by Yoshikawa et al. (1977). These workers showed that the uptake of oxygen could be triggered by the presence of water in the food. This concept was concurrently being applied in the development of iron-based systems and marks the key concept in providing a useful commercial oxygen-absorber system that could be stored and handled before use.

Oxygen absorbers based on sulfur compounds have been replaced by iron-based compositions, although the former are still used in combination with ascorbic acid in oxygen-scavenging closure liners.

The use of oxidase enzymes for the removal of oxygen from food packages has been discussed by Brody and Budny (1995) and Brody et al. (2001). The earliest known application of an oxygen absorber in a sachet was reported to be that of Scott (1958). This system involved the oxidation of glucose catalyzed by glucose oxidase in the presence of water. The hydrogen peroxide formed was removed by the action of catalase. The concept was commercialized by Scott's company, Fermco Laboratories, using the trade name "Oxyban". A commercial enzymic oxygen scavenger in a sachet is marketed internationally by Bioka, a Finnish company.

The oxidation of hydrogen to form water may appear to be a very attractive mechanism for oxygen scavenging. This process has been used by microbiologists for deoxygenating anaerobic jars for cultivation of anaerobes for many years. The process was proposed for the packaging of milk powder in cans by King (1955) and subsequently by Abbott et al. (1961). The process involved flushing cans of milk powder with a mixture of hydrogen (7%) in nitrogen. The hydrogen reacts with oxygen on the surface of palladium-coated steel attached by means of adhesive tape to the inside of the lid. The particular benefit of this process was the removal of oxygen released from pores in the spray-dried powder over several days following closure.

A variety of other systems, such as catechols, glycols, and boron compounds, have been the subject of patents or have been released for commercial sale. Both the Toppan Printing Company and the Mitsubishi Gas Chemical Company have developed ascorbic acid-based sachet systems for use where fast oxygen absorption is required in the presence of carbon dioxide. Generally, these compositions are nonmetallic and do not place restrictions on the use of metal detectors on packaging lines.

9.3.2 Packaging Materials as Oxygen Scavengers

Although the performance of oxygen-absorbing sachets was quite satisfactory for a wide range of food storage conditions, a number of limitations to their use in practice were recognized. The esthetics of inserts, coupled with a concern about possible ingestion or rupture, as well as their unsuitability for use with beverages, drove researchers to seek package-based solutions. The approach of using the packaging material as the medium for the oxygen-scavenging chemistry was developed independently in several laboratories and countries. Not surprisingly, the reactions were initially the same as used in the sachet technologies, but eventually it was recognized that the restrictions applying to package inserts need not apply to the package. This has allowed a multiplicity of oxygen access problems, arising from quite disparate packaging factors, to be addressed, thus permitting targeting of problems at their source rather than waiting for the oxygen to enter the package to be absorbed by an insert, such as a sachet. Some of the chemistries and reaction media used in packaging-material-based systems are summarized in Table 9.1.

Table 9.1 Oxygen Scavengers with Different Chemistries

Substrate	Medium	Structure	Application	Commercial
Hydrogen	Pd/alumina	Sandwich	Foil laminates	Briefly
Singlet oxygen acceptors	Plastics	Homogeneous plastic	Plastics packaging	No
Sulfites	Salt blend	Sandwich	Laminates	No
Sulfites	Solution	Sandwich	Bag-in-box	No
Sulfites/ascorbate	Plastics	Compound	Closure liner	Yes
Aromatic polyamide	Polymer/ blend	Mono/multilayer	PET bottles	Yes
Iron powder	Plastics	Compound	Plastics packaging	Yes
Reducible compounds	Plastics	Blend/polymer	Plastics packaging	No
Polymer-bound olefins	Plastics	Coextrusions	Flexibles	Yes
Polydiene block copolymers	Plastics	Blend/multilayer	PET bottles	Yes

The use of palladium on alumina as a catalyst is common in organic chemistry. Its use in a sandwich of the powder in a laminate containing a polyvinyl alcohol barrier layer and the polyolefin heat-seal layer offered a number of advantages as a headspace scavenger (Kuhn et al., 1970). The packages of intermediate moisture foods or milk powder were flushed with a mixture of hydrogen, 5%, in nitrogen and sealed. The hydrogen and nitrogen both diffuse through the sealant to the powdered palladized alumina. The water formed on the catalyst surface is absorbed by the alumina. The packaging is expensive to fabricate, and the use of hydrogen mixtures is not popular in the industry. None of this detracts from the inherent high efficiency of the process, which demonstrated quite early that high permeability of the sealant layer is beneficial in oxygen scavenging.

Farrell and Tsai (1985) introduced the concept of dealing with the enhancement of oxygen permeability of plastic packages during and after retorting. They noted that the quantity of water permeating the package was enough to hydrate the sulfite or another hygroscopic salt mixed with it. They took advantage of this fact to provide a concentrated aqueous solution of the oxidizable sulfite between two layers of the packaging material to achieve a high rate of oxygen removal at retort temperature.

The problem of enhanced permeability of EVOH barrier layers to oxygen during retorting has been approached by Tsai and Wachtel (1990) by attempting to keep the EVOH dry or by Bissot (1990) by including microscopic inorganic platelets in the polymer to introduce a longer diffusion path. It appears that a combination of the oxygen-scavenging packaging coupled with the use of a desiccant might reduce the access of oxygen to the packaged food during the postretorting period when the EVOH slowly loses water, thereby increasing its barrier action.

Scholle (1977) advanced the concept of using an aqueous solution of the sulfite trapped between the layers of a multiwall package, such as bag-in-box. This concept was directed at the rapid removal of headspace and dissolved oxygen from liquid foods and beverages such as wine. This is a particular problem associated with bag-in-box, where it is difficult to avoid air headspaces due to both filling, and that already between the webs used to make up the bag.

Cook (1969) described the use of an all-organic system involving a plastic bilayer separated by a solution of common antioxidants in a minimum quantity of a high-boiling organic solvent. Antioxidants are normally designed to trap free radicals originating from the first step of autoxidation, so the claimed reduction in oxygen permeability is a surprising discovery. This system was designed to reduce the oxygen permeability of the bilayer primarily for meat packaging, with one example being a sandwich between two layers of PVDC.

Plastics with blended sulfites have also been used to remove oxygen diffusing under bottle closures. Teumac (1995) has summarized commercial developments since 1989, and describes the compositions as including up to 7% sodium sulfite and up to 4% sodium ascorbate. In some patents, the use of isoascorbic acid has been proposed. In the sulfite-free compositions, the quantity of ascorbate determines the scavenging capacity while the amount of catalyst determines the rate. A parallel development in Japan by Toyo Seikan Ltd involved the use of iron in the closure liner.

The success of iron in package inserts gave momentum to research into the potential use of iron in plastic-based compositions. In the early 1990s, several companies launched products based on compounds of iron with polyolefin polymers. These were launched in Japan (Toyo Seikan's Oxyguard) and in the United States of America (Amoco Chemicals' Amosorb 1000 and 2000). The latter became Shelfplus when bought by Ciba Specialty Chemicals. These resins are extrudable under normal conditions of temperature, and are used in oxygen-barrier laminations to packages, particularly for foods subjected to conditions of high temperature and humidity and especially in thermoformed trays. Toyo Seikan produced pouches for blood-product bags with one transparent side and one white-pigmented Oxyguard side. These developments were accompanied by several similar proposed compositions, which did not reach commercialization.

Incorporation of iron into resin strips placed in sachets has been utilized by the Mitsubishi Gas Chemical Company as an alternative to filling the sachets loosely with reduced iron powder. The sachets contain polyolefin strips, which are microporous, and the pores allow the oxygen and water vapor increased access to the iron particles compared with the same composition in a continuous film strip. This innovation addresses the need for sachets that do not interfere with microwave reheating of the food, such as semiaseptic rice. Another welcome benefit is removal of the danger of accidental release of iron powder if the sachet is ruptured when the package is opened, for example with a knife. Brody et al. (2001) describe a patent by Kawatiki et al. (1992) involving a seemingly related concept involving microvoids generated by stretching an iron-loaded strip of plastic.

Homogeneous Plastic Structures

The progress from package insert to reactive polymers, via various blends of solids (or inclusion of trapped liquid scavenger solutions), also included homogeneous solutions of reagents in polymers. This provided the opportunity for increased clarity of flexible and rigid packaging and reduced interference with the inherent properties of the polymers used. This also had the potential to reduce limitations on the component polymers, which might be desired in particular packaging structures.

There was the first multilayer plastic structure in which antioxidants were claimed to function as oxygen "getters". According to Brody et al. (2001), the process involved dispersing very minor portions of conventional antioxidants in or between layers in a multilayer. The process appears not to have advanced from that point.

The first plastic to incorporate dissolved reagents with known oxidation chemistry involved the light-energized excitation of oxygen diffusing into the plastic (Rooney and Holland, 1979). The substrate for oxidation does not react with ground-state oxygen, so the oxygen to be scavenged had to be excited to the singlet state. This was achieved by including a photosensitizing dye and exposing the scavenger film to visible light. The process occurs only while the scavenger film is exposed to the light, as shown in Figure 9.1.

The laminate consisting of polyethylene/polyamide 6/cellulose acetate contained a singlet oxygen acceptor, 1,3-diphenylisobenzofuran, 8×10^{-2} M, and methylene blue dye, 10^{2} M. The laminate separated the two compartments of a permeability cell, air was placed on the polyamide side, and nitrogen with a small oxygen residue was placed on the scavenger side. In darkness the laminate displayed its normal permeability characteristics, but when illuminated it not only prevented permeation but also scavenged oxygen that had permeated during the previous dark period. This process continued until the concentration of scavenger was reduced to a point at which scavenging was now incomplete and some oxygen permeation occurred. This research demonstrated, for the first time, activation by light as well as the finite oxygen-scavenging capacity of film-based scavengers—a topic that has subsequently become commercially important.

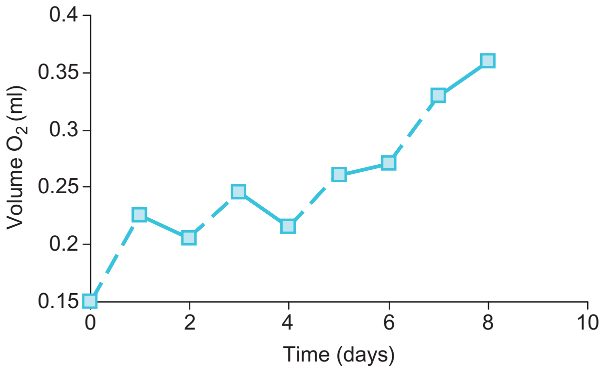

Figure 9.1 Effect of illumination (solid line) and darkness (dashed line) on the cumulative volume of oxygen permeating a scavenger film laminate.

Plastics compositions with a higher scavenging capacity for oxygen were subsequently investigated by the same research team (Rooney and Holland, 1979), and the factors affecting the rate of oxygen scavenging by solutions of singlet oxygen acceptors in polymers were elucidated. During the 1980s, there appears to have been no reported research other than this academic work focusing on the polymer as a reaction medium for diffusing oxygen molecules (Rooney et al., 1981). It was shown that ascorbic acid could perform as a singlet oxygen acceptor and that the photochemistry imposed limits on the scavenging rate (Rooney et al., 1982). The use of one polymer as both the reagent and the reaction medium was investigated using natural rubber (Rooney, 1982). This work was extended to other rubbers which display different inherent reactivities with singlet oxygen while having similar values of oxygen permeability. The process was applied in a poly(furyloxirane) designed to have an even higher reactivity toward singlet oxygen (Maloba et al., 1994).

A more practical approach to creating a polymeric total barrier to oxygen permeation based on the transition-metal-catalyzed oxidation of aromatic polyamides was developed by the Carnaud Metal Box Company under the trade name Oxbar™ (Cochran et al., 1991). The key advantage initially seen for such a process was the ability to blend the polymer plus catalyst with polyethylene terephtalate (PET) in the manufacture of bottles for wine and beer. Few polymers are compatible with PET, so this approach constituted a breakthrough in the development of PET bottles for oxygen-sensitive beverages in general. It was shown that around 200 ppm of cobalt is necessary in a 7% blend of MXD-6 polyamide in PET in order to generate a total barrier to oxygen permeation (Folland, 1990). Several developments by competing companies have resulted in approaches that use this chemistry either in a PET matrix or in a separate MXD-6 polyamide layer coinjected with two layers of PET. One such patent involves use of a blend of MXD-6 polyamide, polyester, and a cobalt salt in the core layer of bottles (Collette, 1991). Other commercial approaches have been to incorporate the cobalt into a thin (10 μm) layer of MXD-6 sandwiched between PET layers in bottles.

An alternative approach to dealing with the PET compatibility issue was devised in Amoco Chemicals (Cahill and Chen, 1997). This approach involved making a block copolymer of a polybutadiene with PET with the trade name Amosorb™ 3000, sold by BP Amoco. The PET caused the compatibilization while the polybutadiene was the oxidizable polymer. The process is catalyzed by means of a transition metal salt. This polymer lent itself to use in PET bottle manufacture, since the catalyst can be added at a late stage in the injection-molding process, and premature oxidation can be minimized. Even though the injection-molded preforms have been heated while containing the catalyst, they have a substantial shelf life due to the low permeability of the thick layers of PET, especially when the Amosorb™ 3000 is in a buried layer. Perhaps, an improvement would be to include some form of triggering or activation closer to the time of filling the bottle.

Triggering of oxygen-absorbing sachets was an essential feature present from the time they were initially introduced commercially. In that case the trigger was the water necessary for the rusting of iron by the oxygen. In general, this water came from the food and the sachets were not prematurely activated unless exposed to the air for too long. The concept of triggering an otherwise unreactive plastic system was also demonstrated in the 1970s in the singlet oxygen approach to oxygen scavenging (Rooney and Holland, 1979). Around the same time, Rabek and Ranby (1975) showed that the oxidative degradation of a plastic in sunlight was substantial if a photosensitizer and a transition metal salt were dispersed therein. Against this background, the breakthrough concept of single-dose triggering has been developed and introduced commercially. Speer et al. (1993) were the first to claim that films of unsaturated polymers, such as poly(1,2-butadiene), could very effectively scavenge ground-state oxygen provided they contained a transition metal catalyst and a photosensitizer. The use of pendant C=C double bonds was designed to minimize rupture of the polymer backbone during oxidation. This overcame one of the significant drawbacks of the process of Rooney (1982). Speer's process has been developed with a large number of patents and has been marketed by the Cryovac division of Sealed Air Corporation under the trade name OS 1000™.

The approach of using autoxidation of unsaturated groups on a polymer as a basis for oxygen scavenging has been taken up by Chevron Chemical Company, in a further development of the Cryovac concept. In this case, the oxidizable moiety is a cyclohexene side group bound to the backbone, for instance by transesterification (Ching et al., 1994). The novelty of this process lies in its apparent "tasteless" achievement of oxygen removal. The earlier approaches involving autoxidation of noncyclic side groups are claimed to have imparted some taste to the food.

The chemistries employed in the oxidation of aromatic polyamides and of hydrocarbon polymers with various side groups have the common theme of using light-triggering to produce enough free radicals to remove the antioxidants remaining after extrusion. The transition metal catalysts then facilitate the rupture of the hydroperoxides formed and accelerate the ongoing chain reactions.

A radically different process also triggered by light has been developed without the use of photoinitiation. This process involves the light excitation of a photoreducible component, such as a quinone, followed by its photoreduction. This new photoreduced species is then oxidized by the oxygen that it scavenges. In this case, the polymer was inactive until exposure to, for example, ultraviolet light—something that might not be applied until immediately before package filling (Rooney, 1993). The species reactive toward oxygen is therefore not present during thermal processes such as extrusion and blow molding.

There have been other approaches to scavenging oxygen from food packs or to enhancing the barrier of packs such as bottles. These have generally been variants on those mentioned here, and some have been reviewed elsewhere (Brody et al., 2001; Rooney, 1995). The processes that have progressed to the market or which are undergoing commercial development are described in ever-increasing detail in the forest of patent applications that have been published. Despite the density of this forest, it is clear that several different food distribution problems can be solved by using these scavengers. These problems have their genesis in the nature of the newer packages as well as the requirements of high-speed filling and the use of distribution temperatures that impose demands upon the packaging. Perhaps the greatest demand has been made by the shift from glass and metal cans to substantially plastic packs.

The requirements of foods that impact on package selection involving oxygen scavenging can basically be subdivided into enhancement of barrier and headspace scavenging (Figure 9.2). Frequently both requirements are present, but the most economical approach to package selection may be made by using oxygen scavenging to address one problem or the other.

Barrier enhancement is commonly needed where the product is packaged in an impermeable package with a closure allowing oxygen entry, or when the product has a very low headspace and the oxygen ingress needs to be prevented while maintaining a thin barrier layer. The latter limitation may be a requirement of the package for other reasons, such as in aseptic brick packs or with close-fitting thermoformed films used for vacuum packaging. The most recent need for barrier enhancement is found in PET bottles for beer, where beer is packaged with a very low oxygen concentration but is degraded by oxygen permeating the PET.

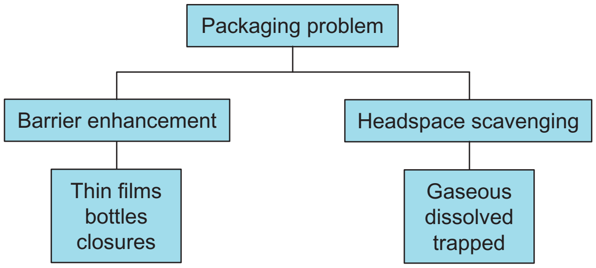

Figure 9.2 Roles for oxygen-scavenging packaging plastics.

Headspace scavenging is beneficial when, even though the package may provide a high barrier, the residual oxygen is not readily removed to the necessary level by conventional means. This is typically the case with beverages and products with a porous structure not economically deoxygenated by evacuation or gas flushing. Such products include bakery items and spray-dried and freeze-dried foods. Beverages that are not readily deoxygenated include those that froth readily yet contain air bubbles due to the presence of fruit pulp.

9.4 Application to Food and Beverage Packaging

The interest in, and adoption of, oxygen-scavenging systems has been driven by the wide range of mechanisms by which oxygen can contribute to loss of food quality. These mechanisms include:

- nutrient loss,
- discoloration,
- microbial spoilage,
- rancidity,
- organoleptic deterioration,
- infestation by insects and vermin.

Pathogen growth is not included in the above list, as measures to prevent their growth should already be in place. Each one of these mechanisms has its own kinetics and level of sensitivity at which the effect on the food becomes unacceptable. Table 9.2 shows a selection of foods that benefit from oxygen scavenging and indicates the importance of the speed at which quality deterioration occurs. Hence, although a pack of full-cream milk powder which has been nitrogen flushed may have an oxygen content of around 5% after desorption from the pores, the oxidation occurs sufficiently

Table 9.2 Oxygen Sensitivity of Some Foods

Food/ Beverage	Substrate	Rate
Milk powder	Fat	Slow
Cheese	Mold	Slow
Beer	Flavors	Moderate
Wine	Preservatives	Moderate
Juice	Vitamin C	Fast
Fish	Oil	Fast

slowly to present only a minor problem. Beer, on the other hand, is similarly sensitive to oxidation of oils which cause off-flavor development. However, the damage done by the initial oxygen uptake results in flattening of the flavor and can take some months off the potential shelf life. This is crucial to the introduction of PET packaging for this beverage.

The choice of packaging for preserved fish products is severely limited by the rapid oxidation of the polyunsaturated oils present. Indeed, a variety of fish-oil products cannot be packaged in glass jars because the residual oxygen present is sufficient to cause unacceptable levels of both discoloration and rancid odor. Packaging that scavenges oxygen at a rate much greater than the food oxidation calls for rapid scavenging coupled with package design that maximizes the area of scavenger available.

Prevention of mold growth is a major role for oxygen scavenging (Smith et al., 1995). Although mold is one of the major causes of food quality loss, the slow rate of growth in many foods provides an opportunity for oxygen scavenging to reduce oxygen levels to around 0.1%, which inhibits such growth. The capacity of oxygen scavenging to prevent mold growth on processed meat was addressed by Randell et al. (1995). They demonstrated that even in the presence of a pinhole in the seal of packages, an oxygen-absorber sachet could suppress growth for useful periods. They found that the concurrent degradation of the meat color by the action of the fluorescent display lights on the oxidation reaction was also prevented.

Color loss due to photo-oxidation is not limited to processed meats. It has also been shown that the flavor and color degradation of Havarti cheese is strongly enhanced by fluorescent display lights (Randell et al., 1995). These authors showed that by reducing the headspace oxygen in these packs to 0.1%, the formation of pentanol (the indicator of quality loss) could be essentially eliminated, regardless of the illumination conditions tested. The benefit demonstrated by such work is that oxygen scavenging can contribute not just to the package properties but also to the conditions under which a food might be distributed.

The oxidation of vitamin C in orange juice occurs rapidly, and this reaction usually results in substantial deoxygenation of the juice in ambient barrier packaging in aseptic brick packs. The result is the loss of the vitamin, coupled with the consequent generation of browning products several months later. Beverages do not lend themselves to protection by oxygen-absorber sachets or labels, so overcoming this problem has been delayed pending the development of plastics with scavenging capability.

The development of these plastics has been described largely in patents, so there are very few peer-reviewed research results published. One such investigation, from the author's laboratory, involved the measurement of dissolved oxygen concentrations, ascorbic acid, and total vitamin C assays, and browning of the juice when stored in an oxygen-scavenging laminate under refrigerated and ambient conditions (Zerdin et al., 2003). The laminate (OS) pouches consisted of EVOH/oxygen-scavenger film/EVA, and the pouches contained orange juice from freshly packed aseptic brick packs. The juice was resterilized with dimethyldicarbonate on repacking in the pouches in order to avoid microbial oxygen uptake. The scavenger film was an improved version of one that involved photoreduction of a polymer-bound reducible compound that had been described previously (Rooney and Horsham, 1998). It was found that the oxygen was scavenged in less than 3 days at ambient temperature, and that the quantity of ascorbic acid lost during that time was reduced compared with that in the control pouches. The loss of ascorbic acid from the juice packed in the scavenger pouch was consistently less than that in the reference over a period of 1 year (Figure 9.3). The extent of browning of the juice was reduced by around 33% when the juice was packaged with the scavenger laminate. Results broadly similar to these were reported by Rodgers (2000), whose results were obtained by an independent laboratory and used the

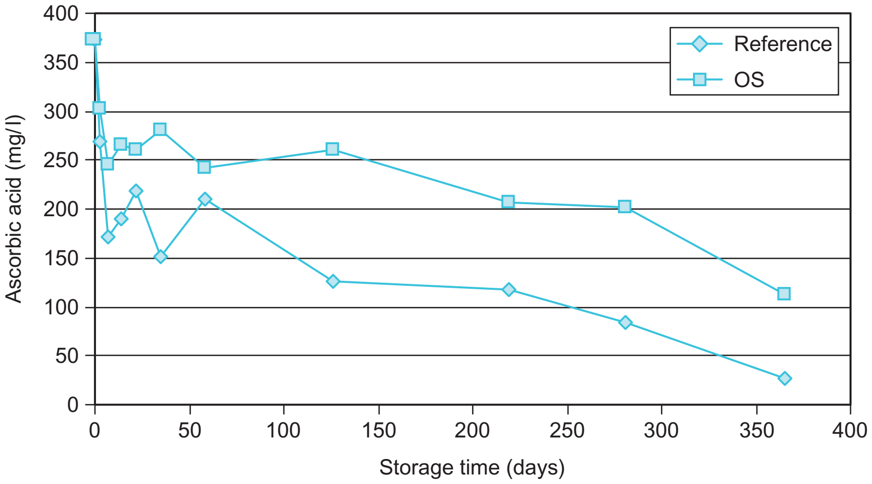

Figure 9.3 Concentration of ascorbic acid in orange juice packed in oxygen scavenging and reference pouches stored at 25°C.

metal catalyzed and photoinitiated polymer-bearing cyclohexenyl groups.

The results obtained at refrigerator temperature by Zerdin et al. (2003) were similar to those obtained under ambient conditions. The oxygen concentration was similar after 3 days. The browning was suppressed at low temperature in both the control and test pouches. Thus, oxygen scavenging may be significantly more necessary where aseptic packs are distributed under ambient conditions than where short shelf-life juices are distributed chilled.

Besides the direct effects of suppressing oxidation or microbial growth on the food, there are other aspects of food quality that can be influenced by use of oxygen scavengers. Chilled beef is conventionally distributed at the wholesale level as primal cuts weighing several kilograms, vacuum-packaged in shrink bags with low oxygen permeability, at 0°C. The drip, or liquid exudate lost under these circumstances has been minimized, but recent research into the use of nonvacuum packaging with the presence of an oxygen-scavenger sachet has revealed a further improvement (Payne et al., 1998). These investigators found that drip loss could be substantially reduced by avoiding the compression effect of evacuation and removing the residual oxygen by using an oxygen-absorber sachet (Ageless™ Z50). Results like these are indicative of the potential for oxygen scavenging to contribute to quality and logistic parameters associated with food distribution in the wider sense.

The application of oxygen scavenging has not been limited to plastic packages. The shelf life of cracker biscuits in metal cans, as measured by hexanal formation and peroxide value development, was almost doubled at 25°C (Berenzon and Saguy, 1998). It was found that with the addition of oxygen-absorber sachets, no oxidative odors were observed after 44 weeks at 25°C and 35°C. Results such as these support the view that the method of oxygen scavenging will vary with the food/package combination, and that no one approach is likely to satisfy the varying demands of food and beverage packaging.

9.5 Future Opportunities

The field of oxygen scavenging using plastics is still largely under development, even though the use of sachets, labels, and closure liners is well established. The introduction of new technologies will depend upon the drivers revealed in the food and packaging industries. The major driver should be the curiosity of food technologists interested in seeking better outcomes when they introduce new or modified products. This in turn may be expected to be a result of the education process. Another driver of importance will be the need to achieve current (or better) quality levels as packaging is changed, especially when newer materials are used. This is being observed already with the introduction of PET bottles and jars in place of rigid metals and glass. Even in the latter packaging, there are ample opportunities to enhance the product quality for the consumer by scavenging of the headspace already present therein. The potential impact on canned foods can only be guessed at currently.

Regulation by both food authorities and those caring for the environment will also have major impacts. A variety of scavenging systems have already been approved in Japan, the United States of America, and European countries, among others. The expected amendment of the Food Packaging Directive by the European Commission in late 2004/2005 to address active packaging will make the future paths to introduction clearer, even though oxygen removal is not really the main thrust of the expected changes. The potential for reduction in the complexity of multilayer plastics structures and the reduction in rigid packaging use following the use of oxygen scavenging may be expected to have favorable outcomes for the environment, as long as there are no adverse impacts in the manufacturing process.

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10 Antimicrobial Packaging Systems

Jung H. Han
PepsiCo Corporate Research, PepsiCo Inc., Plano, TX 75024 USA

10.1 Introduction

The quality of foods has been defined as their degree of excellence and includes factors such as taste, appearance, and nutritional content. Quality is a composite of characteristics that have significance and make for acceptability. However, acceptability can be highly subjective. Based on deterioration factors and determination procedures, quality may include various aspects such as sensory quality, microbial quality, and toxicological quality. These aspects are not separate from one another—for example, microbial contamination damages sensory quality and safety. Microbial food quality relates to all three groups of factors, since the growth of bacteria generates undesirable odors and life-threatening toxins; it changes the color, taste, and texture of food; and also reduces the shelf life of the product. Microbial growth in packaged foods significantly decreases its safety and the security of public health. In our society, fast foods, convenience foods, and fresh foods are essential elements. Many food industries produce minimally processed foods, precut fruits/vegetables, and ready-to-eat foods for the purpose of maximum convenience and freshness. In food manufacturing on a mass-production scale, food safety is a top priority for producers, the food industry, governments, and public consumers. Improper treatment and accidental cross-contamination of foods can cause major problems of recall and serious food-borne illnesses. Furthermore, the safety of food and related public health issues can be jeopardized by malicious tampering, extortion for benefits, trials to obtain public attention for any reasons, and terrorism (Kelly et al., 2003). Since the 2001 tragedy of the World Trade Center, consideration of food and water safety has assumed major importance, and protecting food chains against bioterrorism is regarded as a significant aspect of public safety (Nestle, 2003). Food safety has become a significant subject of trends in food packaging, logistics, trade, and consumer studies.

10.2 Food Safety

10.2.1 Spoilage of Food Products

Most foods are perishable. Food spoilage is caused both biologically and chemically. In addition to the chemical degradation of food ingredients through oxidation processes, most spoilage processes are due to biological mechanisms such as auto-degradation of tissues by enzymes, viral contamination, protozoa and parasite contamination, microbial contamination, and attack by rodents and insects. The growth of microorganisms is the major route for food spoilage, leading to degraded quality, shortened shelf life, and changes in natural microflora that could induce pathogenic problems. Microbial spoilage of food products is caused by many bacteria, yeast, and molds; however, their growth is dependent on nutrients, pH, water activity, and presence of oxygen. Therefore, the many different potential microorganisms that could contaminate food products and the various growth environments present difficult problems in preventing the spoilage.

For the food industries, the prevention of food spoilage is a very important issue in determining profit. Furthermore, reducing food spoilage can prolong the shelf life of food products and accordingly extend market boundary, resulting in increased profit.

10.2.2 Food-Borne Illness

Food-borne illness is caused by contamination of food products by microorganisms or microbial toxins. Many food processing technologies have been developed to prevent such contamination by the

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inactivation of pathogens. Traditionally, thermal processes such as blanching, pasteur, and commercial sterilization have been used for the elimination of pathogens from food products. Currently, various new nonthermal technologies are being studied to assess their effectiveness and mechanisms. Such new processes include irradiation, pulsed electric fields, high-pressure processes, and the use of new antimicrobial agents. However, these new technologies cannot completely prevent the contamination and/or growth of pathogens. Some of these methods still require regulatory permission for their commercial use. It is also very hard to control pathogens because of the wide variety of microbial physiology, pathogenic mechanisms, and passage of contamination; the complexity of food composition; their sensitivity to antimicrobial agents; the mass-production nature of food processing; and difficulties in early detection.

There are many prevention systems that are used by the food industry, such as hazard analysis and critical control points (HACCP), sanitation standard operating procedures (SSOP), good manufacturing practice (GMP), and various inspections. The good practice of these quality systems is much more important and effective in eliminating pathogen problems from food system than is the use of reliable new technologies.

10.2.3 Malicious Tampering and Bioterrorism

One of the primary functions of food packaging is to protect food from unintentional contamination and undesirable chemical reactions as well as to provide physical protection. However, recently, the need has arisen for packaging systems to be capable of protecting food from intentional contamination—that is, malicious tampering (Kelly et al., 2003). To secure food safety from tampering and bioterrorism, many systematic protocols are required—such as new food and drug regulation, and new security acts (e.g., bioterrorism acts and Homeland Security guidelines for imported goods). Enhanced traceability is also required so that any potentially tampered goods can be removed from the food chain. Security against tampering and terrorism can be improved by systematic preparation, practical regulation, inspection, emergency response training, and other systematic protocols. However, issues such as traceability, food security, and safety enhancement involve technical development, such as a database for tracking products, intelligent packaging for monitoring foreign matters in products, robotic automation for warehousing, and new security seals on distribution packages.

The protective function of food packaging has become more significant with respect to safety enhancement. Among all of the potential technologies, practical approaches to enhance the safety of food products include the use of advanced tamper-evident or tamper-resistant packaging, and intelligent packaging that indicates any tampering and contamination and has a high-barrier design (Rodrigues and Han, 2003). The use of tamper-evident packaging and intelligent packaging is highly desirable to minimize the risk of the malicious activities of terrorists endangering public safety through the food product chain. In addition to the visual indication of disintegration and contamination of packages, antimicrobial packaging systems can kill or inhibit the growth of pathogenic microorganisms that may be injected into packaged foods without any visual evidence of tampering. With the positive contribution to food safety of the new smart design of food packaging, antimicrobial packaging systems can also protect food products more actively.

Tamper-evident packaging and intelligent packaging are considered to be passive monitoring systems. Antimicrobial packaging can reduce the risk of tampering and bioterrorism by eliminating contaminating microorganisms as well as maintaining the quality of packaged food products by reducing the potential for cross-contamination of food products with spoilage and pathogenic microorganisms.

10.3 Antimicrobial Packaging

Antimicrobial packaging is a system that can kill or inhibit the growth of microorganisms and thus extend the shelf life of perishable products and enhance the safety of packaged products (Han, 2000). Antimicrobial packaging can kill or inhibit target microorganisms (Han, 2000, 2003a). Antimicrobial functions of packaging materials/systems can be achieved by creating unfavorable environments to target microorganisms by eliminating their essential growth requirements and rendering contact of antimicrobials to the target microorganisms (Cho et al., 2009). These systems are constructed either by containing antimicrobial agents in an independent device (e.g., sachet or pad) or in the packaging materials (Lopez-Carballo et al., 2012). Among many applications such as oxygen-scavenging packaging and moisture-control packaging, antimicrobial packaging is one of the most promising innovations of active packaging technologies (Floros et al., 1997). It either uses antimicrobial packaging materials and/or antimicrobial agents inside the package space or inside foods. Most food packaging systems consist of the food products, the headspace atmosphere, and the packaging materials. Any one of these three components could incorporate an antimicrobial element to increase antimicrobial efficiency.

Antimicrobial packaging research generally started with the development of antimicrobial packaging materials that contain antimicrobial chemicals in their macromolecular structures. However, without the use of alternative packaging materials, common packaging materials can be utilized for antimicrobial packaging systems when there is antimicrobial activity in packaged foods or in the in-package atmosphere. Edible antimicrobial agents can be incorporated into food ingredients, while antimicrobial resources can be interleaved in the in-package headspace in the form of sachets, films, sheets, or any in-package supplements to generate antimicrobial atmospheres.

Besides the use of antimicrobial packaging materials or antimicrobial inserts in the package headspace, gaseous agents have been used to inhibit the growth of microorganisms. Common applications include carbon dioxide for modified atmosphere packaging, sulfur dioxide for berries, and ethanol vapor for confections. These gases are injected into the package headspace or into palletized cases after shrink-wrapping of a unit load on a pallet. Vacuum, nitrogen-flushing, and oxygen-scavenging packaging, which were originally designed for preventing the oxidation of packaged foods, also possess antifungal and antimicrobial properties which act against aerobic bacteria, since these microorganisms are restrictively aerobic (Han, 2003b; Smith et al., 1990). However, these technologies, which control the low oxygen concentration to inhibit the growth of aerobic microorganisms, could cause anaerobic microbial growth. Controlling anaerobic bacteria in modified atmosphere packaging is a very important issue in maintaining the quality and safety of the products.

10.4 Antimicrobial Agents

Various antimicrobial agents could be incorporated into conventional food packaging systems and materials to create new antimicrobial packaging systems. The food-grade condition of an antimicrobial agent is the most essential requirement for constructing antimicrobial packaging system (Lopez-Carballo et al., 2012). Table 10.1 shows potential antimicrobial agents and food-grade preservatives. They can generally be classified into three groups: chemical agents, natural agents, and probiotics.

10.4.1 Chemical Antimicrobial Agents

For the purpose of food preservation, all packaging ingredients must be food grade. Chemical agents can be mixed with food ingredients, incorporated into packaging additives, or inserted into the headspace atmosphere. The antimicrobial agents will be in contact with and consumed alongside the food products in these applications. Therefore, the chemical antimicrobial agents should be controlled as food ingredients regardless of where the chemical antimicrobial agents were positioned initially—in the food products, in the packaging materials, or in the package headspace atmosphere. In the case of nonfood-grade chemicals, the only way to incorporate the chemical into the food packaging system is to bind it chemically to the polymers of the packaging material (immobilization). In this case, the migration of residual amounts of the nonfood-grade chemical into the food products is prohibited by regulation. Therefore, it is necessary to verify that there is no migration of the chemical from packaging material to food, and there is no residual free chemical after the immobilization reaction. There will be detailed explanation of immobilization systems later in this chapter.

The most common chemical antimicrobials used by researchers are the various organic acids. Organic acids are widely used as chemical antimicrobial agents because their efficacy is generally well understood and they are cost effective. Many organic acids, including fatty acids, are naturally

Table 10.1 Examples of Potential Antimicrobial Agents for Antimicrobial Food Packaging Systems

Classification	**Antimicrobial Agents**
Organic acids	Acetic acid, benzoic acid, lactic acid, citric acid, malic acid, propionic acid, sorbic acid, succinic acid, tartaric acid, mixture of organic acids
Acid salts	Potassium sorbate, sodium benzoate
Acid anhydrides	Sorbic anhydride, benzoic anhydride
Para-benzoic acids	Propyl paraben, methyl paraben, ethyl paraben
Alcohol	Ethanol
Bacteriocins	Nisin, pediocin, subtilin, lacticin
Fatty acids	Lauric acid, palmitoleic acid
Fatty acid esters	Glycerol monolaurate
Chelating agents	EDTA, citrate, lactoferrin
Enzymes	Lysozyme, glucose oxidase, lactoperoxidase
Metals	Silver, copper, zirconium
Antioxidants	BHA (butylated hydroxyanisole), BHT (butylated hydroxytoluene), TBHQ (tert-butylhydroquinone), iron salts
Antibiotic	Natamycin
Fungicides	Benomyl, Imazalil, sulfur dioxide
Sanitizing gas	Ozone, chlorine dioxide, carbon monoxide, carbon dioxide
Sanitizers	Cetyl pyridinium chloride, acidified NaCl, triclosan
Polysaccharide	Chitosan
Phenolics	Catechin, cresol, hydroquinone
Plant volatiles	Allyl isothiocyanate, cinnam-aldehyde, eugenol, linalool, terpineol, thymol, carvacrol, pinene
Plant/spice extracts	Grape seed extract, grapefruit seed extract, hop beta acid, *Brassica* erucic acid oil, rosemary oil, oregano oil, basil oil, other herb/spice extracts, and their oils
Probiotics	Lactic acid bacteria

Source: Modified from Han (2000, 2003a,b) and Suppakul et al. (2003a).

existing chemicals and have been used historically. Currently, most are produced by chemical synthesis or are chemically modified natural acids. Organic acids have characteristic sensitivities to microorganisms. For example, sorbic acid and sorbates are very strong antifungal agents, while their antibacterial activities are limited—they have various antimicrobial mechanisms. Therefore, the correct selection of organic acids is essential to produce effective antimicrobial agents. Mixtures of organic acids have a wider antimicrobial spectrum and stronger activity than a single organic acid.

Fungicides are also common antimicrobial agents. Imazalil has been incorporated into the wax coating of oranges and other citrus fruits. Since fungicides are not permitted as a direct food preservatives, they cannot be mixed into food ingredients or added to food-contact packaging materials as food-contact substances. Therefore, it is necessary to design antimicrobial food packaging systems when nonfood-grade antimicrobial agents, such as fungicides, are used. Food sanitizers and another chemical antimicrobial groups are included in Table 10.1. They are food cleansing agents, food-contact substances, or food-contact surface sanitizers. Residual food sanitizers on foods are permitted, with specific control limits. Thus, the use of food sanitizers has many advantages over the use of other nonfood-grade antimicrobial agents such as fungicides.

Various inorganic compounds are also used as active antimicrobial agents when incorporated in packaging materials. Silver, and its complexes with porous materials such as zeolite are used as antimicrobial particles in addition to polymeric films or surface coating (Pehlivan et al., 2005). Silver, especially in nanoparticle form, shows strong antimicrobial activity against bacteria, molds, and yeasts. It acts by disturbing cell-wall permeability, respiration, and cellular replication (Feng et al., 2000; Li et al., 2010; Saulou et al., 2010). Titanium oxide (TiO_2) is a nontoxic Food and Drug Administration (FDA) approved (as GRAS) food-contact material exhibiting strong antimicrobial activity with a similar mode of action to silver after UV excitement (Chawengkijwanich and Hayata, 2008; Cho et al., 2007; Kikuchi et al., 1997).

Some gases act as effective antimicrobial agents when vaporized in the package headspace and dissolution onto the food surface (Han, 2000). Gases commonly used for this purpose are carbon dioxide, sulfur dioxide, chlorine dioxide, ethanol, and ozone (Han, 2005; Suppakul et al., 2003a).

Chitosan, a deacetylated chitin, possesses antimicrobial and film-forming ability (Dutta et al., 2009; Joerger, 2007). In spite of the popularity of chitin as a raw material in antimicrobial polymer research, it is still not listed as a GRAS status material by FDA.

10.4.2 Natural Antimicrobial Agents

Table 10.1 includes herb extracts, spices, enzymes, and bacteriocins as naturally occurring antimicrobial agents. Due to consumer demand for chemical-preservative-free foods, food manufacturers are now using naturally occurring antimicrobials to sterilize and/or extend the shelf life of foods. Herb and spice extracts contain multiple natural compounds and are known to have a wide antimicrobial spectrum of activity against various microorganisms. Major components of these extracts and essential oils are phenolics, terpenes, and aliphatic alcohols whereas compounds such as ketones and aldehydes are minor components (Tiwari et al., 2009). Apart from antimicrobial activity, they offer other advantages including antioxidative activity and their effect as alternative medicines. However, their mode of action and kinetics are generally unknown, and their chemical stability is also of concern. In addition, they create some problems with respect to flavors.

Specificity of enzymes should be considered carefully, since antimicrobial activity is very sensitive to environment and substrate. As an example, the activity of lysozyme can be significantly affected by temperature and pH. In most cases, lysozyme is not effective against gram-negative bacteria. This is due to the complex cell-wall structure of gram-negative bacteria and the specificity of lysozyme for peptidoglycan. Many research results demonstrate the efficient antimicrobial activities against spoilage and pathogenic microorganisms, including gram negatives in combination with lysozyme and other bacteriocins such as nisin, and chelating agents such as EDTA after incorporating into edible biopolymer coatings or plastic films (Coma, 2008; Conte et al., 2007; Güçbilmez et al., 2007; Han, 2005).

Various bacteriocins, such as nisin, pediocin, lacticin, propionicin, etc., can be incorporated into foods and/or food packaging systems to inhibit the growth of spoilage and pathogenic microorganisms (Daeschul, 1989). Bacteriocins are peptidic toxins produced by bacteria to inhibit the growth of similar bacterial strains (Lopez-Carballo, 2012). The extracted bacteriocins, which are generally small molecular weight peptides, can be utilized in various ways; however, it is very important to characterize their resistance to thermal treatment and pH. In the case of fermented food products, live bacteria that produce bacteriocins can be intentionally added as probiotics in the packaged food system to obtain antimicrobial effectiveness.

10.4.3 Probiotics

Table 10.1 also shows the possible use of probiotics (*Lactobacillus reuteri*) to control *Escherichia coli* O157:H7 (Muthukumarasamy et al., 2003).

Various microorganisms, for example, lactic acid bacteria, produce bacteriocins and nonpeptide growth-inhibiting chemicals such as reuterin. These naturally produced antimicrobials can inhibit the growth of other bacteria. Probiotics can therefore effectively control the competitive undesirable microorganisms. Many traditional fermented food products contain antimicrobial probiotics. There has been much research and development regarding the function of antimicrobial probiotics for the preservation of fermented foods. Currently there is only limited research into the use of probiotics for the purpose antimicrobial of packaging design. With the of development new technology for the delivery of live probiotics, their use as an antimicrobial source for antimicrobial food packaging will increase in future due to its safety and effectiveness.

10.5 System Design

There are various factors to be considered in designing antimicrobial systems. Antimicrobial systems can be constructed by using antimicrobial packaging materials, antimicrobial inserts (such as sachets) to generate antimicrobial atmosphere conditions inside packages, or antimicrobial edible food ingredients in the formulation of foods. Since antimicrobial packaging systems are designed to control the growth of microorganisms in packaged foods, the systems essentially consist of packaging materials (or packages), foods, the in-package atmosphere, target microorganisms, and antimicrobial agents. These five elements are related to one another and to the final system design features.

To study the effectiveness of antimicrobial food packaging systems with respect to the relative effects of these elements, many choices of combinations should be examined using real food systems. The majority of research has been conducted using culture media, which provides the richest nutritional quality and the most favorable environment for microbial growth, and antimicrobial packaging materials. Most microorganisms in culture media are not stressed compared to microorganisms under normal conditions in foods. Many antimicrobial systems that show strong antimicrobial activity against target microorganisms in culture media do not demonstrate the same antimicrobial activity when they are actually incorporated into food systems. This clearly shows the interactive effects of food ingredients, microorganisms, and antimicrobial agents. All of these are complex systems that cannot be explained by a single chemical mechanism. Therefore, it is strongly recommended that experiments examining the efficiency of an antimicrobial packaging system should be conducted using a real food instead of culture broth or agar media. Table 10.2 lists examples of antimicrobial food packaging systems that have been tried, mostly by university researchers, over the past two decades.

10.5.1 Antimicrobial Mechanisms

An antimicrobial agent has specific inhibitory activity and mechanisms against each microorganism. Therefore, the selection of antimicrobial agents is dependent on their efficacy against a target microorganism. There is no “magic bullet” antimicrobial agent that will work effectively against all spoilage and pathogenic microorganisms because all antimicrobial agents have different activities that affect microorganisms differently. This is due to the characteristic antimicrobial mechanisms and the differences in physiology of the microorganisms. Simple categorization of microorganisms may be very helpful to select specific antimicrobial agents, which may be categorized by oxygen requirement (aerobes or anaerobes), cell-wall composition (gram-positive and gram-negative), growth stage (spores or vegetative cells), optimal growth temperature (thermophilic, mesophilic, or psychrotrophic), or acid/osmosis resistance. In addition to the microbial characteristics, the antimicrobial characteristics of the agent are also important in understanding the efficacy as well as its limits. For example, some antimicrobial agents inhibit essential metabolic (or reproductive genetic) pathways of microorganisms, while others alter cell membrane/wall structure. Two major mechanisms of microbial inhibition are microbiocidal and microbiostatic effects, which are discussed below.

10.5.2 Microbiocidal

It is expected that antimicrobial packaging systems would kill target spoilage and pathogenic bacteria, since the system could eliminate any microorganisms from the food/packaging system.

Table 10.2 Antimicrobial Food Packaging Systems Constructed by Researchers

Antimicrobial Agents	Packaging Materials	Foods	Microorganisms	Researchers
Organic acids				
Benzoic acids	PE	Tilapia fillets	Total bacteria	Huang et al. (1997)
	Ionomer	Culture media	*Penicillium* spp., *Aspergillus niger*	Weng et al. (1997)
Para-benzoate	LDPE	Simulants	Migration test	Dobias et al. (2000)
	PE coating	Simulants	Migration test	Chung et al. (2001a)
	Styrene-acrylate	Culture media	*Saccharomyces cerevisiae*	Chung et al. (2001b)
Benzoic and sorbic acids	PE-*co*-met-acrylate	Culture media	*Asp. niger*, *Penicillium* spp.	Weng et al. (1999)
Sorbates	LDPE	Culture media	*S. cerevisiae*	Han and Floros (1997)
		Pastry dough	Total bacteria	Silveira et al. (2007)
	PE, BOPP, PET	Water, cheese	Migration test	Han and Floros (1998a,b)
	LDPE	Cheese	Yeast, mold	Devlieghere et al. (2000a)
	MC (methyl cellulose)/ palmitic acid	Water	Migration test	Rico-Pena and Torres (1991)
	MC/HPMC/ fatty acid	Water	Migration test	Vojdani and Torres (1990)
	MC/chitosan	Culture media		Chen et al. (1996)
	Starch/ glycerol	Chicken breast		Baron and Sumner (1993)
	WPI (whey protein isolate)	Culture media	*S. cerevisiae*, *Asp. niger*, *Penicillium roqueforti*	Ozdermir (1999)
	CMC/paper	Cheese		Ghosh et al. (1973, 1977)
	PE	Culture media	*S. cerevisiae*, molds	Weng and Chen (1997); Weng and Hotchkiss (1993)
	Cellulose	Pastry dough	*Staphylococcus* spp., mesophilics, psychrotrophs	Silveira et al. (2007)
Sorbate and propionates	PE/foil	Apples	Firmness test	

(*Continued*)

Table 10.2 (Continued)

Antimicrobial Agents	**Packaging Materials**	**Foods**	**Microorganisms**	**Researchers**
				Yakovleva et al. (1999)
Acetic and propionic acids	Chitosan	Water	Migration test	Ouattara et al. (2000a)
Na-lactate, K-sorbate, Na-diacetate	Chitosan	Smoked salmon	*Listeria monocytogenes*	Neetoo et al. (2008b); Ye et al. (2008a)
Enzymes				
Lysozyme	PVOH	Water	Migration test	Buonocore et al. (2003)
Lysozyme, nisin	Ca-alginate	Smoked salmon	*Lis. monocytogenes*, *Salmonella anatum*	Datta et al. (2008)
Lysozyme, nisin, EDTA	SPI, zein	Culture media	*Escherichia coli*, *Lactobacillus plantarum*	Padgett et al. (1998)
Lysozyme, nisin, propyl paraben, EDTA	WPI	Culture media	*Lis. monocytogenes*, *Salmonella typhimurium*, *E. coli* O157:H7, *Brochothrix thermosphacta*, *Staphylococcus aureus*	Rodrigues and Han (2000)
Immobilized lysozyme	PVOH, polyamide, cellulose acetate	Culture media	Lysozyme activity test	Appendini and Hotchkiss (1996, 1997)
Glucose oxidase		Fish		Fields et al. (1986)
Bacteriocins				
Nisin	PE	Beef	*B. thermosphacta*	Siragusa et al. (1999)
	LDPE	Smoked salmon	*Lis. monocytogenes*	Neetoo et al. (2008a)
	HPMC	Culture media	*Lis. monocytogenes*, *S. aureus*	Coma et al. (2001)
		Hot dog	*Lis. monocytogenes*	Franklin et al. (2004)
	HPMC/ stearic acid	Culture media		Sebti et al. (2002)

(*Continued*)

Table 10.2 (Continued)

Antimicrobial Agents	**Packaging Materials**	**Foods**	**Microorganisms**	**Researchers**
			Lis.	
	Corn zein	Shredded cheese	Total aerobes	Cooksey et al. (2000)
	Corn zein, wheat gluten	Culture media	*L. plantarum*	Dawson et al. (2003)
	Ethylene-*co*-acrylic	Culture media	*Lactobacillus leichmannii*	Leung et al. (2003)
	PVC	Chicken	*Sal. typhimurium*	Natrajan and Sheldon (2000)
	Chitosan	Milk, orange juice	Yeast, total bacteria	Lee et al. (2004)
Nisin, lacticins	LDPE, polyamide	Culture media	*Aspergillus flavus*, *Lis. monocytogenes*	An et al. (2000)
	LDPE, polyamide	Oyster, beef	Total aerobes, coliform bacteria	Kim et al. (2002a,b)
Nisin, EDTA	PE, PE–PE oxide	Beef	*B. thermosphacta*	Cutter et al. (2001)
Nisin, citrate, EDTA	PVC, polyamide, LLDPE	Chicken	*Sal. typhimurium*	Natrajan and Sheldon (2000)
Nisin, organic acids mixture	Acrylics, PVA-*co*-PE	Water	Migration test	Choi et al. (2001)
Nisin, lactate	PP	Cooked ham	*Lis. monocytogenes*	Jofre et al. (2008)
Nisin, enterocin, sakacin	PP	Cooked ham	*Lis. monocytogenes*	Jofre et al., 2007
Nisin, lauric acid	Zein	Simulants	Migration test	Hoffman et al. (2001)
	Soy protein	Turkey bologna	*Lis. monocytogenes*	Dawson et al. (2002)
Nisin, pediocin	Cellulose casing	Turkey breast, ham, beef	*Lis. monocytogenes*	Ming et al. (1997)
Pediocin	WPI	Culture media	*Listeria innocua*	Quintero-Salazar et al. (2003)
Polymers				
Chitosan		Cheese	*Lis. monocytogenes*, *Lis. innocua*	Coma et al. (2002)
		Pork	Total bacteria	Yingyuad et al. (2006)

(*Continued*)

Table 10.2 (Continued)

Antimicrobial Agents	**Packaging Materials**	**Foods**	**Microorganisms**	**Researchers**
	Chitosan/paper	Strawberry	*E. coli*	Yi et al. (1998)
	Chitosan/PE	Turkey breast	*Lis. monocytogenes*	Joerger et al. (2009)
	Chitosan/Surlin	Ham	*Lis. monocytogenes*	Ye et al. (2008b)
Chitosan, herb extracts	LDPE	Culture media	*L. plantarum*, *E. coli*, *S. cerevisiae*, *Fusarium oxysporum*	Hong et al. (2000)
Chitosan acetate		Culture media	*E. coli*, *Vibrio vulnificus*, *Sal. typhimurium*, *Salmonella enteritidis*, *Shigella sonnei*	Park et al. (2003)
UV irradiation, excimer laser	Polyamide	Culture media	*Pseudomonas fluorescens*, *Enterococcus faecalis*, *S. aureus*	Paik and Kelly (1995); Paik et al. (1998)
Natural extracts				
Grapefruit seed extract	LDPE, polyamide	Ground beef	Total aerobes, coliform bacteria	Ha et al. (2001)
	LDPE	Lettuce, soy sprouts	*E. coli*, *S. aureus*	Lee et al. (1998)
Grapefruit seed extract, lysozyme, nisin	Na-alginate, kappa-carrageenan	Culture media		Cha et al. (2002)
Clove extract	LDPE	Culture media	*L. plantarum*, *F. oxysporum*, *E. coli*, *S. cerevisiae*	Hong et al. (2000)
Herb extract, Ag-zirconium	LDPE	Lettuce, cucumber	*E. coli*, *S. aureus*, *Leuconostoc mesenteroides*, *S. cerevisiae*, *Asp. niger*, *Aspergillus oryzae*,	An et al. (1998)

(*Continued*)

Table 10.2 (Continued)

Antimicrobial Agents	**Packaging Materials**	**Foods**	**Microorganisms**	**Researchers**
			Penicillium chrysogenum	
	LDPE	Strawberry	Firmness test	Chung et al. (1998)
Cinnam-aldehyde, eugenol, organic acid	Chitosan	Bologna, ham	*Enterobacter*, lactic acid bacteria, *Lactobacillus sakei*, *Serratia* spp.	Ouattara et al. (2000a,b)
Cinnam-aldehyde, catechin	Algae film	Sausage	*E. coli* O157:H7, *Lis. monocytogenes*	Ku et al. (2008)
Horseradish oil	Paper in pouch	Ground beef	*E. coli* O157:H7	Nadarajah et al. (2002, 2003)
Horseradish extract and *Lactobacillus reuteri* (probiotics)	PE/EVOH/PET pouch	Ground beef	*E. coli* O157:H7	Muthukumarasamy et al. (2003)
Lemon extract	Agar	Mozzarella cheese	Total bacteria	Conte et al. (2007)
Allyl isothiocyanate	PE film/pad	Chicken, meats, smoked salmon	*E. coli*, *Sal. enteritidis*, *Lis. monocytogenes*	Takeuchi and Yuan (2002)
	Paper pad	Cheese	*Penicillium*, *Geotrichum*, *Aspergillus* spp.	Winter and Nielsen (2006)
Green tea extract (catechins)	PVA/starch	Culture media	*E. coli*	Chen et al. (2003)
Carvacrol	EVOH	Culture media	*Lis. innocua*, *E. coli*, *Salmonella* spp.	Cerisuelo et al. (2010a,b)
Basil extract	LDPE	Culture media	*E. coli*	Suppakul et al. (2003b)
		Cheese	Total bacteria	Suppakul et al. (2008)
Others				
Benomyl	Ionomer	Culture media		Halek and Garg (1989)
Imazalil	LDPE	Bell pepper		Miller et al. (1984)
	LDPE	Cheese		Weng and Hotchkiss (1992)
Ageless	Sachet	Bread	Molds	Smith et al. (1989)

(*Continued*)

Table 10.2 (Continued)

Antimicrobial Agents	Packaging Materials	Foods	Microorganisms	Researchers
O_2 absorber	Sachet	Sponge cake	Molds	Guynot et al. (2003)
BHT	HDPE	Breakfast cereal		Hoojjatt et al. (1987)
Ethanol	Silica gel sachet	Culture media		Shapero et al. (1978)
	Silicon oxide sachet	Bakery		Smith et al. (1987)
Hinokithiol	Cyclodextrin sachet	Bakery		Gontard (1997)
Chlorine dioxide	Plastic films		Migration test	Ozen and Floros (2001)
	Sachet	Chicken	Total bacteria	Cooksey (2005)
Sulfur dioxide	Paper, sachet	Grapes	*Botyris cenerea*	Scully and Horsham (2007)
Titanium oxide	PP	Lettuce	*E. coli*	Chawengkijwanich and Hayata (2008)
Hexanal, hexenal, hexyl acetate	Modified atmosphere packaging	Sliced apple	*E. coli*, *Sal. enteritidis*, *Lis. monocytogenes*	Lanciotti et al. (2003)
Carbon monoxide	Modified atmosphere packaging	Pork chops	Total bacteria, lactic acid bacteria	Krause et al. (2003)
Carbon dioxide	Sachet	Fresh meats	*Pseudomonas* spp.	Coma (2008)
Triclosan	Styrene-*co*-acetate	Culture media	*Enterococcus faecalis*	Chung et al. (2003)
	LDPE	Chicken breast	*Lis. monocytogenes*, *S. aureus*, *Sal. enteritidis*, *E. coli* O157:H7	Vermeiren et al. (2002)
Hexamethylenetetramine	LDPE	Orange juice	Yeast, lactic acid bacteria	Devlieghere et al. (2000b)
Silver zeolite	LDPE	Cucumber	Total bacteria	An et al. (1998)
		Oolong tea	*E. coli*	An et al. (1998)
Silver zeolite, silver nitrate	LDPE	Culture media	*S. cerevisiae*, *E. coli*, *S. aureus*, *Sal. typhimurium*, *Vibrio parahaemolyticus*	Ishitani (1995)
Natamycin	Cellulose	Cheese	*P. roqueforti*	

(*Continued*)

Table 10.2 (Continued)

Antimicrobial Agents	Packaging Materials	Foods	Microorganisms	Researchers
				Oliveira et al. (2007)
			Total bacteria, molds	Pires et al. (2008)
Antibiotics	PE	Culture media	*Sal. typhimurium*, *Klebsiella pneumoniae*, *E. coli*, *S. aureus*	Han and Moon (2002)

BOPP, biaxially oriented polypropylene; CMC, carboxyl methyl cellulose; EVOH, ethylene vinyl alcohol; HPMC, hydroxypropyl methyl cellulose; LDPE, low-density polyethylene; LLDPE, linear low-density polyethylene; MC, methyl cellulose; PE, polyethylene; PVA, polyvinyl acetate; PVOH, polyvinyl alcohol; PET, polyethylene terephthalate; PP, polypropylene; SPI, soy protein isolate; WPI, whey protein isolate.

Though in practise it is very hard to remove all microorganisms, microbiocidal antimicrobial system may kill the target microorganisms when the antimicrobial concentration goes above the minimum inhibitory concentration (MIC) for a while. With other treatment to encourage the antimicrobial activity of the packaging system, such as refrigeration, the antimicrobial effectiveness will be increased; however, generally refrigeration is not necessary when all of the system factors satisfy the requirements. Refrigeration may be very effective in inhibiting the growth of untargeted (unexpected) microorganisms. If the initial concentration of microbiocidal antimicrobial systems is lower than the MIC of the target microorganisms, and the concentration has never been above the MIC, the agent may show a microbiostatic instead of a microbiocidal effect. Therefore, it is very important to maintain the antimicrobial concentration above the MIC for certain critical periods to eliminate the target microorganisms. If the package has been hermetically sealed, the packaged foods may not contain any live microorganisms even when the concentration decreases to below the MIC due to the migration or loss of the agent after the critical period.

10.5.3 Microbiostatic

Microbiostatic agents can inhibit the growth of microorganisms above a certain critical concentration (i.e., MIC). However, when the concentration is lower than the critical concentration, or when the agent is removed from the packaging systems through a seal defect, leakage, opening, or any other means, the suppressed microorganisms can grow or their spores can germinate. Therefore, it is critical to maintain the concentration of the antimicrobial agent above the MIC during the entire shelf life of the packaged foods. Chemical indicators that show the concentration or microbial growth would be very beneficial in microstatic antimicrobial packaging systems, and this is one concept of intelligent packaging (Rodrigues and Han, 2003).

10.5.4 Functioning Modes and Volatility

Microorganisms grow primarily on the surfaces of most packaged solid or semisolid foods (Brody et al., 2001). Therefore, antimicrobial activity should take effect on these surfaces. The antimicrobial activity may be located in the packaging materials, in the in-package atmosphere, or in the headspace, varying by incorporation method. The antimicrobial activity should be transferred to the surface of the food to suppress the microbial growth. Therefore, incorporation methods and transfer techniques are critical in designing effective antimicrobial packaging systems. As examples of incorporation methods, antimicrobial agents have been impregnated into packaging materials before final extrusion (Han and Floros, 1997; Nam et al., 2002), dissolved into coating solvents (An et al., 2000), added in edible coating materials (Rodrigues and Han, 2000; Rodrigues et al., 2002), and mixed into sizing/filling materials such as paper and cardboard (Nadarajah et al., 2002). Gaseous antimicrobial agents can also be added to the package atmosphere (Krause et al., 2003; Lanciotti et al., 2003).

The edible coating system has various benefits due to its edibility and biodegradability (Krochta and De Mulder-Johnston, 1997). The edible coating may be either a dry coating or a wet battered coating. Dry coatings can incorporate chemical and natural antimicrobials, and play the role of a physical and chemical barrier as well as a microbial barrier (Han, 2001, 2002). Wet coating systems may need another wrapper. However, the wet system can carry many different types of functional agents as well as probiotics and antimicrobials (Gill, 2000). Lactic acid bacteria can be incorporated into the wet coating system to control the competing undesirable bacteria. Such a system may be very beneficial to the fresh produce, meats, and poultry industries. For edible coating purposes, various biopolymers are used as an antimicrobial hosting matrix, including chitosan, soy protein, whey protein, corn zein, methyl cellulose, hydroxypropyl methyl cellulose, starch, and other gums (Han, 2005; Min and Krochta, 2007).

Chemical immobilization covalently binds the agents into the chemical structures of packaging materials when regulations do not permit the migration of agents into foods (Appendini and Hotchkiss, 1996, 1997; Halek and Garg, 1989; Miller et al., 1984). The immobilized antimicrobial agents will inhibit the growth of microorganisms on the contact surfaces of packaged products.

10.5.5 Nonvolatile Migration

The mass transfer of nonvolatile antimicrobials is dominated by diffusional migration. Nonvolatile agents will be positioned initially in the packaging materials or between the package and the surface of the food. If nonvolatile antimicrobial agents are incorporated into packaging material matrix, diffusivity of the agents is a primary kinetic constant of the transfer in the matrix to the surface of the matrix that governs the overall migration profile from the matrix to contacted food surface (Choi et al., 2005; Han, 2000). If the agent is sprayed onto the surface of food, the initial surface concentration will be very high and then start to decrease due to dissolution and diffusion of the agent toward the center of the food. Therefore, the solubility (or partition coefficient) as well as diffusivity of the agent in the food are very important characteristics to maintain the surface concentration above the effective MIC during the expected shelf life. If the agent is incorporated into packaging material initially, it should escape from the packaging material and dissolve into the food before diffusing into the food core. Therefore, the significant characteristic constants of the mass transfer profile are the diffusivity of the agent in the packaging material, the solubility (or partition coefficient) of the agent in the food at the surface, and the diffusivity of the agent in the food. It is important for the food/packaging/antimicrobial agent system to have mass transfer kinetics appropriate to the microbial growth kinetics in order to provide efficient antimicrobial activity. To understand the concentration distribution profile, it is necessary to use mass transfer models that have more than two-layer diffusion and interface partitioning (or dissolution). Since the migrating agent is nonvolatile, this system requires intact contacting between the packaging materials and the food surface. The food should be a continuous matrix form without significant pores, holes, air gaps, or heterogeneous particles, due to the interference of the latter with diffusion. One-piece, solid, semisolid (soft solid) foods and liquid products are good examples of products that could use this nonvolatile migrating antimicrobial packaging system.

Practical examples of this system may include cured or fermented meats and sausages battered with antimicrobial agents, natural cheeses sprayed with potassium sorbate before packaging, antimicrobial plastic films for deli products, antimicrobial wax coatings on fruits, and antimicrobial cleansing of fruits/vegetables before packaging. The advantages of this nonvolatile migrating system are the simplicity of the design, which could be installed ahead of the current packaging process without high investment, and the easy maintenance required to control its effectiveness.

10.5.6 Volatile Migration

Many researchers have claimed that it is necessary to have intact contact of the antimicrobial material with the food surface to facilitate the migration of the active agent for maximal effectiveness (Suppakul et al., 2003a; Vermeiren et al., 2002). However, this is not necessary when using volatile antimicrobial agents. To maintain the surface concentration above a certain MIC, it is very important to control the headspace gas concentration, since the volatile agent's concentration in the headspace has been equilibrated with the concentration on the food surface and in the packaging materials. Initially the volatile agent is placed in the packaging material, whether it is a film, container, sachet, or tray. After packaging the food, the volatile agent vaporizes into the headspace, reaches the surface of the food, and is absorbed by the food. The mass transfer of a volatile agent in the packaging system is more dynamically balanced. The release rate of the volatile agent from the packaging system is highly dependent on its volatility, which relates to the chemical interaction between the volatile agent and the packaging materials. There are ways to control the volatility of the agent in the packaging system, including the use of oil, cyclodextrin, or microencapsulation. These techniques can control the volatility of the agent and, eventually, the headspace concentration. The absorption rate of headspace volatiles into the food surface is related to the composition of the foods, as the ingredients undergo chemical interactions with the gaseous agents. Since most volatile agents are generally lipophilic, the lipid content of the food is an important factor in determining the headspace concentration.

Volatile antimicrobial agents have many advantages. They can be used effectively for highly porous, powdered, shredded, irregularly shaped, and particulate foods, such as ground beef, shredded cheese, small fruits, mixed vegetables, etc. Because the majority of volatile antimicrobial agents are natural herb and spice extracts are this system is linked to the nutraceutical research and development area as well as being easily accepted by consumers and governmental regulatory agencies.

10.5.7 Nonmigration and Absorption

The nonmigration system uses nonmigratory antimicrobial polymers, in which the antimicrobial agent does not migrate out of the polymer because it is covalently attached to the polymer backbone (Steven and Hotchkiss, 2003). Besides the antimicrobial agents, other bioactive agents (such as enzymes, proteins, and other organic compounds) can be attached to the polymer through covalent cross-linkers. Since the agents are not mobile, their activity is limited to the contact surface only. This limitation is more critical in solid or semisolid foods. However, in liquid foods, the disadvantages of this nonmigration characteristic may be minimal. This system could be designed for large-size membrane reactors or processing units to convert any preexisting substrates into valuable compounds using immobilized enzymes. For the future, it is important that this packaging system be evaluated to assess whether it can be used effectively as a unit operation substituting reaction process during any necessary timed processes such as aging, chilling, tank-holding, etc.

As a food packaging system, this nonmigration system has unique advantages in marketing and regulation. Since the active agents cannot migrate, this system requires a very small amount of attached agents. This may reduce the overall cost of packaging systems that use very expensive antimicrobial agents. A nonmigrating system can include agents that are not permitted as food ingredients or food additives. With the verification of nonmigration, the packaging material may contain any food-contact substances. From the marketing point of view, this system is attractive because the food does not contain any chemical antimicrobial agents throughout its shelf life. However, in contrast to the benefits, this system may use only a very limited selection of antimicrobial agents and may also be limited in application to certain types of foods.

10.5.8 Shapes and Compositions of Systems

Packaging is a system used to contain and protect enclosed products, which consists of a product, a package, and the in-package atmosphere. Antimicrobial agents may be incorporated in the nonfood parts of the packaging system, which are the package or the in-package atmosphere. Antimicrobial agents can be incorporated directly in packaging materials in the form of films, overcoating on films, sheets, trays, and containers, or in the in-package space in the form of inserts, sachets, or pads. Edible coatings also can contain edible antimicrobial agents, protecting the coated foods from microbial degradation (Han, 2001). Figure 10.1 illustrates some possible forms of antimicrobial packaging systems (Han, 2003a).

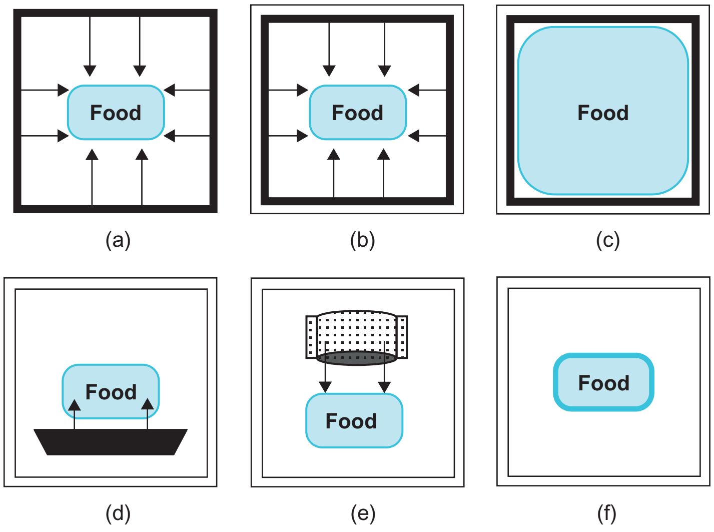

Figure 10.1 Possible ways to construct antimicrobial food packaging systems. (A) The use of antimicrobial packaging materials, (B) antimicrobial coating on conventional packaging materials, (C) immobilization of antimicrobial agents in polymeric packaging materials, (D) the use of antimicrobial trays or pads, (E) the use of sachet/insert containing volatile antimicrobial agents, and (F) antimicrobial edible coating on foods. *Source: Adapted from Han (2003b).*

10.6 Commercialization

Some commercial antimicrobial packaging systems are listed in Table 10.3. Most systems consist of silver-containing active agents. Table 10.4 lists potential applications of antimicrobial packaging and food groups. Since foods are complex systems, there are many factors to be considered in commercializing antimicrobial packaging systems.

10.6.1 Technical Factors

Compatibility of Process Conditions and Material Characteristics

There are three methods for manufacturing commercial antimicrobial packaging materials other than independent antimicrobial inserts such as sachets, labels, or pads: (1) coating of antimicrobial packaging material mix on films or paper surfaces, (2) blending antimicrobials with plastic resins for extrusion film processes, and (3) immobilization of antimicrobials on film surfaces (Han, 2000). Film/container casting methods, that is, extrusion coating or wet casting, are important to maintain antimicrobial effectiveness. In the case of extrusion, the critical variables related to the residual antimicrobial activity are extrusion temperature and specific mechanical energy input. The extrusion temperature is related to the thermal degradation of the antimicrobial agent, and the specific mechanical energy indicates the severity of the process conditions that also induce the degradation of the agents. Nam et al. (2002) showed a severe decrease in the activity of lysozyme in an extruded starch container as the extrusion temperature increased. In many cases, this thermal degradation is the reason for selecting solvent compounding (i.e., wet casting/coating) methods (Cho et al., 2009; Han et al., 2007). In the case of wet casting (i.e., using solvent to cast films and containers such as cellulose films and collagen casing), the solubility and reactivity of the antimicrobial agents and polymers to the solvents are the critical factors. The solubility relates to the homogeneous distribution of the agents in the polymeric materials, while the reactivity relates to the activity loss of the reactive antimicrobial agents.

The physical properties of the antimicrobial agent, such as its solubility, are also important. For example, when water-soluble agents are mixed into plastic resins to produce antimicrobial films, the extrusion process may be beset with various problems, including crevice hole creation in the films, powder-blooming, the loss of physical integrity, and/or the loss of transparency due to the heterogeneous

Table 10.3 Examples of Commercial Antimicrobial Packaging Products and Manufacturers

Trade Name	Active Compounds	Manufacturer	References
Piatech	Ag oxide	Daikoku Kasei Co. (Japan)	Brody et al. (2001)
Silvi Film	Ag oxide	Nimiko Co. (Japan)	Brody et al. (2001)
Okamoto Super Wrap		Okamoto Industries, Inc. (Japan)	Brody et al. (2001)
Apacider	Ag zeolite and others	Sangi Co. (Japan)	Brody et al. (2001)
Zeomix	Ag zeolite	Shinanen New Ceramics Co. (Japan)	Brody et al. (2001)
Bactekiller		Kanebo Co. (Japan)	Brody et al. (2001)
Cleanaid		Gyunghyang Ind. Co. (Korea)	Cho et al. (2009)
AgION		AgION Technologies LLC (USA)	Suppakul et al. (2003a); www.agion-tech.com
MicroFree	Ag, copper oxide, zinc silicate	DuPont (USA)	Brody et al. (2001); Vermeiren et al. (2002)
Novaron	Ag-zirconium phosphate	Milliken Co. (USA)	Vermeiren et al. (2002)
Surfacine	Ag-halide	Surfacine Development Co. (USA)	Vermeiren et al. (2002)
Ionpure	Ag/glass	Ishizuka Glass Co. (Japan)	Vermeiren et al. (2002)
Microban	Triclosan	Microban Products Co. (USA)	Brody et al. (2001)
Sanitized, Actigard, Saniprot	Triclosan and others	Sanitized AG/Clariant (Switzerland)	Suppakul et al. (2003a); Vermeiren et al. (2002)
Ultra-Fresh	Triclosan and others	Thomson Research Associates (Canada)	Vermeiren et al. (2002)
WasaOuro	Allyl isothiocyanate	Green Cross Co. (Japan)	Brody et al. (2001)
Wasa Power		Sekisui Plastic Co. (Japan)	Cho et al. (2009)
MicroGarde	Clove and others	Rhone-Poulenc (USA)	Brody et al. (2001)
Take Guard	Bamboo extract	Takex Co. (Japan)	Brody et al. (2001)
Acticap	Ethanol	Freund Industrial Co. (Japan)	Smith et al. (1987)
Ageless SE		Mitsubishi Gas Chemical (Japan)	Cho et al. (2009)
Biocleanact	Antibiotics	Micro Science Tech Co. (Korea)	Han and Moon (2002)
Microatmosphere	Chlorine dioxide	Southwest Research Institute (USA), Bernard Technologies Inc. (USA)	Brody et al. (2001)

(*Continued*)

Table 10.3 (Continued)

Trade Name	Active Compounds	Manufacturer	References
Microsphere (Microgarde)		MicroActive Corp. (USA)	Scully and Horsham (2007)
Knick'n Clean		Helrik Bobke (Germany)	Cho and Han (2009)
Grape Guard	Sulfur dioxide	Quimica Osku S.A. (Chile)	Scully and Horsham (2007)
Uvasy		Grapetek (S. Africa)	Scully and Horsham (2007)

blending of the hydrophilic agents with the hydrophobic plastics. Therefore, the compatibility of antimicrobial agent and packaging material is an important factor. Various spice extracts and essential oils could be blended with plastic resins such as polyethylene or ethylene vinyl alcohol due to their compatible hydrophobicity to form plastic coating layers or free-standing films (Cerisuelo et al., 2010a, b; Farris et al., 2010; Hernandez-Muñoz, 2005). The pH of the system is also important. The activity of most antimicrobial chemicals changes with pH. The pH of the packaging system mostly depends on the pH of the packaged foods, and therefore consideration of the food composition along with the chemical nature of the antimicrobial agent is important as well as consideration of the packaging material reaction with the chemical nature of the agents (Han, 2003b).

Storage and distribution conditions are also significant factors, including storage temperature and time. This time–temperature integration affects the microbial growth profile, chemical reaction kinetics, and the distribution profile of antimicrobial agents in the food. To prevent microbial growth, storage at a temperature range favorable for microbial growth should be avoided or minimized for the whole period of storage and distribution.

In the case of modified atmosphere packaging with antimicrobial gas, the active gas permeation through the packaging materials may change with temperature and time during the whole period of storage and distribution. When the gas composition is altered through active gas permeation, unexpected gas invasion, or a seal defect, microorganisms that are not considered as target microorganisms may spoil the packaged foods.

Physical Properties of Packaging Materials

The physical and mechanical properties of packaging materials are affected by the incorporated antimicrobial agents. If the antimicrobial agent is compatible with the packaging materials, a significant amount of the agent may be impregnated into the packaging material without any deterioration of its physical and mechanical integrity (Han and Floros, 1997). However, excess antimicrobial agent that is not capable of being blended with packaging materials will decrease physical strength and mechanical integrity (Cooksey, 2000). Polymer morphology studies are very helpful in predicting possible loss of physical integrity when the antimicrobial agent is added to the packaging material. Small-sized antimicrobial agents can be blended with polymers and may be positioned in the amorphous regions of the polymeric structure without significantly interfering with polymer–polymer interactions. If a high level of antimicrobial agent is mixed into the packaging materials, the space provided by the amorphous region will be filled and the mixed agent will start to interfere with the crystalline region. Although there is no damage to the physical integrity at low levels of antimicrobial agent addition, optical properties can be changed—for example, there may be a loss of transparency or a change in the color of the packaging materials (Han and Floros, 1997).

Controlled Release Technology

The design of an antimicrobial packaging system requires a balanced consideration of controlled release technology and microbial growth kinetics.

Table 10.4 Potential Applications of Antimicrobial Food Packaging

Antimicrobials	Meat/Poultry	Dairy	Seafood	Produce	Bakery	Beverage	Minimally Processed
Organic acids and their salts	Fresh meat, sausage, ham, chicken	Cheese		Fruits, vegetables, jam/jelly		Fruit juice, wine	Precut salad, noodle, pasta, steamed rice, sauce/dressing
Ethanol				Nuts	Bread, cakes, cookies		Noodles, pasta, sandwiches
Bacteriocins	Fresh meat, sausage, ham, chicken	Cheese	Fish, shellfish				Ham/egg sandwiches
Enzymes	Fresh meat, sausage, ham, chicken	Cheese	Fish, shellfish				Ham/egg sandwiches, meatball pasta
Chelating agents	Fresh meat, sausage, ham, chicken	Cheese	Fish, shellfish	Fruits, jam/jelly		Fruit juice	Precut fruits, sauce/dressing
Fungicides				Citrus, berries, nuts			
Sanitizers	Fresh meat, chicken		Fish, shellfish	Fruits, vegetables			Precut salad
Volatile essential oils	Fresh and processed meats, ground beef, chicken nuggets	Shredded cheese	Fish, shellfish, dried fish	Berries, nuts, jam/jelly	Bread, cakes, cookies	Fruit juice	Noodles, pasta, steamed rice, sandwiches, hamburgers, precut salad, sauce/dressing
Spices	Fresh and processed	Cheese				Fruit juice	Noodles, pasta, steamed rice,

(*Continued*)

Table 10.4 (Continued)

Antimicrobials	Meat/Poultry	Dairy	Seafood	Produce	Bakery	Beverage	Minimally Processed
	meats, fresh and cooked chicken		Fish,				sandwiches, sauce/ dressing
Probiotics	Fresh and processed meats, cured meats	Cheese, yogurt		Fermented vegetables			Deli mix
Oxygen scavengers	Fresh and processed meats, ground beef, dried meats, chicken	Shredded cheese	Dried fish	Nuts, jam/ jelly	Bread, cakes, cookies	Fruit juice, wine	Noodles, pasta, steamed rice, sandwiches, hamburgers, sauce/ dressing

When the mass transfer rate of an antimicrobial agent is faster than the growth rate of the target microorganism, loaded antimicrobial agent will be diluted to less than the effective critical concentration (i.e., MIC) before the expected storage period is complete, and the packaging system will lose its antimicrobial activity because the packaged food has almost infinite volume compared to the volume of packaging material and the amount of antimicrobial agent. Consequently, the microorganism will start to grow following depletion of the antimicrobial agent. On the other hand, when the migration rate is too slow to maintain the concentration above the MIC, the microorganism can grow instantly, before the antimicrobial agent is released. Therefore, the release rate of the antimicrobial agent from the packaging material to the food must be controlled specifically to match its mass transfer rate with the growth kinetics of the target microorganism. Controversially, in the case of antimicrobial edible coating systems, the mass transfer of antimicrobial agents is not desirable, since the migration of the incorporated antimicrobial agents from the coating layer into the food product dilutes the concentration in the coating layer. Compared to the volume of the coating layer, the coated food has almost infinitive volume. Therefore, the migration will deplete the antimicrobial agent in the coating layer, decrease the concentration below the MIC, and thus reduce the antimicrobial activity of the coating system. The migration of incorporated antimicrobial agents contributes to antimicrobial effectiveness in the case of packaging systems; on the contrary, no migration is beneficial in the coating system.

The solubility of the antimicrobial agents in the foods is a critical factor in its release. If the antimicrobial agent is highly soluble in the food, the migration profile will follow unconstrained free diffusion, while very low solubility creates a dissolution-dependent monolithic system. For example, when highly soluble potassium sorbate was incorporated in packaging materials (e.g., plastic films or papers) and the antimicrobial packaging materials were used for semisolid or high-moisture foods, such as paste, yogurt, fruit jelly, soft cheese, and sliced ham, the potassium sorbate dissolved in the food immediately after packaging. The potassium sorbate concentration increased very rapidly on the surface of the foods and the surface concentration decreased slowly as the potassium sorbate diffused into the food. Rapid diffusion of the antimicrobial agents in the food decreased the surface concentration rapidly. The surface concentration is highly dependent on the release rate from the packaging materials (diffusivity of packaging materials) and the migration rate through the foods (diffusivity of the foods). Since the flux of the release from the packaging materials decreases as the amount of antimicrobials in the packaging materials decreases with release time, the period in which the surface concentration is maintained above the MIC needs to be carefully estimated, considering its rapid decay profile (Figure 10.2A).

When the solubility of antimicrobial agents in the packaged food is very low, the antimicrobial concentration on the contact food surface is the maximum that its solubility will allow. Since the release rate is slower than unconstrained free diffusion, the period at which the concentration can be maintained above the MIC in slow-release systems is generally longer than in free diffusion systems. If the antimicrobial agents are impregnated into the polymeric packaging materials, the diffusivity of the agent through the polymeric matrix will control the release rate. This system, shown in Figure 10.2B, may include, for example, sorbic acid anhydride or propyl-*para*-benzoic acid in plastic films that wrap high-moisture foods such as fruit jelly or soft cheese. Since the antimicrobial agents are less soluble in water, the release of these agents from hydrophobic plastic will be very slow. It takes more time to reach the maximum peak concentration, and there will be a longer period above the MIC than in the system shown in Figure 10.2A. After the agents initially located on the surface of plastic films have migrated into the food, the release flux will decrease because the agents positioned inside the plastic film should diffuse to the surface of the plastic film. Because of this internal diffusion, the release kinetics do not show a zero-order profile with a constant release flux. The concentration on the food surface will decrease due to the migration of the agent into the contained food products as well as the reduction of release flux.

Figure 10.2C illustrates the longer period of concentration above the MIC given by membrane systems, which consist of a permeable membrane that controls the release rate. In the case of liquid pharmaceuticals, the release rate will be controlled by the permeability of the liquid agents through the control layer. Until the liquid agent is depleted, the

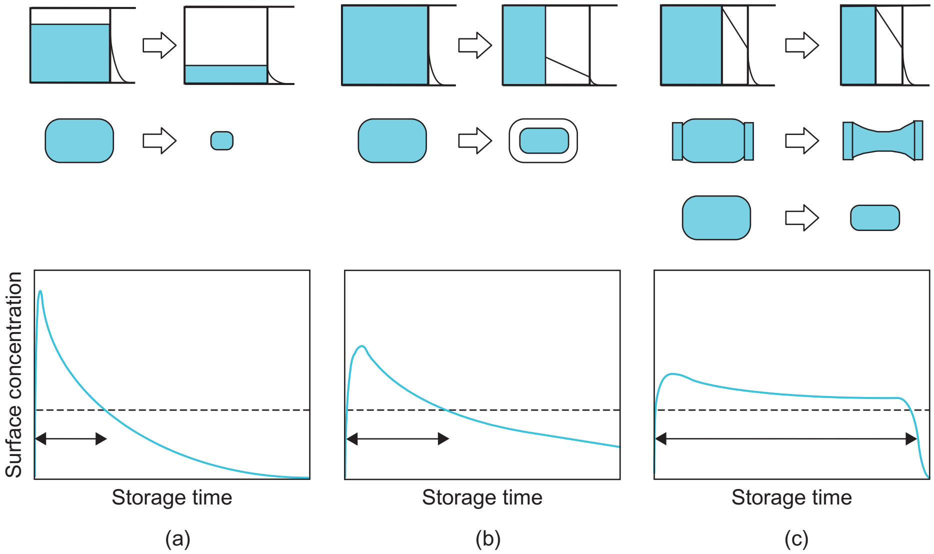

Figure 10.2 Release profiles of antimicrobial agents from various systems. (A) Unconstrained free diffusion from packaging materials or fast dissolution from antimicrobial tablets, (B) slow diffusion of very low solubility agents from monolithic packaging materials, and (C) membrane (reservoir) system with constant flux of permeation, slow dissolution from antimicrobial powder/tablets, or gaseous agent release from concentrated antimicrobial sachets/tablets with constant volatility in a closed packaging system. Dashed lines and arrows indicate the minimum inhibitory concentration (MIC) of a target microorganism and the period of shelf life maintaining the surface concentration over the MIC, respectively.

system maintains a zero order of release with a constant permeation flux. This system may include volatile agent concentrates, such as horseradish oil. Horseradish oil contains allyl isothiocyanate, which is a strong, volatile flavoring and antimicrobial agent. The volatile agent will partition between the oil and the headspace of packages. If there is enough oil in the package, the headspace concentration will equilibrate and stay above the MIC until the oil has disappeared. Such equilibrated partitioning is an important factor in controlling the release rate as well as the headspace concentration.

Extra Advantages

Traditional preservation methods sometimes include antimicrobial packaging concepts—for example, the sausage casings of cured/salted/smoked meats, smoked pottery/oak barrels for fermentation, and brine-filled pickle jars. The basic principle of these traditional preservation methods and antimicrobial packaging is one of hurdle technology applications. The extra antimicrobial function of the packaging system is another hurdle to prevent the degradation of quality and improve the safety of packaged foods, in addition to the conventional protective functions of providing moisture and oxygen barriers as well as physical protection. The effectiveness of antimicrobial packaging is generally enhanced by combination with other preservation hurdles, such as modified atmosphere packaging, low pH, high pressure, or low water activity (Cooksey, 2005; Jofre, 2008; Vartiainen et al., 2003). The microbial hurdle provides the extra function of protection against microorganisms, which has never been achieved by conventional moisture- and oxygen-barrier packaging materials. Therefore, antimicrobial packaging is an active packaging and hurdle technology application. The hurdle technology concept of antimicrobial packaging systems can enhance the efficiency of other sterilization processes, such as aseptic processes, nonthermal processes, and the conventional thermal process, where the sterile foods are packaged in the antimicrobial packaging systems.

Since such systems can incorporate natural antimicrobial agents such as plant and herb extracts or probiotics, it is considered that natural antimicrobial packaging design development has a connection to nutraceutical research and pharmacognosy. This relationship may be helpful in transferring food packaging knowledge to the area of

Table 10.5 Factors to Be Considered for Marketing of New Antimicrobial Packaging Systems

Advantages	Disadvantages
Safety enhancement	Changes in culinary culture
Security achievement	Lifestyle changes of consumers
Shelf-life extension	Cost of new materials and systems
Health promoting effect	Regulation conflict
Market attention	Market conflict with conventional packaging, political decision making

nutraceutical and pharmaceutical research because of the studies on the barrier properties of materials against volatile active ingredients and the studies on the clinical effectiveness of natural active agents.

10.6.2 Regulatory, Marketing, and Political Factors

The use of antimicrobials should follow the guidelines of regulatory agencies (Brody et al., 2001; Han, 2003a,b; Meroni, 2000; Vermeiren et al., 2002). Antimicrobial agents are additives of packaging material, not food ingredients; however, when the antimicrobial agents migrate into foods, they also require food ingredient approval—as for food-contact substances and packaging additives. Therefore, the use of natural antimicrobial agents included in plant extracts or spices is a very promising alternative because of their appeal as natural products, consumers' preference, and because they do not conflict with regulations.

For the commercialization of antimicrobial packaging systems, various marketing factors are involved—for example, logistics, cost, and consumer acceptance (Meroni, 2000). The use of antimicrobial packaging systems should not create any conflict with the current logistic systems of the food industry. If new packaging systems require totally new transportation, distribution, and warehousing systems, it would not be feasible to commercialize them. The antimicrobial packaging systems should be manageable within current packaging-related logistic systems. Reasonable cost recovery should be promised for the commercialization of new packaging systems. Consumers' acceptance of the use of new antimicrobial packaging systems is critical. This acceptance may be related to the convenience and easiness of the use of a new system, any conflict of the new system with their culture and lifestyles, and other various reasons.

Table 10.5 summarizes the pros and cons of the new antimicrobial packaging systems in terms of marketing. From the consumer's standpoint, other than increased cost, the broad utilization of antimicrobial packaging should not require any significant changes in the organoleptic properties of foods (Gutierrez et al., 2009) or their lifestyle.

Since the antimicrobial agent is in contact with or migrating into food, the organoleptic properties and toxicity of the antimicrobial agent should be adequate to avoid quality deterioration and to maintain the safety of the packaged foods. The antimicrobial agents may possess a strong taste or flavor, such as a bitter or sour taste, as well as an undesirable aroma that can affect sensory qualities adversely. In the case of antimicrobial edible protein film/coating applications, the allergenicity or chronic disease caused by the edible protein materials, such as peanut protein, soy protein, and wheat gluten, should be considered before use (Han, 2001).

The legality of antimicrobial activity in new packaging systems has many critical controversial aspects. For example, research and development departments would not like to claim "antimicrobial activity" on their products for commercial use, since there is no antimicrobial agent that can eliminate all types of microbial growth. The potential growth of microorganisms in their new antimicrobial packaging systems could therefore reduce the company's creditability as well as being a possible cause for a serious law suit. However, for marketing purposes, there is no point in using a new antimicrobial packaging system, as far as profits are concerned, if the company cannot claim "antimicrobial activity". This example shows that the use of antimicrobial packaging systems possesses a political aspect.

Most foods are perishable, and most medical/sanitary devices are susceptible to contamination. Therefore, the primary goals of an antimicrobial packaging system are as follows:

1. Safety assurance
2. Quality maintenance
3. Shelf-life extension

This is in reverse order to the primary goals of conventional packaging systems. Nowadays, food security is a big issue in the world, and antimicrobial packaging could play a role in food security assurance, comprehensively agreed with industrial sectors, farmers/producers, wholesalers/retailers, governments, and consumer groups. Owing to the political aspects of food safety and security matters, the use of antimicrobial packaging technology is also politically influenced regarding commercialization.

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11 Damage Reduction to Food Products During Transportation and Handling

Jay Singh[a] and S. Paul Singh[b]

[a]California Polytechnic State University, San Luis Obispo, CA, USA; [b]Michigan State University, East Lansing, MI, USA

11.1 Introduction

Packaging plays a key role in protecting the product from contamination by external sources, and reducing damage during its transportation and handling in the supply chain from the producer and manufacturer to the consumer. In the United States alone, estimated annual losses due to damaged products exceed $10 billion. This covers processed foods, perishables, consumer products, and electronic and hardware products sold in retail stores. A major portion of this loss is in the fresh and processed food category. The use of proper packaging materials and methods to minimize food losses and to provide safe and wholesome food products has always been a primary focus of food packaging. New packaging technologies are constantly being challenged to provide better quality, wholesome, and safe foods with extended shelf life, while limiting the environmental pollutions and disposal problems. Packaging is also designed to play a significant marketing role with strong appeal through the use of logos and company brands to display food products in an attractive form. Packaging shapes and forms have been widely adopted for brand recognition. This is evident when considering shaped packages by Coca Cola Company in the beverage sector. The choice of packaging materials and forms is dictated primarily by economic, technical, and legislative factors.

11.2 Functions of Packaging

Packaging has been defined as all products made of any materials of any nature to be used for the containment, protection, handling, delivery, and presentation of goods, from raw materials to processed goods, and from the producer to the user or the consumer (Packaging Regulations, 2004). The aim of packaging is to protect the goods purchased by the consumer from wastage and damage. Without packaging, handling many products would be messy, inefficient, costly, and in some cases impossible.

The United Kingdom Institute of Packaging provides the following definitions of packaging (Gawith and Robertson):

- a coordinated system of preparing goods for transport, storage, retailing, and end use;
- a means of ensuring safe delivery to the ultimate consumer in a sound condition at minimum cost; and
- a techno-economic function aimed at minimizing costs of reusing, recycling, or disposing while maximizing sales (and hence profit).

According to Abbott (1989), the term “packaging,” as defined by the Packaging Institute, USA, and used in both teaching and practice, is the enclosure of products in a container to perform one or several of the major functions described in the following sections.

11.2.1 Containment

This function refers to the containment of the product for handling, transportation, and use and is often considered to be the “original” package function required to move products in various forms and shapes. The different product forms, such as solids, liquids, and gases, can make this function a critical factor in the selection process for the type of material and package system. A package must be able to contain a product in order to protect it from various environments. For example, fresh produce (fruits and vegetables) needs to be able to fit well inside the container with little wasted space (Boyett et al., 1996). Delicate and irregularly shaped produce

Ebnesajjad: Plastic Films in Food Packaging. DOI: http://dx.doi.org/10.1016/B978-1-4557-3112-1.00011-9

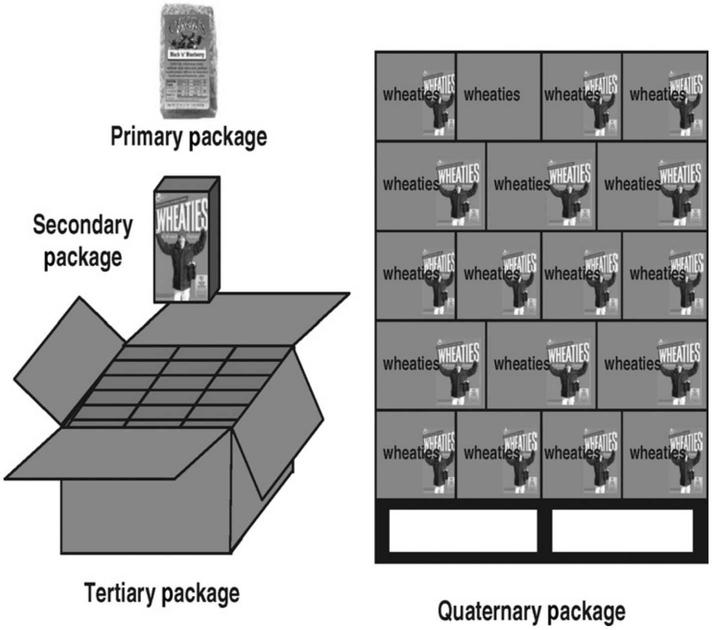

Figure 11.1 Layers of packaging.

such as asparagus, berries, or soft fruit may require specially designed containers to accommodate them. From a distribution system approach, packaging may be broken down by layers (Figure 11.1):

- *Primary*: The primary package has direct contact with the product (an example of this is a pouch for cereals). It provides the initial and the major protective barrier from moisture. The materials and printing inks used are regulated by government agencies to ensure that any toxic chemicals do not migrate and transfer to the product.
- *Secondary*: The secondary package contains and/or unitizes primary package(s) (an example of this is the paperboard carton containing the cereal). They contain and protect the primary units placed inside throughout the handling, transportation, and warehousing environments. Sometimes secondary packaging may be specially designed and printed to display primary packages on the sales floor.
- *Tertiary*: Refers to the shipping package (an example of this is a corrugated fiberboard shipping case containing several cereal boxes). This is used predominately for shipment and warehousing purposes.
- *Quaternary*: Unitized shipping package (an example of this is a pallet load of stretch wrapped, corrugated fiberboard shipping cases filled with cereal cartons).

11.2.2 Protection

The second function, protection, relates to protecting the contents from deterioration due to physical and climatic changes during normal transportation and storage. This could mean protecting the product from shock (drops) and vibration (transportation) by using cushioning. It could also mean using a high-barrier film to prevent oxygen and moisture from entering a package and causing spoilage to a food product. The protection function also relates to protecting the outside environment from contamination by the contents, especially if they are hazardous materials (HazMat). Examples of these protection functions are seals and valves specifically designed to contain contents in HazMat packages.

Sometimes the element of protection also aids in food preservation. For example, produce containers need to be designed to provide an optimum environment for the longest shelf life possible. These containers may include special materials to deliberate water loss, insulate from heat and cold, or provide a favorable mix of oxygen and carbon dioxide.

Aseptically packaged dairy products will only remain shelf stable for as long as the integrity of the package is not compromised. As a rule, once the integrity of the package is breached, the food product will no longer stay preserved.

Proper packaging is an important component in both food production and related industries. Products must be adequately protected to ensure integrity and safety at all destinations in the supply chain. Many damaging hazards exist between harvest and the time when products reach consumers' hands. A properly designed package can ensure adequate protection from the most adverse of conditions, whether initially caused by human, machine, or environmental issues, or a combination of all three. Products need protection during transport and distribution, from climatic effects such as heat, cold, moisture, drying, hazardous substances, contamination, and infestation.

A majority of groceries are subject to biological spoilage caused by the normal enzyme-induced maturation and by microbiological putrefaction caused by molds, bacteria, and yeasts. Packaging can decrease or retard this spoilage. Synthetic packaging can also contaminate the product, for example, plastic packaging can contaminate some foods with toxic petrochemical-based chemicals, additives, inks, or sealants.

11.2.3 Communication

The third function, communication, is often used to identify the contents, quality, quantity, and manufacturer, etc. There are also various federal and state requirements that may be required as part of this function, depending on the product to be packaged and the choice of packaging materials used. An example of this is the nutrient information label requirement on all food packages. Additional features, such as precautionary labeling, helps provide information for safe use, handling, and storage of the container. Flavors, alcohols, preservatives, and cooking wines are examples of food products that may require HazMat packaging, depending on quantity and shipping method. Pictorial markings are used to mark and identify a package and are often used both for domestic and international labels to identify the safe handling, storage, and human interaction with the container.

Legal/regulated information on the package label includes net quantity declaration, ingredients listing, nutritional label, health claims, and reduced-calorie statements (The Clemson University Cooperative Extension Service, 2002). These fall under the Fair Packaging and Labeling Act and the Nutrition Label and Education Act. Emotional/motivational/selling information is intended to gain interest and help sell the product such as purchase incentives, recipes, contests, logos, color, overall design, photographic images, and illustrations (The Clemson University Cooperative Extension Service, 2002).

11.2.4 Utility

Lastly, utility relates to the ease of use or performance of the package system. This includes the ease of opening and closing (if required), reuse, application, dispensing, and especially a provision for instructions and directions Singh and Singh, 2005. One of the main reasons for the dramatic rise in food packaging is convenience. Consumers are demanding convenience and quick food preparation. Packaging that allows bagged salads, fresh-cut vegetables for stir-fry, case-ready meat, and bag and boil pasta or rice are all examples of food packaging that allow convenience to the consumer to prepare good-quality and multi-ingredient healthy meals in a short time. Additional examples of convenience packaging include easy-open beverage and food cans, frozen food packs, microwavable containers, wine cardboard casks, individually wrapped butter and stock cubes, and controlled dispensing with spouts, squeeze bottles, spray cans, aerosols, etc. for sauces, cooking oils, jellies, pastes, and sauces (Reduce Packaging, 2005). Figure 11.2 shows examples of various convenience packages for soups. Among notable trends in soup packaging are easy-open tops on metal cans and microwavable primary packaging in the form of plastic single-serve cups and stand-up pouches.

Most specialty packaging today often has several features that address the utility function of a package and is often the driving force for the sales of the product. An example would be a tamper-evident, child-resistant closure used for a pharmaceutical product that provides an easy-to-open feature for the elderly. Various research studies are being conducted as the pool of elderly with limiting dexterity pose a greater challenge for easy access to packaged contents for foods and pharmaceuticals.

One or more of these primary functions are essential in characterizing a container or system to

Figure 11.2 Examples of convenience packaging for soups.

Figure 11.3 Examples of single-serve cereal packaging.

Figure 11.4 Meat trays using prepacked case-ready meat using Sealed Air modified packaging.

be termed as a package. Packaging comes in many forms, such as convenience foods, individually packed serves, microwaveable meals, easy-opening packaging, secure packaging for hazardous chemicals and pharmaceutical drugs, and packaging of fresh food for transport and display (Reduce Packaging, 2005). The form of the package is determined to some extent by the functions of the packaging to contain, preserve, protect, and communicate information. Figure 11.3 shows the trends in the breakfast cereal products. Note the single-serve packages.

The growth in the packaging industry has led to greater specialization and sophistication based on the health and environmental friendliness of the packaging material. So to meet the goal of packaging it is necessary to develop the right type of packaging materials, form, machinery, and process.

11.3 Food Product Categories

11.3.1 Meats

Meats pose special problems for the packaging industry, due to the highly perishable and biologically active nature of the product (Sacharow, 1980). On average, they have a maximum 2–3 day shelf life in tray packs. Color changes due to oxidation will also reduce consumer acceptance and potential sales (Sacharow, 1980). Traditional meat packaging methods are not intended to prevent bacterial contamination. Meat is handled so frequently for retail sale that contamination is inevitable (Sacharow, 1980). The principal role of packaging meats is to prevent moisture loss, exclude foreign odors and flavors, and to reduce the effects of oxidation. To ensure these targets are met, the packaging used needs to have good tear and puncture resistance, while providing a pleasing appearance for the purchaser in a retail store temperature-controlled display environment (Sacharow, 1980). Figure 11.4 shows meat trays using prepacked case-ready meat using Sealed Air® modified packaging.

In supermarkets, fresh meat is placed in rigid thermoformed plastic trays and overwrapped with a transparent or heat-shrink film. The tray is usually expanded polystyrene (EPS) of a contrasting color to promote the freshness and quality look of the meat it contains. Blotters or absorbent pads are placed underneath the meat to absorb excess juices.

New retailing methods such as case-ready meat for beef, ground beef, pork, chicken, turkey, lamb, and veal strive to reduce handling and contamination (Salvage, 2005). This practice streamlines distribution and reduces time for products to move through the supply chain from manufacturer to customer. Case-ready meat is prepared in a central location and shipped to individual supermarkets already packaged and ready for immediate sale. Most products prepared this way are identical in packaging as meat cut and packaged by a butcher in a store (Salvage, 2005). This centralized system is common in Europe, but has only recently been introduced into the United States by leading retailer WalMart Stores Inc. using packaging innovation developed by companies such as Sealed Air Corporation and Pactiv Inc. Case-ready red meat is still growing, but benefits include extended shelf life, hermetically sealed and leak-free packs, and better food safety because of reduced human contact (Salvage, 2005). Stores that have adopted this program now include Albertsons, Kroger, Safeway, Target, and WalMart, among others (Salvage, 2005).

11.3.2 Seafood

Retail fresh seafood sales are growing, up by 13% each year, thanks to innovative methods for commercially raising fish and advancements in packaging materials. These factors help bulk retailer Costco sell approximately 30,000 tons of salmon fillets and shrimp per year. New packaging materials are important because they prolong shelf life while maintaining freshness of the product. This is possible because the packaging prevents damage during transportation and addresses temperature concerns (Barry, 2003). Examples of seafood packaging for an imported product are shown in Figures 11.5 and 11.6.

Fresh seafood has an extremely limited shelf life. This timeframe may be reduced to a few hours if proper packaging methods are not followed to prevent spoilage, such as dehydration, natural juice loss, odor permeation, bacterial growth, and incorrect temperature control (Sacharow, 1980). Fish must be immediately gutted and cleaned prior to packaging, and refrigerated transportation is necessary to prevent enzymatic and bacterial contamination (Sacharow, 1980). Temperature control is extremely critical to maintain a high quality and unspoiled product. The rate of spoilage doubles for every 5.5° of increase in temperature (Sacharow, 1980).

Figure 11.5 Seafood (shrimp) in display ready from Thailand for Kroger Inc. in vacuum packaging.

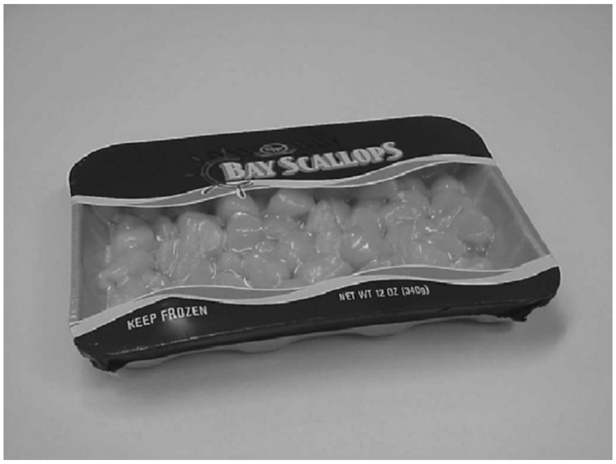

Figure 11.6 Seafood (scallops) in display ready from China for Kroger Inc. in vacuum packaging.

Once seafood is harvested and packaged, temperatures need to be quickly reduced to prevent microbial growth, and flavor and texture loss. The potential for botulism reproduction is also a reason why the Food and Drug Administration (FDA) maintains strict guidelines for seafood packaging. Seafood must be in contact with a limited oxygen flow to prevent deadly anaerobe microbial growth (Barry, 2003). Also, too much contact with oxygen and improper temperatures will allow the natural fish oils and fats to rapidly oxidize and go rancid.

Fresh seafood is transported by air to reach markets faster. Lightweight protective containers are necessary for distribution. Bulk containers are usually wax-coated corrugated boxes that help promote insulation and efficiently reduce the amount of required refrigeration.

11.3.3 Vegetables and Fruits

Fruits and vegetables purchased at supermarkets are living plant organs which, when growing, exhibit features such as respiration, transpiration, synthesis, and degradation of chemical constituents. When harvested, the produce is removed from a source of water and mineral and organic nutrients, but remains living. Greening and sprouting of stored onions and root tubers and the sweating of produce in polythene bags as a result of transpiration and water loss are just a few examples of this retention of living processes. As soon as produce is harvested, the processes leading to breakdown begin and cannot be stopped. However, the rate at which breakdown occurs can be slowed and losses minimized by employing the correct handling methods after harvest.

Major retailers, such as WalMart and Sam's Club, have pushed the produce industry to adopt a modular and interlocking common footprint container solution for use in transportation, storage, and floor displays. Common footprints require standardized dimensions and stacking features to ensure compatibility between differing container manufacturers and materials (Major, 2003). These containers are packed in the fields with the desired crop then distributed to stores without repackaging (Fibre Box Association, 2005). Citing improvements in product integrity, reduced shrinkage, better space efficiency, and reduction in labor costs, the supermarket and bulk club industries have found container standardization to be an important development (Paperboard Packaging, 2000, 2002). No longer will boxes and cartons of varying size be transported, warehoused, and produce repackaged. There are two competing systems on the market; returnable plastic containers (RPCs) and the corrugated common footprint (CCF).

Corrugated Common Footprints

Recyclable CCFs were introduced in 2000 as a response to the emergence of common footprint RPCs. RPC display-ready bins promised to improve efficiency, durability, airflow, and to attack corrugated's 98% dominance of the produce market (Major, 2003). The Corrugated Packaging Alliance responded to this threat by developing the CCF. Corrugated containers offer superior protection because the fluted material provide built-in air cushioning and minimize damage from abrasion and bruising. In the near future, CCFs are expected to have a 5:1 market share over RPCs (Fibre Box Association, 2005).

The Fibre Box Association (FBA) and the European Federation of Corrugated Board Manufactures (FEFCO) have outlined standards to ensure compatibility between different manufacturers in the United States and Europe. According to these associations, a full stack of containers will be 597 mm × 398 mm, while a half-stack will be 398 mm by 298 mm. Footprint configurations may not overhang any European or American standard pallets, which are 1200 mm × 1000 mm or 40 in. × 48 in., respectively. Also, these containers must be able to stack in mixed loads with other FBA- and FEFCO-approved containers, regardless of manufacturer, without sacrificing load stability or container integrity (Paperboard Packaging, 2000).

Reasons to choose CCFs include savings on shipping costs, and these versatile containers double as point-of-purchase displays. Corrugated weight is much lighter than plastic and can fit 7.5–22% more products per truckload (Fibre Box Association, 2005). Once the displays reach stores, they can be sent directly to the floor. High-quality printing will attract customer attention. Paperboard Packaging (2000) reports that the FBA and the FEFCO standards allow significant design flexibility. Containers from different manufactures may vary in style, depths, venting features, graphics, colors, and self-locking mechanisms, while still conforming to the common footprint design (Figure 11.7). This provides the flexibility to create a container that offers maximum protection and marketability for specific fruits and vegetables (Fibre Box Association, 2005).

However, CCFs are limited to one-time use. This is an environmental waste concern. The corrugated industry is quick to point out that approximately 74% of all box material manufactured today is recycled (Fibre Box Association, 2005). Grocery retailers recycle at even higher rates because they earn money when used boxes are recovered (Fibre Box Association, 2005).

Figure 11.7 A corrugated common footprint tray.

Returnable Plastic Containers

RPCs share common footprint, tab, and receptacle locations with CCFs. A joint study by the Corrugated Packaging Alliance and the Reusable Pallet and Container Coalition (RPCC) indicates that when mixed together on a pallet, both offer similar performance (Harper, 2004). In other words, the mixed loads containing RPCs and CCFs performed as well as loads of either 100% CCFs or RPCs (Harper, 2004). This allows supermarkets flexibility regarding how fruits and vegetables are shipped on the same pallet.

The California Strawberry Commission financed a study to determine which material provided a faster cool-down rate, an important factor with perishable produce. Initial results indicated that CCFs beat RPCs. However, revised findings found "no measurable difference in cooling..." between corrugated and plastic containers (Zind, 2003).

According to the RPCC, plastic is less detrimental to the environment than the one-time use corrugated system. The study showed that plastic required 39% less total energy, produced 95% less total solid waste, and generated 29% less total greenhouse gases (Figure 11.8) (RPCC, 2005).

11.3.4 Processed Versus Nonprocessed

Food processing is a \$500 billion industry in the United States (Hormel, 2005). Processors offer an almost limitless supply of foods. These items come packaged in various ways to meet consumer demand for safety, convenience, and nutrition. Widely used methods for food processing include canning, freezing, refrigeration, dehydration, and aseptic processes. Processing technologies are designed to rid foods of harmful organisms and make products shelf stable (Hormel, 2005). The United States Department of Agriculture (USDA) even has a special Processed Foods Unit. According to the USDA, the idea of this specialized research team is to enhance the marketability and healthfulness of agricultural commodities and processed products to better benefit consumers.

Figure 11.8 A returnable plastic container.

Nonprocessed foods are the raw materials and agricultural commodities that are turned into processed foods ready for consumer use.

11.4 Food Product Distribution Environment

11.4.1 Harvesting

Harvesting is the initial stage in supply chain distribution (Figure 11.9). This is a critical time for growers, as overall integrity cannot improve after this point (FAO, 1989). Therefore, items will need to be packed and shipped with care to avoid additional and preventable damage. Produce prices are dependent on physical condition (FAO, 1989).

Fruits and vegetables are still considered to be living organisms after harvest. However, postharvest longevity is limited. The rate of deterioration depends on how fast water and nutrient reserves are depleted (FAO, 1989). If harvested crops sustain damage, the rate of deterioration increases. Therefore, careful harvesting is the first step for a successful and safe journey to retail outlets.

Figure 11.9 Harvesting of grapes.

Figure 11.10 Empty CCF trays.

11.4.2 Packing

Fruits and vegetables are especially sensitive foods. Large produce quantities need proper packaging to minimize losses in the most cost-effective way. Each time crops are handled or repackaged, the chance of irreversible damage increases.

To protect crops during this stage, certain precautions need to be taken. Wooden crates may have rough surfaces, sharp nails, and staples. If containers are overpacked, compression damage will occur when they are stacked. Dropping and/or throwing containers, as well as any additional rough handling, will cause further damage.

Container sizes used should be easy to handle and maneuver. A standardized system such as RPCs and CCFs is one example (Figure 11.10). These containers are of a uniform size that reduce excess handling and provide better stacking and loading qualities (FAO, 1989).

11.4.3 Shipping

Food is transported from producers to packing houses or processing plants and from processors to retail markets. It is important that fresh foods are shipped quickly and efficiently since they are perishable and susceptible to injury. Refrigerated trucks, railroad cars, and cargo ships are all modes of transportation used, sometimes in conjunction with each other on long journeys. Airplane use is typically reserved for highly perishable items, such as fish, or expensive foods, such as live lobsters.

Throughout the shipping stage, food products need to be carefully loaded and protected to prevent damage from a wide assortment of potential hazards. Loads need to be positioned accordingly to fit inside transportation containers efficiently and remain stable. For example, proper stacking is necessary to prevent shifting or collapsing. In other cases, foods need to be protected from vibrations and jolts. This may be achieved by special packaging materials or if being shipped by truck, equipping the trailer with shock absorbers and low-pressure tires (FAO, 1989).

11.4.4 Storage and Shelf Life

Storage for most meats, seafood, and produce involves some sort of refrigeration. Their storage and shelf lives are dependent upon biological and environmental conditions (FAO, 1989). Warm temperatures will increase the natural enzymatic breakdown rate in foods. Since produce is considered a living organism after harvest, food and water reserves will become depleted causing spoilage. Microbiological organisms may also penetrate natural openings or broken surfaces causing decay. Cool storage temperatures slow down natural biological processes and decay in the foods we eat.

Many fresh seasonal and highly perishable food crops are processed to preserve nutrients and avoid wastage. Processing expands consumer choices and allows for greater flexibility (FAO, 1989).

11.5 Major Causes of Food Spoilage/Damage in Supply Chain

United Nation statistics indicate that half of the third-world population does not have access to adequate food supplies. In addition, 25% of food that is successfully produced will be lost after harvest due to mishandling, spoilage, or pest infestation (FAO, 1989). Even food with small amounts of damage may have properties such as taste, visual blemishes, and the rate of deterioration adversely affected (FAO, 1989). Proper packaging helps alleviate some of these issues. Developed countries, such as those in Europe and in North America, have access to better packaging methods and technology. As a result, these countries experience substantially lower rates of spoilage and wastage.

Most packaged food deterioration and spoilage occurs when the container is opened or compromised to the external environment (Robertson, 1993). Knowledge of the various types of spoilages and contaminants allows packing and processing firms to choose the correct materials for their products.

11.5.1 Microbiological Spoilage

This is a major factor in food spoilage. A host of microorganisms may flourish in foods. They multiply rapidly within the food and produce by-products that cause chemical changes to affect color, texture, flavor, or nutritional value. These containments may also release toxins, which lead to illness or even death.

11.5.2 Biochemical

Biochemical refers to enzymatic deterioration. Enzymes are naturally found in plant and animal tissue that control digestion and respiration. Upon harvest, these enzymes begin to destroy the tissue and cause spoilage. Some enzymes come in contact with the food as a consequence of microbial growth. They have several main functions of which food processors and packaging professionals should be aware. First, enzymes act as catalysts and accelerate the rate of chemical reactions that occur. Second, specific enzymes may be modified to produce desired longevity effects. Proper packaging methods and materials can slow enzymatic activity. Containers that maintain low temperatures, protect water activity levels, and maintain appropriate oxygen flow will help keep foods fresher longer.

11.5.3 Chemical

Oxidation is the major chemical reaction that leads to spoilage. Certain components and characteristics contained in foods, such as fats and vitamins, are susceptible to atmospheric oxygen. It also promotes mold growth. Other sources of chemical changes are caused by light and components in the packaging material. These reactions cause flavor alteration, discoloration, surface damage, and decay (FAO, 1989).

11.5.4 Macrobiological Spoilage

Macrobiological spoilage is caused by insects, rodents, birds, and pilfering by humans (FAO, 1989). Initial damage incurred by these factors may be minor and could be overlooked. However, even the most minor tissue wounds will make food more susceptible to microbial damage, causing the food to be inedible and leading to sickness or death.

11.5.5 Physical

Physical injuries can be classified as either mechanical or physiological. Mechanical damage leads to spoilage because it may cause bruising or deep punctures that cause water loss and rapid decay in fruits and vegetables or other undesirable effects in other food products. Mechanical effects may result from impact or shock associated with dropping, throwing, or sudden starting and stopping of a vehicle. Vibration damage also may result from various transportation methods including truck, train, airplane, and boats. Compression and crushing are caused by flimsy or oversized containers, overfilled containers, or containers stacked too high and unable to support heavy loads. Physiological deterioration may increase natural deterioration because of high temperatures, low humidity, or other physical injuries.

11.6 Packaging Materials

Packaging is essential. It is designed to surround, enhance, and protect. Packaging perishable food products is particularly cumbersome. The supply chain, which starts at the grower, ultimately ends up at the supermarket and the consumer. Bags, crates, hampers, baskets, cartons, bulk bins, and palletized containers are all examples of the various types of containers that may be used in different parts of the journey. There are approximately 1500 different types of packages that may be used, sometimes in conjunction with each other (Boyette et al., 1996). According to one study, a significant percentage of produce buyer and consumer complaints may be traced to container failure because of poor design or inappropriate selection and use (Boyette et al., 1996).

A World Health Organization study has indicated that in developed countries with sophisticated storage, packaging, and distribution systems, wastage of food is estimated at only 2–3%. In developing countries without these systems, wastage is estimated at between 30% and 50% (Soroka, 2002).

According to the United Nations (1969), food is packaged for two main reasons; to preserve it and to present it in an attractive form to the buyer. In order to successfully satisfy these requirements, various materials are used. The factors involved in selecting these materials include:

- the composition of the food product and its physical state;
- nature of deteriorative reactions that may occur;
- modes of transportation used to bring the product to market;
- time before consumption;
- who the target consumer will be; and
- overall budget for the product.

Ideally all food containers should exhibit the following properties:

- Sanitary
- Nontoxic
- Transparent
- Tamperproof
- Easily disposable
- Protective against light
- Easily opened or closed
- Impermeable to gases or odors
- Resistant to chemical or mechanical damage
- Easily printed or labeled.

The following is a brief overview of the packaging materials commonly used for packing as standalone packaging or in conjunction with each other.

11.6.1 Paper

Cardboard and pasteboard are both terms used for corrugated fiberboard, a material commonly used for boxes. This paper-based product is available in many different styles and weights made to accommodate a wide variety of food products. Demand for corrugate has been growing steadily at an average of 2–3% per year in Europe, where it dominates with a 63% market share over other packaging material alternatives such as plastics (FEFCO 2011).

According to the Corrugated Packaging Council, the product is easy to identify. Corrugated, in its most basic design, has two main components, an arched, wavy, layer called “fluting”, which is glued in between two smooth sheets called “liners” (The Corrugated Packaging Allowance, 2005). Together they form a double face. The fluted liner can be made in varying sizes, each size denoted by a letter, A to E. Size A has the largest flutes and E the smallest. The grades are assigned according to paper weight and thickness.

The flutes are the essential component in corrugated material. They give containers strength and add protection. When the flutes are anchored to the linerboard with adhesive, they resist bending and pressure from all directions (fibrebox.org). When a piece of corrugated fiberboard is placed on its end, the flutes form rigid columns, capable of supporting weight without compressing. This allows many boxes to be stacked on top of each other. When pressure is applied to the side of the board, the space in between the flutes serves as a cushion to protect the container’s contents, thus providing shock protection. The flutes also provide insulation against sudden temperature changes. The liners placed on the outer sides protect the flutes from damage and increase the container’s overall strength.

For produce transportation, double-faced corrugate is commonly used. The materials used on the inner and the outer layers are determined by the product it will hold. For example, the inner layer may be coated to resist moisture while the outer layer will usually be printed to identify the contents and for display inside retail outlets (FEFCO, 2011).

Corrugated materials have standards to ensure boxes shipped by rail or truck do not fail during transportation. The first rules established in the United States were in 1906. Corrugated fiberboard must protect from bursting to withstand forces during rough handling, be able to withstand weight placed on top of the box, and allow for a maximum weight of contents that can be safely placed in the box. These measurements are usually printed on the outside of the container.

11.6.2 Plastic

Plastics are a versatile medium used to protect and prevent damage to a variety of food products. They are available in a variety of thick, thin, rigid, or flexible forms, ranging from bottles to liners, to accommodate almost any food product. Traditionally, this material is only considered for primary or secondary packaging. This is changing as manufacturers and distributors have adopted RPCs for tertiary packaging use with fresh produce. Now plastics use may be considered at all levels in the supply chain (APME, 2001). According to the American Plastics Council, each pound of plastic can prevent up to 1.7 lb of food from being wasted due to spoilage, contamination from foreign substances and organisms, or packaging failure (APC, 2005).

Since plastic is light in weight, it also saves costs in transportation and is therefore a cost-effective material. Plastic also extends the life of perishable produce to eliminate waste and preservatives. The transparent nature allows people to look at food and touch it without causing bruising or other damage (APME, 2001). The shatterproof material keeps the package intact, and prevents chips or shards from contaminating the food. Polyethylene (PE) films are the dominant material for fruit and vegetable packaging in retail stores. Produce remains fresh during transportation and handling because the material is breathable, allowing the correct ratio of oxygen, carbon dioxide, and water vapor to fill the bag. Some produce varieties can be protected by rigid clamshells (Figures 11.11 and 11.12). This inexpensive package encloses high-value items such as fruit, berries, precut salads, and mushrooms and prevents delicate items from crushing (The Clemson University Cooperative Extension Service, 2002).

PE is the dominant plastic material in use today, with a 56% market share. Other types of plastic used are polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS), polyvinyl chloride (PVC), EPS, low-density polyethylene (LDPE), and high-density polyethylene (HDPE).

Material descriptions according to the American Plastics Council (2005) are as follows:

- *PET*: Clear and tough material. Has good gas and moisture barrier properties. Commonly used for beverage containers, food containers, boil-in food pouches, and processed meat packages.
- *HDPE*: Used for milk, juice, and water bottles, as well as cereal box liners. Translucent material is well suited for products with a short shelf life. Has good strength, stiffness,

Figures 11.11 and 11.12 Bunches of grapes being packed in plastic clamshell trays.

toughness, and chemical resistance. Gases are permeable.

- *PVC*: Widely used for construction applications because of stable properties. This rigid plastic is commonly used for clear food packaging such as food wrap, vegetable oil bottles, and blister packaging. It has great strength and toughness and resistance to chemicals, oils, and grease.
- *LDPE*: This plastic is predominant for film applications. It is tough and flexible, while still maintaining transparency. It makes sealing easy and is a good barrier to moisture. Common applications include shrink-wrap, plastic bags, and squeezable food bottles.
- *PP*: This strong material has a high melting point, making it a good candidate for hot-fill liquids. Resistant to other chemicals, grease, oil, and moisture. Commonly used for margarine and yogurt containers, caps for containers, wrapping to replace cellophane, and medicine bottles.
- *PS*: Can come in two different forms, either rigid or foamed. Usually, it is clear, hard, brittle, and has a low melting point. Typically used for protective packaging such as egg cartons, containers, lids, fast-food trays, disposable plastic cutlery, and cups.

11.6.3 Metal

In the 1790s, Nicolas Appert became the first person to conserve food in a metal container. Today, commercial canning is made possible by materials such as steel, aluminum, tin, and chromium. Each material offers food processors different properties and preservation methods. Producers choose metal for food and beverages for reasons including mechanical strength, low toxicity, superior barrier properties to gases, moisture and light, and ability to withstand a wide extreme of temperatures. These qualities help ensure the integrity and safety of a wide variety of food products.

The most commonly used metals for packaging are tinplate, tin-free steel, and aluminum. Tinplate comprises of low carbon steel with a thin layer of tin. The tin layer may be as thin as 0.38 μm (Soroka, 2002). Tinplate is nontoxic and corrosion resistant and is well suited for conversion into packaging due to its excellent ductility and drawability.

Tin-free steel comprises of low carbon steel and a thin coating of chromium, aluminum, or enamel. Cans made from this material can no longer be soldered and must be welded or cemented.

Tinplate and tin-free steel are commonly used to manufacture three-piece cans. These cans can be mechanically seamed, bonded with adhesive, welded, or soldered (Soroka, 2002). Soldered food cans are no longer permitted in North America. Three-piece cans are the most popular worldwide because they are cheap to produce, and since all pieces are made from flat sheets with no stretching required.

Aluminum is the most abundant metallic constituent used for packaging. Often referred to as the transportation metal, aluminum alloys with magnesium for strength provides one-third the strength of steel at one-third the weight. Among its notable properties, aluminum is light, weaker than steel, easy to work with, inexpensive, nontoxic, a good barrier down to 1 ml thickness, nonmagnetic, does not rust, no “taste”, and has an excellent recycle record.

Aluminum cans are often two piece in construction with a seamless body plus a top cap. They are very popular in the US beverage industry. The machinery used to manufacture these cans is costly compared to three-piece cans because the process stretches metal. The two most commonly used processes in manufacture of two-piece cans are draw and iron, and draw and redraw.

11.6.4 Glass

Glass refers to an inorganic material fused at high temperature and cooled quickly so that it solidifies in a vitreous or noncrystalline state. The main constituent of glass, silica, is an abundantly available element because it exists in the form of sand. Lime and soda are the other two major components of glass. Cullet or recycled glass is often desired as one of the primary constituents because it provides excellent energy efficiency and saves time for the manufacturers. Large-scale glass manufacturing for food products was introduced in the late 1800s. Today’s glass containers are lighter and stronger than their predecessors. Amber and green glass provides light protection for sensitive foods.

Glass is impermeable to gases, moisture, odors, and microorganisms and is probably the most inert packaging material available today. Glass also provides other benefits such as it can be molded into a variety of shapes and sizes, is ideal for high-speed filling lines, is made from abundant raw materials, and is reusable, recyclable, and resealable. Among its greatest drawbacks are the facts that glass is brittle and usually breaks under an applied tensile strength and has the least ability to withstand sudden temperature change, unlike other packaging materials.

The manufacture of glass containers involves either blow-and-blow process used in manufacturing narrow mouth containers, press-and-blow process used for wide mouth applications, and the most recent one, narrow-neck-press-and-blow process gaining favor for manufacture of narrow mouth containers, due to its ability to distribute the material more evenly thereby requiring less material.

11.7 "Smart" Packaging

With modern development and enhancements in packaging technology, today's packaging is providing more than just the basic functions. Smart packaging is a term coming into use more frequently and covers a number of functionalities, depending on the product being packaged, which includes food, beverage, pharmaceutical, and household products (Butler, 2001). Examples of current and future functional "smartness" include the following points:

- packages that retain integrity and improve the shelf life;
- enhances the product attributes such as its flavor, aroma, and taste;
- assists with product access and indicates seal integrity;
- responds actively to changes in product or package environment; and
- confirms product authenticity.

11.7.1 Active Packaging

Traditional "passive" packaging techniques that only allow for a short shelf life are being consistently improved upon to play an "active" role by slowing down quality-impairing processes within the packaging itself, due to the advances in polymer chemistry. Examples of active packaging systems include use of oxygen scavengers, ethylene absorbers, moisture regulators, taint removal systems, ethanol and carbon dioxide emitters, and antimicrobial-releasing systems.

In active packaging, a substance or substances are incorporated into the packaging to fulfill an active role in protecting the foodstuff against contamination, such as aroma components of microorganism growth. Until recently, carbonated beverages in plastic bottles tended to have limited durability compared with conventional glass bottles. With recent developments, the shelf life of beer in 0.33 l PET bottles has been increased from 6 to 9 months (Beverage Machines Magazine, 2006).

As a majority of food products are light sensitive, ultraviolet light barriers, which preserve the transparency of the bottles or containers, are being incorporated into the substrates of the packages. As related to informative packaging, external or internal indicators that document quality alterations during the storage period, such as temperature changes or interruptions in the cold chain, are rapidly coming into use. Active packaging is also being used as security features in the form of labels that track manipulation or misuse of the product prior to its sale.

11.7.2 Modified Atmosphere Packaging

Food preservation technology accounts for two main factors of ever-increasing importance, extending product life and reducing the amount of additives used. Modified atmosphere packaging (MAP) allows for these demands to be met. MAP involves modifying the atmosphere surrounding the product inside the package. This in turn allows chemical, enzymatic, or microbiological reactions to be controlled and therefore reduces or eliminates the main processes of deterioration in the product. The package usually has a low permeability to gas, so that the initial concentrations of the added gases remain unchanged after the package is sealed.

MAP can be used to extend the shelf life of many fruit and vegetables. Most fruit and vegetables age less rapidly when the level of oxygen in the atmosphere surrounding them is reduced. This is because the reduced oxygen slows down the respiration and metabolic rate of the products and therefore slows down the natural aging process. Elevating the level of carbon dioxide to levels of 2% or more can also be beneficial. Elevated CO_2 levels can reduce the product's sensitivity to ethylene and can also slow the loss of chlorophyll. High CO_2 levels can also slow the growth of many of the postharvest fungi that cause rot. All these effects can help to extend the storage and shelf life of fresh produce (Joblin, 2001).

11.7.3 Controlled Atmosphere Packaging

The major difference between controlled atmosphere packaging (CAP) and MAP is that the concentrations of the gases in a MAP package may change after sealing, due to use of oxygen and the expelling of carbon dioxide by microbes and because of the slightly permeable nature of the package. In a CAP package, the gas concentrations do not change during storage. To achieve this, the use of a gas-impermeable package, such as metal or glass is preferred, and also provides a way of controlling the atmosphere inside the package.

11.7.4 Intelligent Packaging

The stakes in food cold chains are high and the loss of a trailer of food due to improper handling or transport is measured in hundreds of thousands of dollars. Because of the financial pressure and increasing regulatory demands for better recordkeeping resulting from the Bioterrorism Act, suppliers and logistics service providers are turning to systems that combine radio-frequency identification (RFID) with temperature and humidity sensors.

RFID is an age-old technology that has recently realized its potential in supply chain systems. Traditional supply chain management systems produce information regarding "transactions" (orders, shipments, and payments) and "location" (warehousing, traffic, and inventory). However, perishable goods also require information regarding their "condition" (time and temperature) as they change in value while in the supply chain. RFID promises to provide real-time tracking of goods while in transit, thereby providing a clearer picture of the distribution environment.

With mandated use of this technology by major suppliers to industry giants such as WalMart, Albertsons, and Tesco, this technology is already being adopted in the consumer goods supply chains. With standardization and reduced costs, this noncontact technology is set to be as commonplace as barcodes.

11.8 Trends in Protective Food Packaging of 2000 and Beyond

The following sections discuss some of the food packaging trends and damage reduction trends in food packaging (Figures 11.13–11.15).

11.8.1 Food Packaging Trends

This is a broad overview of major packaging changes that have occurred in recent years and are playing a dominant role in food packaging. While the general transition to plastics rather than glass and metal as primary packaging materials continues, the more recent and revolutionary introduction of biobased and biodegradable plastic materials continues to lead. Innovations are going on every day, leading the effort in specialty coatings directly on food products to enhance shelf life and quality aspects such as texture, aroma, and flavor. In addition, the US market continues to develop more cost-effective packaging methods for palletized quantities led by club stores such as Costco Inc.

Figure 11.13 A packed CCF tray with four clamshell containers.

Figure 11.14 A pallet load of grapes being protected until shipment.

Figure 11.15 Palletized loads of grapes being prepared for shipment.

Figure 11.16 Stand-up pouch and juice box.

Figure 11.17 Flexible pouch and metal can packaging for seafood.

and Sam's Club (WalMart Stores Inc.). These concepts significantly reduce the amount of secondary and tertiary packaging compared to retailers that display merchandise on store shelves. Some key primary packaging evolutions of recent times are as follows:

1. *Stand-up pouches replacing metal cans*: High-barrier foil laminated or metalized flexible packaging continues to replace metal cans. Multilayer plastics in flexible pouches are replacing traditional paperboard juice boxes. Examples include CapriSun fruit juice for young children and tuna fish introductions by Star Kist (Figures 11.16 and 11.17).
2. *Plastic bottles replacing glass bottles*: There is a continuous shift in the beverage industry from glass to plastic bottles. Most blow-molded plastic bottles can be made in-house which reduces dependency on external suppliers and shrinks the supply chain. Also, by using shrink-sleeve labels, multiple product lines can be filled in the same blow-molded bottle without major changeovers. Glass bottles are still holding their competition for high value and premium beverage launches. Shaped primary packages are easy to produce with plastic, provide new product launches with shorter lead times and provide market share in a competitive environment. Heinz used this to launch specialty ketchups and sauces for children (Figure 11.18).

3. *Convenience for on-the-go food packages*: The US customer continues accepting packaging launches that provide convenience while driving and placing in cup holders in automobiles (Figure 11.19). Products range from snack foods, cereal with milk, and salads. An examples range is Frito Lays Inc., who offer a range of snack foods in blow-molded plastic bottles with shrink labels that fit automotive cup holders and allow consumption while driving. These replace the traditional bag and pouch.
4. *Clear plastics packaging*: The consumer continues to demand more esthetically pleasing containers for food packaging. Product visibility plays a key role from bagged salads, to fresh produce in thermoformed containers, to spices. However, the gas transmission requirements for these plastics vary from extremely high barrier in the case of spices to low barrier for salads. The customer wants more visibility of the actual product being purchased (Figures 11.20 and 11.21).

Figure 11.18 Some plastic ketchup bottle forms.

Figure 11.19 Convenience-driven snack food packaging.

11.8.2 Damage Reduction Trends

The various innovations and trends discussed in the previous section all lead to a reduction of damage in shipment. Protection (physical and chemical) is an underlying function of a package, and generally all package improvement and changes will usually result in reduction of damage as protection is increased. In addition, there are some key changes that clearly can help reduce damage beyond the primary package change.

Use of good-quality pallets is the key to reducing damage to both rigid and flexible primary packages. The most widely used pallets to distribute food products, both fresh and processed, are made of wood. Low-quality lumber, protruding nails, insufficient deck or base coverage, moisture content, and infestation are all factors that can lead to damage of food products and packages when shipped on wooden pallets. For this reason, most retailers use reusable plastic pallets in downstream shipping between distribution centers to stores. An alternate to a single-use wooden pallet are high-quality wooden pallets that can be leased and reused. These are often an economically better choice but also offer additional benefits due to the high-quality construction.

Figure 11.20 Vine ripe tomatoes in a biodegradable PLA plastic thermoformed container.

Figure 11.21 Bagged salads with brand identity in see-through packaging.

Today, most companies leasing wooden pallets to the food industry (CHEP USA Inc.) offer a picture-frame bottom section and a large percentage of the top deck covered with deck-boards to reduce damage from stacked products and packages. Also these are true four-way entry block-style pallets that can be easily handled with fork trucks and pallet jacks. Reduced handling results in lower damage as compared to products on conventional stringer pallets. In addition to the quality of pallets, the placement of products on pallets is critical. Both underhang and overhang can greatly affect the load transfer in stacked loads and thereby result in damage. Use of slip sheets to distribute load among layers and the pallet surface is a common way to address these issues.

The unitization method of loads on a pallet is also critical. Choice of appropriate shrink-wrap, stretch wrap, banding, netting, gluing, and strapping are all choices that need to be examined for specific product and packaging needs. Use of corner posts and top caps can reduce damage in caseless palletized loads designed for club store shipments.

Most of these issues and potential solutions should be addressed by using lab-based accelerated test evaluations. The use of test methods developed by American Society of Testing and Materials and the International Safe Transit Association allow users to conduct preshipment tests on palletized configurations to simulate different distribution methods from truckload to less than truckload to single parcel shipments. It is important to test a few pallets of the product and identify damage reduction solutions than launch a massive new product in a retail distribution and be subject to a major recall or loss.

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12 Food Packaging Machinery

Harold A. Hughes
Michigan State University, East Lansing, MI, USA

12.1 Introduction

Packaging is an essential activity in the food industry. Virtually every food product is packaged one or more times before it reaches the ultimate consumer. Packages are used at each stage in the process of production and distribution of food products: from farms to processing plants, between processing plants, from processing plants to warehouses to retail outlets, and from retail outlets to consumers. A package can hold a food product, several food products, or packages of food products. There are many package forms including wraps, pouches, bags, boxes, cups, trays, cans, tubes, and bottles.

Packages perform one or more of the following four basic functions: containment, protection, communication, and utility. Each function is discussed briefly in the following sections.

12.1.1 Containment

Many food products, especially liquids and free flowing solids, are contained in packages to facilitate convenient handling and to avoid spillage and loss of the product. Table salt and granulated sugar are examples of free flowing solids. Liquid food products include water, milk, fruit juices, and a wide assortment of other products.

12.1.2 Protection

Food products must be protected against contamination by microorganisms and a wide array of other hazards. Depending on the characteristics of the product and other factors, it may be necessary to provide protection against gain or loss of moisture, oxygen, CO_2, and other constituents, from crushing and other distribution damage, from improper temperature, from light, from tampering and theft, and against numerous other hazards.

12.1.3 Communication

Every package communicates information. The communication may be simple and straightforward, such as a label listing the contents and showing the source and destination. However, most retail food packages include expensive and elaborate multicolored labels, bar codes, and radio-frequency tags. Every retail food package must include a nutritional label.

12.1.4 Utility

Some packages and package components are designed to add value to the packaged product. Spout shakers and similar fitments enable consumer to apply spices, salt, and similar materials more easily and accurately. Printed directions add convenience. Handles enable small children to handle large packages conveniently and safely.

The modern food production and distribution system could not function without packaging. Even fresh food, such as bananas, oranges, tomatoes, or lettuce, is packaged for transport from the store to the consumer's residence. The packages may be made of corrugated board, mesh bags, paper bags, or plastic containers. A large percentage of the fresh products are packaged by hand.

However, unlike the fresh products mentioned above, most modern food products are prepared or processed in factories and then packaged for distribution to warehouses and stores and ultimately to consumer's residences. Most of the packaging is done by machines set up into systems. The packaging equipment often receives the prepared product from an adjacent preparation area. Four example production and packaging systems are described in Table 12.1.

The descriptions illustrate two important principles about packaging machines. The first is that packaging machines are generally set up as a system. It is unusual for a packaging operation to have only one machine. Rather, there is nearly always a

Ebnesajjad: Plastic Films in Food Packaging. DOI: http://dx.doi.org/10.1016/B978-1-4557-3112-1.00012-0
Adapted from a chapter in: Kutz, *Handbook of Farm, Dairy, and Food Machinery* (2008).

Table 12.1 Description of Some Typical Food Packaging Systems

Product	**Steps in the Preparation/Packaging System**
Milk in one gallon plastic jugs	1. Milk is received at the plant, filtered, processed as necessary, and stored in large stainless steel tanks 2. Plastic jugs are manufactured on site by blow molders and placed into temporary storage 3. The jugs and the milk are conveyed to a filling machine, which meters one gallon of milk into each container 4. The filled jugs are capped, washed, and labeled 5. The completed gallon packages of milk are placed into plastic crates for handling 6. The crates are stacked and conveyed to a refrigerated temporary holding area
Soup in metal cans	1. The constituents for the soup are delivered to the plant 2. The metal cans, labels, and other packaging components are delivered to the plant 3. The soup is prepared and conveyed to the packaging line 4. The cans are depalletized and conveyed into the packaging line 5. The cans are cleaned as necessary 6. Empty cans and the soup are conveyed to a filling machine and the soup is metered into the cans 7. The can end is applied 8. The filled cans are retorted 9. Labels are applied to the cans 10. Completed cans are packed into corrugated trays 11. The filled trays are wrapped with shrink-wrap and palletized
Granulated sugar in multiwall paper bags	1. Sugar is extracted from sugar cane or sugar beets and transported to a temporary holding area 2. Preprinted, multiwall paper bags and rolls of heavy Kraft paper are delivered to the plant 3. Empty bags are held open by the filling machine and the specified weight of sugar is metered into the bag 4. The top of the bag is rolled over, crimped, and glued shut 5. Bags of sugar are bundled together and wrapped in Kraft paper 6. The bundles of sugar are palletized and moved to a warehouse
Assorted chocolates in paperboard cartons	1. Decorated paperboard cartons, plastic trays, plastic overwrap, corrugated shipping containers, labels, and other packaging components are delivered to the plant 2. Chocolates are manufactured and placed into temporary holding locations in the packaging area 3. Empty cartons are conveyed past the filling station where a robot picks up individual pieces of chocolate and places them into particular locations in a thermoformed plastic tray 4. Filled trays are placed into cartons 5. A lid is placed on the cartons 6. Completed cartons are wrapped in plastic film 7. Wrapped cartons are placed into the shipping containers, which are closed, taped, labeled, and palletized 8. The loaded pallets are moved to a warehouse for temporary storage

series of machines. For example, the milk system generally includes a filler, a capper, a labeler, and other machines. The packages go down the packaging line, moving from machine to machine as different operations are performed.

The second principle is that there are almost always options in the way that a particular operation can be performed. The options may be provided by different machines. Alternatively, there may be a choice to not use a machine. For example, in the candy packaging system, the individual pieces of candy could be placed into the carton by a robot or by people working with their hands.

The next portion of this chapter will discuss some of the different types of packaging machines that are available, including machine capacity, operating principles, and other characteristics. The discussion will start with filling machines.

12.2 Filling Machines

The filling machine is usually the most important machine in a food packaging line. The filler performs two critical functions. It measures out a specific quantity of a food product and places that metered quantity of food into a package. The machine may also perform other functions, such as making and closing the package. Most fillers can be set up to work on many different products. For example, a machine that is used to meter water into 12 oz. plastic bottles could also be used to meter 1 qt of motor oil into different plastic bottles or 2 qt of milk into paperboard or gable-topped cartons. However, since this chapter addresses only food products, motor oil and other nonfood products will be ignored. Filling machines used in food systems measure out a quantity of product by volume or weight.

12.3 Volumetric Fillers

Volumetric fillers deliver a measured volume of product into each container. Volumetric systems are flexible and can be adapted to a wide variety of products, ranging from water to thick pastes or powders, and other dry products.

Most fillers can be adjusted to deliver a desired quantity of product. A typical unit can be adjusted over a 10-fold range. For example, a particular machine might be adjusted to deliver any volume from 2 fluid ounces to 20 fluid ounces.

12.3.1 Piston Fillers

Piston fillers (Figure 12.1) are the most common type of volumetric fillers. Piston fillers measure and deliver the product by the action of a single piston. On the intake stroke, the piston draws product out of a supply tank, through a directional valve, and into the measuring chamber which houses the piston. Then, on the following delivery stroke, the valve leading to the container is opened

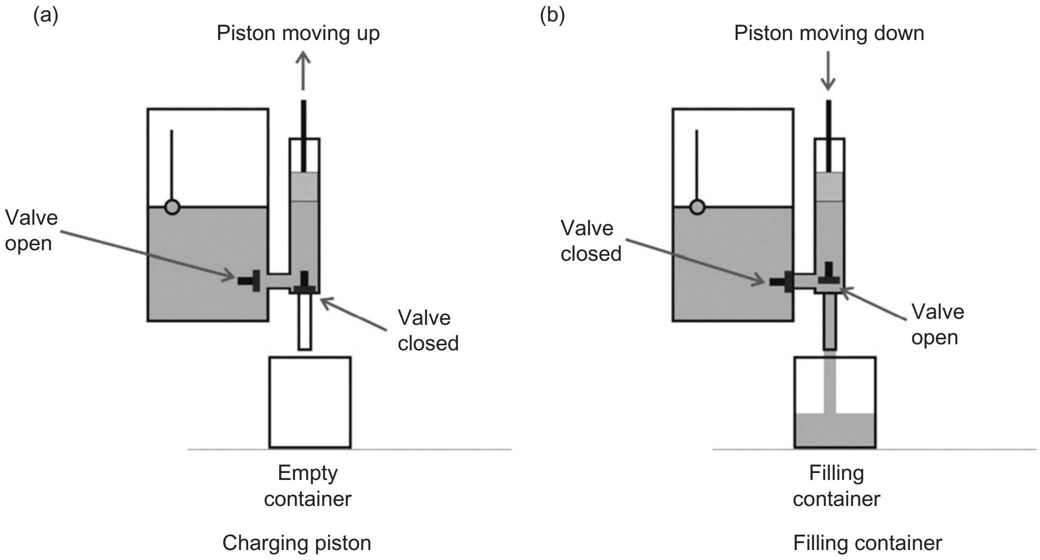

Figure 12.1 Piston filler operation.

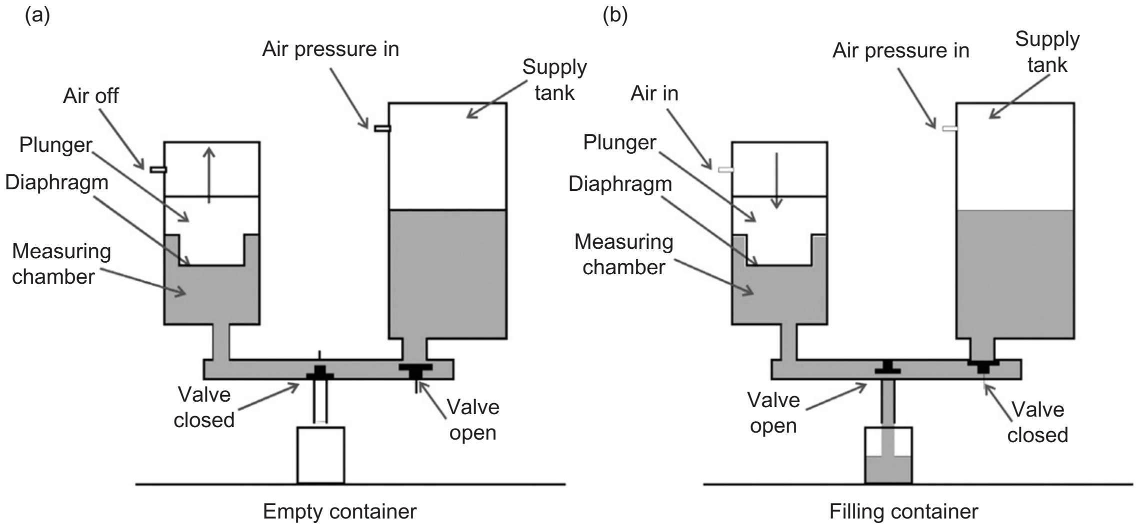

Figure 12.2 Diaphragm filler operation.

and the valve leading to the supply chamber is closed causing the product to flow out of the chamber and into the container. The filled container is then conveyed away and replaced by another empty container and the process repeats.

The length of the stroke and the diameter of the chamber determine the volume of product that is metered out. To alter the quantity of product, either the stroke length or the chamber diameter (or both) must be changed. On most machines, the stroke length can be adjusted easily. However, to change chamber diameter, the entire chamber must be removed and replaced, a relatively complex and time-consuming operation on most machines and not possible on some machines.

12.3.2 Diaphragm Fillers

Diaphragm fillers (Figure 12.2) are similar in principle to piston fillers. Instead of a rigid piston and cylinder, a diaphragm filler has a flexible diaphragm which can be distorted to adjust its volume. The operation of a diaphragm filler is straightforward. When the cycle starts, the valve at the bottom of the supply tank is opened and the valve to the empty container is closed. Air pressure in the supply tank forces the product out of the tank and into the measuring chamber. The top of the chamber is formed by the diaphragm with the plunger above. As product flows into the chamber, the diaphragm and plunger are lifted. When the plunger reaches a preset position, the valves are reversed and air pressure is applied to the top of the plunger, forcing the product out of the chamber and into the container. The filled container is then conveyed away and replaced by another empty container and the process cycle repeats.

12.3.3 Timed Flow Fillers

If a liquid product flows through a tube of specific size at a constant rate, the total quantity of product delivered depends on the length of time that the product flows. For example, if one cup flows through the tube in 1 s, two cups will flow through the tube in 2 s, 3 cups in 3 s, etc. The accuracy of the metering process depends on smoothness of flow and the precision of the timing mechanism (Figure 12.3). The equipment set includes a supply tank and a pump, along with a timer and various pipes (Figure 12.4). To fill larger containers, the timer setting is increased. To adjust the filling speed (volume/unit of time) is increased or decreased.

The fillers that have been discussed so far are mostly intended for use with liquids, such as milk, water, pancake syrup, cooking oil, alcoholic beverages, and other thin liquids. There are equipment variations that enable the machines to be used with thicker products.

12.3.4 Auger Fillers

Auger fillers are a widely used type of volumetric filling equipment used for many types of dry products and thick pastes (Figure 12.5). The product is held

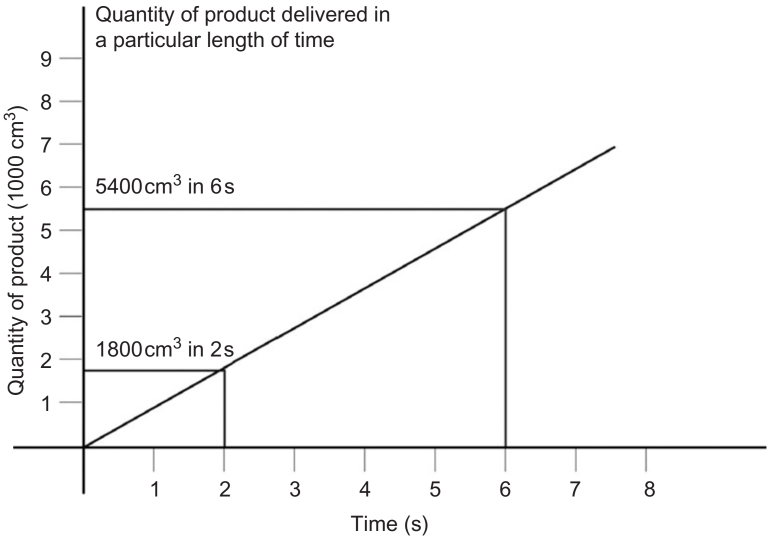

Figure 12.3 Delivery of product from a timed flow filler.

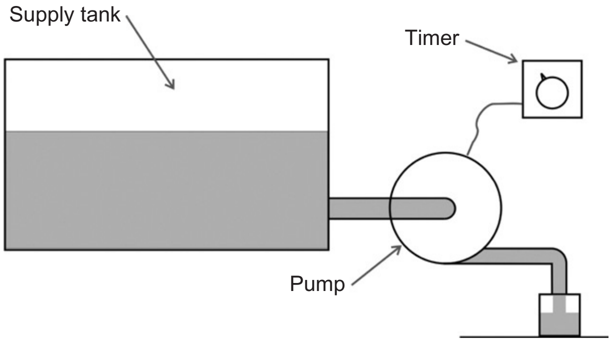

Figure 12.4 Timed flow equipment arrangement.

temporarily in a conical shaped bin and metered and conveyed out through an opening at the bottom by an auger. The auger must be specially designed and manufactured to suit the product. The filler manufacturer or a specialty manufacturer should be contacted to make the augers. The volume of product to be delivered is directly related to the number of degrees that the auger rotates. The control can be based on time, which requires that the speed of rotation be constant, or it can be based on the degrees of rotation. To change the volume of product delivered, the time that the auger rotates can be increased or decreased.

Some powders tend to bridge in the hopper and not flow into the auger. To prevent bridging, manufacturers make various types of agitators that rotate together with the auger. The agitator breaks up the bridged product and keeps the product flowing smoothly to the auger.

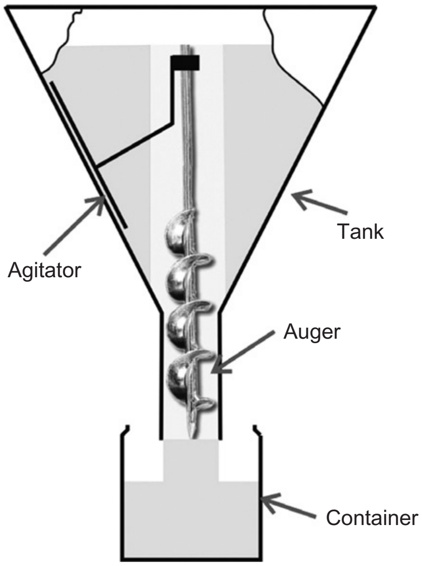

Figure 12.5 Auger filler.

If the density of the product is constant, metering a specific volume of product also defines a particular weight of product. Volumetric filling is a good choice for products of this type.

12.4 Weight Filling

Weight filling is used to meter products that do not have uniform density and for products that require more accurate metering than is possible using volumetric fillers. There are two types of weight filling: gross weight and net weight.

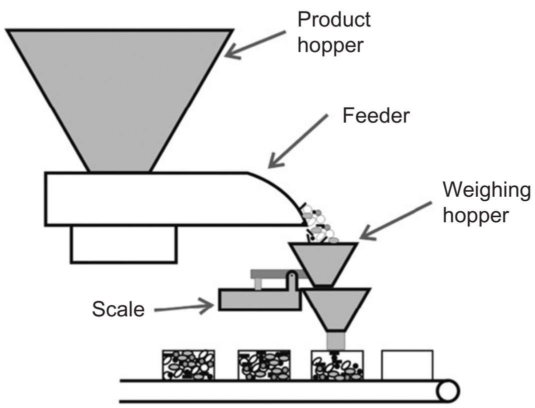

Figure 12.6 Net weight filler.

12.4.1 Net Weight Fillers

Net weight fillers (Figure 12.6) measure out the desired weight of product and convey the measured product to the container. The metering step is done inside the machine, before the product is introduced into the container. The scale measures only the weight of the product. When the weight of the product in the hopper reaches the preset value, the feeder stops and the hopper opens to discharge the product into a funnel which guides the product into the container. After the product has been placed into the container, the filled container is moved away and an empty container is moved into position to be filled.

12.4.2 Gross Weight Fillers

A gross weight filler (Figure 12.7) measures the combined weight of the product and the package. Before the filling operation begins, a sample of packages are weighed individually and the average is calculated. The metering scale is then preset with the sum of the desired product weight and the average weight of a container. The product is metered directly into a container until the scale determines that the proper (combined) weight has been reached. At that time, the product flow is terminated, the filled container is moved out and an empty container is moved into position to be filled.

There are several machine arrangements that can be used to improve the accuracy of weight filling equipment. From Figure 12.7, it can be seen that there is some product in the fill tube when the valve closes. This product, of course, still falls into the container after the valve closes. A method of compensating for this product is required or every container will be overfilled. One approach is to set the scale to “underweight” the container. Another approach is to change the machine design. Simply locating the cutoff valve closer to the container will reduce the amount of product in the fill tube when the valve closes, so the container is filled more accurately.

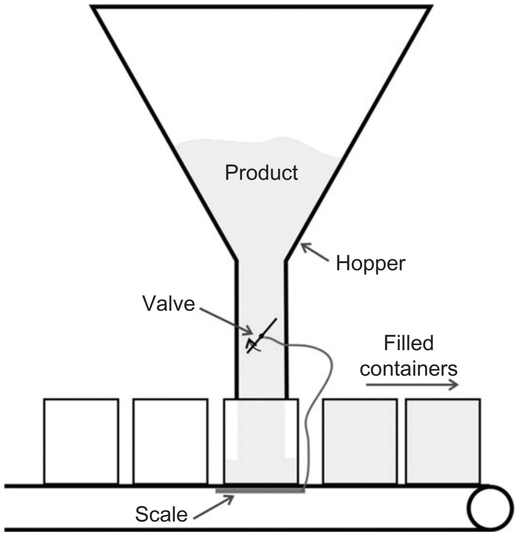

Figure 12.7 In-line filler.

Gross weight fillers are less complicated and less costly than net weight units. In addition, because the weight of the containers is preset into the scale rather than being weighed, as is done by the net weight units, gross weight fillers tend to be less accurate than net weight fillers. Therefore, gross weight equipment tends to be selected for lower value products. In addition, net weight fillers handle the product more times than gross weight fillers. Therefore, gross weight fillers tend to be the more popular choice when brittle or fragile products, such as potato chips, are being packaged.

12.5 In-Line or Rotary Fillers

There are two basic arrangements of fillers: in-line and rotary. Each will be described and discussed here.

12.5.1 In-Line Fillers

In-line fillers (Figure 12.8) are widely used for filling liquid and paste food products, such as

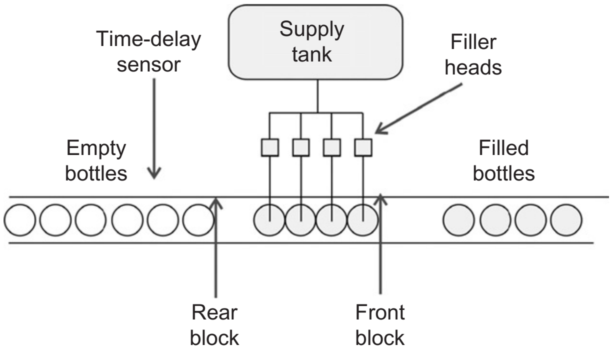

Figure 12.8 Gross weight filler.

water, beverages, fruit juices, ketchup, mayonnaise, and many other products, into metal cans, glass bottles, and other containers. Obviously, an in-line filler must have at least one filling head but most have six or more heads. An in-line filler, including a short section of conveyor belt, is usually positioned in a packaging line between an in-feed conveyor and an out-feed conveyor. Typically, the conveyors are a little wider than the diameter or width of the containers.

The following description of the operation of an in-line filler refers to the four head unit shown in Figure 12.8. The filling procedure starts when empty containers are conveyed into the filler in single file by the in-feed conveyor. The containers are held in position by the rear block as shown in Figure 12.8 until the four containers have been filled properly. Then, the filler heads are raised and moved back out of the way, allowing the four newly filled containers to start moving down the line toward the out-feed conveyor. After a time delay (set on the time-delay sensor), the rear block is moved back and out of the way, allowing empty containers to start moving into position for filling. After the four filled containers have moved past the front block, it is repositioned to prevent the next set of containers from simply passing through the machine unfilled. After four containers pass the rear block, the rear block is repositioned, the filler heads move into position and the cycle repeats.

12.5.2 Rotary Fillers

Rotary fillers (Figure 12.9) remove empty containers from the in-feed conveyor and place them on the rotating turret of the filler. As the containers travel around the periphery of the filler, they are filled and then placed onto the out-feed conveyor.

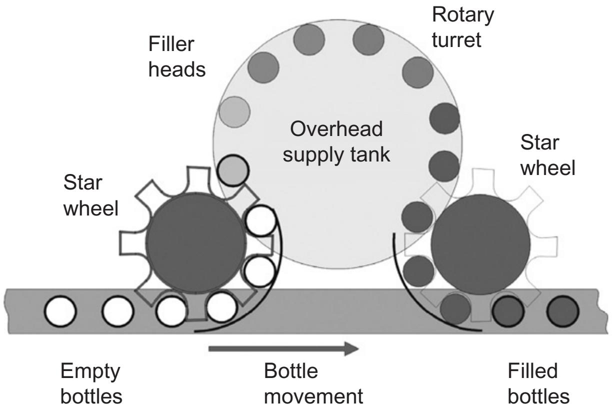

Figure 12.9 Rotary filler.

Rotary units range in size from as few as 4 heads to as large as 140 heads or even more. The large units are used on high-speed beverage lines of the type used for filling metal cans with beer or soft drinks. Lines for these products can operate as fast as 2500 cans per minute or 1600 glass bottles per minute. Slower lines are used for milk, pancake syrup, juices, and many other products. The rotational speed of the in-feed star wheel and the rotating turret must be synchronized so that each empty container is placed in the proper position below a filler head on the turret. Similarly, the star wheel on the out-feed side must align with the filled containers as they are taken off the turret and placed back on the conveyor.

Any of the volumetric or weight filler heads can be used on either in-line or rotary fillers. Filler heads are usually a major portion of the cost of a large rotary filler.

12.6 Cap Application Machines

After a container has been filled, it continues downstream to the next machine which is usually the capper. Like fillers, cappers can be set up in either an in-line or rotary arrangement.

Simultaneously, caps are fed down a chute from a cap orienting machine which puts all caps into the same orientation. Like fillers, cappers can be set up in either an on-line or rotary arrangement. When an in-line capper is being used, the containers pass under the end of the cap chute which is adjusted so that the upper portion of the leading edge of the container catches the lower edge of the

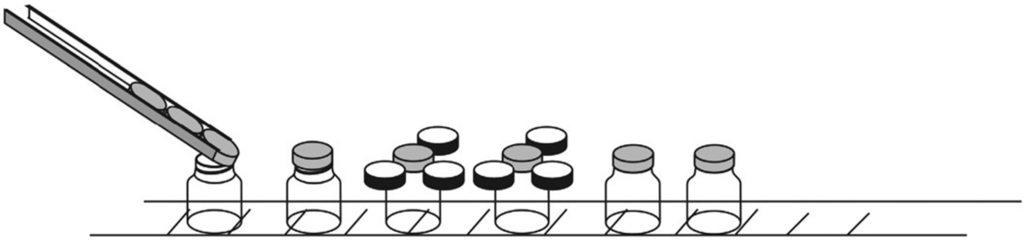

Figure 12.10 Cap chute and spinning disk tightener.

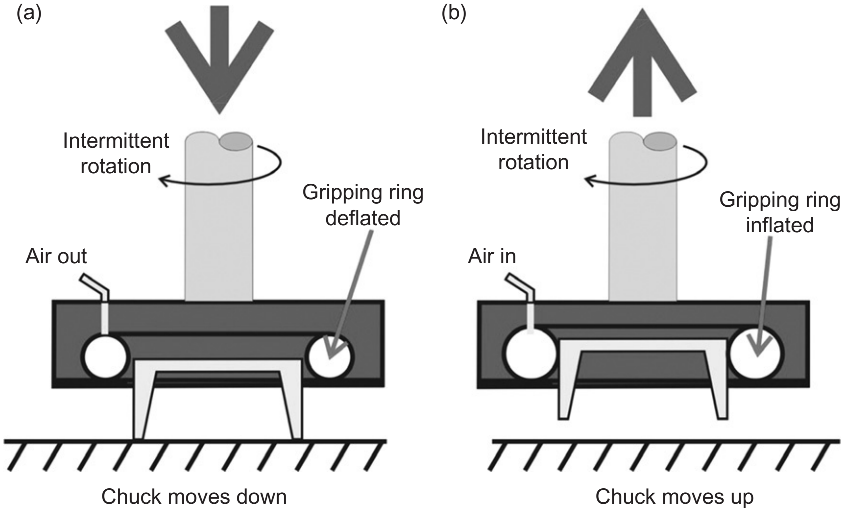

Figure 12.11 Operation of pneumatic chuck.

cap, pulling it out of the chute and setting it in place on top of the container. Then the container, with the cap, passes through a set of spinning disks which tighten the cap to the desired application torque (Figure 12.10).

The in-line arrangement shown in Figure 12.10 is very popular, but like in-line fillers, there is an upper limit on capping speed. For lines that exceed the capacity of in-line equipment, rotary cappers can be used. The arrangement of capping heads around the periphery of a rotary capper is similar to the arrangement of rotary filler. The filled containers are removed from the line by the entrance star wheel and placed on the capper. As the capper rotates, the caps are applied and tightened. Then, the filled and capped containers are set back onto the line to be moved to the next station. The spinning disk arrangement used on in-line cappers cannot be used on rotary cappers because the filled containers move with the turret, and there is no relative motion that would cause the containers to pass between the disks. Instead, a spindle capping setup is used. A spindle (Figure 12.11) is mounted on a vertical shaft that rotates as the spindle travels around the periphery of the machine. The spindle has a "chuck" at the lower end with a torque-limiting clutch above.

The operating cycle described here is for a machine applying screw caps. The cycle of steps is essentially the same whether metal or plastic screw caps, metal lug caps, or some other type of cap is being applied.

The operating cycle begins when a cap is delivered to the capping machine. In one system, as the capper rotates, a peg on the outside of the frame of the capper pulls a cap out of the chute in a fashion similar to the way that a container pulls a cap out the end of the chute in an in-line setup. In another system, the empty chuck passes over a swinging arm holding a cap. The chuck is lowered over the cap and picks it up. The arm then moves back to pull another cap from the chute.

When the cap is in the correct position, the spindle moves down and the chuck opens to fit over the cap. Then, the chuck closes to grip the cap and the spindle moves away, carrying the cap with it. While the spindle is picking up the cap, the container is moved into position. Then, the spindle begins to turn and simultaneously moves downward screwing the cap onto the container. When the required (preset) application torque is reached, (i) the clutch opens and stops driving the chuck or (ii) the chuck opens and starts to slip around the cap. In either case, the spindle lifts away, releasing the container to be discharged through the exit star wheel and back onto the conveyor to travel to the next machine.

Only one spindle is involved in capping each container. Capping speed can be increased by using a machine with more spindles. Each spindle and container goes through the same sequence of operations. While a peg is picking up a cap at one spindle, another spindle is moving into position, another spindle is applying a cap, another spindle is releasing the container, and a container is leaving the machine through the exit star wheel. Depending on the number of spindles on the capper, the sequence may be divided into even more steps. A rotary capper typically has 3–12 or even more spindles, depending on the filling speed that is required.

12.6.1 Chucks and Clutches

Screw caps can be applied by rotary capping machines that have spindles with pneumatic chucks, mechanical chucks, or roller mechanisms (Figure 12.11) The pneumatic type is illustrated in Figure 12.11. The doughnut-shaped gripping ring is relaxed or deflated when the chuck is lowered to pick up a cap. The ring is made of soft, pliable material that will not scratch or mar the surface of the cap. When the ring is inflated, it grips the cap, enabling it to be picked up. Different sized rings can be installed in the chuck to provide gripping characteristics that are suitable for a particular bottle and cap combination. Also, variations exist in the method for applying the force. One variation has a solid gripping ring with an area above where pressure can be applied, causing the ring to expand in the horizontal direction to grip the cap.

Mechanical chucks operate in a similar fashion except that the jaws are held closed by a spring linkage. The linkage opens when the preset application torque is reached while the cap is being applied.

12.6.2 Chuck-Type Press-On Cappers

The operation of a chuck-type press-on capper is similar to the operation of screw-type cappers, except that the twisting motion used to screw the cap down is not required. Instead, the cap is held in the chuck while it is positioned and pressed straight down onto the top of the bottle. The application force can be controlled in several ways. The spring-operated capper head application pressure can be regulated by adjusting the collar that sets the spring tension. Similarly, the movement of the capper head can be controlled by air pressure in a pneumatic unit. Chuck-type press-on cappers can be designed to suit caps and bottles of almost any size and shape.

12.6.3 Roller-Type Press-On Cappers

In roller-type press-on cappers (Figure 12.12), the cap is dropped or otherwise placed on the top of the bottle. It is then passed under rollers that press the tap tightly onto the containers. A shallow cap may be pressed on by a single roller. Deeper caps may require two or even three rollers to push them on completely. Roller cappers are generally used to apply caps with flat tops. The first roller levels and seats the cap. The remaining rollers press the cap further onto the bottle. Irregular shapes often cause problems when they pass under the rollers.

12.7 Induction Cap Sealing

Today, increasing numbers of rigid and semirigid food packages are fitted with induction-welded inner seals. The Food and Drug Administration requires this type of technology for many pharmaceutical products. The rules were instituted following a famous product tampering incident. Inner seals are not required for food products. However, manufacturers are adopting the technology to

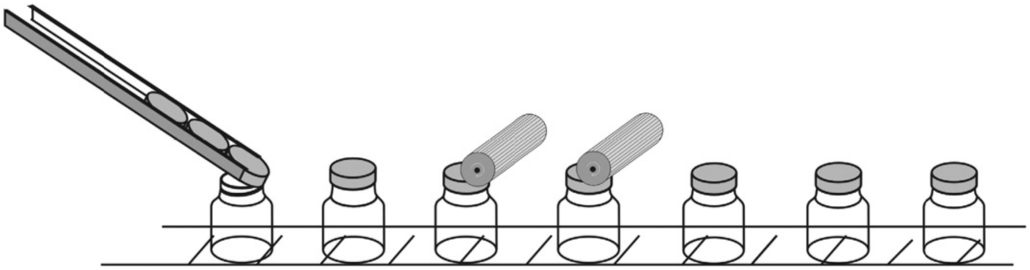

Figure 12.12 Roller-type press-on capper.

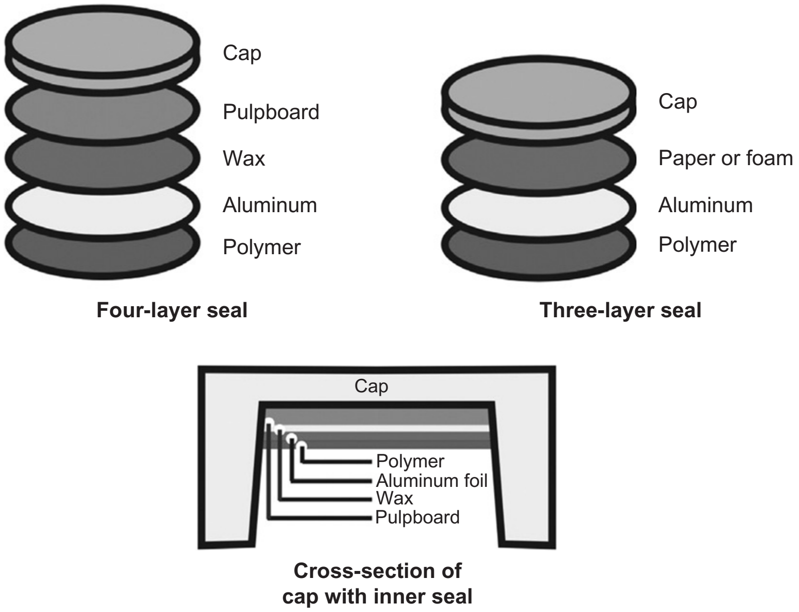

Figure 12.13 Induction inner seals and cap with seal included.

prevent spills and for product protection. Food products that are packaged with inner seals include peanut butter, edible oils, ketchup, honey, spices, jellies, and syrups.

There are two primary types of inner seals (Figure 12.13). The four-layer seal shown on the left was originally developed when induction inner seals were first applied to packaging. The three-layer inner seal was a later development.

An induction sealing system may consist of a power supply, a sealing coil, a sealing coil mount, a water recirculating system, and necessary electrical cables to connect the power supply and the sealing coil. The power supply converts regular line electrical current into the necessary power and frequency needed to seal bottles. The output energy is transmitted to the sealing coil by the cables. The coil mount supports the coil over a conveyor. An alternating magnetic field is produced around the coil. Several thousand times a second, the field expands and contracts and then expands and contracts in the opposite direction. The water cooling system removes excess heat from the cables and the coil. Modern systems are more efficient, so the water cooling system is often not required.

Seals are provided by the cap supplier. Each of the four layers of the seal has a specific function, as described here. A seal is held inside a cap by friction or a small glue spot (Figure 12.13). Caps are applied to bottles and tightened in the usual fashion, as discussed previously. The capped bottles leave the capper and are carried down a conveyor to the induction sealing coil. As the bottles pass under the sealing coil, the lines of magnetic force in the alternating magnetic field cut through the aluminum layer in the inner seal inducing a current to flow the surface of the aluminum layer. The aluminum is not a perfect conductor, so it has some electrical resistance. As a result, heat is produced in the aluminum. The heat causes the wax layer to melt and be adsorbed into the pulp board layer. It also softens the polymer which seals the aluminum to the top of the bottle as it cools. The heating process often loosens the cap. Retorqueing, using a unit similar to an in-line disk-type cap lightener, is generally used.

12.8 Flexible Packaging

The discussions above have primarily addressed glass and plastic bottles, jugs, and similar rigid or semirigid containers. However, many food products are packaged in pouches, bags, wraps, and other forms of flexible packaging. Flexible packaging is probably the oldest form of packaging. Ancient hunter gatherers used available natural materials, such as leaves, and animal parts to form flexible containers to wrap food products for protection and for carrying and storing convenience. Of course, all of their packaging was done by hand.

12.9 Form-Fill-Seal Equipment

A form-fill-seal (ffs) machine performs three distinct operations:

1. form the package,
2. close and seal the package.

Form-fill-seal equipment is popular because it can be used on a wide variety of products ranging from dry powders, such as cake mixes, to liquids, such as salad dressings or pizza sauce. There are three types of ffs equipment:

1. vertical form-fill-seal (vffs) machines,
2. horizontal form-fill-seal (hffs) machines,
3. thermo form-fill-seal (tffs) machines.

12.9.1 Vffs Equipment

Vffs machines are popular and widely used to package a vast array of food products, including dry cereals, granular sugar, cake mixes, flour, and many others. The operation of an ffs machine is easy to understand. As the name indicates the material being packaged flows vertically down the machine as the various package forming, filling and sealing operations are performed.

The web of material (usually plastic or a laminate) that will be formed into packages is fed into the machine from a roll (Figure 12.14). The web is usually printed with the manufacturer's logo, product illustrations, nutritional labels, and other information.

The web is threaded through a series of rollers, guides, and tensioning devices. Even movement of the material is critical for smooth machine operation. The web is then fed over a specially shaped former (Figure 12.14). As the web travels over the wings of the former, it is automatically wrapped around the outside of the filler tube and the edges are brought together and positioned for sealing the back seam that will form a tube of the flexible material.

The package material passes down the outside of the filler tube. As it moves, the edges are heat

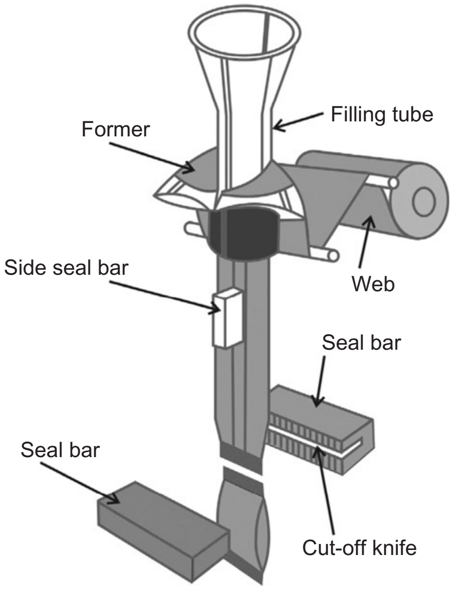

Figure 12.14 Operation of a vffs machine.

sealed together, forming a tube. At the bottom of the filler tube, a pair of heat seal jaws closes on the tube, flattening it and simultaneously sealing the top of a filled pouch and then forming the bottom of the next pouch. Then a heated knife cuts off the bottom pouch which is conveyed away.

At the same time, the product is loaded into the pouch through the filler tube. As the tube of material continues moving downward, the heat sealing mechanism forms the top of a filled pouch and the bottom of the next pouch.

The sealing jaws are often triggered by an electric eye mechanism which reads a black registration spot printed in the web. In this way, the preprinted graphics will appear correctly on the completed package. The pouch length can be adjusted easily. However, the filler tube must be replaced to change the diameter of the package.

Aseptic Packaging

A specialty form of vffs machinery is used to make aseptic packaging of the type often called “Brick-Pack” or “drink box”. Aseptic packaging is sterilized in a hydrogen peroxide dip and formed into a package. Then the product which has also been sterilized is piped into the newly formed box by double-wall pipe which has sterile air in the outer layer. Aseptic technology is also used to package products into premade containers. The system is essentially the same, except that the container forming step is skipped.

12.9.2 Hffs Equipment

The flow of material in a hffs machine is essentially horizontal. The package forming process starts when a flat web of material, usually plastic film or a laminate with a heat sealable surface, is unwound from a roll (Figure 12.15). The web is threaded through a series of rollers, guides, and tensioning devices. Uniform tension on the material is critical for smooth machine operation.

Packaging material from a preprinted supply roll is folded in half. Side and bottom seals are applied. A cutoff device separates the individual pouches which are transferred to clamps on a conveyor chain which, in turn, moves them past the stations for other operations. Just ahead of the filling position, the clamps are moved closer together, causing the pouch tops to open. Filling can be done in one or two steps. A two-step filling setup is illustrated in Figure 12.15. The first filler head utilizes rapid flow and the second filler “tops off” the filling operation. After filling has been completed, the clamps are pulled apart, causing the top of each pouch to close. The pouches are then heat sealed. In the final step, the pouches are picked off the conveyor chain and placed directly into a shipping container or onto a belt conveyor.

12.9.3 Tffs Equipment

Tffs equipment uses two films to make packages. In the most common arrangement, one plastic web is thermoformed into a tray and the other is heat sealed onto the tray to form the cover (Figure 12.16). The bottom material unrolls from the supply roll and passes initially into a section of the tffs machine equipped with heaters to soften the plastic web. As the material moves forward, it passes next into the forming section where a combination of pressure and vacuum pulls the plastic into

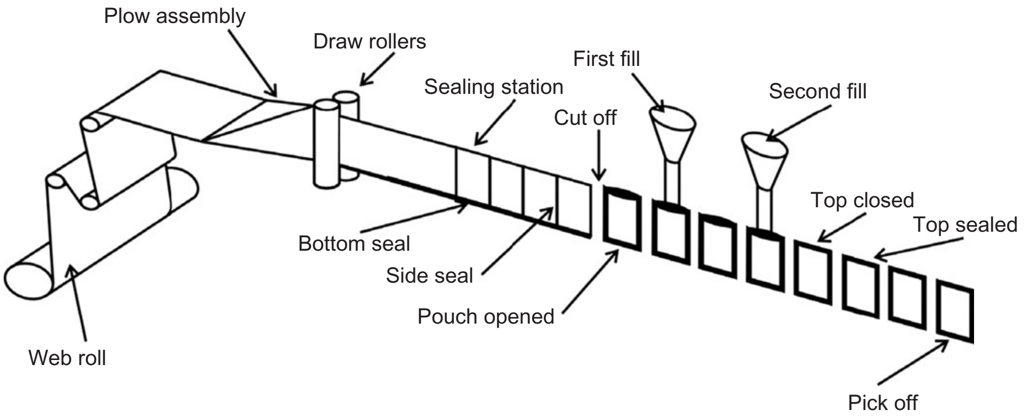

Figure 12.15 Operation of a hffs machine.

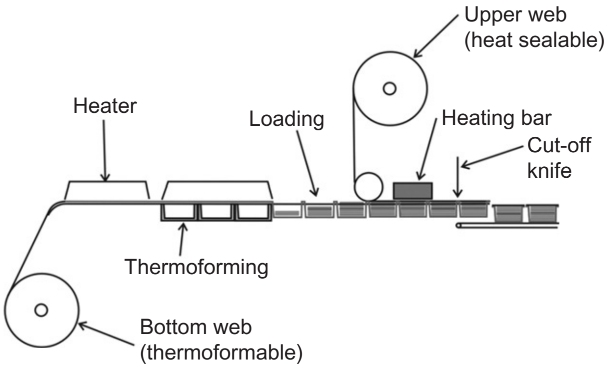

Figure 12.16 Operation of a tffs machine.

the shape of a tray to be used as the bottom of the package. The thermoformed plastic then moves into the loading section where the food product is placed into the tray cavities. The loading operation can be done by hand, by robots, or by various metering devices similar to the dry products and liquid products discussed previously. After the trays are loaded, the second plastic web (often transparent) is fed in from the top and heat sealed onto the edges of the trays.

The final operation is to cut the individual trays apart and send them on down the line for any further packaging steps.

Tffs machines are used to package sandwich meat, pasta products, cut meat, medical products, and many other products, even nails, bolts, saw blades, and other hardware. The machines are available in a variety of sizes, both in length and width. Such machines are used in food plants and in the meat departments of grocery stores. Depending on the kind of product, the filled packages can be shelf stable, refrigerated, or frozen.

12.10 Canning Machinery

Two types of cans are available: three-piece and two-piece. Cans are made by can manufacturers and delivered to the user's location in pallet load lots. The three-piece cans leave the can company with one can end attached to the sidewall of the can, forming what is essentially a deep cup. Two-piece cans are formed into a single-piece deep cup and leave the can company in that form. Cans are palletized in layers separated by sheets of corrugated board, heavy paperboard, plastic sheeting, or similar material.

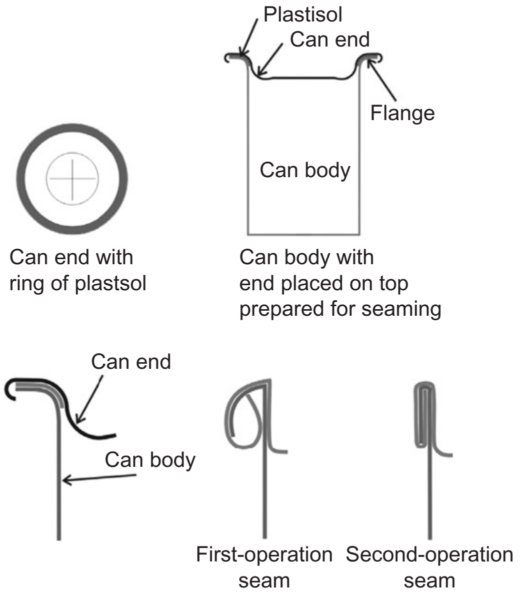

Figure 12.17 Can seaming.

At the food or beverage plant, the cans are taken off the pallets by depalletizing machines. They travel down a conveyor to the can washer and onto the filler. Except in very small systems, cans are filled by a rotary filler of the type discussed earlier. After the cans have been filled, the can end is placed on the top of the can cylinder. The projection of the can end and the flange on the can are then folded tightly together around the periphery, forming a tight seal (Figure 12.17) known as a double seam.

The folding and sealing operation, which attaches can ends and closes the cans, is done by a can seamer or can closer. When used at a can manufacturing plant, the machine is known as a double seamer. Can seamers can be used on metal cans, either two-piece or three-piece cans and on cans made of other materials, particularly plastic. The operation is essentially identical for all can types.

A double seam consists of a "first operation" which curls the outside of the can end around the can flange and a "second operation" which forms and irons out a tight hermetic seal between the can and the can end. Hermetic seals are secure against the entry of microorganisms and maintain the sterility of the food or beverage that has been packaged in the can.

There are two general types of seamers: head-spin and can-spin. On a head-spin seamer, the can

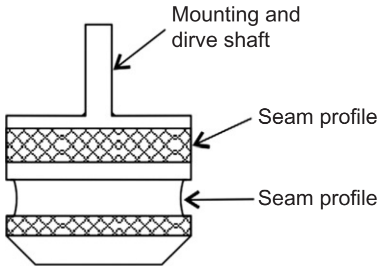

Figure 12.18 Roller for can seamer.

is held while the seaming head, which has first-operation and second-operation seaming rolls (Figure 12.18), rotates around the can and gradually forms the can end and the can flange into a tight seam. On a can-spin seamer, the can is rotated around its center axis. The seaming rolls, mounted on levers, are moved into position in a sequence to engage the can and form the seam. A variation of the can-spin process uses a seaming rail which has been machined to the desired final shape of the seam. The top of the rotating can is forced against the rail to form the seam.

Seamers used in the food industry can be semiautomatic or automatic. Semiautomatic seamers are motor-driven single station units used on low-speed lines and for making test packages in laboratories. Automatic seamers are single or multiple head machines used to close cans of vegetables, soups, beverages, and other food products, mostly for commercial trade. On food or beverage packaging lines, the can closing speed can range from as low as 100 cans per minute to as high as 2500 cans per minute.

Can seamers are designed for a particular can-diameter range, can height range, and speed range. Canning speed is expressed in cans per minute or hour. A seamer which is in service can be modified to run any can and end within the designated diameter and height range by fitting the proper can and end change parts.

12.11 Carton Filling and Closing Machinery

Cartons are paperboard containers that are manufactured by converters and then filled and closed in a food packaging plant. Cartons are made in a wide variety of sizes and shapes, and in numerous designs. Tube and tray-type cartons are made from single paperboard blanks that are scored, folded, and glued to form the carton. Cartons are economical. The material is inexpensive compared to other packaging materials. Cartons can be collapsed to take up minimal space in shipment to the user. A carton provides protection for a product, makes it easier to handle, supplies a surface that can be printed and attractively decorated to add sales appeal to the product, and makes it possible to market several items in a single package. Cartons can be creased and folded into shapes which are semirigid or rigid. However, while cartons are used as containers for many products, they are not generally rigid enough to be used as shipping containers.

Cartons are used to package candy, pasta, dry cereal, beans, and other dry products, as well as liquid products, such as milk and orange juice. In addition, several packages of other products can be packed into a carton. An example is a pizza kit in a carton which contains a paper pouch of a dry crust mixture, a second pouch containing powdered cheese, and a metal can of tomato sauce.

12.11.1 Carton Filling

The following brief description of the operation of a typical cartoner will demonstrate the features and capabilities required by users. There is a great variety of machines for setting up and closing cartons. Some are high speed and automatic and some are semiautomatic and of lower capacity. The most common is the horizontal cartoner for tuck end cartons (Figure 12.19).

The collapsed cartons are taken from the shipping container, loaded into the magazine on the cartoner, and held in place by spring pressure or a weight. A single carton is pulled off the front or bottom of the stack by a swinging or rotating arm with vacuum cups attached. The flat carton is then held in place by a pocket on a conveyor chain. At the same time, a pusher bar applies pressure to the trailing edge, forcing it to open and holding it against the front corner of the chain pocket. The combination of vacuum cups pulling and the pressure from the pusher bar holds the carton securely in position as it opens.

As the carton moves along with the chain, the product is pushed into the carton by hand, by pneumatic cylinder, or by a cam-operated mechanism that travels along next to the chain. Then, the

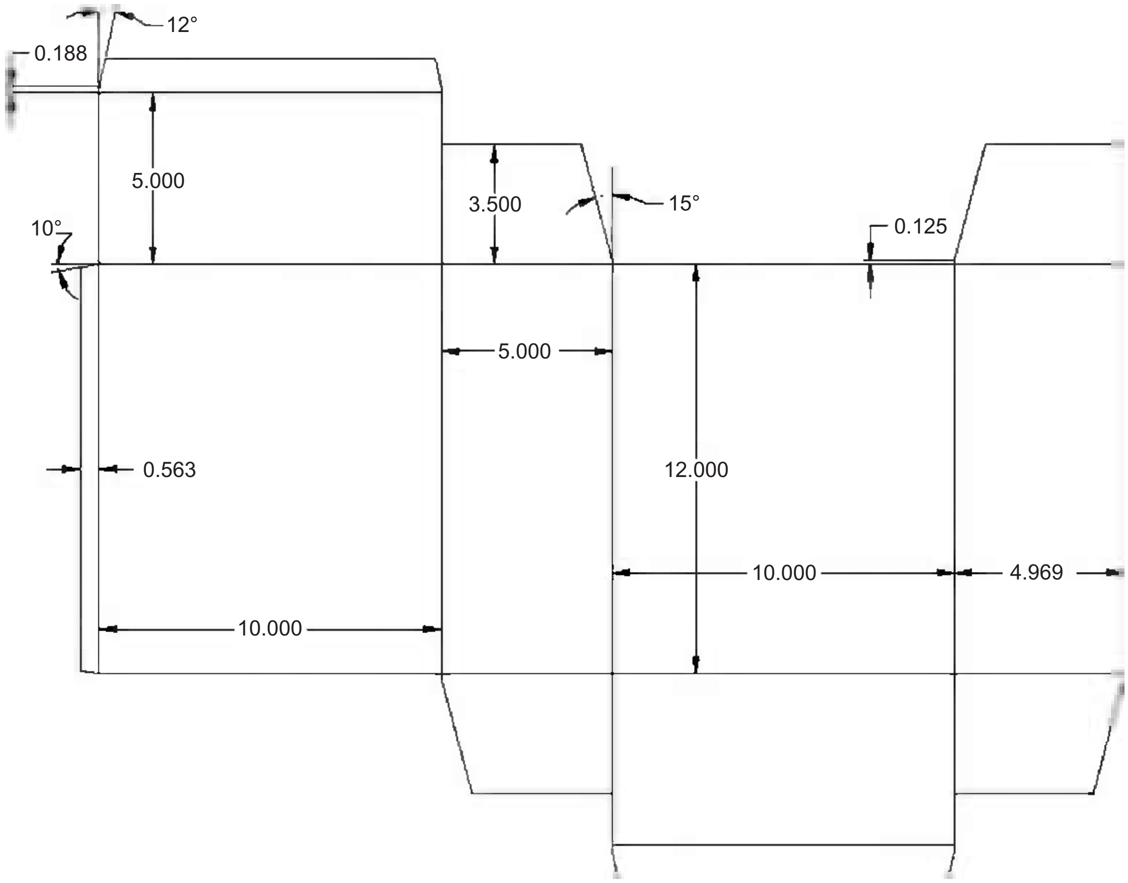

Figure 12.19 Reverse tuck carton.

carton is closed. The dust flaps on the leading edge are wiped into position by stationary bars as the carton moves along. Trailing flaps are folded forward by mechanical fingers that move faster than the carton travel speed. Then, the tucks are folded in by curved bars that bend the score lines and guide the tuck flaps into the proper slots.

Since cartons move rapidly into, through, and out of the cartoner, the carton design must be precise and the manufacturing must be workmanlike. If not, carton jams will occur.

Other factors that will influence the machinability of the cartons are the weather and storage conditions. In the winter, the air is cold and holds less moisture. As a result, the cartons are usually dryer, flatter, and easier to run. However, as the season progresses and the temperature rises, the air takes up more water. The cartons absorb moisture from the air and often take on a twisted or curved shape because the absorption is not uniform in all areas of the carton blank. The twists and curves make it more difficult for the cartoner to perform the folding and tucking actions involved in closing a carton. As a consequence, jams become more common. One solution is to store the unused cartons in an environmentally controlled space or at least give the stored cartons time to equalize moisture before attempting to run them on the machine.

12.12 Metal Detectors

Metal is a potential hazard in all types of food products. The hazard can be reduced greatly by using proper equipment and an effective program to manage the so-called “tramp metal”. Metal detection is also an issue in pet food systems, but this discussion will focus on human foods and beverages.

Metal in food can cause injury to people, pets, and other animals. It often leads to a loss of good will. Incidents of product contamination routinely receive attention from the media, both local and national. A contamination incident can damage a company's reputation. Metal in the food can cause damage to machinery. Finally, the contamination could lead to an expensive product recall.

The consequences are serious enough to warrant a carefully planned program to find and remove unwanted metal contamination, including the use of metal detection equipment. There are many sources of metal in a typical food plant. Broken machinery is an obvious source. Most food products are processed in metal equipment and packaged by metal equipment. Moving parts wear and eventually small pieces of metal fall from a machine. Some of the small pieces fall into the food product. Dropped tools are another source of metal as are items which fall from workers' clothes. Items that could cause contamination in this way include nuts and bolts, screws, nails, pens, rulers, etc. Jewelry worn by workers can fall off and get into the food. Examples include rings, watches, and earrings. And sometimes the contamination is not an accident. Systems may be sabotaged by individuals who wish to damage the company or make a legal claim for monetary damages.

The metal detection process that will be discussed is based on the magnetic induction process, the same process that is used to heat the caps in an induction cap sealing system and which makes most electric motors spin.

In simple terms, the metal detector produces an oscillating electromagnetic field. The food products and packages pass through the field. The presence of metal causes a disturbance in the field which can be detected and used to trigger an action to reject the contaminated product, whether or not it is in a package.

12.12.1 Typical Metal Detectors

A common type of metal detector (Figure 12.20) consists of a heavy metal case and a control unit. The case has an aperture (opening) large enough for a conveyor carrying packages and/or products to pass through. However, there are other arrangements that may be advantageous in certain circumstances. For example, a metal detector can be mounted around the filler tube on a vffs machine. It detects metal in the free-falling stream of product passing through the tube as the pouch is filled. A metal detector has three coils. The front and rear coils are connected to the same AC power supply, but the rear coil is the reverse of the front coil (Figure 12.20). The center, detector, coil is connected to the control unit. The front and rear coils produce alternating magnetic fields which are balanced and out of phase with each other. Each of the end coils induces a voltage in the middle coil. When the detector is empty, the voltages cancel each other out so that there is no output signal in the detector coil. This situation will remain unchanged as packages pass through the unit unless there is metal in the package.

When a piece of metal is moved through the aperture into the detector unit, the metal will interact with the front coil and cause a voltage to be induced in the piece of metal. This voltage, in turn, will cause a current to flow on the piece of metal. That current on the piece of metal causes an unbalanced condition on the middle (detector) coil which can be sensed and used to trigger an automatic rejection device.

Nonconducting objects can pass by the sensor without causing a disturbance of the balance on the sensor coil, but the metal detector will pick up both ferrous and nonferrous metals since the detection process depends on the electrical conducting properties of the metals.

For this reason, food packaged in aluminum trays, cups with aluminum foil covers, and similar

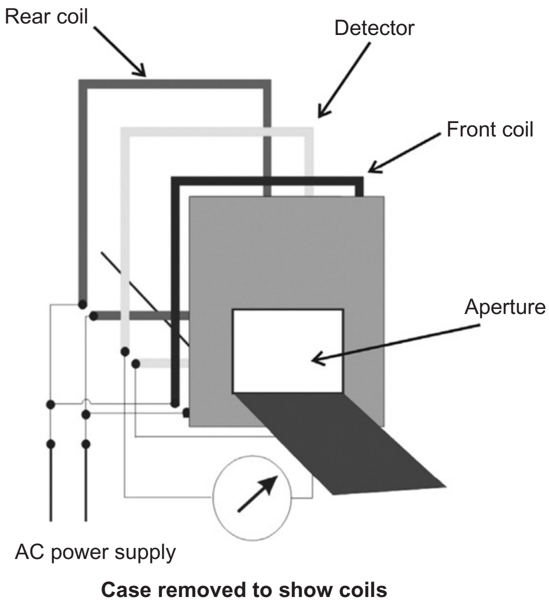

Figure 12.20 Metal detector.

packages cannot be inspected by a metal detector. There is an alternate design, using a static electromagnetic field that can be used on aluminum packages because it will only detect ferrous metals.

A metal detector, by itself, will not provide assurance that all metal has been detected and removed. For best results, the metal detector should be a part of a quality assurance program specifically designed for each product.

13 Compostable Polymer Properties and Packaging Applications

Ewa Rudnik
Scientific and Research Centre for Fire Protection – National Research Institute,
Józefów, Poland

13.1 Introduction

Compostable polymers have been designed to be disposed of after their useful life by means of organic recycling, that is, composting, and are one of the strategic options available for the management of plastic waste. Composting is an attractive alternative for reducing solid waste and is especially suitable for those segments of conventional plastics for which recycling is difficult or economically not feasible. Use of compostable polymers for packaging applications, especially in food packaging is still growing (Mahalik et al., 2010; Mensitieri et al., 2011; Siracusa et al., 2008).

Growing environmental awareness and new rules and regulations, as well as new trends in solid waste management have led scientists to increase their investigations into the design of compostable polymer materials that easily degrade under well-defined environmental conditions.

ASTM (ASTM D, 6400-04) and ISO (ISO, 17088) Standards define "compostable plastic" as: "a plastic that undergoes biological degradation during composting to yield carbon dioxide, water, inorganic compounds and biomass at a rate consistent with other known compostable materials and leaves no visually distinguishable or toxic residues."

The difference between biodegradable and compostable polymers lies in additional requirements related to the latter. Besides biodegradation into carbon dioxide, water, inorganic compounds, and biomass, compostable polymers must fulfill other criteria such as compatibility with the composting process, no negative effect on quality of compost, and a degradation rate consistent with other known composting materials.

It is noteworthy that compostable plastics are a priori designed for a given method of safe disposal, that is, composting. This means that after their useful life they will biodegrade in a composting process. The idea of compostable polymers is in agreement with life cycle thinking.

To summarize, the requirements a material must satisfy to be termed "compostable" include mineralization (i.e., biodegradation to carbon dioxide, water, and biomass), disintegration into a composting system, and completion of its biodegradation during the end-use of the compost, which, moreover, must meet relevant quality criteria, for example, no ecotoxicity. The satisfaction of requirements should be proved by standardized test methods.

Compostable polymers can be classified according to their source of origin or method of their preparation (Figure 13.1).

On the basis of origin, compostable polymers are derived from renewable or petrochemical resources.

The potential uses for biodegradable packaging materials include (Tharanathan, 2003):

1. use and throw, disposable packaging materials,
2. routine consumer goods for day-to-day use, such as plates, cups, containers, and egg boxes,
3. disposable personal care napkins/sanitary pads, diapers, etc.,
4. lamination coating,
5. bags for agricultural mulching (nursery).

The field of applications of compostable polymer in food-contact articles includes disposable cutlery, drinking cups, salad cups, plates, overwrap and lamination film, straws, stirrers, lids and cups, plates, and containers for food dispensed at delicatessen and fast-food establishments (Siracusa et al., 2008).

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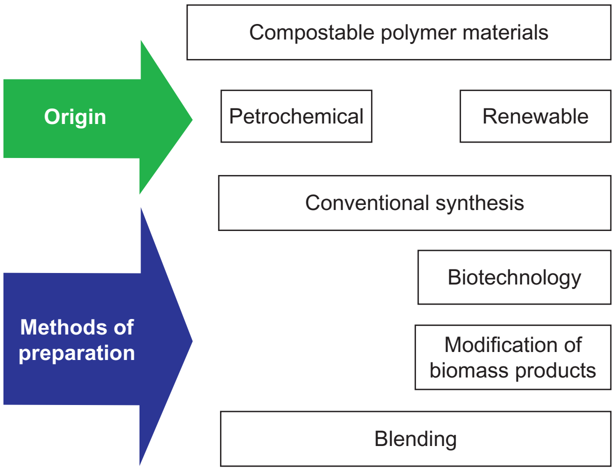

Figure 13.1 Classification of compostable polymers.

13.2 Biodegradable Polymers from Renewable Resources

13.2.1 Poly(lactic acid)

Properties

Poly(lactic acid) (PLA) exhibits a balance of performance properties that are comparable to those of traditional thermoplastics (Vink et al., 2004). PLA can be fabricated in a variety of familiar processes and brings a new combination of attributes to packaging, including stiffness, clarity, dead fold and twist retention, low-temperature heat sealability, as well as an interesting combination of barrier properties including flavor, aroma, and grease resistance (Table 13.1).

PLA polymers range from amorphous glassy polymers with a glass transition temperature of about 50–60°C to semicrystalline products with melting points ranging from 130°C to 180°C, depending on the sequence of enantiomeric repeating units (L and D) in the polymer backbone (Jamshidi et al., 1988).

Generally, commercial PLA grades are copolymers of poly(L-lactic acid) (PLLA) and poly(D,L-lactic acid) (PDLLA), which are produced from L-lactides and D,L-lactides, respectively (Martin and Avérous, 2001). The ratio of L- to D,L-enantiomers is known to affect the properties of PLA, such as melting temperature and degree of crystallinity. Enantiomerically pure PLA, poly(L-lactide) is a semicrystalline polymer with a glass transition temperature (T_g) of about 55°C and melting point (T_m) of about 180°C (Lunt, 1998; PROBIP, 2004; Södergård and Stolt, 2002). Introduction of stereochemical defects into poly(L-lactide) (i.e., mesolactide or D-lactide incorporation) reduces the melting point, rate of crystallization, and extent of crystallization of the resulting polymer but has little effect on glass transition temperature (Drumright et al., 2000). After roughly 15% incorporation of mesolactide, the result is no longer crystallizable. For example, introduction of mesolactide depresses the crystalline melting point to 130°C (Lunt, 1998).

The molecular weight, macromolecular structure, and the degree of crystallization of PLA vary substantially depending on the reaction conditions in the polymerization process (Gupta and Vimal Kumar, 2007).

Of the three possible isomeric forms, PLLA and poly(D-lactic acid) are both semicrystalline in nature, and poly(mesolactic acid) or PDLLA is amorphous. Racemic PLA—synthesized from petrochemicals—is atactic, that is, it exhibits no stereochemical regularity of structure, is highly amorphous, and has a low glass transition temperature. Amorphous grades of PLA are transparent (Table 13.1).

PLA has good mechanical properties, thermal plasticity and biocompatibility, is readily fabricated, and is thus a promising polymer for various end-use applications. From a physical property standpoint, it is often loosely compared to polystyrene (PS) (Drumright et al., 2000). Like PS, standard-grade PLA has high modulus and strength and is lacking in toughness. The toughness of PLA can be dramatically improved through orientation, blending, or copolymerization (Drumright et al., 2000).

PLA possesses high transparency and is an excellent material for packaging (Gupta and Vimal Kumar, 2007). PLA is an inherently polar material due to its basic repeated unit of lactic acid. This high polarity leads to a number of unique attributes such as high critical surface energy that yields excellent printability. Another benefit of this polar polyester polymer is its resistance to aliphatic molecules such as oils and terpenes (Gupta and Vimal Kumar, 2007; Hartmann and Whiteman, 2000). Apart from this, PLA possesses stiffness, clarity and twist retention, low-temperature heat sealability, as well as an excellent combination of barrier properties including flavor and aroma barrier characteristics. Possible application of PLA in liquid and juice packaging

Table 13.1 Properties of Some Commercially Available PLA

	Nature Works® PLA (PROBIP, 2004)	**Nature Works® PLA Resin General purpose (NatureWorks)**	**Biomer® L9000 (PROBIP, 2004)**	**Hycail HM 1011 (Hycail)**
Physical properties				
Melt-flow rate (MFR) (g/10 min)		10–30	3–6	2–4
Density (g/cm^3)	1.25	1.24	1.25	1.24
Haze	2.2			
Yellowness index	20–60			
Clarity		Transparent		
Mechanical properties				
Tensile strength at yield (MPa)	53	48	70	62
Elongation at yield (%)	10–100	2.5	2.4	3–5
Flexural modulus (MPa)		3828	3600	
Flexural strength (MPa)		83		
Notched Izod impact (J/m)		0.16		
Thermal properties				
HDT (°C)	40–45, 135			
Vicat softening point (°C)	Not determined[a]		56	
Glass transition temperature (°C)	55–65			60–63
Melting point (°C)	120–170[b]			150–175
Barrier properties[c]				
Transmission rate: oxygen (cm^3-mil/m^2/24 h atm)		550		
Transmission rate: carbon dioxide (cm^3-mil/m^2/24 h atm)		3000		
Transmission rate: water vapor (g-mil/m^2/24 h atm)		325		
Optical properties[c]				
Haze (%)		2.1		
Gloss, 20°		90		

[a] *Close to glass transition temperature.*

[b] *Amorphous and crystalline, respectively.*

[c] *NatureWorks® PLA Polymer 4042D (Technical Data Sheet); All properties measured on 1.0 mil film; O_2 and CO_2 at 23°C; 50% RH; H_2O at 38°C; 90% RH.*

was suggested based on permeability studies of a variety of polymers to D-limonene, a major component of orange juice flavor (Hartmann and Whiteman, 2000). Upon testing, no D-limonene could be detected passing through the PLA film.

An overview of polylactides as packaging materials, summarizing the main properties of PLA, was given by Auras et al. (2004). PLA films have better UV light barrier properties than low-density polyethylene (LDPE), but they are slightly worse than those of cellophane, PS and poly(ethylene terephthalate) (PET) (Auras et al., 2004). PLA films have mechanical properties comparable to those of PET and better than those of PS. The CO_2, O_2, and water permeability coefficients of PLA are lower than those of PS and higher than those of PET.

Processing

PLA resin can be tailor-made for different fabrication processes, including injection molding, sheet extrusion, blow molding, thermoforming, film forming, or fiber spinning (Drumright et al., 2000). The key is controlling certain molecular parameters in the process, such as branching, D-isomer content, and molecular weight distribution. Injection molding of heat-resistant PLA products requires rapid crystallization rates, which can be achieved by using PLA that contains less than 1% D-isomer and often by the addition of nucleating agents (Drumright et al., 2000). Extrusion-thermoforming is optimized at a D-isomer content that does not allow crystallization to occur during the melt processing steps, with 4–8% D-isomer content being the effective range.

The recommended process temperature for Hycail PLA is 190–240°C (Hartmann and Whiteman, 2000).

The processing temperature profile of Nature Works PLA 3001 D-polymer, designed for injection-molding applications, comprises melt temperature 200°C, feed throat 25°C, feed temperature (crystalline pellets) 165°C, feed temperature (amorphous pellets) 150°C, compression section 195°C, metering section 205°C, nozzle 205°C, and mold 25°C (Gupta and Vimal Kumar, 2007). For extrusion grades the processing temperature profile ranges from 180°C to 210°C.

Applications

PLA products are finding uses in many applications, including packaging, paper coating, fibers, films, and a host of molded articles.

The first products were aimed at packaging film and fibers for textiles and nonwovens. For packaging, clear films with good barrier properties but low heat-seal properties can be produced. For fibers it could mean apparel with better drape and moisture management and industrial clothing with better UV resistance, reduced flammability, and good resistance to soiling and staining (Additives for Polymers, 2000). Cargill Dow's PLA has been designated as a new generic fiber type by the US Federal Trade Commission. PLA now joins other classifications including cotton, wool, silk, nylon, and polyesters as a recognized fiber category. Examples of main applications of PLA are given in Table 13.2.

Business segment opportunities and examples of commercially available products are listed below (Vink et al., 2004).

1. Rigid thermoforms (clear fresh fruits and vegetable clamshells, deli meat trays, opaque dairy (yogurt) containers, bakery, fresh herb and candy containers, consumer displays and electronics packaging, disposable articles, and cold drink cups),
2. Biaxially oriented films (candy twist and flow wrap, envelope and display carton windows, lamination films, product (gift basket) overwrap, lidding stock, die cut labels, floral wrap, tapes, shrink sleeves, stand-up pouches, cake mix, cereal, and bread bags),
3. Bottles (short shelf-life milk, edible oils, and bottled water).

In addition to traditional food packaging applications, several companies are exploring nonfood packaging applications for PLA, including (Vink et al., 2004):

- Mitsui-Chemical telephone cards,
- Sanyo compact disk,
- Matsushita (Panasonic) battery packaging,
- Fujitsu PC body components.

13.2.2 Polyhydroxyalkanoates

Properties

The family of polyhydroxyalkanoates (PHAs) exhibits a wide variety of mechanical properties from hard crystalline to elastic, depending on the

Table 13.2 Main Applications for PLA

Sector	Examples
Packaging	Food packaging, films, rigid thermoformed food, and beverage containers, carrier bags and labels, coated papers and boards, battery packaging, windows for envelopes
Agriculture	Sheet or molded forms for time-release fertilizers, plant clips
Transportation	Parts of automobile interiors (head liners, upholstery, spare tire covers)
Electric appliances and electronics	CD, computer keys, cases for Walkmans, wrappers for CDs
Houseware	Carpets
Other (fibers and fabrics)	Textiles and nonwovens

composition of monomer units (Khanna and Srivastava, 2005). Solid-state poly(3-hydroxybutyrate) (P(3HB)) is a compact, right-handed helix with a two-fold screw axis (i.e., two monomer units complete one turn of the helix) and a fiber repeat of 0.596 nm (Braunegg et al., 1998). The stereoregularity of P(3HB) makes it a highly crystalline material. Its melting point is around 177°C, close to that of polypropylene (PP), with which it shares other similar properties, although the biopolymer is stiffer and more brittle.

The densities of crystalline and amorphous PHB are 1.26 and 1.18 g/cm^3, respectively (Khanna and Srivastava, 2005).

P(3HB) is water insoluble and relatively resistant to hydrolytic degradation. This differentiates P(3HB) from most other currently available bio-based plastics which are either moisture or water soluble. Mechanical properties like Young's modulus and tensile strength of PHB are close to that of PP though extension to break is markedly lower than that of PP (Table 13.3) (Khanna and Srivastava, 2005; Lee, 1996). However, due to the high stereoregularity of biologically produced macromolecules, PHB is a highly crystalline polymer that is stiff and brittle. It is also thermally unstable during processing (Padermshoke et al., 2005). The molecular weight of PHB degrades significantly at temperatures just above the T_m. This unfortunate aspect poses a limitation of, for example, the application to a flexible film, which is one of the largest uses of biodegradable polymers. As a consequence, many attempts to copolymerize a different comonomer with PHB monomer to improve its mechanical properties have been made. One idea is to include a more bulky comonomer to reduce the crystallinity and presumably increase the flexibility of the resulting copolymer. The copolymerization with 3-hydroxyvalerate (3HV) was the first attempt performed by ICI (Imperial Chemical Industries) in the early 1980s. However, the crystallinity of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (P(3HB-*co*-HV)) never falls below 50% due to the isodimorphism of the P(HB-*co*-HV) copolymer. It has been reported that poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (P(HB-*co*-HHx)) shows a greater T_m, at a given mol% comonomer, in comparison to P(HB-*co*-HV). Interestingly, hexanoate and larger comonomers depress T_m in the same manner regardless of their molecular sizes. This feature indicates the breakdown of the isodimorphism occurring in the P(HB-*co*-HV) copolymer by the incorporation of comonomer units with three or more carbon units (Padermshoke et al., 2005).

Incorporation of other hydroxy acid units to form PHA copolymers can improve properties such as crystallinity, melting point, stiffness, and toughness (Khanna and Srivastava, 2005). As the fraction of 3HV increases, the copolymer becomes tougher (increase in impact strength) and more flexible (decrease in Young's modulus). The increase in melting temperature with increasing 3HV fraction without affecting degradation temperature allows thermal processing of copolymer melts without thermal degradation. The melting temperature (T_m) of P(3HB) homopolymer was 178°C, and the copolymer P(3HB-*co*-3HV) with a 95 mol% of 3HV was 108°C (Kunioka et al., 1989). A minimum value (around 75°C) of melting temperature was observed at approximately 40 mol% 3HV, where

Table 13.3 Comparison of Mechanical Properties of PHAs and PP (Khanna and Srivastava, 2005; Lee, 1996)

Polymer	Copolymer Content	Melting Temperature (°C)	Young's Modulus (GPa)	Tensile Strength (MPa)	Elongation at Break (%)
PP	–	170	1.7	34.5	400
P(3HB)	–	179	3.5	40	5
P(3HB-*co*-3HV)	3 mol% 3HV	170	2.9	38	–
P(3HB-*co*-3HV)	9 mol% 3HV	162	1.9	37	–
P(3HB-*co*-3HV)	14 mol% 3HV	150	1.5	35	–
P(3HB-*co*-3HV)	20 mol% 3HV	145	1.2	32	–
P(3HB-*co*-3HV)	25 mol% 3HV	137	0.7	30	–
P(3HB-*co*-4HB)	3 mol% 4HB	166	–	28	45
P(3HB-*co*-4HB)	10 mol% 4HB	159	–	24	242
P(3HB-*co*-4HB)	16 mol% 4HB	–	–	26	444
P(3HB-*co*-4HB)	64 mol% 4HB	50	30	17	591
P(3HB-*co*-4HB)	90 mol% 4HB	50	100	65	1080
P(4HB)	–	53	149	104	1000
P(3HHx-*co*-3HO)		61	–	10	300
P(3HB-*co*-6 mol% 3HA)		133	0.2	17	680
P(3HB-*co*-3HHx)		52	–	20	850

the crystal lattice transition took place. For copolymers poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate)s (P(3HB-*co*-4HB)), the T_m value decreases from 178°C to 150°C as the 4HB content increases from 0 to 18 mol%, then is almost constant in the composition range from 18 to 49 mol% 4HB.

PHAs made of longer monomers, such as medium chain length mcl-PHAs, that is, with $C_6 - C_{14}$ monomers, are typically elastomeric, sticky materials, which can also be modified to make rubbers (Suriyamongkol et al., 2007). PHA copolymers composed of primarily HB with a fraction of longer chain monomers, such as HV, HH or HO, are more flexible and tougher plastics.

The copolymer P(3HB-*co*-3HV) has lower crystallinity and improved mechanical properties (decreased stiffness and brittleness, increased tensile strength and toughness) compared to P(3HB), while still being readily biodegradable. It also has a higher melt viscosity, which is a desirable property for extrusion blowing (PROBIP, 2004). Copolymers polyhydroxybutyrate-*co*-valerate (PHBV) and Poly

Table 13.4 Properties of P(HB-*co*-HHx)s (Narasimhan, 2004)

% C6 (hexanoate)	Melting Point, T_m (°C)		Applications
0 (PHB)	180	Hard, brittle, crystalline	
4	150	Hard, some elasticity	Molded articles
6	145	Hard, elastic, flexible	Fibers
10	125	Soft, elastic, flexible	Films
18	95	Soft, rubbery	Coatings

(3-hydroxybutyrate-*co*-3-hydroxyhexanoate)s have a range of properties depending on composition (Table 13.4).

P(HB-*co*-HHx) combines the thermomechanical properties of PE (strength, flexibility, ductility, toughness, and elasticity) with the physicochemical properties (compatibility) of polyesters (printability, dyeability, and barrier performance). It forms blends with PLA and thermoplastic starch (TPS).

The oxygen permeability of commercial PHA was investigated and compared to oil-based polymers conventionally used in the food packaging domain (Corre et al., 2012). PHAs show intermediate to high oxygen barrier properties depending on the considered grade and compared to PA6 MXD6 which has very high oxygen barrier properties and PS 1560 which presents low ones.

Properties of some commercial PHAs are given in Table 13.5.

The possibility for using PHB or P(3HB) in food packaging was investigated (Bucci et al., 2005). It was found that PHB can be used in injection-molding processes for the manufacture of packaging for food products with the same equipment used for PP package injection. However, the process conditions must be adjusted to the characteristics of the polymer and a specific mold must be used.

The performance of the PHB packaging (500 ml packaging (jar-cap set)) was evaluated through physical tests (visual analysis and light transmission), comparing it with PP packaging, migration tests of packaging components, and biodegradation assays (Bucci et al., 2007). The evaluated PHB was shown to be promising for use in food packaging, since it acts as a good barrier to light incidence in the UV range. In relation to the migration of components, pigmented PHB packaging can be recommended for different foods under conservation conditions in the long and short terms.

Processing

Homopolymer P(3HB) has good thermoplastic properties (melting point 180°C) and can be processed as classic thermoplast and melt-spun into fibers. It has a wide in-use temperature range (articles retain their original shape) from −30°C to 120°C. Articles made of P(3HB) can be autoclaved. However, it is fairly stiff and brittle, and it has somewhat limited applications. PHB has a small tendency to creep and exhibits shrinkage of 1.3%.

A comparison of injection-molding conditions between homopolymer PHB and PP is given in Table 13.6 (Rabetafika et al., 2006).

PHBV is thermoplastic and can be processed by injection molding, extrusion, blow molding, film and fiber forming, and lamination techniques.

The Nodax family of PHAs is suitable for different conversion processes, including injection molding, cast film, cast sheet for thermoforming, melt-extruded paper, and board coatings (www.nodax.com/).

Applications

Cups based on polylactate (PLA) and PHB were found to be as effective as high-density polyethylene (HDPE) cups in protecting an orange juice simulant and a dressing from quality changes during storage (Haugaard et al., 2003). The orange juice simulant and the dressing were stored in PLA, PHB, and HDPE for 10 weeks at 4°C under fluorescent light or in darkness. The suitability of PLA and PHB compared to HDPE was investigated by determination of color changes and loss of ascorbic acid of the juice simulant, and by determination of color changes, primary (peroxide value) and secondary lipid oxidation (volatiles determined by static headspace) products and reduction of α-tocopherols of the dressing.

Table 13.5 Properties of Commercial PHAs (PROBIP, 2004)

	P(3HB) Biomer P240	**P(3HB) Biomer P226**	**P(3HB-*co*-3HV) Biopol**	**P(3HB-*co*-3HHx) Kaneka, Nodax**
Physical properties				
MFR (g/10 min)	5–7	9–13		0.1–100
Density (g/cm^3)	1.17	1.25	1.23–1.26	1.07–1.25
Transparency (%)			0.7	White powder/ translucent film
Mechanical properties				
Tensile strength at yield (MPa)	18–20	24–27		10–20
Elongation at yield (%)	10–17	6–9		10–25
Flexural modulus (MPa)	1000–1200	1700–2000	40	Several orders of magnitude
Thermal properties				
HDT (°C)	–	–		60–100
Vicat softening point (°C)	53	96		60–120

Table 13.6 Injection Molding Conditions of PHB and PP (Rabetafika et al., 2006)

Parameters	**PHB**	**PP**
Melt temperature (°C)	160	180
Hopper temperature (°C)	25	25
Fill temperature (°C)	130	230
Clamp zone (°C)	140	250
Mixture zone (°C)	150	250
Nozzle (°C)	160	250
Mold (°C)	10–15	10–15

Initially, PHAs were used in packaging films mainly in bags, containers, and paper coatings (Khanna and Srivastava, 2005; Lee, 1996; Reddy et al., 2003). Similar applications in conventional commodity plastics include disposable items such as razors, utensils, nappies, feminine hygiene products, cosmetic containers, shampoo bottles, and cups (Kunioka et al., 1989). P(3HB-*co*-3HHx) (Nodax) has applications in flushable materials (e.g., feminine hygiene products), coatings, synthetic papers, heat-formed products, binding materials, and films. Markets for the Nodax family of PHAs (www.nodax.com/) include:

- Packaging
- Single use and disposable items
- Housewares
- Appliances
- Electrical and electronics

Table 13.7 Glass Transition Temperatures of TPS Using Different Plastification Levels (Avérous and Fringant, 2001)

% Starch	Plasticizer Level (wt%)	Glycerol Content (wt%)	Water Content (wt%)	Glass Transition (°C)
74	26	10	16	43
70	30	18	12	8
67	33	24	9	−7
65	35	35	0	−20

- Consumer durables
- Agriculture and soil stabilization
- Adhesive and soil stabilization
- Adhesives, paints, and coatings
- Automotive

13.2.3 Thermoplastic Starch

Properties

The glass transition temperature (T_g) of dry amorphous starch is experimentally inaccessible owing to the thermal degradation of starch polymers at elevated temperatures (Poutanen and Forsell, 1996). It is estimated that the T_g of the dry starch is in the range of 240−250°C (Poutanen and Forsell, 1996). Native starch is a nonplasticized material because of the intra- and intermolecular hydrogen bonds between hydroxyl groups of starch molecules. During the thermoplastic process, in the presence of a plasticizer, a semicrystalline granule of starch is transformed into a homogeneous material with hydrogen-bond cleavage between starch molecules, leading to loss of crystallinity.

The physical properties of the TPS are greatly influenced by the amount of plasticizer present. In most literature covering TPS, polyols were usually used as plasticizers, of which glycerol is the most common. The effect of plastification level on glass transition of TPS is presented in Table 13.7.

According to the plasticizer/starch, TPS presents a large range of properties. A number of studies on the effects of plasticizers on the properties of TPS have been carried out. Plasticizers used include polyols such as glycerol, glycol, xylitol, sorbitol, and sugars, and ethanolamine (Avérous and Fringant, 2001; Da Roz et al., 2006; De Graaf et al., 2003; Forsell et al., 1997; Huang et al., 2005; Rodriguez-Gonzalez et al., 2004; Van Soest et al., 1996a,b,c). Plasticizers containing amide groups such as urea, formamide, and acetamide or a mixture of plasticizers have been also studied (Ma and Yu, 2004; Ma et al., 2005, 2006; Shogren et al., 1992; Thunwall et al., 2006).

The mechanical properties of a low- and a high-molecular mass TPS were monitored at water contents in the range of 5−30% (w/w). The stress-strain properties of the materials were dependent on the water content. Materials containing less than 9% water were glassy with an elastic modulus between 400 and 1000 MPa (Avérous and Fringant, 2001). Different starch sources were extruded with the plasticizer glycerol, and glass transition temperatures and mechanical properties were evaluated (Avérous and Fringant, 2001). Above certain glycerol contents, dependent on the starch source, a lower glass transition temperature T_g resulted in decreased modulus and tensile strengths and increased elongations. For pea, wheat, potato, and waxy maize starch, the T_g was 75°C,143°C, 152°C, and 158°C, respectively. Properties of potato and wheat and TPS are given in Table 13.8.

The effect of the type and amount of plasticizer on the mechanical, thermal, and water-absorption properties of melt-processed starch was investigated (Huang et al., 2005). It was reported that, in general, monohydroxyl alcohols and high-molecular weight glycols failed to plasticize starch, whereas shorter glycols were effective.

The mechanical properties of starch-based plastics of native corn, potato, waxy corn, and wheat starch, produced by compression molding of native starch and glycerol in the weight ratio 0−3, were strongly dependent on the water content and starch source (Yang et al., 2006).

The mechanical and melt-flow properties of two thermoplastic potato starch materials with different

Table 13.8 Properties of TPSs

	Potato TPS (Hulleman et al., 1998)	**Wheat TPS (Avérous, 2004)[a]**
MFR (g/10 min)		
Density (g/cm^3)		1.34–1.39
Transparency (%)		
Mechanical properties		
Tensile strength at yield (MPa)	22	1.4–21.4
Elongation at yield (%)	3	3–104
Tensile modulus (MPa)	1020	11–1144
Thermal properties		
Glass transition temperature (°C)		(−)20–43
α-transition (DMTA) (°C)		1–63

[a] *Properties after equilibrium at 23°C and 50%, 6 weeks; glycerol to starch ratio: 0.135–0.538; water content: 9–13 wt%.*

amylose contents were evaluated (Da Roz et al., 2006). After conditioning at 53% relative humidity (RH) and 23°C, the glycerol-plasticized sheets with a high amylose content (HAP) were stronger and stiffer than the normal TPS with an amylose content typical for common potato starch. The tensile modulus at 53% RH was about 160 MPa for the HAP and about 120 MPa for the plasticized native potato starch (NPS). The strain at break was about 50% for both materials.

Processing

Various industrial processing techniques have been used to prepare starch plastics, including kneading, extrusion, compression molding, and injection molding (Van Soest and Kortleve, 1999). Processing temperatures are in the range of 100–200°C, although care has to be taken at temperatures above 175°C because of starch molecular breakdown (Van Soest, 1997; Van Soest and Kortleve, 1999; Van Soest and Vliegenthart, 1997). Most research has been focused on water and glycerol as the most important additives. As melt-flow accelerators lectin, glycerin monostearate, and calcium stearate have been studied. Several native starches have been processed, such as wheat, rice, corn, waxy maize starch, high amylose corn starch, and NPS (Van Soest and Kortleve, 1999). The dimensions of molded objects from hydrophilic polymers such as starch depend on their water content (Stepto, 2006). If precise dimensions are required, processing should be carried out so that products are formed at approximately the equilibrium in-use water content. For potato starch, for example, this means water contents of around 14% for use under ambient conditions (50% RH, 20–25°C) (Stepto, 2006). If higher water contents are used in processing, distortion and shrinkage will occur as the equilibrium water content is naturally achieved after processing. In addition, higher water content can induce more hydrolytic degradation of the starch chains during processing and also gelatinization rather than melt formation. If lower water contents are used, thermal degradation can occur during processing, as well as swelling after processing.

Applications

The first commercial product made of injection-molded TPS was the drug-delivery capsule Capill, and further products are gradually appearing, for example, golf tees, cutlery, plates, and food containers (Stepto, 2006). In addition, extrusion has been applied to produce rigid foams, suitable for loose-fill packaging. Starch can be transformed into a foamed materials using water steam, replacing the PS foam as packaging material (Siracusa et al., 2008). Packaging is the dominant application area for starch-based polymers (PROBIP, 2004). Main application areas include:

- foams (for the loose-fill foam market),
- films (for agriculture, e.g., mulch films),
- shopping bags,
- moldable products (pots, cutlery, fast-food packaging).

13.2.4 Other Compostable Polymers from Renewable Resources

Cellulose

Properties

Cellulose esters, besides cellulose esters of inorganic esters and cellulose ethers, were pioneer compounds of cellulose chemistry, and they remain the most important technical derivatives of cellulose (Klemm et al., 2005). Unlike commodity plastics such as polyolefins, cellulose cannot be processed thermoplastically. However, derivatization, that is, esterification, can yield materials suited for thermoplastic processing. Cellulose esters, such as cellulose acetate (CA), cellulose acetate propionate (CAP), and cellulose acetate butyrate (CAB), are thermoplastic materials produced through the esterification of cellulose (Mohanty et al., 2003). A variety of raw materials such as cotton, recycled paper, wood cellulose, and sugarcane are used in making cellulose ester biopolymers in powder form. Such powders combined with plasticizers and additives are extruded to produce various grades of commercial cellulosic plastics in pelletized form. Of great interest as potential biodegradable plastics are also long-chain aliphatic acid esters of cellulose (Edgar et al., 2001; Joly et al., 2005).

Cellulose esters are characterized by their stiffness, moderate heat resistance, high moisture vapor transmission, grease resistance, clarity and appearance, and moderate impact resistance (Edgar et al., 2001).

Some properties of commercial cellulose esters are given in Table 13.9.

Processing

Cellulose esters are easy materials to extrude and injection mold (Edgar et al., 2001). Some of their innate properties include a relatively narrow window between the melt-flow temperature and the decomposition temperature. Therefore, in most commercial applications, plasticizers are used in conjunction with cellulose esters. Triethyl citrate is usually used for CA and dioctyl adipate for CAP.

Through plasticization of CA by an environmentally friendly triethyl citrate plasticizer, the CAs are processable at 170–180°C, much below the melting point of CA (233°C) (Mohanty et al., 2003). Materials processed by extrusion followed by injection molding exhibited better properties compared to those processed by extrusion followed by compression molding, as additional shear forces applied during injection molding resulted in a stiffer product. Cellulosic plastics fabricated through injection molding at a higher temperature (190°C) exhibited better tensile properties than their counterparts injected molded at a comparatively lower temperature (180°C) (Mohanty et al., 2003).

Applications

Materials such as metal, plastic, wood, paper, and leather are coated with polymers primarily for protection and for improving their properties. For this purpose, CA, CAP, and CAB are the most important classical and solvent-based cellulose esters of the coating industry (Klemm et al., 2005). Cellulose esters are widely used in composites and laminates as binder, filler, and laminate layers. In combination with natural fibers, they can be used to some extent as composites from sustainable raw materials with good biodegradability. An additional domain of cellulose esters is their use in controlled-release systems, as well as membranes and other separation media (Edgar et al., 2001; Klemm et al., 2005). In the field of controlled-release systems, cellulose esters are used as enteric coatings, hydrophobic matrices, and semipermeable membranes for applications in pharmacy, agriculture, and cosmetics.

CA is widely used in food packaging (baked goods and fresh produce; Weber, 2000). CA possesses relatively low gas and moisture barrier properties and has to be plasticized for film production.

Other applications of cellulose esters include:

- thin films,
- containers,
- handles,
- optical applications,
- automotive applications,

Table 13.9 Properties of Cellulose Esters (www.ides.com/)

	CAP Albis CAP CP800 (10% Plasticizer)	**CAB Albis CAB B900 (10% Plasticizer)**
Physical properties		
MFR (g/10 min)		
Density (g/cm^3)	1.21	1.19
Water absorption at 24 h	1.6	1.4
Mechanical properties		
Tensile strength at yield (MPa)	31.7	28.3
Elongation at break (%)	30	30
Flexural modulus (MPa)	1240	1170
Flexural strength (MPa)	41.4	37.2
Thermal properties		
HDT (°C)		
Vicat softening point (°C)	102	104
GTT (°C)		
Melting point (°C)		

- toys,
- writing instruments,
- electric insulation films, lights, and casings.

Chitosan

Properties

Chitin and chitosan are examples of highly basic polysaccharides. Chitin is highly hydrophobic and is insoluble in water and most organic solvents. It is a hard, white, inelastic, nitrogenous polysaccharide (www.ides.com/). An important parameter, which influences its physicochemical and biomedical characteristics, is the degree of N-acetylation, especially in chitosan. Converting chitin into chitosan lowers the molecular weight, changes the degree of N-acetylation, and thereby alters the net charge distribution, which in turn influences the degree of agglomeration (Srinivasa and Tharanathan, 2007). The average molecular weight of chitin is $1.03-2.5 \times 10^6$ Da, but upon N-deacetylation, this reduces to $1.0-5 \times 10^5$ Da. Chitosan is soluble in dilute acids such as acetic acid and formic acid. Chitosan has many useful characteristics such as hydrophilicity, biocompatibility, biodegradability, and antibacterial characteristics (Di Martino et al., 2005; Srinivasa and Tharanathan, 2007; www.ides.com/). Chitin and chitosan degrade before melting, which is typical of polysaccharides with extensive hydrogen bonding (www.ides.com/).

Chitosan can form transparent films, which may find application in a variety of packaging applications (Kumar, 2000; www.ides.com/). In 1936, Rigby was granted a patent for making film from chitosan and a second patent on making fibers from chitosan (www.ides.com/). The films were described as flexible, tough, transparent, and colorless with a tensile strength of about 6210 kPa.

Plasticizing agents are essential generally to overcome the brittleness of the biopolymeric films. Chitosan films were prepared by blending with polyols (glycerol, sorbitol, and polyethylene glycol (PEG)) and fatty acids (stearic and palmitic acids), and their mechanical and barrier properties were studied (Kumar, 2000). The tensile strength of the blended films decreased with the addition of polyols and fatty acids, whereas the percent elongation was increased in polyol blend film, but fatty acid blend films showed no significant differences. Glycerol blend film showed a decrease, whereas sorbitol and PEG blend film showed an increase in water vapor permeability values.

The effect on the quality of mango fruits (*Mangifera indica*) during modified atmosphere packaging was investigated (Srinivasa et al., 2002). The fruits were kept in carton boxes whose top surface was covered with either chitosan film or with LDPE (positive control) or kept as such (control) and stored at room temperature (27 ± 1°C at 65% RH). The CO_2 and O_2 levels measured on day 3 were 23–26% and 3–6%, and at the end of the storage period they were 19–21% and 5–6%, respectively. The fruits stored as such had a shelf life of 9 ± 1 days, whereas those stored in LDPE showed off-flavor due to fermentation and fungal growth on the stalk and around the fruits, and they were partially spoiled. On the other hand, fruits stored in chitosan-covered boxes showed an extension of shelf life of up to 18 days and without any microbial growth or off-flavor.

The antimicrobial activity of chitosan and its derivatives against different groups of microorganisms such as bacteria, yeast, and fungi are used in food packaging applications (Honarkar and Barikani, 2009).

Processing

Chitosan possesses an excellent ability to form porous structures (Di Martino et al., 2005). It can be molded in various forms as porous membranes, blocks, tubes, and beads. Chitosan also readily forms films and produces material with very high gas barrier. Chitosan films are prepared by dissolving chitosan in dilute acid and spreading on a leveled surface and air-drying at room temperature (Srinivasa and Tharanathan, 2007). Films are also prepared by drying at 60°C in an oven by spreading the solution on plexiglass.

Applications

Chitosan has prospective applications in many fields such as biomedicine, waste water treatment, functional membranes, and flocculation (Kurita, 2001; Rinaudo, 2006; Srinivasa and Tharanathan, 2007). Chitosan has been used in the purification of drinking water and in cosmetics and personal care products. They have excellent biological properties such as biodegradation in the human body, biocompatibility, and immunological, antibacterial, and wound-healing activities and also a variety of medical uses such as wound dressings, drug delivery, and encapsulation (Kurita, 2001). Chitosan has found a potential application as a support material for gene delivery, cell culture, and tissue engineering. It is also known as an adsorptive material, for example, sorbent for heavy metal ions. It has been used for the production of edible coatings. Chitosan films were used in extending the shelf life of vegetables (Srinivasa and Tharanathan, 2007).

Proteins

Properties

Until recently, the only uses and applications for proteins were in food sciences (Swain et al., 2004). The development of studies on nonfood uses of agricultural raw materials initiated an interest in protein-based plastics. A number of proteins of plant origin have received attention for the production of biodegradable polymers. These proteins are corn zein, wheat gluten, soy protein, and sunflower protein.

The major drawback of protein-based plastics, apart from keratin, is their sensitivity to RH. For example, it was reported that after being submerged in water for 20 h, soy protein sheets absorbed up to 180% water (Zheng et al., 2003).

Soy protein plastics are rigid, but tend to be brittle and water sensitive (Mo and Sun, 2003; Zheng et al., 2003). The water resistance of soybean protein-based plastics can be improved by chemical modification or blending, for example, with polyesters (Mo and Sun, 2003). The flexibility of soybean protein-based plastics can be improved by adding various plasticizers (Mo and Sun, 2003; Zheng et al., 2003). It was reported that depending on the moisture and glycerol contents, soy protein plastic sheets displayed properties from rigid to soft (Zheng et al., 2003). The glass transition temperature of the sheets varied from approximately −7°C to 50°C with moisture contents ranging from 26% to 2.8% and 30 parts of glycerol.

Among proteins, wheat gluten with its unique viscoelastic properties and its water insolubility is of particular interest for the preparation of biodegradable polymer materials. To control the brittleness of protein-based materials and to lower their shaping temperature, the addition of plasticizer is generally required (Pommet et al., 2005). Water and glycerol are common plasticizers of wheat gluten. Other compounds including polyols, sugars, ethylene glycol and its derivatives, lipids, and emulsifiers have been tested as gluten plasticizers. Various compounds, differing in their chemical functions, number of functional group and degree of hydrophobicity, including water, glycerol, 1,4-butanediol, lactic and octanoic acids, have been tested as wheat gluten plasticizers in a thermoplastic process (Pommet et al., 2005).

The glass transition temperature (Tg) of hydrophobized and native wheat gluten and its protein fractions, with water mass fraction from 0 to 0.2, was studied using modulated differential scanning calorimetry (DSC) (Mo and Sun, 2003). The T_g values of unplasticized products were approximately 175°C whatever the treatment (hydrophobization) or the fraction tested, except for the gliadin-rich fraction (162°C) (Micard and Guilbert, 2000). Thermal properties of corn gluten meal and its proteic components were investigated by Di Gioia et al. (1999) (Table 13.10).

Processing and modification routes to produce and improve properties of biodegradable plastics from soy isolate have been studied (Vaz et al., 2005). Soy isolate, acid-treated soy, and cross-linked soy were subsequently compounded, extruded, and injection molded. The obtained plastics were rigid and brittle with stiffness ranging from 1436 MPa for soy, to 1229 MPa for glyoxal cross-linked soy, up to 2698 MPa for heat-treated soy. Mechanical properties of soy protein materials plasticized with glycerol, and wheat gluten materials plasticized with water are given in Table 13.11 and Table 13.12, respectively.

The influence of a set of hydrophilic plasticizers varying in their chain length (ethylene glycol and longer molecules) on the tensile strength and elongation at break of cast gluten films was studied (Mangavel et al., 2003). Properties of deamidated gluten films enzymatically cross-linked were studied (Larré et al., 2000). The action of transglutaminase with or without the addition of external diamines induced a simultaneous increase in tensile strength and elongation at break but tended to decrease the contact angle between the film surface and a water droplet.

The effect of various cross-linked or hydrophobic additives (aldehydes, plant tannins, alcohols, and fatty acids) on the mechanical properties and water resistance of thermomolded films made from a sunflower protein isolate plasticized with glycerol have been studied (Larré et al., 2000). The use of octanoic acid resulted in high tensile strength (7 MPa), whereas the use of octanol resulted in a great increase in tensile elongation (54%). Several polyalcohols (glycerol, ethylene glycol, diethylene

Table 13.10 Glass Transitions Temperatures of Protein Materials (Di Gioia et al., 1999)

Material	Glass Transition Temperature (°C)	Conditions	Technique
Corn gluten material	176	0% moisture	DMTA; MDSC
Extracted proteic component of corn gluten (zein)	164	0% moisture	DMTA; MDSC
Extracted proteic component of corn gluten (glutelin)	209	0% moisture	DMTA; MDSC

Table 13.11 Mechanical Properties of Soy Protein Sheets (Zhang et al., 2001)

Glycerol (Parts)	Stress at Yield Point (MPa)	Elongation at Yield Point (%)	Tensile Strength (MPa)	Young's Modulus (MPa)	Toughness (MPa)
10	40.6	2.4	40.6	1226	0.4
20	33.9	7.9	34.0	1119	21.2
30	15.0	8.8	15.6	374	18.8
40	1.6	2.5	9.1	176	13.0
50	1.5	4.3	7.1	144	11.1

Table 13.12 Mechanical Properties of Wheat Gluten Materials Plasticized with Different Amounts of Water (Zhang et al., 2006)

Sample	Water Content (%)	Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)
W1	13.8	13.6	19.2	219.3
W2	15.7	7.5	57.4	143.0
W3	18.8	4.9	79.2	104.8
W4	21.2	3.0	91.4	67.5
W5	24.2	2.3	84.3	77.8

glycol, triethylene glycol, and propylene glycol) were tested as sunflower protein plasticizers (Honarkar and Barikani, 2009). The additives produced soft, brown, and smooth films with good mechanical properties ($\sigma_{\max} = 6.2\text{–}9.6$ MPa; $\varepsilon_{\max} = 23\text{–}140\%$) with a high level of impermeability to water vapor ($1.9\text{–}9.9 \times 10^{-2}$ g m^{-1} s^{-1} Pa^{-1}). However, these films were only moderately resistant to water. Glycerol and triethylene glycol were proposed as the most suitable plasticizers for sunflower proteins.

With a worldwide production estimated at about 33 million metric tons, cottonseed is the most important source of plant proteins after soybeans (Orliac et al., 2002). The viscoelastic behavior of cottonseed protein isolate, plasticized with glycerol, was characterized in order to determine the temperature range within which cottonseed protein-based materials can be formed by extrusion or thermomolding (Orliac et al., 2002). The results indicated that cottonseed proteins are thermoplastics with a T_g ranging from 80°C to 200°C when the glycerol content varies from 0% to 40% (w/w, dry basis).

Processing

Two important processes are used to make protein-based films: a wet process based on dispersion or solubilization of proteins, and a dry process based on thermoplastic properties of proteins under low water conditions (Rinaudo, 2006).

Effects of molding temperature and pressure on properties on soy protein polymers were evaluated (Mo et al., 1999). The maximum stress of 42.9 MPa and maximum strain of 4.61% of the specimen were obtained when soy protein isolate was molded at 150°C. Native soy protein was converted into a thermoplastic material in a corotating twin-screw extruder in the presence of 35% water and 10% glycerol (w/w relative to the protein amount) (Vaz et al., 2005). The extrusion was carried out at temperatures ranging from 70°C to 80°C (temperature necessary for the splitting of the disulfide bridges and loss of the tertiary structure of the protein). Glycerol-plasticized wheat gluten sheet was produced by extrusion at the barrel and die set temperature of 130°C (Hochstetter et al., 2006).

Applications

Protein-based plastics have been used, alone or in mixtures, to obtain edible films and coatings. They have been used to protect pharmaceuticals and to improve the shelf life of food products. Some commercialization of protein films has been realized in collagen sausage casing, gelatin pharmaceutical capsules, and corn zein protective coatings for nutmeats and candies (Irissin-Mangata et al., 2001).

Soybean protein can be used to produce a wide variety of nonfood products, including plastic films, building composites, insulating foams, plywood adhesives, and other wood bonding agents (Kumar et al., 2002).

The thermoplasticity and good film forming properties of wheat gluten may be used to produce natural adhesives (Day et al., 2006). Gluten's adhesive properties make it useful in pressure-sensitive medical bandages and adhesive tapes. Gluten has the ability to provide edible protection for food or food components against interactions with the environment as they can serve as barriers to mass transfer (e.g., oxygen, water vapor, moisture, aroma, lipids) (Day et al., 2006).

Some example applications of proteins from various sources are given in Table 13.13.

Table 13.13 Examples of Proteins Technical Applications (IENICA, 1996–2000)

Protein	Technical Application
Soybean protein	Paper coatings, plywood adhesives
Maize zein	Printing inks, floor coatings, grease-proof paper
Keratin	Textiles, cosmetics
Rapeseed meal protein	Adhesives, plastics
Wheat gluten	Adhesives, coatings, cosmetics

13.3 Biodegradable Polymers from Petrochemical Sources

13.3.1 Aliphatic Polyesters and Copolyesters

Properties

Poly(butylene succinate) (PBS) is a commercially available, aliphatic polyester with many interesting properties, including biodegradability, melt processability, and thermal and chemical resistance (Fujimaki, 1998; Sinha Ray and Bousmina, 2005; Uesaka et al., 2000). PBS has excellent processability, so can be processed in the field of textiles into melt blow, multifilament, monofilament, flat, and split yarn and also in the field of plastics into injection-molded products, thus being a promising polymer for various potential applications (Fujimaki, 1998).

Commercial aliphatic polyesters and copolyesters under the trade name Bionolle (Showa Highpolymer, Japan) are white crystalline thermoplastics, have melting points ranging from about 90°C to 120°C, glass transition temperatures ranging from about −45°C to −10°C, and a density of about 1.25 g/cm^3. The main physical and mechanical properties of various Bionolle grades, including 1000 series (PBS), 2000 and 3000 series (poly(butylene succinate adipate), PBSA), and 6000 series (poly(ethylene succinate)) are given in Table 13.14.

The effects of ethyl and *n*-octyl branches on the properties of PBS and poly(ethylene adipate) (PEAd) were investigated (Jin et al., 2000). Glass transition and melting temperature, crystallinity, melt viscosity, and spherulite growth rate decreased with an increase in the degree of chain branching. The addition of *n*-octyl branches improved the elongation and tear strength of PBS considerably without a noticeable decrease of tensile strength and modulus. The influence of polyester composition on the thermal and mechanical properties of a series of aliphatic homopolyesters and copolyesters prepared from 1,4-butanediol and dimethyl esters of succinic and adipic acids was studied by Tserki et al. (2006a,b). The homopolymer PBS is a highly crystalline polymer exhibiting a melting point (T_m) of 114.1°C and heat of fusion (ΔH_f) of 68.4 J/g, while for poly(ethylene adipate), which is a less crystalline polymer, the corresponding values are 60.5°C and 52.8 J/g, respectively. Copolyesters exhibited an intermediate behavior depending on their composition. Glass transition temperature T_g decreased with increasing adipate unit content from −31.3°C to −60.7°C. The homopolymer PBS exhibited the highest tensile strength, which decreased with increasing adipate unit content, passed through a minimum at copolyester close to equimolarity and then increased toward the value of poly(ethylene adipate). It was observed that in contrast to tensile strength, the elongation at break increased for adipate unit content of 20–40 mol%. Chain extension reaction resulted in increase of polyester molecular weight leading to increased tensile strength (Tserki et al., 2006). Polyester crystallinity and melting temperature decreased upon chain extension, while glass transition temperature increased.

Crystallization and melting behavior of polyesters based on succinic acid and respective aliphatic diols, with 2–4 methylene groups were studied by (Papageorgiou and Bikiaris, 2005). The equilibrium melting points were found to be 114°C, 133.5°C, and 58°C for poly(ethylene succinate), PBS, and poly(propylene succinate), respectively. The corresponding values for enthalpy of fusion were 180, 210, and 140 J/g. Poly(propylene succinate) exhibited the slowest crystallinization rates and lowest degree of crystallinity among these polyesters.

Table 13.14 Properties of Typical Grades of Bionolle (Fujimaki, 1998)

Property	PBSU #1000	PBSU #2000	PBSU #3000	PESU #6000	LDPE F082	HDPE 5110	PP 210
MFR$^{190^\circ C}$ (g/10 min)	1.5	4.0	28	3.5	0.8	11	3.0[a]
Density (g/cm^3)	1.26	1.25	1.23	1.32	0.92	0.95	0.90
Melting point (°C)	114	104	96	104	110	129	163
Glass transition temperature (°C)	−32	−39	−45	−10	−120	−120	−5
Yield strength (kg/cm^2)	336	270	192	209	100	285	330
Elongation (%)	560	710	807	200	700	300	415
Stiffness 10^3 (kg/cm^3)	5.6	4.2	3.3	5.9	1.8	12.0	13.5
Izod impact strength[b] (Kg-cm/cm) 20°C	30	36	>40	10	>40	4	2
Combustion heat (cal/g)	5550	5640	5720	4490	>11,000	>11,000	>11,000

[a] MFR was measured at 230°C.
[b] Izod impact strength was measured with notched samples.

Processing

PBS may be processed using conventional polyolefin equipment in the range 160−200°C (Fujimaki, 1998). Injection, extrusion, or blow molding is suitable for processing PBS.

Applications

Applications include mulch film, cutlery, containers, packaging film, bags, and "flushable" hygiene products (Fujimaki, 1998).

13.3.2 Aromatic Polyesters and Copolyesters

Properties

As an engineering thermoplastic, poly(trimethylene terephthalate) (PTT) has a very desirable property set, combining the rigidity, strength, and heat resistance of PET with the good processability of poly(butylene terephthalate) (PBT) (PROBIP, 2004).

PTT is crystalline, hard, strong, and extremely tough. The density of PTT is slightly lower than PET and similar to PBT. The tensile strength and flexural modulus decrease between PET, PTT, and PBT, respectively (Table 13.15). The thermal and relaxation characteristics of PTT are intermediate to the properties of PET and PBT, and are typical of those encountered with semiflexible polymers of low to medium crystallinity (Kalakkunnath and Kalika, 2006). The reported equilibrium melting temperature for PTT is approximately 237°C, with a corresponding 100% crystalline heat of fusion estimated to be 30 kJ/mol (Pyda et al., 1998).

To improve the thermal and mechanical properties of biodegradable aliphatic polyesters, introducing aromatic terephthalate units into the main chain of aliphatic polyesters has been considered to produce aliphatic−aromatic copolyesters with better physical properties as well as still having biodegradability (Gan et al., 2004).

The solid-state microstructures and thermal properties of aliphatic−aromatic copolyesters of poly

Table 13.15 Properties of PTT (PROBIP, 2004; www.ides.com/)

	PTT (PROBIP, 2004)	**PTT RTP 4700 (www.ides.com/)**	**PET (PROBIP, 2004)**	**PBT Celanex 1300 A (www.ides.com/)**
Physical properties				
MFR (g/10 min)				90
Density (g/cm^3)	1.35	1.33	1.40	1.31
Haze (%)			2–3	
Mechanical properties				
Tensile strength at yield (MPa)	67.6	61	72.5	55.2
Elongation at yield (%)		>10%		
Tensile modulus (MPa)		2551		
Flexural strength (MPa)		98		82.7
Flexural modulus (MPa)	2760	2758	3110	2200
Thermal properties				
HDT (°C)	59		65	
Vicat softening point (°C)			265	
GTT (°C)	45–75		80	60
Melting point (°C)	225			225

(butylene adipate-*co*-butylene terephthalate) were investigated by wide-angle X-ray, solid-state ^{13}C nuclear magnetic resonance, DSC, and atomic force microscopy (Gan et al., 2004). Both the melting temperature and crystallinity of copolyesters showed minimum values at around 25 mol% butylene terephthalate content, which is the transition point from PBA crystal structure to PBT crystal structure. It was reported that introducing 40 mol% or more butylene adipate units could reduce the glass transition temperature (T_g) of the copolyesters from 66°C to below −10°C, and reduce the melting temperature T_m from above 200°C to about 100°C (Gan et al., 2004). Biodegradable ideal random copolymer poly(butylene adipate-*co*-terephthalate) (PBAT) was melt-spun into fibers with a take-up velocity up to 5 km/min (Shi et al., 2005). Despite the ideal randomness and composition (1:1) of PBAT copolymers, the PBAT fiber showed a well-developed PBT-like crystal structure, while its melting temperature (approximately 121°C) was over 100°C lower than that of PBT.

Ecoflex (PBAT), a commercialized aliphatic–aromatic copolyester from BASF, was characterized to be an ideal random copolymer with 44 mol% of BT units. The glass transition occurs at −30°C, and the melting point is 110–115°C (Mecking, 2004). The physical and mechanical properties of this soft thermoplastic are similar to those of LDPE, and it can be processed on conventional equipment for LDPE. Ecoflex complies with food safety requirements, is water- and tear-resistant, elastic, printable, and weldable (BASF). Properties of Ecoflex are given in Table 13.16.

Processing

For injection-molding processing of PTT melt and mold temperatures were suggested to be between 232–260°C and 88–121°C, respectively (www.ides.com/). PTT can be spun and drawn at

Table 13.16 Properties of Aliphatic–Aromatic Copolyesters (www.ides.com/)

	Ecoflex® F [a] (www.ides.com/)
Physical properties	
Melt volume flow rate (cm^3/10 min)	3.5
Density (g/cm^3)	1.26
Transmittance (%)	82
Mechanical properties	
Tensile strength at yield (MPa)	35–44
Tensile strength at break (%)	560–710
Tensile modulus (MPa)	
Flexural strength (MPa)	
Flexural modulus (MPa)	
Shore D hardness	332
Thermal properties	
HDT (°C)	
Vicat softening point (°C)	80
GTT (°C)	
Melting point (°C)	112
Barrier properties [b]	
Permeation rate: oxygen (ml/(m^2 d bar))	1400
Permeation rate: water vapor (g/(m^2 d))	170

[a] *A copolyester mainly based on 1,4-butanediol, adipic acid, and terephthalic acid.*
[b] *Ecoflex F BX 7011 (BASF).*

high speeds, resulting in a fiber suitable for applications such as sportswear, active wear, and other specialty textiles (PROBIP, 2004). PTT has been melt-spun at various take-up velocities from 0.5 to 8 km/min to prepare fiber samples (Wu et al., 2002). The effect of take-up velocity on the structure and properties of as-spun fibers has been characterized through measurements of fiber fringence, density, wide-angle X-ray scattering, DSC melting behavior, tensile properties, and boiling water shrinkage.

The processing temperature of Ecoflex copolymer is 140–170°C (melt temperature) (www.ides.com/).

Applications

PTT is an opaque rigid thermoplastic useful for many structural applications, for example, in carpet, textile, film and packing, and other engineering thermoplastic markets, where rigidity, strength, and toughness are required (Shafee, 2003).

PTT may be used to produce fibers for carpets and industrial textiles where it has good resilience and the wearability of nylon, combined with the dyeability, static resistance, and chemical resistance of PET (PROBIP, 2004). As a spunbond fiber for apparel, its property set includes good stretch recovery, softness, and dyeability.

Main applications include:

- Fibers (textile, carpet, apparel),
- Packaging (films).

According to the manufacturer (BASF), Ecoflex has been developed for the flexible films sector. Typical applications include agricultural films, carrier bags, and compost bags. The material is marketed as a compostable packaging film, as a hydrophobic protective coating for food containers, and as a blend component (Mecking, 2004). Ecoflex is suitable for food packaging as a protective film or as component of laminated paper (BASF). Example of application include: wrapping paper, drink cartons, fast-food packaging, and drink cups. Copolyesters with a higher terephthalic acid unit have been reported to be suited for fiber applications.

13.3.3 Poly(caprolactone)

Properties

Polycaprolactone (PCL) was developed as a biodegradable plastic of aliphatic polyester type derived from the chemical synthesis of crude petroleum (Funabashi et al., 2007). It has a low-melting point (approximately 60°C), low melt viscosity, and is easy to process (Funabashi et al., 2007). PCL has good water, oil, and chlorine resistance.

The PCL chain is flexible and exhibits high elongation at break and low modulus. The elongation at break and tensile strength of PCL films have been reported to be between 450% and 1100% and 25 and 33 MPa, respectively (Koening and Huang, 1995; Matzinos et al., 2002). These values are quite high as compared with the elongation at break, 500−725%, and tensile strength, 9.7−17.2 MPa, of LDPE (Matzinos et al., 2002). The main drawback of PCL is its low melting point, which can be overcome by blending it with other polymers or by radiation cross-linking processes, which result in enhanced properties suitable for a wide range of applications (Sinha Ray and Bousmina, 2005).

Properties of commercially available CAPA and Tone PCLs are given in Tables 13.17 and 13.18 (Solvay; Union Carbide).

Processing

PCL can be processed by the usual thermoplastic processing techniques, including blow and slot cast film extrusion, sheet extrusion, and injection molding. The low melting point of PCL polymers requires lower temperatures than polyethylene and other polyolefins.

According to the manufacturer's information, the extrusion parameters for PCLs are: 70−120°C (CAPA 6500) and 130−165°C (CAPA 6800) (Solvay).

Applications

PCL is recognized as a biodegradable and nontoxic material. Its high permeability to low molecular species at body temperature and biocompatibility makes PCL a promising candidate for biomedical applications, such as controlled drug delivery (Edlund and Albertsson, 2002). PCL is used mainly in thermoplastic polyurethanes, resins for surface coatings, adhesives, and synthetic leather and fabrics (Funabashi et al., 2007). It also serves to make stiffeners for shoes and orthopedic splints, and fully biodegradable bags, sutures, and fibers (Funabashi et al., 2007). PCL is often mixed with starch to obtain a good, biodegradable, low-cost material.

The main applications of PCL comprise (Solvay):

- biodegradable bottles,
- biodegradable films,
- controlled release of drugs, pesticides, and fertilizers,
- polymer processing,
- adhesives,
- nonwoven fabrics,
- synthetic wound dressings,
- orthopedic casts.

13.3.4 Poly(esteramide)s

Properties

Poly(esteramide)s (PEA) constitute a new series of thermoplastic polymers that can combine high technical performance with good biodegradability (Botines et al., 2002; Ferré et al., 2003; Grigat et al., 1998; Lips et al., 2005; Lozano et al., 2004). BAK 1095 is an example of a poly(esteramide) commercialized by Bayer but its production stopped in 2001. This is a statistical polymer with an amide/ester ratio of 6/4 based on 1,4-butanediol, adipic acid and 1,6 aminohexanoic acid. BAK poly(esteramide)s differing in the amide/ester ratio have been synthesized and characterized (Ferré et al., 2003). Spectroscopic analyses of BAK poly(esteramide)s with 50/50, 60/40, and 70/30 amide/ester ratios showed a random distribution of monomers, which was in agreement with their low crystallinity (12−14%). BAK polymers showed a decrease in the melting and glass transition temperatures when the ester/amide ratio was increased. In the same way, Young's modulus decreased (Table 13.19). The influence of substituting adipic acid by terephthalic acid units on the thermal and mechanical properties of poly(esteramide)s has been investigated

Table 13.17 Properties of CAPA PCLs (Avérous et al., 2000b)

Property	CAPA 6500	CAPA 6800
Molecular weight (M_n)	4750 ± 2000	69,000 ± 1500
Melting point (°C)	60–62	60–62
Heat of fusion (J/g)	76.9	76.6
Crystallinity (%)	56	56
Crystallization temperature (°C)	25.2	27.4
Glass transition (°C)	−60	−60
MFR (g/10 min) (190°C/2.16 kg)	28	7.29
Tensile yield stress (MPa)	17.2	14
Tensile modulus (MPa)	430	500
Strain at break (%)	>700	920
Flexural modulus (MPa)	411	nd
Hardness (Shore D)	51	50
Viscosity (Pa · s) (70°C, 10.1/s)	2890	12,650
Viscosity (Pa · s) (100°C, 10.1/s)	1353	5780
Viscosity (Pa · s) (150°C, 10.1/s)	443	1925

Table 13.18 Properties of Tone PCLs (Wang et al., 2003)

Property	P-767	P-787
Density (g/cm^3)	1.145	1.145
MFR (g/10 min) (190°C)	30	4
Tensile strength (MPa)	21.3	39.7
Tensile modulus (MPa)	435	386
Ultimate elongation (%)	600–800	750–900
Flexural modulus (MPa)	575	514
Flexural stress at 5% strain (MPa)	23.4	21.0
Izod impact (J/m) (notched)	82	350
Izod impact (J/m) (unnotched)	No break	No break
Water absorption	0.3508	0.3295
Hardness (Shore D)	55	55

(Lozano et al., 2004). A regular increase in glass transition and melting temperatures with the aromatic content was observed. Moreover, the mechanical properties showed an increase in chain stiffness with the aromatic content.

High molecular weight segmented poly(esteramide)s comprising different ester to amide ratios have been prepared by melt polycondensation of a preformed bisamide-diol, 1,4-butanediol, and dimethyl adipate (Lips et al., 2005). The polymers had a low and a high melt transition, corresponding with the melting of crystals comprising single esteramide sequences and two or more esteramide sequences, respectively. The low melt transition is between 58°C and 70°C and is independent of polymer composition. By increasing the hard segment content from 10 to 85 mol%, the high melt transition increased from 83°C to 140°C while the glass transition temperature increased from −45°C to −5°C. Likewise, the elastic modulus increased from 70 to 524 MPa, the stress at break increased from 8 to 28 MPa, while the strain at break decreased from 820% to 370%.

Processing

The processing conditions of BAK poly(esteramide) are similar to those of polyolefins (Grigat et al., 1998). BAK 1095 resin can be processed into film and also into extruded or blow-molded parts on conventional machinery used for processing thermoplastics. Processing conditions are given in Table 13.20.

Applications

Potential applications for BAK 1095 resin include uses in the horticulture, agriculture, and food sectors. Specific examples are biowaste bags, agricultural films, plant pots, plant clips, cemetery decoration, and one-way dishes (Grigat et al., 1998).

13.3.5 Poly(vinyl alcohol)

Properties

Poly(vinyl alcohol) (PVA) is a water-soluble polymer based on petroleum resources with interesting properties such as good transparency, luster, antielectrostatic properties, chemical resistance, and toughness (Gohil et al., 2006). It has also good gas barrier properties and good printability. The final properties of PVA depend on the properties of its parent polymer, that is, poly(vinyl acetate), its polymerization conditions, and degree of hydrolysis. Basic properties of PVA and PVA-based systems also depend upon the degree of polymerization, distribution of hydroxyl groups, stereoregularity, and crystallinity (Chiellini et al., 1999). For example, the degrees of hydrolysis and polymerization affect the solubility of PVA in water (Hassan and Peppas, 2000). PVA grades with high degrees of hydrolysis have low solubility in water. The presence of acetate groups affects the ability of PVA to crystallize upon heat treatment (Hassan and Peppas, 2000). PVA grades containing high degrees of hydrolysis are more difficult to crystallize.

Commercial PVA grades are available with various degrees of hydrolysis and polymerization.

Processing

Two technologies are used for PVA film production—casting from viscous water solution or blown extrusion from melt. Plastic items based on PVA film are mainly obtained using casting techniques (Chiellini et al., 2003). However, due to interest in biodegradable PVA-based film, melt-processing technology has been developed. The main difficulty in PVA thermal extrusion processing is the close proximity of its melting point and decomposition

Table 13.19 Properties of PEAs (Ratto et al., 1999; Wang et al., 2001)

Property	BAK 1095 (Wang et al., 2001)	BAK 70/30 (Ratto et al., 1999)	BAK 60/40 (Ratto et al., 1999)	BAK 70/30 (Ratto et al., 1999)
Density (g/cm^3)				
MFR (g/10 min) (190°C)				
Tensile strength (MPa)	27	29	27	11
Tensile modulus (MPa)	250	285	250	128
Elongation at break (%)	570	432	570	24

temperature (Chiellini et al., 2003). The thermal degradation of PVA usually starts at about 150°C or above, depending upon the PVA grade (degree of hydrolysis and pH). In order to improve the thermal stability and processing properties of PVA, the use of plasticizers is required. Various plasticizers such as water, glycerol, ethylene glycol, and its dimer and trimer, amine alcohols, and polyvalent hydroxyl compounds have been applied.

Applications

PVA is largely used as fiber, film, in the paper industry, in textile sizing, as a modifier of thermosetting resins, in plywood manufacture, as pressure-sensitive adhesives, and as an emulsifier (Chiellini et al., 1999; Gohil et al., 2006). It is mainly used as a sizing agent or stabilizer of dispersion systems. In particular, the four major segments of PVA consumption comprise warp sizing, paper coating, coatings, and films (Chiellini et al., 1999).

PVA applications include textile-sizing agents, paper processing agents, emulsification dispersants, films and general industrial use, in particular:

- Textile sizing and finishing,
- Laminating adhesives,
- Size in paper and paperboard manufacture,
- Water-soluble films for packaging and release applications,
- Protective colloid in emulsion polymerization processes,
- Photosensitive coatings,
- Binders for building products such as ceramics, ceiling tiles, floor coatings, and paper board,
- Binders for pigmented paper coatings, ceramic materials, and nonwoven fabrics.

13.4 Blends

In order to obtain compostable polymer materials with the best compromise between mechanical and processing properties and cost, as well as compostability, various blends of biodegradable polymers have been studied. For example, blends such as PLA/PHA, and PLA/starch have improved performance with respect to degradation rate, permeability characteristics, and thermal and mechanical properties. Overall processability is thus improved and the range of possible applications for PLA is broadened. Blends of PLA and natural fibers have increased durability and heat resistance and resulted in a lower cost to weight ratio compared to unblended PLA (PROBIP, 2004).

All possible systems, including blends of polymers based on renewable and petrochemical resources have been developed. However, most attention is given to starch-based blends (Avérous, 2004; Avérous et al., 2000b; Bastioli, 1998; Wang et al., 2003). Starch is one of the most inexpensive and most readily available of compostable polymers. The renewability of starch is another of its advantages. The major drawback of TPS is its sensitivity to water and poor mechanical properties. TPS is a hydrophilic material. To overcome moisture sensitivity and changes in mechanical properties of TPS in relation to the crystallinity and the contents of plasticizer and water, during aging, blending TPS with other biopolymers has been commonly performed (Avérous et al., 2000b). Associations between TPS and other biopolymers include aliphatic polyesters such as PCL, PLA, PHBV, and polyesteramide (PEA). Some

Table 13.20 Processing Conditions for BAK (Wang et al., 2001)

	BAK 2195	BAK 1095
Melting point	175°C	125°C
Mass temperature	180–200°C	140–220°C
Mold temperature	50°C	30–40°C
Deforming	Good	Reasonable
Fogging	No	No
Corrosion	No	No
Drying conditions	2 h at 70°C	2 h at 90°C

starch-based blends have been commercialized such as Mater-Bi (Novamont) or Bioplast (Biotec).

The properties of commercially available starch-based blends are summarized in Table 13.21.

Different compositions of wheat TPS and PCL were melt blended by extrusion and injected (Avérous et al., 2000b). It was noticed that the addition of PCL to the TPS matrix allowed the weakness of pure TPS to be overcome: low resilience, high moisture sensitivity, and high shrinkage, even at low PCL concentrations, for example, 10 wt%. However, a fairly low compatibility between both polymeric systems was reported. For PCL-based blends, the resulting mechanical properties depend both on plasticization level and PCL content (Table 13.22).

PCL, due to its low melting point (~65°C), is difficult to process by the conventional techniques used for thermoplastic materials. Blending of starch with PCL improves its processability and furthermore promotes its biodegradation. Poly(ε-caprolactone)/plasticized starch blends varying in starch content were processed by conventional extrusion, injection molding, and film blowing techniques (Matzinos et al., 2002). Blending plasticized starch with PCL increased the modulus and decreased the other mechanical properties (i.e., strength and elongation at yield and break) of both injection-molded specimens and films.

The processability, mechanical and thermal properties, and biodegradability of PBSA/starch films containing up to 30 wt% corn starch were studied (Ratto et al., 1999). Increasing the starch content led to an increase in modulus and decrease in tensile strength, elongation to break and toughness.

Mechanical properties of TPS blended with poly (hydroxy butyrate) (PHB) confer higher performance than those of pristine TPS (Lai et al., 2006). In particular, a significant increase in tensile strength and tear strength is observed for TPS (potato starch) blended with PHB at low-gelatinization degree. For example, for TPS blended with 7% PHB, the tear strength reaches 44.1 kJ/m^2, a 12-fold increase over unfilled TPS at 25% glycerol content.

The properties of blends of starch and aliphatic biodegradable polyesters, including poly(ε-caprolactone), PBS, and a butanediol-adipate-terephthalate copolymer were studied (Mani and Bhattacharya, 2001). To improve the compatibility between the starch and the synthetic polyester, a compatibilizer containing an anhydride functional group incorporated into the polyester backbone was used. The addition of a small amount of compatibilizer increased the strength significantly over the uncompatibilized blend. For the compatibilized blend, the tensile strength was invariant with starch content when compared to the original polyester, while it decreased with increase in starch content for the uncompatibilized blend.

The interfacial interaction between PLA and starch was improved, and mechanical properties of PLA blends with starch were enhanced by adding methylene diisocyanate (Wang et al., 2001, 2003).

Blending TPS with other biodegradable polyesters such as PEA could be an interesting way to produce new biodegradable starch-based materials (Avérous et al., 2000a). A range of blends was studied with glycerol (plasticizer)/starch contents ratios varying from 0.14 to 0.54 (Avérous et al., 2000a). BAK PEA concentrations were up to 40 wt %, TPS remaining as the major phase in the blend. It was reported that the addition of BAK to the TPS matrix allowed the weaknesses of pure TPS to be overcome: low mechanical properties, high moisture sensitivity, and high shrinkage in injection, even at 10 wt% BAK. The tensile yield properties of PEA blended with granular corn starch or potato starch over a range of strain rates were investigated (Willett and Felker, 2005). Yield stress increased relative to unfilled PEA with starch volume fraction and stress rate when corn starch was the filler. When potato starch was used, the yield stress decreased with starch volume fraction at low strain rates, and increased at high strain rates.

Applications

Commercially available starch-based blends (Novamont Mater-Bi) depending on the grade are used in the following areas (Bastioli, 1998):

Mater-Bi Z Class

Mainly for films and sheets.

Technology: film blowing (ZF03U/A).

Use: bags, nets, paper lamination, mulch films, twines, wrapping film.

Mater-Bi Y Class

For rigid and dimensionally stable injection molded items.

Table 13.21 Properties of Commercially Available Starch-Based Blends (Grevellec et al., 2001; PROBIP, 2004)

	Starch (>85%)/ Copolyester Mater-Bi NF01U (PROBIP, 2004)	**Starch/PCL Mater-Bi ZF03U/A (PROBIP, 2004)**	**Starch/CA Mater-Bi Y1010U (Grevellec et al., 2001)**	**Starch/CA Bioplast GF105/30 (PROBIP, 2004)**	**Modified Starch Cornpol (PROBIP, 2004)**
Physical properties					
MFR (g/ 10 min)	2–8		10–15	5–9	5–6
Density (g/ cm^3)	1.3	1.23	1.35	1.21	1.2
Transparency (%)					
Mechanical properties					
Tensile strength at yield (MPa)	25	31	25–30	44,38	30
Elongation at yield (%)	600	900	2–6	400, 500	600–900
Tensile modulus (MPa)	120	180	2100–2500		10–30
Thermal properties					
HDT (°C)					85–105
Vicat softening point (°C)				65	105–125
GTT (°C)					
Melting point (°C)	110	64			

Samples aged 2 weeks at 23°C and 50% RH.

Technology: injection molding.

Use: cutlery, boxes, flowers pots, seedling plant trays, golf tees, vending cups, and pens.

Mater-Bi V Class

For rigid and expanded items.

Technology: foaming.

Use: loose fillers and packaging foams as a replacement for PS.

Technology: injection molding.

Use: soluble cotton swabs, soluble items.

In general, the main applications of starch-based materials include (PROBIP, 2004):

- Packaging: leaf collection compost bags, packaging films, shopping bags, strings, straws, tableware, tapes, technical films, trays, and wrap film.
- Agricultural sector: mulch film, planters, planting pots, encapsulation and slow release of active agents such as agrochemicals.
- Transportation: fillers in tires.

Table 13.22 Mechanical Properties of TPS/PCL Blends (Srinivasa et al., 2007)

PCL (wt %)	TPS Formula (Components in wt%)	Modulus (Mpa)	Maximum Tensile Strength (Mpa)	Elongation at Break (%)	Impact Strength (kJ/m^2)
100		190	14.2	>550	No break
0	Starch 74/glycerol 10/water 16	997	21.4	3.8	0.63
25	Starch 74/glycerol 10/water 16	747	10.5	2.0	1.57
40	Starch 74/glycerol 10/water 16	585	9.0	2.4	2.99
0	Starch 70/glycerol 18/water 12	52	3.3	126.0	No break
25	Starch 70/glycerol 18/water 12	93	5.9	62.6	No break
0	Starch 67/glycerol 24/water 9	26	2.6	110.0	No break
25	Starch 67/glycerol 24/water 9	80	5.3	42.2	No break
0	Starch 65/glycerol 35	2	0.61	90.7	No break
10	Starch 65/glycerol 35	8	1.05	61.9	No break
25	Starch 65/glycerol 35	36	2.87	43.1	No break
40	Starch 65/glycerol 35	71	5.19	50.4	No break

- Miscellaneous: nappy back sheets, soluble cotton swabs, soluble loose fillers, cups, cutlery, edge protectors, golf tees, mantling for candles and nets.

13.5 Summary

Physical and mechanical properties of the main compostable polymers are summarized in Tables 13.23 and 13.24.

Applications of compostable polymer materials which have been commercialized or are in the development/demonstration stage include (Bastioli, 1998):

- Packaging: films and trays for biscuits, fruit, vegetables and meat, yoghurt cup, nets for fruit, grocery bags, rigid transparent packaging of batteries with removable printed film on back side, trays and bowls for fast-food, envelopes with transparent window, paper bags for bread with transparent window
- Agriculture and horticulture: mulching films, tomato clips
- Short-life consumer goods: hygiene products such as nappies, cotton swabs, stationary, and prepaid cards.
- Long-life consumer goods: apparel, for example, T-shirts, socks, blankets, mattresses, casings for Walkmans, CDs (compact disks), computer keys, small components of laptop housing, spare wheel covers, automobile interiors including head liners and upholstery and possibly for trimmings.

Table 13.23 Summary of Properties of Compostable Polymer Materials Derived from Renewable Resources (Van de Velde and Kiekens, 2002)

Property	PLA	L-PLA	DL-PLA	PHB
Density (g/cm^3)	1.21−1.25	1.24−1.30	1.25−1.27	1.18−1.262
Glass transition (°C)	45−60	55−65	50−60	5−15
Melting temperature (°C)	150−162	170−200	Amorphous	168−182
Tensile strength (MPa)	21−60	15.5−150	27.6−50	40
Tensile modulus (GPa)	0.35−3.5	2.7−1.14	1−3.45	3.5−4
Ultimate tensile strain (%)	2.5−6	3−10	2−10	5−8

Table 13.24 Summary of Properties of Compostable Polymer Materials Derived from Petrochemical Resources (Averous and Fringant, 2001)

Property	PCL	PEA	PBSA	PBAT
Density (g/cm^3)	1.11	1.05	1.23	1.21
Glass transition (°C)	−60	−30	−45	−30
Melting temperature (°C)	60−62	125	92−94	110−115
Tensile strength (Mpa)	20.7−42			
Tensile modulus (Gpa)	0.21−0.44			
Ultimate tensile strain (%)	300−1000			

13.5.1 Major Markets of Compostable Polymer Materials

- Agricultural and fishery (mulch films, pots for transplanting, fishing lines and nets),
- Civil engineering and construction (sand bags, flora sheets, curing sheets),
- Leisure goods (golf tees, marine sports, and mountain climbing),
- Food packaging (trays for perishable food, fast-food containers),
- Packaging (kitchen garbage, composting bags, bin liner bags, shopping bags),
- Textile goods (clothes, mats),
- Daily use (pen cases, disposal shavers),
- Electronic (electronic equipment cases),
- Automotive industry (car parts).

According to the technical market research report, *Biodegradable Polymers* from BCC Research, the global market for biodegradable polymers, reached 245 million kilograms (541 million pounds) in 2007 (Plastics Additives, 2008). This was expected to increase to over 545 million kilograms (1203 million pounds) by 2012, a compound average annual growth rate of 17.3%. This report breaks the market down into applications of compost bags, loose-fill packaging, and other packaging, including medical/hygiene products, agricultural and paper coatings, and miscellaneous. Of these, compost bags have the largest share of the market. At nearly 110 million kilograms (242 million pounds) in 2007, this segment was expected to reach 266 million kilograms (586 million pounds) by 2012. Loose-filled packaging has the second largest share of the market.

At an estimated 73 million kilograms (162 million pounds) in 2007, this segment was expected to reach 97 million kilograms (214 million pounds) by 2012.

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14 Waste Management for Polymers in Food Packaging Industries

Ioannis S. Arvanitoyannis
University of Thessaly, Department of Agriculture Crop Production and Rural Environment Nea Ionia, Magnesia, Greece

14.1 Biodegradable Synthetic Copolymers and Composites

The continuously increasing extent of pollution of the environment has recently given rise to demands for novel biodegradable polymers, mainly for applications related to food packaging and agriculture (Huang, 1985; Kumar, 1987; Schnabel, 1981). The main emphasis was initially focused on the synthesis of novel aliphatic polyesters (Chiellini and Solaro, 1992; Schnabel, 1981; Vert et al., 1992) due to their higher susceptibility to biodegradation with regard to other polymers such as polyamides (PAs) and polyanhydrides (Satyanarayana and Chaterji, 1993; Zhang et al., 1993). Among the aliphatic polyesters, poly(ε-caprolactone) (PCL) (Tokiwa et al., 1983, 1988), poly(β-methyl-δ-valerolactone) (Nakayama et al., 1993, 1995a,b), polylactide (Kim et al., 1992, 1993; Satyanarayana and Chaterji, 1993; Vert et al., 1992), and their copolymers (Den Dunnen et al., 1993; Gaymans and de Haan, 1993; Shiaw et al., 1994) have been suggested as the most promising in terms of potential applications. The low glass transitions and low melting points of most polyesters have oriented several researchers toward exploring other potential avenues, such as the direct polymerization of α-amino acids (Kiyotsukuri et al., 1992; Wu, 1992; Yang et al., 1993) or copolymerization of lactams with lactones (Goodman, 1984; Goodman and Vachon, 1984a,b,c; Goodman and Valavanidis, 1984) in an attempt to synthesize novel polymers with higher thermal resistance. The biodegradability tests conducted on the copolyesteramides were highly promising and favored potential applications (Huang, 1985; Kumar, 1987). However, the difficulties encountered in producing high molar mass and environmentally degradable copolyamides have been restrictive factors, in terms of applications, for the copolyamides (Bera and Jedlinski, 1993; Chen et al., 1993; Yang et al., 1993).

14.1.1 Novel Biodegradable Copolyamides Based on Diacids, Diamines, and α-Amino Acids

The novel copolyamides, based on adipic acid (AA), 1.6-hexane diamine (1.6-HD), isophorone diamine (IPD), bis(*para*-aminocyclohexyl)-methane (PACM-20), and various α-amino acids (L-tyrosine, proline, alanine, glycine, glutamic acid), were synthesized by a two-stage melt polycondensation (100°C and 250°C for 1 and 2 h, respectively). The semicrystalline and, occasionally, amorphous nature of the copolyamides based on the salt of 1.6-HD/AA (1:1 mol/mol)/α-amino acids was shown by wide-angle X-ray diffraction (WAXD). Several biodegradability experiments (burial in soil, alkali and enzymatic hydrolysis) were carried out to test the susceptibility of these polymers to degradation. The physical properties of the copolymers were investigated before and after biodegradability testing. The observed gradual increase in X_c of the NaOH-insoluble fraction of the copolyamides was proportional to their exposure to alkali hydrolysis. It is thought that the initial gradual dissolution of the amorphous parts results in higher crystallinity values, similar to what has been reported for the early stages of in vivo and in vitro degradation of poly-(L-lactide) (PLLC poly(L-lactide-co-caprolactone)), polyglycolide (Chu, 1981), and PCL (Pitt et al., 1981). The degradation process of biodegradable polymers occurs in two steps. In the first stage, chain scission occurs preferentially in the amorphous regions of the semicrystalline polymer. The initial random chain scissions result in a decrease of the degree of entanglement, thus facilitating and even considerably promoting the mobility of nondegradable chain segments in these regions. This mobility promotes crystallization, as reflected by the high X_c values. However, following the dissolution of the amorphous regions, the degradation proceeds to the crystalline

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regions. A substantial decrease in the molar masses of the copolymers was recorded when the copolymers were exposed to NaOH (10% wt/vol NaOH, 80°C) (Arvanitoyannis et al., 1993, 1994a,b,c,d, 1995a,b,c,d,e,f,g). The effect of alkali hydrolysis was very pronounced for the copolymers rich in α-amino acids because they underwent a significant reduction in the molar mass of polymeric chains, thus resulting in number average molecular weights M_n as low as 2100. The tensile strength (TS) and tensile modulus of copolyamides were shown to undergo a sharp decrease after the copolymer samples were treated with alkali solutions for more than 20 h. In fact, a linear dependence of TS on the M_n with regard to the exposure time of alkali hydrolysis was established. The molar mass of copolyamides was not substantially affected when the copolyamides were buried in soil. Overall, when the content of α-amino acids was higher than 15%, they turned from semicrystalline to amorphous according to DTA (differential thermal analysis) and WAXD measurements. The potential degradability of the synthesized copolyamides was confirmed by various biodegradability experiments, such as alkali hydrolysis, microbial-bacterial attack (burial in soil), and enzymatic hydrolysis. It is envisaged that these copolyamides may find various applications because of their enhanced susceptibility to biodegradation.

14.1.2 Novel Biodegradable Copolyesteramides from ε-Caprolactone and Various PA Salts

The biodegradation of synthetic polymers is of considerable interest to environmentalists, industrialists, and academic researchers as well (Chen et al., 1993). Aliphatic polyesters have been long considered as the most promising polymers for applications in which biodegradability is a prerequisite (Kim et al., 1992, 1993; Satyanarayana and Chaterji, 1993; Vert et al., 1992). However, synthetic poly(amino acids) and PAs, though regarded as the analogs of proteins and natural peptides, have not yet found the extent of expected application, mainly because of preparation difficulties (Huang, 1985; Yang et al., 1993). The aliphatic copolyesteramides recently have been suggested and partially investigated as a polymer family with much potential concerning functional performance and susceptibility to degradation (Arvanitoyannis et al., 1994a,b,c,d, 1995a,b,c,d,e,f,g; Goodman and Sheahan, 1990a,b). Synthesis of copolyesteramides has been carried out in a three-stage process: 1.6-HD was mixed with a diacid (AA, sebacic acid (SA), or octadecanedioic acid (ODA)) and ε-caprolactone (ε-CL) and was kept at 120°C, 180°C, and 250°C for 2 h, 2 h, and 0.5 h, respectively (Arvanitoyannis et al., 1994a,b,c,d, 1995a,b,c,d,e,f,g). Although the melting points T_m versus ε-CL content showed eutectic curves (minimum at 20/20/60 for SA, ODA, or AA/1.6-HD/ε-CL), similar to other copolymers (Kehayoglou and Arvanitoyannis, 1990), the melting points versus the ε-CL content were found to give straight lines (Arvanitoyannis et al., 1994a,b,c,d, 1995a,b,c,d,e,f,g). The substantial difference in the heat of fusion between the ester-rich and the amide-rich copolymers possibly could be attributed to the incompatibility of crystal structures (monoclinic or triclinic for PAs in contrast to the orthorombic for PCL) (Arvanitoyannis et al., 1994a,b,c,d). An increase in ε-CL content resulted in broadening of peaks and in decreases in the T_m and T_g values due to the higher flexibility of the polymeric chain imparted by the incorporation of ε-CL. The total organic carbon (TOC) measurements indicated that only the ester-rich copolyesteramides ($>50\%$ ester content) could be considered biodegradable because the TOC values for the amide-rich copolyesteramides were very low (Arvanitoyannis et al., 1994a,b,c,d, 1995a,b,c,d,e,f,g). It was also found that the weight loss percentages of the copolyesteramides after their immersion in alkali solution increased with an increase in ε-CL content. The weight loss rate was greatly enhanced after the first 10 h, reaching up to about 50% (after 30-h exposure) and was accompanied by a substantial decrease in M_n, as determined by GPC (gel permeation chromatography). Enzymatic hydrolysis was also conducted in order to study the degradation products. Nuclear magnetic resonance (NMR) analysis of the degradation products showed that cleavage primarily occurs at ε-CL—ε-CL labile bonds in the polymer backbone, whereas the amide bonds (O=C—NH—) are characterized by low susceptibility to degradation. The thermal properties (T_g, T_m) showed a linear decrease against the CL content, while the TOC increased considerably. Enzymatic and alkali hydrolysis, as well as burial in soil experiments, all showed that an increase in CL content reflected an increase in the susceptibility of copolyesteramides to biodegradation. Chen and his colleagues' (2012) study presented the successful synthesis of amphiphilic mPEG-*b*-PCL-based (N-phthaloylchitosan-grafted poly (ethylene glycol) methyl ether) block copolymers bearing benzyloxy and hydroxyl side groups on the PCL block by ring-opening polymerization of 4-benzyloxy-ε-caprolactone (4-BOCL) and ε-CL with methoxy PEG ($550\ \mathrm{g\ mol}^{-1}$) as the initiator and Tin(II) 2-ethylhexanoate ($SnOct_2$) as the catalyst. These copolymers were differentiated by scanning calorimetry, 1 H NMR, and gel permeation chromatography. The thermal properties (T_g and T_ms) of the block copolymers depend on the polymer composition. Adding a larger amount of 4-BOCL and/or ε-CL to the macromolecular backbone causes a decrease in T_g and an increase in T_ms. The micellar characteristics in the aqueous phase were investigated by fluorescence spectroscopy, transmission electron microscopy (TEM), and dynamic light scattering (DLS).

14.1.3 Novel Star-Shaped Copolylactides

Strong interest in the eventual, and preferably rapid, biodegradation of synthetic polymers has developed only in past years, primarily in response to the growing problem of waste disposal of plastics (Lenz, 1993). Polyesters attracted much research interest in view of their satisfactory performance property wise and their inherent biodegradability. PCL and PLLA (poly(L-lactide)) were the most responsive to biodegradation both in vitro and in vivo (Nishida and Tokiwa, 1992, 1993a,b; Reeve et al., 1994). Apart from these two homopolymers (PCL and PLLA), several copolymers, based on these two components, have been synthesized in an attempt to "tailor" the properties of the homopolymers for special applications (Kricheldorf et al., 1988; Mikos et al., 1993; Zhang et al., 1993). An effective in situ process has been the main incentive for the introduction of a soft segment such as poly(ethylene glycol) in PLLA (Cerrai and Tricoli, 1993; Kobayashi et al., 1991). The difficulties encountered in processing PLLA remained the major limiting factor in applications despite the well-accepted biocompatibility and biodegradability of PLLA (Kim et al., 1992, 1993; Leenslag, 1984). Novel branched star-shaped polymers are envisaged as a potential solution to the processing problem because they can combine high-molecular weight with lower melt viscosities than the linear PLLA (Aragade and Peppas, 1993; Gijpa and Pennings, 1994a,b). The polymerization of L-lactide (LLA) with polyol (i.e., pentaerythritol, glycerol, or sorbitol) was carried out in the presence of two catalysts (stannous octoate (Sn(Oct)2) and tetraphenyl tin (TPhT)) at 130°C for 4 days (Arvanitoyannis et al., 1995a,b,c,d,e,f,g, 1996a,b). The GPC traces of the LLA/GL or LLA/pentaerythritol copolyesters (synthesized with (Sn(Oct)2)) gave monodisperse curves, thus indicating the occurrence of only one mechanism. In contrast, the biomodal GPC traces, recorded when TPhT was used as the catalyst, support the previously expressed suggestion that two mechanisms are in action, one initiated by the polyol and the other via the catalyst. The DSC (differential scanning calorimetry) results (bimodal traces) further support the existence of two mechanisms. The degradation rates of these polyesters were studied by enzymatic and alkali hydrolysis, primarily in terms of changes in weight, M_n, and TOC. NMR analysis of degraded products confirmed the suggested cleavage of hydrolyzable bonds of star-shaped PLLA. High polyol contents strongly favored extensive cleavage of polymeric chains, thus resulting in an increase of crystallinity. It is noteworthy that the theoretical capability of polyols to act as cross-linking agents was not confirmed by solubility experiments on the synthesized copolyesters (Arvanitoyannis et al., 1995a,b,c,d,e,f,g, 1996a,b).

14.1.4 Biodegradable Composite Materials

The development of novel polymeric materials that degrade slowly is considered a very important research area, especially in view of their various current and potential applications as environmentally degradable materials (Albertsson et al., 1994; Storey and Shoemake, 1993). Although D-, or L-lactide and ε-CL seem to be the most popular monomers, especially in the field of polymeric composite materials (Li et al., 1990a,b,c) mainly related to medical applications, PAs are another promising class of polymer that appeals to a wider range of applications (Gonsalves et al., 1993). It is anticipated that these novel thermoplastic materials have a lot of potential because of their inherent advantages over the majority of thermoset materials (Arvanitoyannis and Psomiadou, 1994), namely, control of their percentage crystallinity (physicochemical properties), ease of processing, and “friendliness” to the environment (Arvanitoyannis et al., 1995a,b,c,d,e,f,g). Composites, consisting of AA/1.6-HD/L-proline or L-glycine and short E-glass fibers, were prepared by the hand lay-up method (Srivastava and Lal, 1991). The crystallinity of the copolyamide matrix was determined from WAXD following the generally accepted procedure for constructing the diffraction pattern of a composite material. Determination of percentage of crystallinity in composite materials with DTA is complicated by the occurrence of nucleation fronts on the glass fibers, in addition to the statistical nucleation from the melt, known as transcrystallinity. Therefore, occurrence of multiple melting peaks should be attributed to different spherulite morphologies (Arvanitoyannis and Psomiadou, 1994). Detection of void content is very critical in terms of determining the shelf life and performance of the composite material. The main reasons for the occurrence of voids in the degradable composite materials are the following: entrapment of air within pelletized material, residual moisture, and shrinkage volume of the core region.

14.1.5 Natural–Synthetic Polymer Blends

It has been estimated that approximately 2% of all plastics (mostly nondegradable) eventually end up in the environment, thus contributing considerably to the currently acute ecological problem. The current trend toward protection of the environment is expressed by using degradable polymers and composting or recycling the “recalcitrant” polymers. Blends of natural and synthetic polymers have been considered a promising avenue for preparing polymers with “tailor-made” properties (functional physical properties and biodegradability).

14.1.6 Partially Degradable Blends

Starch-based plastics initially attracted some research interest, but their development was not as expected, mainly because of their inadequacy with regard to mechanical properties and water transmission (Giffin, 1994; Otey et al., 1974). In an attempt to overcome this problem, synthetic polymers/starch blends were investigated (Lawton and Fanta, 1994; Shogen, 1993). The main advantages of these blends can be summarized as follows (Scott and Gilead, 1995):

1. property tailoring by proper selection of components and their ratios,
2. lower cost by using blending (i.e., extrusion, casting) instead of synthetic,
3. routes for production of novel materials,
4. ecological factors (environmentally friendly and usage of plastic wastes).

Mixtures of low-density polyethylene (LDPE) with gelatinized potato, rice, wheat, and soluble starch, with or without ethylene acrylic acid (EAA) as a compatibilizer, were extruded in the presence of 15–20% water. As long as the starch content in the blends does not exceed 20%, the mechanical properties of the LDPE/starch blends still lie within acceptable operational limits. Typical scanning electron microscopy (SEM) microgaphs taken after fracture clearly showed the blend morphology and the distribution of each component (Psomiadou et al., 1998). The wheat starch particles are deformed and interspersed within the LDPE matrix. Although in several previous publications the failure modes of polyethylene (PE) were investigated and analyzed, a tentative failure mechanism of PE/starch blends was only recently put forward (Arvanitoyannis et al., 1997, 1998). Brittleness and ductility are the two main failure modes. Whichever of these two prevails depends not only on the deformation features and fast or slow crack growth (Chudnovsky et al., 1995; Stojmirovic et al., 1992) but also on conditioning of the sample over certain relative humidity environments. Therefore, the ensuing plasticization of the LDPE/starch blends could be due to penetration of water and filling of voids. Constructing a tentative micromechanical model to depict the geometries, arrangements, and interactions of components within a composite material has always been a challenging task (Christensen, 1979). The main difficulties arise from inherent strength variations within the mass of the composite systems and the need for long-term predictions concerning the performance of the composite in terms of the mechanical properties. Although a previously described system (Reifsnider, 1994) was initially suggested for fiber-matrix composite materials, it could possibly be applied in the case of LDPE/EAA/wheat starch composites as well. According to this model, deformed starch particles constitute the core material, and this is surrounded by an LDPE/EAA continuous matrix. Depending on the relative distribution of the EAA, regions of LDPE/starch/EAA vary in their plasticity; a high EAA content promotes greater plasticity in the matrix, while in regions of lower EAA content, debonding and slipping may occur at the matrix/starch particle interface.

Both LDPE and high-density polyethylene (HDPE) were thoroughly investigated with regard to their gas permeability (GP) (Van Krevelen, 1990; Yasuda and Stannett, 1962) because of their extensive use in food packaging applications. LDPE is a semicrystalline polymer of both amorphous (intralamellar, interlamellar, and interspherulitic) and crystalline (ribbon-like lamellae) areas (Michaels and Bixler, 1961). The presence of starch particulates as fillers within the LDPE matrix, apart from disturbing the continuity of the LDPE network and contributing to the inhomogeneity of the system, substantially enhances the GP of the LDPE/starch composite structure because of their strongly hydrophilic character. The water is either strongly bound (0–12%) or is capillary moisture (12–30%). The temperature dependence of GP and gas diffusion (GD) of the blends is described by the well-known Arrhenius equations.

At this point, it is worth emphasizing the importance of the activation energy of diffusion because of its involvement in chain separation, which is necessary for the eventual "loosening" of the structure. Certainly, the incorporation of starch particles disrupts the LDPE network by imparting some flexibility and mobility and thus reducing the required energy per unit chain separation. An increase in temperature enhances the cavity and channel formation even more, thereby facilitating the diffusivity and permeability. The diffusion and the permeation activation energies were found to fall in the following order with regard to the permeating gas: ED $(N_2) < ED(O_2) < ED(CO_2)$. This order is in agreement with other reports, assuming that there is no interaction between the permeant gas and the matrix (LDPE/starch). LDPE/starch blends have been used commercially for the past 15–20 years. The generally accepted degradation scheme of a high molar mass polymer consists of the following stages:

$$\begin{array}{c} O_2 \\ \downarrow \\ \text{High MW} \rightarrow \text{low MW} \rightarrow \text{organic fragments} \rightarrow CO_2 \\ + O_2 + \text{energy} \rightarrow \text{energy biomass} \rightarrow \text{endogenous} \\ \text{respiration, growth, and cell division} \end{array}$$

Both soil burial and bioreactor exposure experiments showed a decrease in percentage elongation and considerable weight loss, which could be described as a two-stage process (Krupp and Jewell, 1992). The first stage consists of partial starch removal, and only at a later stage does a slow rate of degradation of LDPE occur. Most investigations consider enzymatic oxidation, dehydrogenation, and carbon–carbon breaking processes to be the predominant degradation mechanisms of LDPE (Albertsson and Karlsson, 1994; Albertsson and Ranby, 1979; Albertsson et al., 1994). However, the biodegradation rate of LDPE/starch blends can be effectively accelerated only if the starch content is higher than 10%. Similar conclusions were also reached by other researchers (Goheen and Wool, 1991; Gould et al., 1990; Narayan, 1991; Wool, 1995) who, in addition, applied the percolation theory (Stauffer, 1985) assisted by computer simulation (Peanasky et al., 1991). In general, the higher the starch content, the worse the performance of the composite materials will be (lower TS and modulus, higher GP and water vapor transmission rate), but the higher their biodegradability. An increase in moisture or EAA (whenever used) content of these composite materials induced plasticization of the samples. The degradability of LDPE/starch blends was confirmed by weight loss measurements and changes in mechanical properties.

14.2 Chitosan–Poly(Vinyl Alcohol) Blends

Poly(vinyl alcohol) (PVA) can be prepared by hydrolysis of a variety of poly(vinyl esters) and poly (vinyl ethers) and has many applications in pharmaceuticals, cosmetics, and the paper and food industries, either alone or in blends with other polymers, such as poly(3-hydroxy butyrate) (Azuma et al., 1992), polyacrylic acid (Daniliuc and David, 1996), β-chitin (Lee et al., 1996), cellulose (Hasegawa et al., 1992a,b, 1994), among others. Chitosan is the deacetylated product of chitin. Next to cellulose, chitin is the second most abundant polysaccharide in nature (Rathke and Hudson, 1994). Chitin is associated with other polysaccharides in fungal cell walls, while in animal forms, chitin is associated with proteins (Muzzarelli, 1977). The production of chitin is possible primarily as a secondary activity related to the marine food industry (Zikakis, 1984). Chitosan has been used in a very wide range of applications, such as prevention of water pollution by chelating heavy metals or radioactive isotopes, in membrane separation (Aiba et al., 1986), in medicine and biotechnology, and in the food areas, either as a food packaging material because of its antimicrobial action, or as dietary fiber and a potential medicine against hypertension thanks to its scavenging action for chloride ions (Furda and Brine, 1990; Ishikura, 1993; Muzzarelli, 1996; Okuda, 1995). The preparation of chitosan/PVA blends was carried out as follows. The PVA solution was added, under vigorous stirring and heating, to the chitosan solution and then the plasticizer was added and mixed into the solution for 10−15 min until dispersed. Then the solution was cast over plexiglass plates. Low-molecular weight compounds added to chitosan/PVA blends are shown to lower the melting point and the glass transition T_g. Wide-angle X-ray diffraction patterns (WAXDP) showed that PVA has a high percentage crystallinity ($X_c = 54\%$). The observed reduction in percentage crystallinity in chitosan/PVA blends should be due to "crystallization disturbance" of chitosan in the blend state.

Novel chitosan/PVA composite packaging films were prepared by the casting method, and the effects of chitosan concentration on the structures, mechanical properties, permeability for oxygen, and water vapor were presented in the Li et al.'s (2011) study. Mechanical properties of these films, which were evaluated by the tensile test and the barrier properties, showed that the elongation at break (E) of the composite films decreased rapidly with the addition of chitosan, whereas the TS presented an almost opposite trend. Both the water vapor and oxygen transmission rate values were increased with the increasing amount of the chitosan in the composite films. Based on the obtained results, the optimum property of the composite films were chitosan/PVA blends at a weight ratio of 3:5, in which the TS and elongation at break of the packaging films were 34.12 MPa and 40.24%, respectively.

Chitosan/PCL blend has a perspective in biomaterials. However, the correlation between protein adsorption and cell activity on blends is still unknown. The objective is to investigate the correlation between protein adsorption behaviors and cell activities in chitosan/PCL blend films. Chitosan/PCL films with different mass ratios were prepared by spin coating with chitosan/PCL mixture solution. Atomic force microscopy (AFM), drop shape analysis (DSA), quartz crystal microbalance (QCM), and MTT (microwave thermal treatment) methods were used to analyze the surface morphology, hydrophilicity, protein adsorption, and cell metabolic activity of films. These properties are largely related to the mass ratio of chitosan and PCL. The cell metabolic activity observed on hydrophobic PCL films is superior, and cell adhesion level on hydrophilic chitosan films is excellent (Min et al., 2011).

14.3 Landfill

Landfill has served mankind for much longer than any alternative disposal option. Landfilling is defined as the disposal, compression, and embankment fill of waste at appropriate sites. Landfill for the moment is easy, adjustable with lower cost than other disposal methods, and stands alone as the only all waste material disposal method (Clarke et al., 1999; Karakasidis, 1997). Although landfill was traditionally selected by many communities because of its low cost, it has become prohibitively expensive. The costs of landfill rose due to the decreasing number of landfill sites and the more sophisticated techniques and operating practices (Adams et al., 1996; Von Schoenberg, 1995). Important factors that need to be taken into account for the correct function of disposal sites are the selection of the site, its design and organization, operating performance and life cycle, and biodegradability of the wastes (Karakasidis, 1997). The environmental impact of waste landfilling depends on the design and operational mode of the landfill facility and the nature of the waste deposited (Dascalopoulos et al., 1998). The landfill gas generated at landfill sites was considered barely controllable and one of the main disadvantages of this method. However, the production of such gas has recently been perceived as a promising source of highly combustible fuel since it is a clean source of fuel (Clarke et al., 1999; Von Schoenberg, 1995).

In order to comply with the EU ELV (End-of-Life Vehicles) Directive, an increase in the recycling rate of automobiles to 80% by 2006 and 85%

by 2015 must be met (EC, 2000). On average, the plastic content of a car was 9% and the average thermoplastic content is about 45% polyolefin (40% PP, 4–6% PE). The properties of a blow-molded bottle prepared from 100% postconsumer HDPE showed that this recycled polymer exceeded the material specifications for virgin plastic designs. Similarly, a sample of thermoplastic polyolefin (TPO, 100% polypropylene (PP)) obtained entirely from shredder residue (SR) displayed sufficient material strength for future separation and reprocessing (Ambrose et al., 2002).

14.4 Incineration

An alternative method of waste disposal to landfill is waste incineration. Waste incinerators use the process of combustion to convert the waste materials into carbon dioxide and water. Incineration residues usually consist of small quantities of HCl, S, and other volatile compounds and ash (Waite, 1995). However, it is obvious that not all household waste materials are combustible. Reduction of waste volume by 80–90% is achieved with incineration. Therefore, it should be considered as a means of reducing the amount of waste to be disposed of by landfill rather than a method of ultimate disposal on its own (Von Schoenberg, 1995).

Combustion can be regarded either as a pretreatment method for the waste prior to its final disposal or as a means for increasing value to waste by energy recovery (Dascalopoulos et al., 1998). Incineration became an increasingly popular method of waste disposal by the beginning of the 1970s when many incinerators were constructed (Waite, 1995). The effect of polymers on the combustion of municipal solid waste (MSW) has not been satisfactorily assessed in the past. The Association of Polymer Manufacturers in Europe (APME), in conjunction with academia, launched an in-depth program aimed at understanding the role of polymers in MSW combustors. The APME program on energy recovery from used plastics is focused on exploring all technically different means (Mark, 1995). Co-combustion is regarded as one of the most promising means for economic and safety reasons. As a result, conversion of polyurethanes together with other materials such as textiles, wood, paper, and other plastics into energy in "state of art" incinerators, which meet all health and safety requirements and the respective legislative regulations for emissions and environmental standards, would be an important process contributing to the economy and environment, both now and in the future (Bastian et al., 1995). Waste combustion with energy recovery is usually cost-effective only in large, heavily populated metropolitan areas. This approach becomes less appealing with low fossil fuel cost, strong markets for paper, and the necessity for disposing of a substantial volume of residue, a part of which may be hazardous (Mark, 1995). However, the main problems to be addressed prior to extensive utilization of this method are the finite risk of contamination, noise, odor, fire and explosion hazards, vegetation damage, ground water pollution, and air pollution (El-Fadel et al., 1997). The consumption of crude oil, natural gas, and pit coal, normally used in district heating plants, can be substantially lowered by the incineration of plastic waste. Assuming that the efficiency of an incineration plant and a district heating plant is the same (80%), the incineration of 1-kg LDPE releases 43.3 MJ, which corresponds to 0.08-kg crude oil, 0.07-kg natural gas, and 0.25-kg pit coal (Molgaard, 1995). The cost of landfill or incineration varies in different countries, as do the treatment routes employed by different European nations (Morris et al., 1998; Palin and Whiting, 1998; Simons et al., 1995).

14.5 Pyrolysis

High-molecular weight substances cannot be purified by physical processes like distillation, extraction, or crystallization. They can only be recycled by pyrolysis of their macromolecules into smaller fragments. Pyrolysis can be used to convert mixed plastic wastes to oil products, combustible gas and heavy residues. The pyrolysis products may then be suitable for common petrochemical separation processes. Pyrolysis is the thermal degradation of macromolecules in the absence of air, and it generates oils and gases, which are suitable for chemical utilization or generation of energy. In fact, the pyrolysis products consist of 34% ethylene, 9% propane, 39.7% oil (mainly aromatic compounds), and 1.7% residue (Faaij et al., 1998; Kaminsky, 1995).

The Constantinople composting and recycling plant, constructed in 2001, is one of the few composting plants in Turkey. During test operations of the plant, it was reported that the weight of the oversize materials (OM) above an 80-mm sieve was about 40% of the total incoming waste. They mainly consist of plastic bags that were full of garbage, which resulted in operational problems in the plant. In a study, the composition of OM was determined and evaluated, particularly to find the economic losses in the plant. It was determined that approximately 58% of the OM transferred to the landfill area due to operational failures and interruptions could be used at the plant with improved operational conditions. Otherwise, the plant would realize an annual economic loss of about 640−800 million US$. Compost quality in the plant has been satisfactory, but source-separated collection, at least the separation of the wet from the dry fraction, is needed to increase the amount of compost and recovered materials. To increase the amount of compost and captured recyclable materials in the Constantinople plant, all plastic garbage bags should be torn in the first step of the process. However, appropriate waste collection (higher organic and recyclable content) from potential districts of the city is still an important factor for the plant. The best way to improve the situation would be source-separated collection, at least the separation of the wet from dry fractions. In Turkey and some other developing countries, it is difficult to operate plants optimally, especially publicly owned plants, due to investment and administrative problems. The most important inadequacy in any environmental management activity in those countries is the operating problems and the lack of research during operation of the plants (Kanat et al., 2006).

The thermal decomposition of polyalkenes was investigated as a recycling route for the production of a petrochemical feedstock. LDPE and PP were thermally decomposed individually in a batch reactor at 450°C, thus forming oil/wax products. Then these products were dissolved in primary heavy naphtha to obtain steam cracking feedstock. The selectivity and kinetics of copyrolysis for 10 mass % solutions of oil/waxes from LDPE or PP with naphtha in the temperature range from 740°C to 820°C at residence times from 0.09 s to 0.54 s were studied. The decomposition of polyalkene oil/waxes during copyrolysis was confirmed. It was shown that the yields of the desired alkenes (ethene, propene), according to polymer type, increased or only slightly decreased compared to the yields from naphtha. In addition to the primary reactions, the secondary reactions leading to coke formation were also studied. The formation of coke during copyrolysis of LDPE wax with naphtha was comparable to the coking of pure naphtha. Slightly higher formation of coke was obtained at PP wax solution at the beginning of the measurements, on the clean surface of the reactor. After a thin layer of coke covered the walls, the production was the same as that from naphtha. The results confirmed the possibility of polyalkene recycling via the copyrolysis of polyalkene oils and waxes with conventional liquid steam cracking feedstocks in already existing industrial ethylene units (Hajekova and Bajus, 2005). The results obtained proved that the oil/wax fractions obtained from the thermal decomposition of polyalkenes under mild conditions can be added to liquid charges for steam cracking in the amount of 10 mass%. It is not necessary to separate the oil and wax fractions from each other at this level. Such a separation would unnecessarily increase the costs for preparing these raw materials. The gases formed by the decomposition of polyalkenes can be burnt, but in the case of fluid cracking of polyalkenes, they can also be returned to the process as fluidizing gas. They can also be added to the streams of gases that are formed at the steam cracking unit, and thus the already existing equipment for separation of gases from steam cracking can be utilized. A 10 mass% concentration of oil/waxes does not cause any problems on spreading. Slightly warming up the raw material in the tank is sufficient.

14.6 Reuse and Recovery

One of the priorities set in most countries around the world is drastic waste reduction. Where waste cannot be avoided, it must be recovered, preferably in an environmentally friendly way. This simply means recover and reuse something after its initial function has expired. The ways that the recovered material can be used may be similar or dissimilar to their original function (Lemann, 1995). The strategies identified to help waste prevention include material life extension, process management, and reduction of material used (Bergner, 1995). The term "reuse" expresses the identification of the most cost-effective avenue in reusing goods, components, and materials. When a product is designed, the requirements of reuse and collection processes need to be taken into account (Stahel, 1995). Moreover, the recovery and reuse of waste must not result in an enrichment of hazardous substances within the substance life cycle. All plastic materials interact with "products" to a certain extent. This interaction can either be superficial or more extensive, followed by absorption into the body of the plastic. Contamination of refillable containers through migration of substances (i.e., dyes, flavors) into the plastic could occur at various times during the material's shelf life. Although these substances may not be affected by the washing process, they might subsequently be released into the food on their reuse, with serious implications regarding both consumer safety and sensory characteristics of food.

A plastic container is suitable for refilling when it is resistant to the uptake of chemical and microbiological (toxicological) hazards and taints. Exposure to chronic toxins is statistically unlikely to occur with contaminated containers, but a single exposure at a high level could be a major issue (Castle, 1994).

14.7 Composting

MSW composting is an alternative to the disposal of wastes that has attracted interest in the United States and Europe. A study on composting in the United States lists 15 facilities that are currently operational and an additional 23 that are under construction or at planning or designing stages. In Europe, composting facilities are operational or under construction in France, Holland, Switzerland, Italy, Greece, and Spain (Renkow and Rubin, 1998). Composting has been officially recognized as a form of recycling and is expected to play an even more important role in future waste management operations. Although composting has been rapidly gaining importance, the development of suitable technology still relies on practical experience. Composting still has to grow from an art to a well-established technology. Composting refers to a self-heating, aerobic process of organic wastes and other industrial organic compounds in order to convert them to a mature plant compatible substrate. If a material is considered compostable, biodeterioration/biodegradation should transform it into compost (Blanc et al., 1995; Narayan and Snook, 1994; Raschle et al., 1995; Tokiwa et al., 1989). Under optimal degradative conditions, a controlled composting process can be completed within 3 months, while under normal conditions this takes 1 to 2 years (Kaiser et al., 1995). The final product of

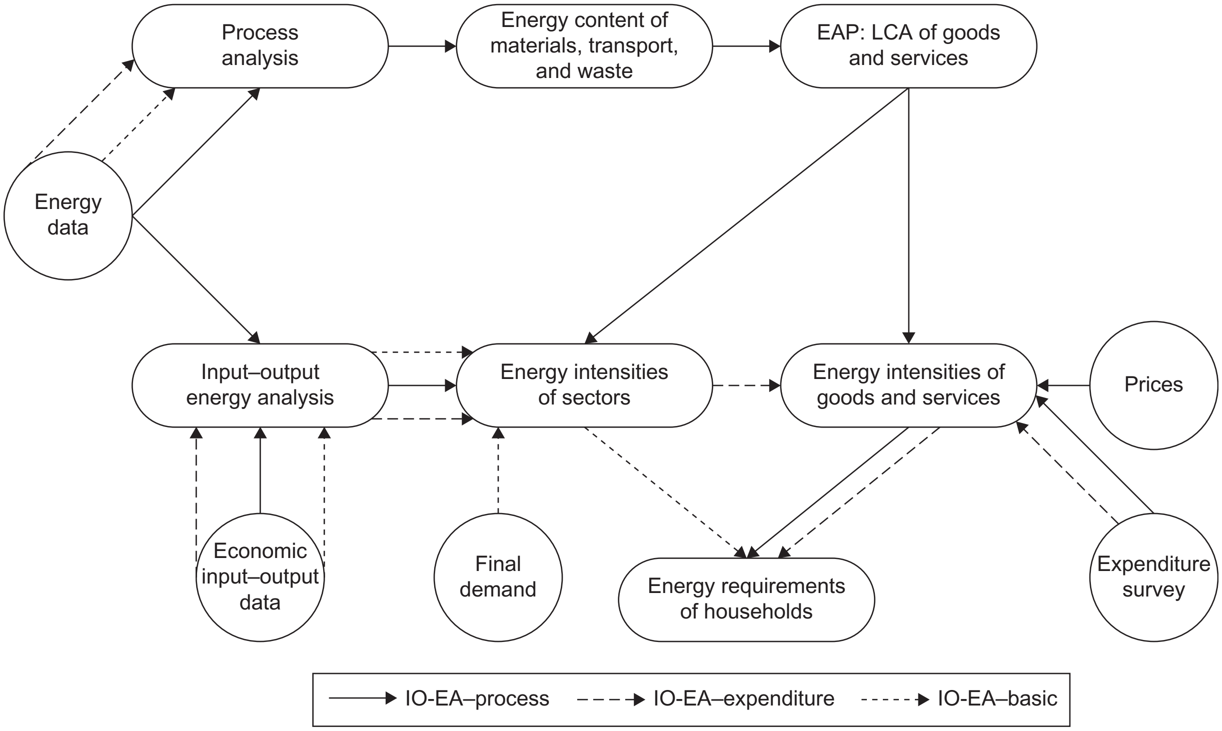

Figure 14.1 Data and operations needed for the three different energy analysis methods. *Source: Adapted from Kok et al. (2006).*

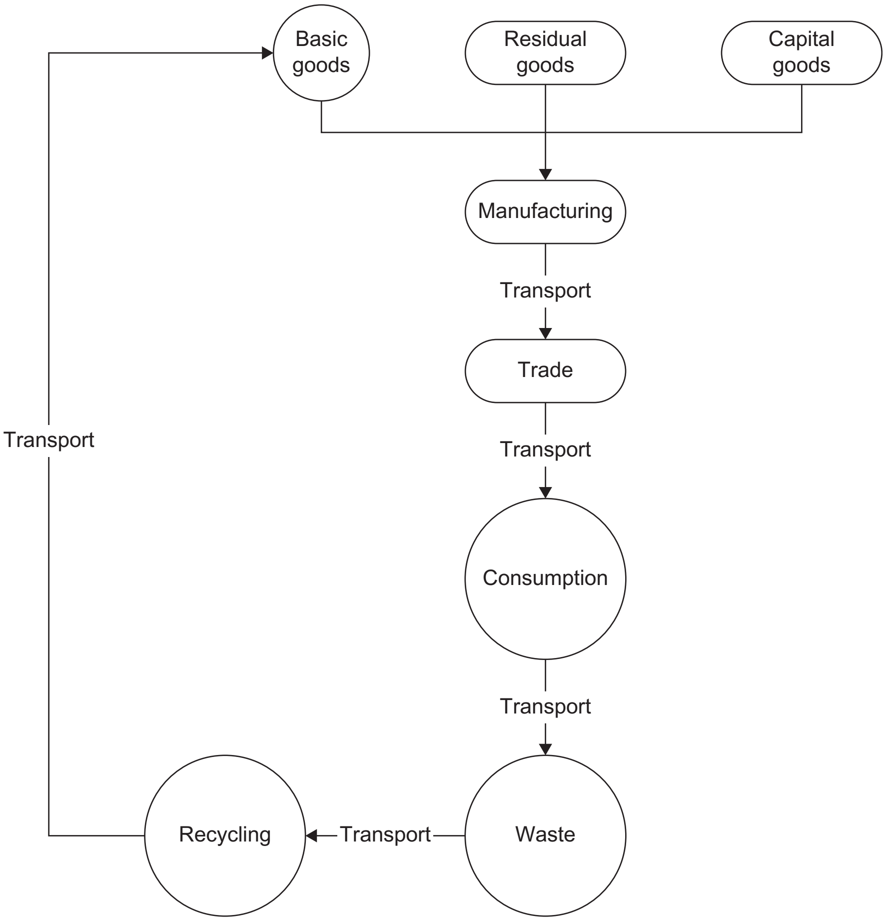

Figure 14.2 Life cycle of a product as used in the IO-EA-process method. *Source: Adapted from Kok et al. (2006).*

composting is rich in organic matter but its concentration of key nutrients, usually too low to compete with commercial fertilizers, improves the soil structure through its enrichment with humic substances (Marilley et al., 1995; Masters, 1998). Besides the microflora required for composting, composts can also harbor potentially pathogenic and/or allergenic bacteria and molds like *Aspergillus fumigatus* (Lott Fischer et al., 1995). The aim of the composting operation is to obtain, preferably in the short term with limited cost, compost with of desired quality. All composting operations should take place under controlled, environmentally safe conditions. During the process, gas and heat may be released that can be used for energy recovery while, at the same time, volume reduction of the original material by up to 40% can be achieved. Furthermore, the process is considered to be "environmentally friendly" and financially viable, but only under proper guidance and management. The basic reaction of the composting process is the oxidation of organic matter with oxygen to carbon dioxide and water by employing thermophilic microorganisms. Under normal temperature conditions (i.e., room temperature), chemical oxidation plays a minor role. At the same time, there is a release of heat resulting in a temperature increase within the composting matter. The process requires a blend of materials with appropriate physical and chemical properties and pertinent management to ensure that suitable process conditions are maintained. The process takes place at temperatures high enough to destroy pathogens. MSW composting treats all readily degradable components of the waste stream such as paper, food, and wood, which account for 55–70% (by weight) of a community's residential solid waste. The two basic processes applied in large-scale composting are classified as windrow-based and in-vessel technologies. In windrow systems, waste is conveyed to a central open-air facility and formed into windrows that are 3- to 5-ft (1- to 1.5-m) high. The windrows are turned periodically to maintain a stable temperature and decomposition rate, and water is periodically added to maintain

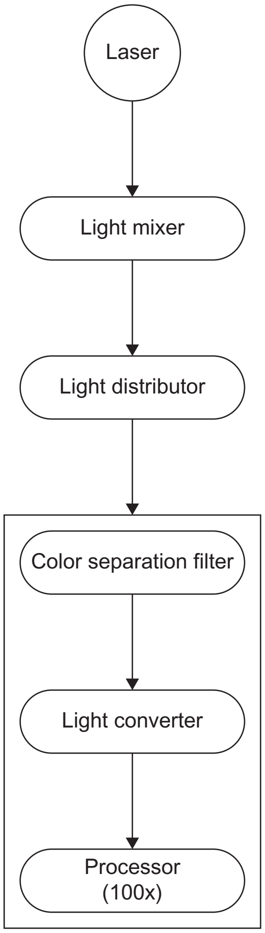

Figure 14.3 Glass laser sorting system. *Source: Adapted from Arvanitoyannis and Bosnea (2001a,b).*

an appropriate moisture content. After the targeted decomposition level has been attained, the composted product is ready for assembly and distribution to end users. Vessel systems employ considerably more sophisticated technologies that offer a highly controlled enclosed environment for effecting the biological decomposition, thus leading to a high-quality product. This system is more capital intensive than windrow technologies, and the sophisticated techniques require highly trained facility operating personnel. Therefore, the composting process is anticipated to play an important ecological role in the promotion of the biological carbon cycle. Similarly to the recycling of other materials, composting requires high-quality raw materials, thereby ensuring that no toxic and hazardous residues are included in the product. In addition to compromising product quality, materials that are resistant to biodegradation may severely affect compost processing. Nondegradable plastic films may interfere with the film screening of the composted product by plugging the screen or reducing the degradation of biodegradable materials by blocking the oxygen flow. The composting process is further affected by temperature, moisture, pH, nutrient supply, and oxygen availability, while temperature also plays an important role in hygiene (Beffa et al., 1995; Gajdos, 1995; Guneklee and Kubocz, 1995; Hamelers, 1994; Hanna, 1994; Neumann, 1995; Peringer et al., 1995; Schaub and Leonard, 1996; Siegenthaler, 1995; Vos, 1994). The composting process is shown in Figure 14.14.

14.8 Recycling

According to Waite (1995), “recycling is a very broad term referring to the conversion of waste into a useful material”. While recycling is second in the priority of waste management options, it has gained ground in many European and American countries as an essential ingredient for the reduction of wastes that would otherwise be landfilled. Over the past decade, the emphasis on the part of MSW management has been on recycling due to the introduction of waste management hierarchy. Recycling is a relatively old method with a well-recorded history. Metals have been recycled since their discovery because of their high value, rarity, and properties that allow near indefinite reprocessing. The recycling of old textiles is equally old since historically they were used for the production of paper. Among the factors which have contributed to improving the recycling process are the decrease in available landfill and the urgent need for raw materials recovery that could be used by reducing the amount of natural resources consumed. Moreover, the increasing public interest in environmental protection has enhanced the importance of recycling as an alternative solution to the constantly escalating waste problem (Alter, 1997; Vogas, 1995).

According to NSWA (National Solid Waste Management Association), recycling consists of six basic steps:

1. Collection and sorting of recyclable materials from the waste stream,
2. Raw material reclamation by special treatment, so that they could replace virgin materials in manufacturing operations,
3. Marketing of the recycling materials,
4. Market establishment for recycled materials,

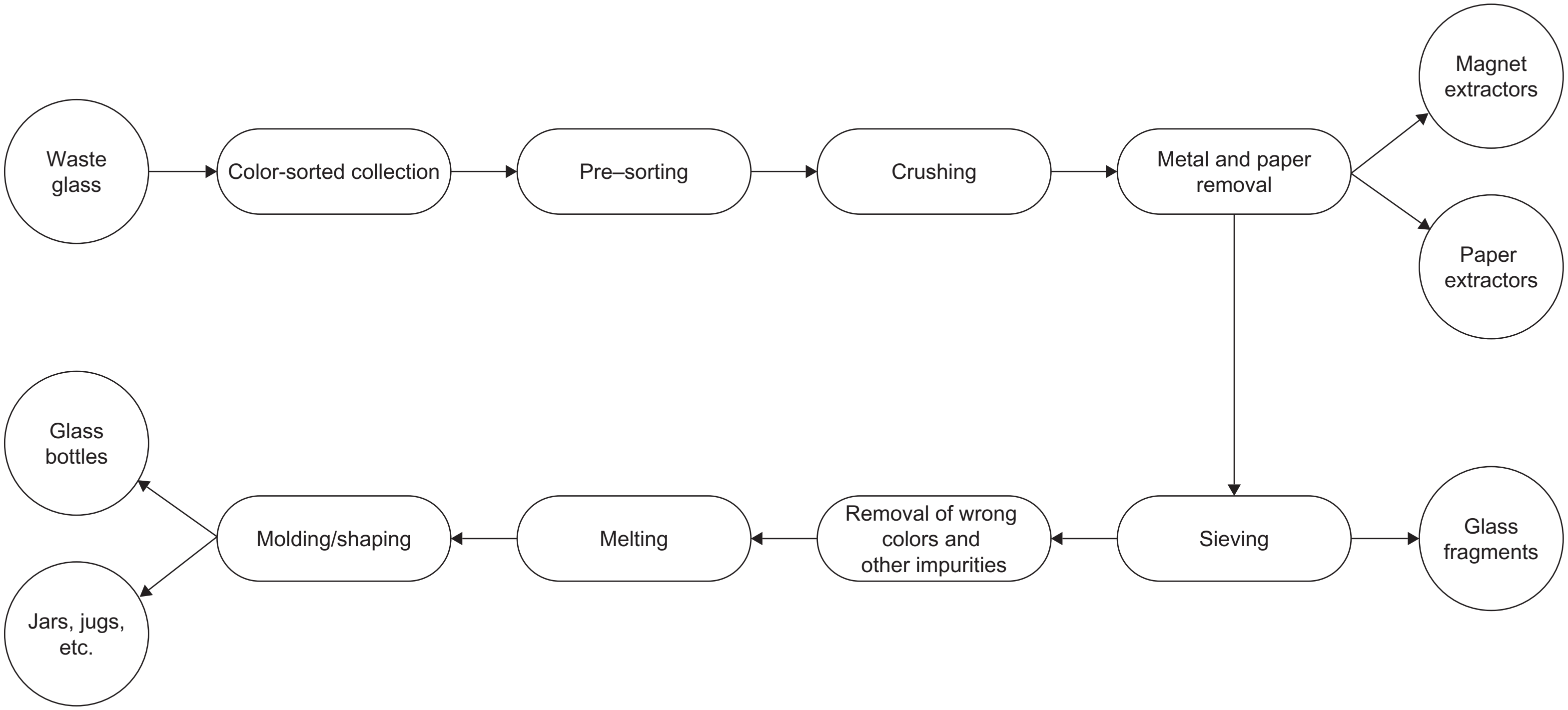

Figure 14.4 Glass recycling process. *Source: Adapted from Arvanitoyannis and Bosnea (2001a,b).*

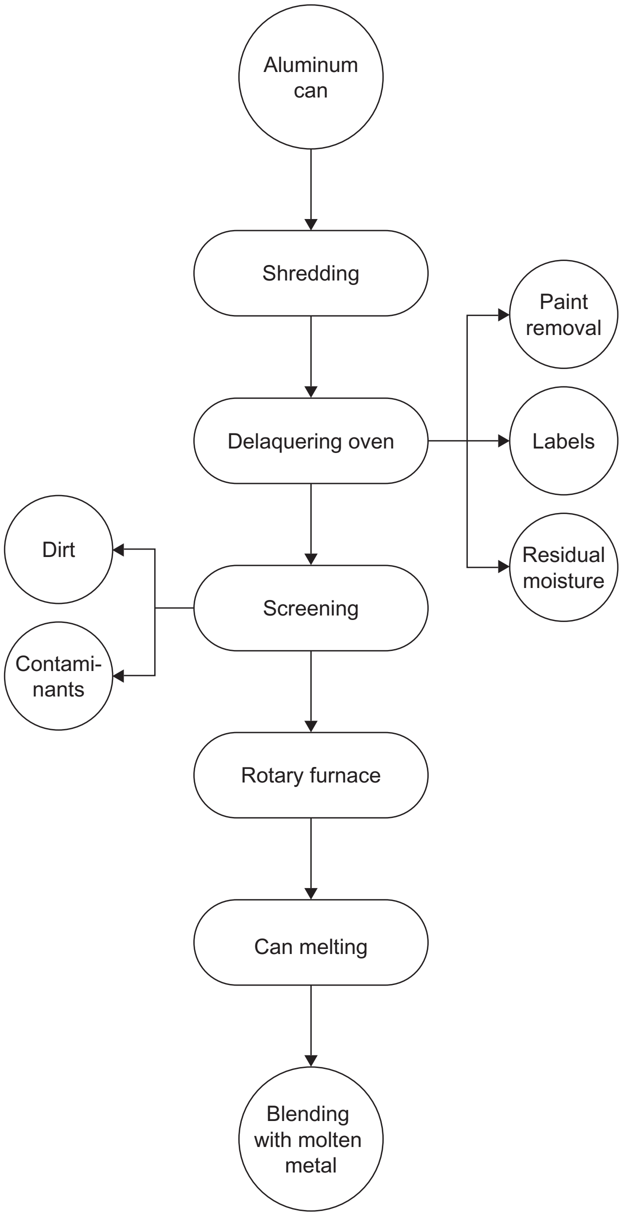

Figure 14.5 Flow diagram for metal recycling.
Source: Adapted from Onusseit (2006).

5. Public involvement in the recycling programs operations,
6. Collection recycling programs target the useless materials from the waste stream and treat them in such a way so that they could return to the industries as raw materials for packaging applications (Vogas, 1995).

Any responsible recycling operation has to meet market, economic, and environmental requirements. The viability of recycling depends on the following factors:

1. the packaging or product design: since the product should be designed for recycling, mixed plastic materials which complicate the recycling operations should be avoided,
2. the raw materials: it is essential that the product does not contain any nonrecyclable raw materials,
3. management operations: that is, identifying distribution channels,
4. legislation: inspection of legislation for packaging and taxes involved to verify that it does not interfere with recycling management options,
5. consumer education concerning recycling: increasing the percentage of informed and educated consumers concerning recycling further promotes the recycling management scheme,
6. technological advances and their applications: this plays an important role in improving the recycling processes (Vogas, 1995).

As far as the economic viability of recycling is concerned, it needs to be measured against the alternative waste management operations. The cost of recycling is mainly governed by three elements (Pearson, 1996):

1. the cost to collect and to sort,
2. minus the cost of landfill avoided,
3. minus the revenue from the recyclable sold by the material recovery facility.

Industrial recycling is so well established that under ordinary commercial practices many secondary materials are destined only for recovery or reclamation and not for discard and final disposal (Alter, 1997). The percentage of recycling of glass, aluminum, and polyethylene terephthalate (PET) in the European Union and the United States is given in Figure 14.15.

14.8.1 Plastic Recycling

The number of recyclable materials collected through the waste stream is quite large and consists of glass, plastic, scrap metal, tins, paper and board, fabrics, oils, construction materials, ash, and organic substances (Waite, 1995). Plastic makes up around 8% of the total waste weight out of which nearly 85% are thermoplastics: these are mainly PET, HDPE/LDPE, polyvinyl chloride (PVC), and

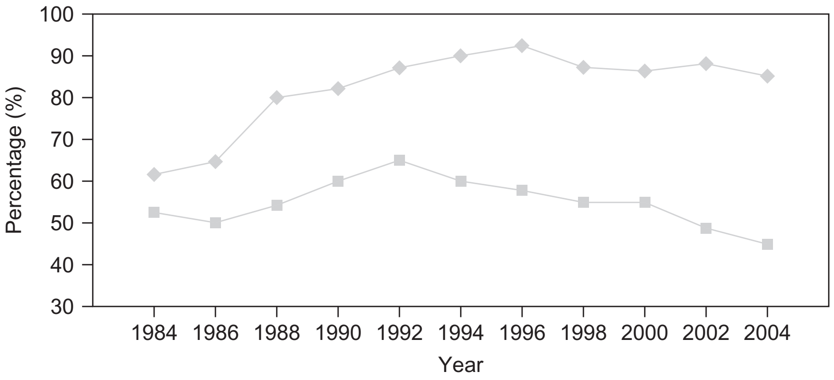

Figure 14.6 Recycling rate for aluminum cans in Sweden and the United States (1984–2004) (♦ Sweden and ■ the United States). *Source: Adapted from http://container-recycling.org/alumrate/gaphs.htm.*

PP. The recycling rate for all plastic bottles dropped from 24.5% in 1996 to 23.7% in 1997. PET soda bottles represent 26% of total plastic bottle production and 40% of total plastic bottles recycled. PET beverage and soda bottles combined represent 44% of total plastic bottle production and 48% of total plastic bottles recycled. The recycling rates for PET soda bottles and for all PET bottles have been in decline for several years in the United States. PET soda bottle recycling rate (36%) was 8% lower than in 1996 and 25% lower than in 1994. Total PET bottle recycling rate (25%) was 9% lower than in 1996 and 18% lower than in 1994. One reason for the drop in the PET bottle recycling rate is the fact that PET resin production increased by 45% between 1994 and 1997. Another is the fact that 60% of the PET soda bottle market is made up of single-serve bottles, and most of those soda bottles are consumed away from home and away from curbside recycling bins. If the major soft drink companies were to use 25% recycled content in their PET soda bottles, they could boost the PET bottle recycling rate from the current rate of 36% to 61%, the total PET bottle recycling rate from 25% to 40%, and the total plastic bottle recycling rate from 24% to 30% (Anonymous, 1994, 1998).

Statistics show that plastic waste is set to become one of the largest categories in MSW. Although only representing around 4% of total oil consumption, plastics represent a valuable resource. The 4% of the world's oil consumption used in plastic products actually helps users of oil (transport, heating, etc.) to become more energy efficient. Therefore, plastic recycling is important to the plastic industry, energy savings, and the environment.

In the United States, plastics account for 13% by weight of waste and are handled by MSW management operations. The United States has historically relied on landfilling as its principal disposal technique. In 1972, approximately 20,000 landfills were operational, while in 1990 this was reduced to 6300 landfills in which over 80% of US MSW was disposed. The number of landfills is expected to decrease even further to 2100 by the end of 2000, while recycling and other waste management techniques would handle the main bulk of wastes (Anonymous, 1990; Jenkins, 1991; Liesemer, 1992). In contrast to the United States, Japan, with a much higher population density, in 1990 employed landfill for only 52% of its solid waste and Western Europe about 60%. Incineration, combined with energy recovery, was widely used in Japan (47% of MSW) as an important method of solid waste disposal in 1990 (Jenkins, 1991). Currently, in Western Europe, about 75% of plastics are landfilled, while 25% are recovered in the form of either new material or useful energy. In 1993, just over 50% of MSW generated in Sweden was incinerated, and the energy recovered was used for district heating (94%) and for electricity (6%) (Tamaddon et al., 1995). Finally, only 8% of MSW in Canada is incinerated, one of the lowest proportions among developed countries. Canada is the leading country in terms of the amount of waste per capita sent to landfill and has below-average rates of diversion to recycling or composting (Gilbert, 1998). Even though recycling is becoming increasingly important, not many comparative figures are available, and there are large differences in performance in recycling rates between countries (APME, 1999). The European community generally recycled by mechanical recycling about 7% of the total plastics consumed in 1995.

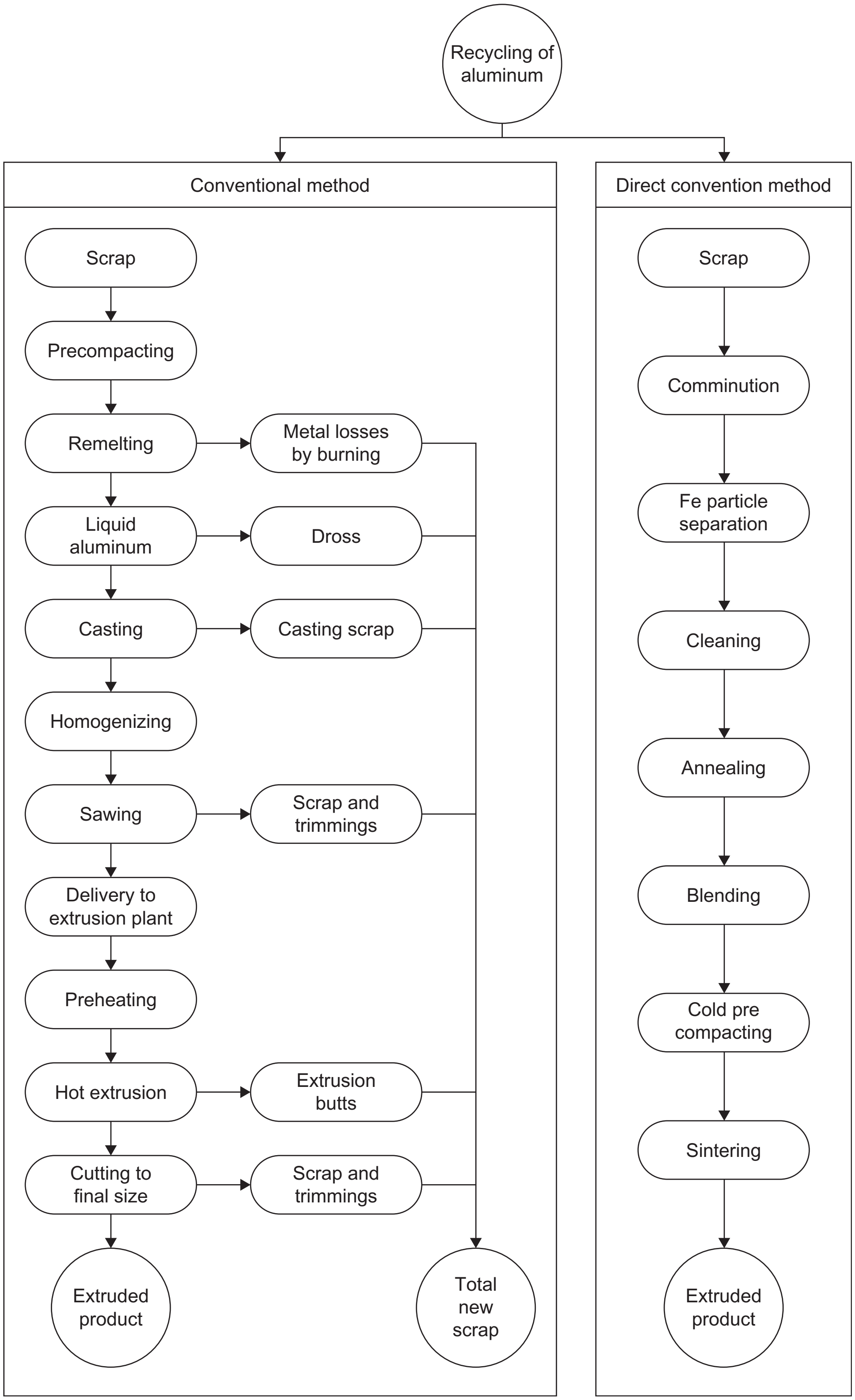

Figure 14.7 Flow charts of recycling aluminum scrap by conventional and direct convention method. *Source: Adapted from Gonostajski et al. (2000), Lazzaro and Atzori (1992), and Samuel (2003).*

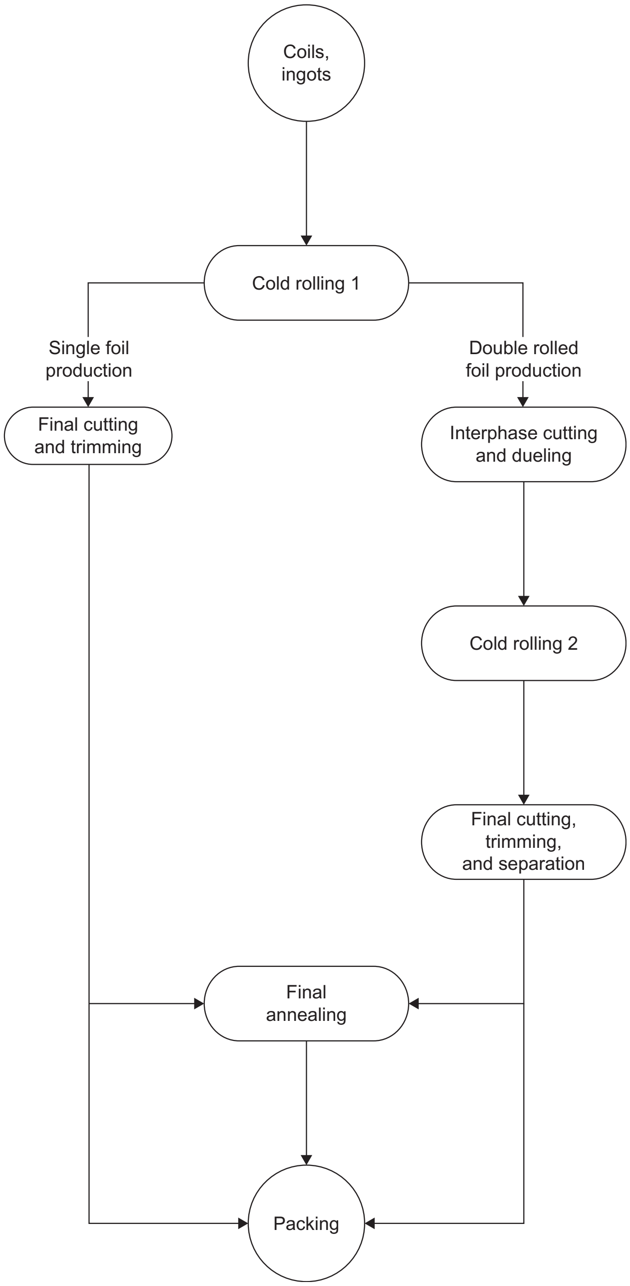

Figure 14.8 Scheme of aluminum foil production unit. *Source: Adapted from Logozar et al. (2006).*

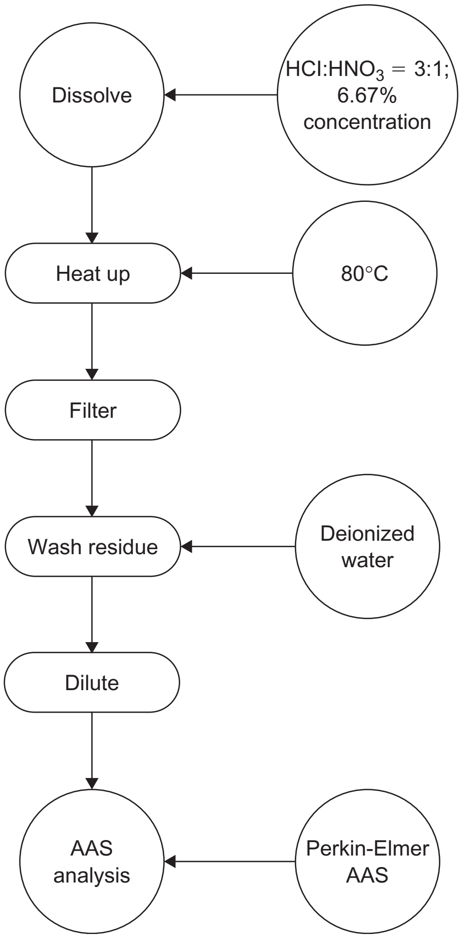

Figure 14.9 Metal assay approach for float and sink products. *Source: Adapted from Zhang and Forssberg (1997).*

In Western Europe, 25% of the plastics consumed during the period 1996–1997 were recovered (4,364,000 t) while, at the same time, there was an 8% increase in total plastics consumption and a 12% increase of recycling volume in 1996. In total, 8% of plastics recovered from Europe's waste stream was mechanically recycled, with agriculture (31%) and distribution sectors (23%) remaining the two sectors with the largest proportions of mechanically recycled plastics. Feedstock recycling rose by 33% from 251,000 t in 1996 to 334,000 t in 1997, but this method is used only in Germany. Europe, in 1997, recycled 14–15% of plastic packaging waste, of which 25 million tons was turned into energy (http://www.apme.org/press/htm/PR030299.htm). In 1995, Germany recycled 60% of consumed plastic of which 20.56% was recycled mechanically, 27.85% was sent abroad, and 9.56% by feedstock recycling. In 1996, the total recycling rate rose by 7.6%. After 1991, when the packaging ordinance was set in Germany, there was an enormous increase in its national recycling rates. In 1991, Germany began a very ambitious plastics recycling plan, the aim of which was to separate and recycle 80% of plastic components in packaging waste (Plinke and Kaempf, 1995). In 1994, it was estimated that 460,000 t was collected, although there was a recycling capacity of only 250,000 t. Unfortunately, this surplus was

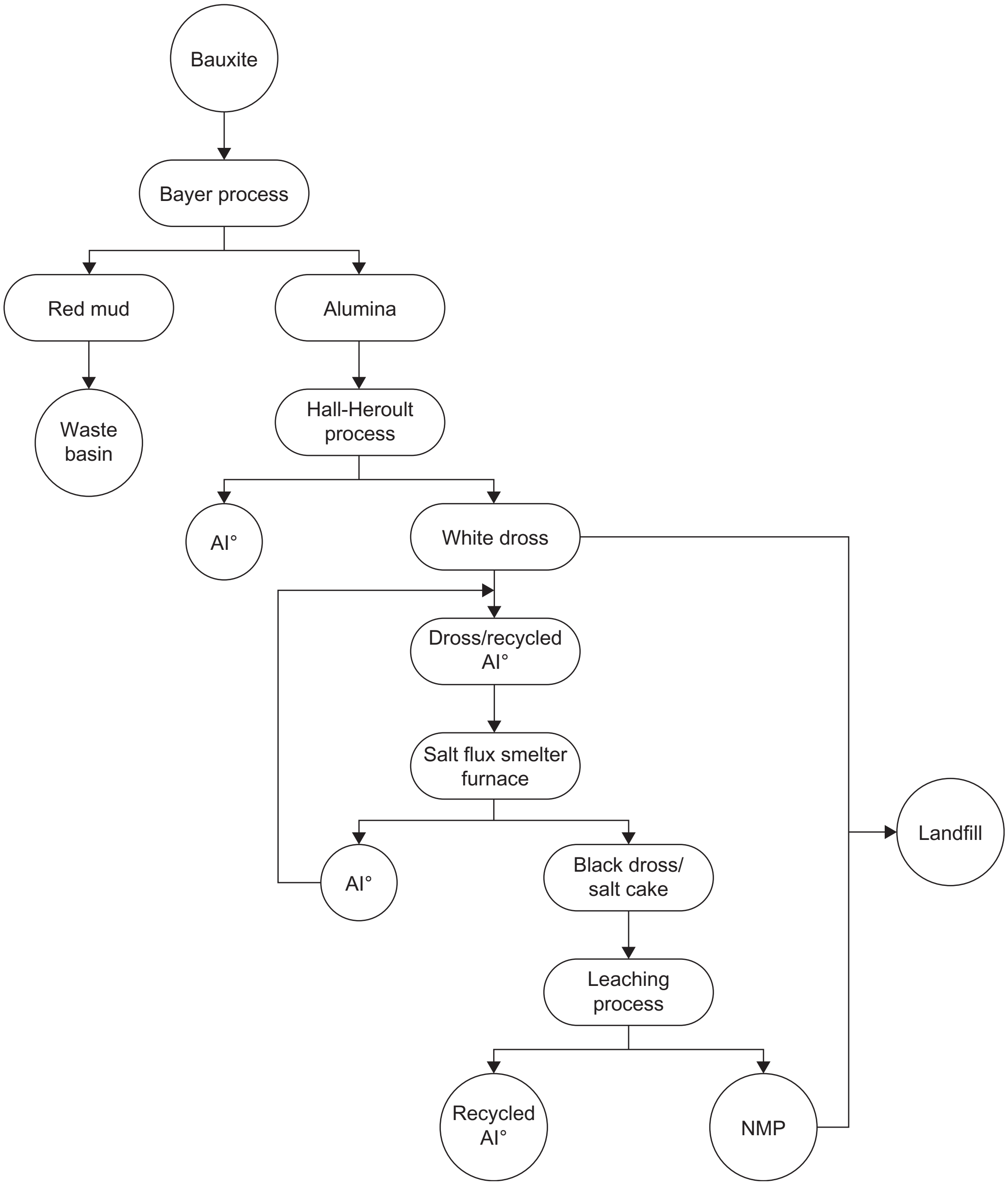

Figure 14.10 Aluminum schematic recycling process in Brazil. *Source: Adapted from Shinzato and Hypolito (2005).*

dumped in other countries, undermining their own recycling industries (Ball and Unsworth, 1995). Italy is the second country in Europe in terms of recycling plastic industries. In 1992, the number of recycling industries that imported recyclable materials from the international market reached a rate of 66.5% (Pinetti, 1995). In 1995, Austria and Switzerland mechanically recycled 15% and 11.9% of plastic waste, respectively (Hertzog, 1995; Mader, 1992). In Switzerland, 80% of household waste was incinerated and 20% landfilled in 1990, while 49% of the remaining urban solid waste was successfully recycled in 1993, which accounts for a total of 1,370,000 t of waste. Out of this waste, 6100 t of PET (72% of beverage containers) were recycled (Fahrni, 1995). Moreover, according to the latest figures from PET Container Recycling Europe, PET recycling had risen by 66% in 1996 throughout Europe. In Switzerland, plastics were collected early on and also used as regranulate, but the recycling rate in Switzerland and neighboring countries is disappointingly low at about 5−6%. It is estimated that

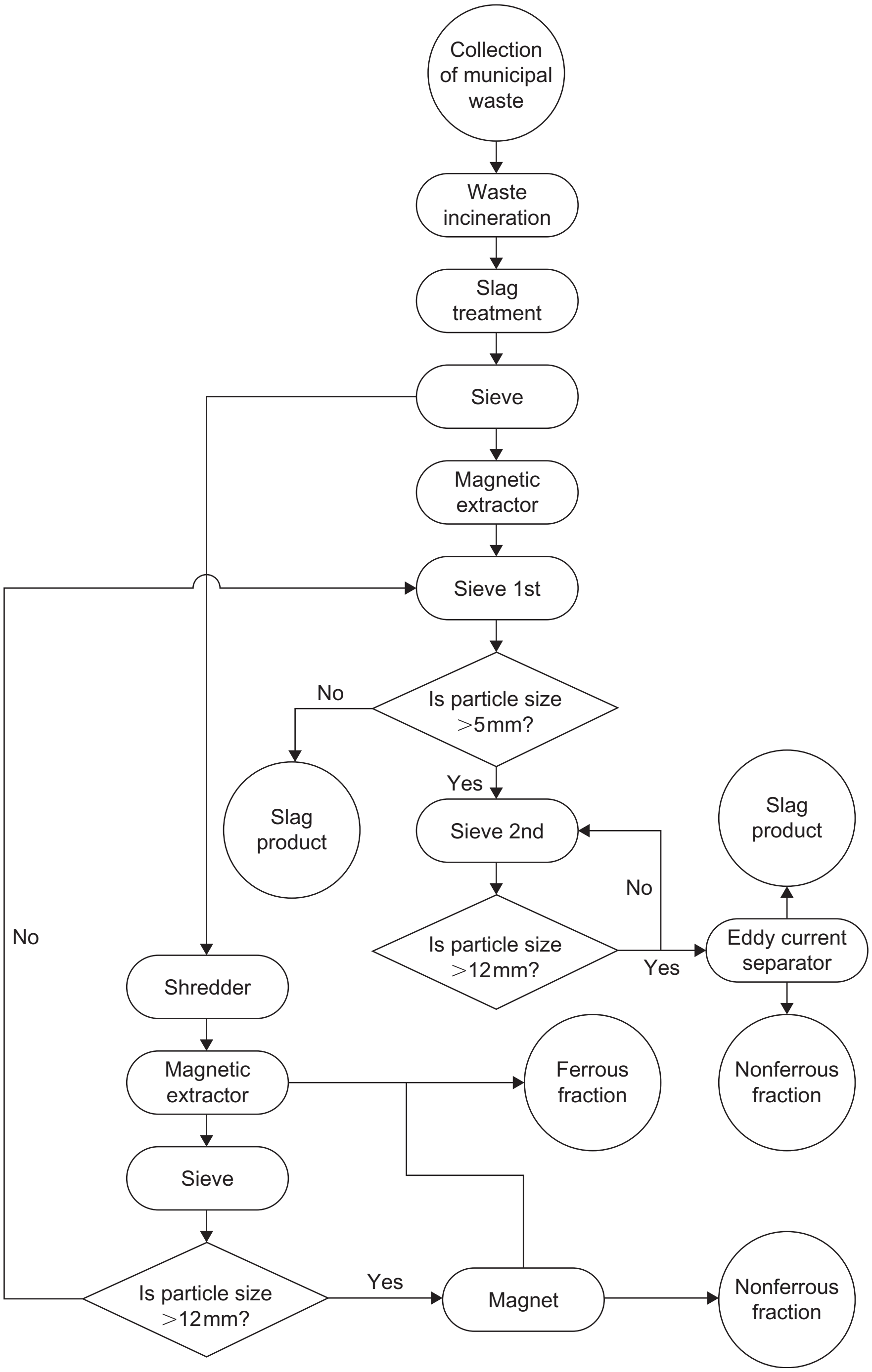

Figure 14.11 Process chain of slag processing with additional steps of metal recovery. *Source: Adapted from Quinkertz et al. (2001).*

more than 700,000 t was consumed in Switzerland, of which only 400,000 t was collected and returned for recycling and only 35,000 t of regranulate was used for further manufacture. The United States recycled about 2% in 1985, less than 5% of total plastic waste in 1994, while there was an increase of about 4% in recycling plastic in 1996 (Jenkins, 1991; Liesemer, 1992). The official recycling rate for the year 1997 increased to 27% of total municipal discards, twice the rate of a decade ago, while 9.5% is mechanically recycled. Nearly 1.4 billion pounds of postconsumer plastic bottles were recycled in 1997, a 4% increase from 1.32 billion in 1996. Even though more plastic bottles were recycled in 1997

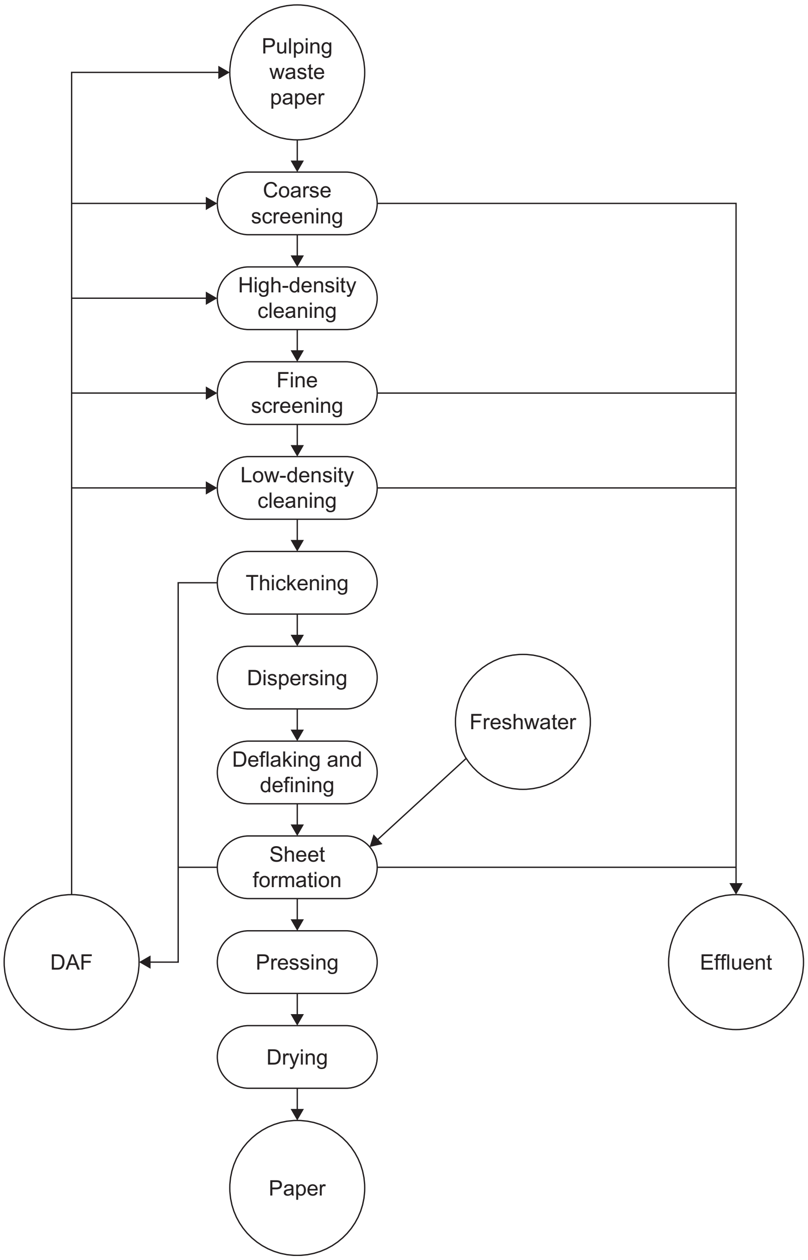

Figure 14.12 Process water usage and wastewater discharged from the board paper mill. *Source: Adapted from Sohair et al. (2006).*

than ever before, the recycling rate for plastic bottles decreased from 24.5% in 1996 to 23.7% in 1997. Recycling of PET soft drink and beverage bottles reached an all-time high of 649 million pounds for 1997. The recycling rate for PET bottles was the highest overall bottle recycling rate of any resin type at 25.4%. HDPE bottle recycling increased 7% in 1997 to 704 million pounds. Both natural and pigmented bottle rates saw significant gains in 1997. In the United States, the percentages of recycled plastics for 2004 were 22, 26, and 3.2 for PET, HDPE, and PP, respectively. As regards the United States, the postconsumer bottles recycle rate in 2005 was 24.3% (www.plasticsresource.com) (Tables 14.4 and 14.5).

In Australia, recycling comprised about 11% of the semirigid and rigid plastics disposal operations in 1992 and it involved about 42% of HDPE, 29% of PET, and 6% of vinyl polymers in 1996. As far as Japan is concerned, in 1995, 28% of total plastic

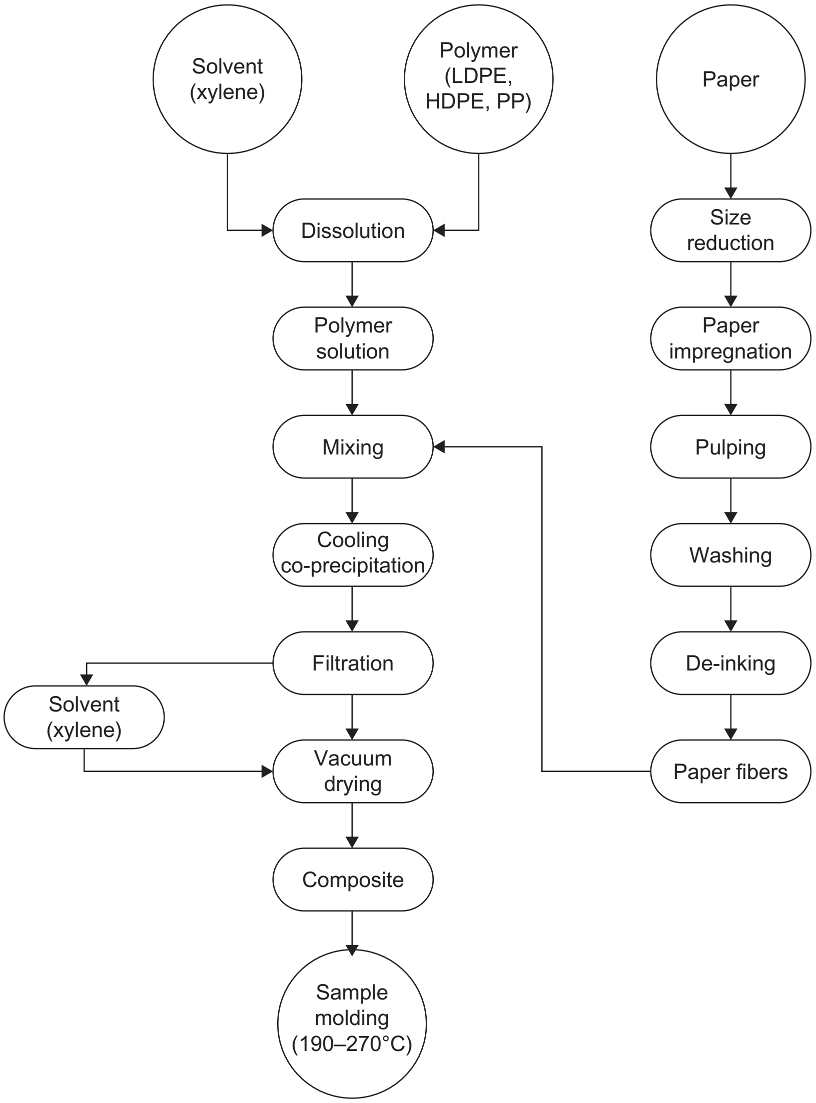

Figure 14.13 Polyolefin/newspaper fiber composites preparation and characterization flow sheet. *Source: Adapted from Baroulaki et al. (2006).*

waste was recycled: 11% mechanically and 17% by thermal recycling, 35% of plastic went for incineration, and 37% was dumped on reclaimed land without any prior recycling. Furthermore, it was expected that by the beginning of 2000, more than 90% of plastics would be recycled in Japan (20% mechanically and 70% by thermal recycling), while landfilling would account for less than 10% in waste management operations. Hong Kong recycles much of its industrial and commercial paper and plastics, with this taking place entirely on the basis of existing market prices. However, in the case of domestic solid wastes, the level of recycling is generally low. Although aluminum cans are nearly 100% recovered, only small amounts of consumed plastics and paper are recycled (Barron and Ng, 1996; Okawa, 1995). In the EEC (European Economic Community), it is expected that 50−65% of packaging materials would be recovered, and 25−45% would be recycled by a minimum for each material of 15% by weight. In developing countries such as India, the problem of waste becomes a major issue since its collection, transportation, and disposal are unscientific and chaotic. Since formal investment on infrastructure is not increasing, most of these countries have to rely on private-sector initiatives for waste disposal (Dasgupta and Sharma, 1995; Gupta et al., 1998).

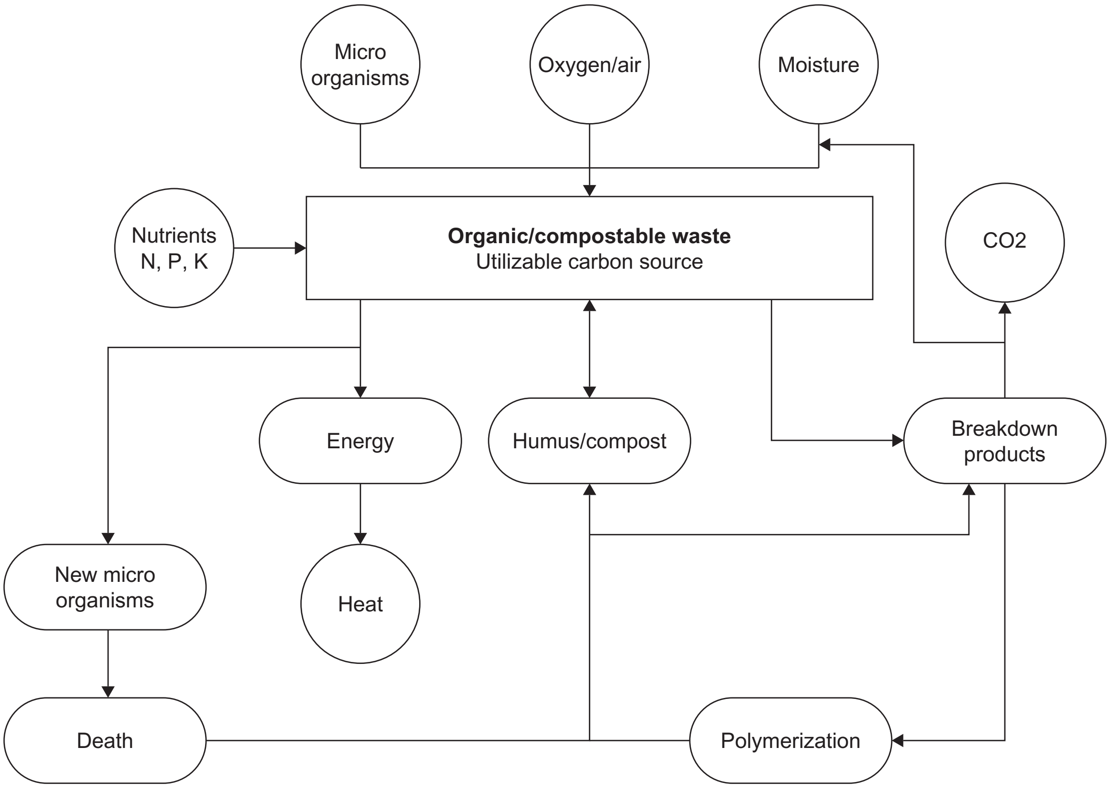

Figure 14.14 Composting process. *Source: Adapted from Arvanitoyannis (1999).*

Collection of Recyclable Materials

In most countries, the collection of MSW falls under the jurisdiction and direction of local authorities. Such authorities could be district councils, municipalities, or county councils. Each waste collection authority is responsible for organizing the collection of MSW for a particular area and delivering the waste to a point of disposal as directed by each country's ministry or responsible nationwide authority. This is an enormous task for the authorities because communities have to learn how to transform the collection to an economically viable enterprise. Traditionally, trash has been collected at the curbside of the homeowner. In such cases, it is possible to obtain 70% or more of the recyclables from the household wastes. In contrast, voluntary drop-off and payback approaches to gathering the recyclables from household wastes amount to only 20% and 10%, respectively. In several cases, a mixed system of collection has been endorsed (Chang et al., 1995; Chiellini, 1994). As far as hazardous household waste is concerned, several countries have already introduced national legislation for centralized collection schemes. It has been estimated that plastics constitute about 40% of the total volume of hospital waste. Many pilot plants have been set in various hospitals because it was proven that packaging waste is more easily collected and recycled in hospitals than private households provided that the required infrastructure and management are in place. Research and commercial experience clearly show that the more complicated the job becomes for the householder, the less recyclable materials are likely to be obtained. Since the capital cost for equipment to collect material at the curb and the labor associated with getting the material into the truck represent about 70% of total collection costs, which equals to 50% of total handling cost, it is essential for the authorities to design a highly efficient collection system (Beattie and Kerell, 1995; Gellenbeck, 1995; Gordon, 1991; Organisation for Economic Co-operation and Development (OECD), 1987; Young and Gordon, 1991).

Drop-Off Centers

This is the simplest method for collection of recyclable materials. The system operates by placing specially designed buckets of large capacity at strategic spots in the municipality. The public is asked to

Table 14.1 Recycling Data for Metals (kg/ton)

Parameter	**Aluminum**		**Ferrous Metal**	
	Virgin	Recycled	Virgin	Recycled
Energy (GJ)	140.00	11.70	25.20	9.43
Air emissions				
CO_2	2900.00	4.36	1820.00	595.00
PFC (perfluorocarbons) (CO_2 eq.)	2226.00	0.00	0.00	0.00
CH_4	6.53	2.71	0.0097	1.29
NO_x	17.30	0.62	2.76	1.77
VOCs (volatile organic compounds)	24.50	0.30	0.23	0.02
SO_x	47.60	2.88	5.11	2.98
PM (particulate matter)	10.00	0.00	1.31	7.22
Pb	1.93×10^{-3}	0.38	7.60×10^{-4}	6.59×10^{-4}
Hg	n/a	n/a	n/a	n/a
Cd	n/a	4.37×10^{-5}	n/a	n/a
HCl	0.81	5.81×10^{-2}	8.57×10^{-2}	0.10
Water emissions				
Pb water	1.47×10^{-7}	0.00	2.92×10^{-2}	2.90×10^{-2}
Hg water	0.00	0.00	n/a	n/a
Cd water	0.24	0.06	9.75×10^{-5}	9.38×10^{-5}
TCDD (tetrachlorodibenzo-p-dioxin) eq. water	1.20×10^{-6}	4.42×10^{-8}	n/a	n/a

Source: Adapted from Haight (2004).

collect the recyclable materials and transfer them by their own means to the drop-off centers. Then the local authorities are responsible for delivering the materials to the waste operation facilities. Basic advantages are the low capital cost necessary and the possibility for a 24-h operation. Usually, lack of public cooperation in this collection scheme is its main disadvantage. It is quite inconvenient for the public to collect and dispose the materials at the drop-off centers, while there is also the contamination problem of the recyclable materials. It is difficult for the collection scheme to result, by itself, in high recycling rates. Many local authorities who operate such drop-off centers have concluded the following:

1. Sites must be selected to provide maximum access but minimum nuisance to neighbors.
2. All centers should be frequently emptied to ensure that there is always capacity to deposit delivered materials.
3. It is essential to maintain sites and to manage the littering problem, thus avoiding any health implications (NSWA, 1990).

Payback Centers

These are centers where the consumer deposits the recyclable materials and receives a compensation to ensure that cooperation will be maintained. The basic advantage is the high quality of obtained material and high public involvement rates. Long distances between consumers and these centers make the operation of this method rather difficult (Pearson, 1996; Vogas, 1995).

Combination of Systems

There are numerous examples of how an appropriate combination of the above-mentioned methods results in viable and successful results (Brandrup, 1992). The method that each local authority will use depends on waste collection operations, experience

Table 14.2 Recycling Data for Glass (kg/ton)

Parameter	**Glass**	
	Virgin	Recycled
Energy (GJ)	14.10	9.23
Air emissions		
CO_2	632.00	278.00
PFC (CO_2 eq.)	0.00	0.00
CH_4	1.11	0.83
NO_x	2.73	1.69
VOCs	0.24	0.17
SO_x	4.37	3.11
PM	0.89	0.43
Pb	5.01×10^{-6}	1.15×10^{-6}
Hg	1.30×10^{-6}	3.00×10^{-7}
Cd	1.35×10^{-5}	2.95×10^{-6}
HCl	5.96×10^{-2}	0.98
Water emissions		
Pb water	3.60×10^{-8}	1.90×10^{-8}
Hg water	2.55×10^{-8}	1.95×10^{-8}
Cd water	2.20×10^{-4}	2.55×10^{-4}
TCDD eq. W	n/a	n/a
BOD (biochemical oxygen demand)	6.9×10^{-3}	5.1×10^{-3}

Source: Adapted from Haight (2004).

obtained by other municipalities, possibilities provided by the particular site, population characteristics, convenience to the consumer, recycling goals, number of individual materials, contamination issues, capital and operational costs, raw materials market, public behavior, current working positions, available technology, legislation, weather conditions, hygiene issues, and political factors. It is important to realize that recycling is not only a collection and recovery method of waste but is also the last part of the life cycle of the materials in which the consumer/recycler is a key factor (Vogas, 1995).

14.8.2 Sorting

After collection, the recyclables are conveyed to a facility for processing into a form suitable for sale as raw materials. Plastic and glass can first be separated from each other by mechanical or manual means and then once more according to their type. Sorting is carried out in specially designed sorting plants that employ semi- or fully automatic processes, depending on the type, size, and technical standards of the plant. The introduction and use of automated plastic sorting systems have lowered processing cost and improved the purity of the separated plastics over the past few years, thereby increasing the quantity of recycled plastics.

Various separation systems are used in different countries, each having different capacity and sensor types, such as the OTTO system (Germany), PET recycling Schweiz (Switzerland), P & R environmental (United States), and Ipia (Novate Milanese, Italy). The technologies for separating postconsumer plastics into their appropriate components fall into two categories: macro-separation and micro-separation.

Macro-separation involves removing discarded materials from waste and separating them into different components by handling the individual items manually or automatically. Macro-separation allows separation of a wide range of materials from each other. The following techniques and methods fall under these categories:

1. Gravity/centrifugation
2. Methods based on the shape of the individual fragments (manual, 3-D measuring devices)
3. Optical (X-ray, infrared (IR), near infrared (NIR), fluorescence, etc.)
4. Metal detectors
5. Sonic techniques (ultrasonic technique)

Micro-separation involves separating polymers by type after they have been shredded and chopped into small pieces of approximately 1/8 to 1/4 in. (0.3−0.6 cm) in diameter. This category comprises techniques based on the following:

1. Geometry (air classification, micronization)
2. Density (hydrocyclone, swim/sink)
3. Melting point (heated rolls)
4. Electrostatic
5. Mechanical (peeling)
6. Solving behavior (temperature gradient)

Table 14.3 Recycling Data for Paper Products (kg/ton)

Parameter	**Newspaper**		**Fine Paper**		**Corrugated Board**		**Mixed Paper**	
	Virgin	Recycled	Virgin	Recycled	Virgin	Recycled	Virgin	Recycled
Energy (GJ)	46.43	25.57	43.05	23.40	29.23	13.64	36.85	26.21
Air emissions								
CO_2	2400.00	1385.00	1100.00	1507.00	896.00	1019.00	1304.00	1752.00
PFC (CO_2 eq.)	0.00	-3060.00	0.00	-4580.00	0.00	-4580.00	0.00	-4580.00
CH_4	0.03	0.02	0.02	0.02	0.01	0.01	0.02	0.01
NO_x	10.40	5.26	8.74	5.38	6.25	5.56	7.94	5.44
VOCs	11.20	7.19	8.27	18.47	3.87	35.40	6.86	23.89
SO_x	16.30	9.40	12.88	9.80	7.74	10.40	11.23	9.99
PM	4.63	2.80	4.81	3.10	5.07	3.56	4.89	3.25
Pb	4.52×10^{-4}	2.63×10^{-4}	3.52×10^{-4}	2.67×10^{-4}	2.03×10^{-4}	2.73×10^{-4}	3.05×10^{-4}	2.69×10^{-6}
Hg	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Cd	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
HCl	n/a	3.87×10^{-6}	3.57×10^{-6}	4.51×10^{-6}	8.93×10^{-6}	5.46×10^{-6}	5.29×10^{-6}	4.81×10^{-6}
Water emissions								
Pb water	1.63×10^{-7}	6.35×10^{-8}	1.46×10^{-7}	6.59×10^{-8}	1.20×10^{-7}	6.95×10^{-8}	1.38×10^{-7}	6.71×10^{-8}
Hg water	3.82×10^{-8}	2.33×10^{-8}	2.69×10^{-8}	1.40×10^{-8}	9.92×10^{-9}	0.00	2.15×10^{-8}	9.51×10^{-9}
Cd water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BOD	3.51	3.09	2.71	3.29	1.52	3.58	2.33	3.38

Source: Adapted from EPA (2002) and Haight (2004).

Table 14.4 Recycling Parameters for Plastics (kg/ton)

Parameter	**PET**		**PE**		**PP**		**PS**		**PVC**	
	Virgin	Recycled	Virgin	Recycled	Virgin	Recycled	Virgin	Recycled	Virgin	Recycled
Energy (GJ)	107.15	46.07	79.76	19.94	76.42	19.87	84.8	11.63	59.8	9.13
Air emissions										
CO_2	2363	163	2400	163	2100	942	2200	942	2000	942
PFC (CO_2 eq.)	25	0.016	28	0.016	28	0.016	24	0.016	22	0.016
CH_4	9.5	0.081	6.5	0.081	6.4	0.081	6.9	0.081	6.3	0.081
NO_x	7.2	6.95	7.8	6.95	7.7	6.95	5.9	6.95	5.8	6.95
VOCs	14	n/a	4.9	n/a	5.4	n/a	5.2	n/a	5.3	n/a
SO_x	4.6	n/a	1.5	n/a	1.7	n/a	2.4	n/a	1.4	n/a
PM	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Pb	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Hg	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Cd	0.058	n/a	0.011	n/a	0.014	n/a	0.014	n/a	0.016	n/a
HCl	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a

Source: Adapted from Molgaard (1995), Eulalio et al. (2000), EPA (2002), and Haight (2004).

Table 14.5 Treatment Routes Employed by European and Other Nations (%MSW)

Nation	Recycled and Composted	Incineration	Landfill
Switzerland	29	59	12
Denmark	23	48	29
Sweden	19	47	34
France	13	42	45
The Netherlands	19	35	45
Germany	18	36	46
Austria	24	11	65
Norway	11	22	67
Finland	15	2	83
Belgium	3	54	43
Italy	10	16	74
Spain	30	6	65
Ireland	3	0	97
Luxembourg	3	75	22
Portugal	15	0	85
United Kingdom	2	10	88
Canada	12	8	80
United States	17	16	67
Greece	0	0	100

Source: Adapted from Onusselt (1997).

Table 14.6 Glass Container Recycling Rates in Europe (%)

Country	2006	2007	2008	2009	2010	2011
Germany	18.04	18.19	18.70	18.81	18.17	18.72
France	17.77	16.69	16.16	15.70	15.12	15.24
Italy	16.47	16.14	16.59	16.59	16.82	16.43
Poland	5.19	5.48	3.94	4.52	4.73	4.56
United Kingdom	10.02	10.00	10.97	10.53	11.11	10.64
Spain	9.97	9.90	9.68	9.60	9.50	9.51
Portugal	5.08	5.48	5.65	6.41	6.29	6.22
Austria, Belgium, Denmark, Estonia, Sweden, Switzerland, The Netherlands	9.31	9.58	9.36	9.45	9.35	9.40
Bulgaria, Czech Republic, Greece, Hungary, Romania, Slovakia	5.33	5.36	5.44	5.30	5.12	5.64
Turkey	2.77	3.14	3.56	3.05	3.74	3.78

Source: Adapted from FEVE (2012).

Table 14.7 Energy and Emissions from Recycled and Virgin Glass Production

Source	Recycled Glass (100%)/Tons Produced	Virgin Glass/Tons Produced	Savings/Tons Recycled Glass Produced	Savings/Tons Recovered Glass Used
Energy consumption (GJ)	5.8	9.6	3.8	3.7
Air emission (g) particles	428	17,780	17,352	16,831
CO	57	105	48	47
NO_x	1586	2270	684	663
N_2O	12	106	94	91
SO_x	2652	3927	975	946
HCl	6	75	69	67
HF	2.4	1	− 23	− 22
Ammonia	2	4	2	1.9
Lead	16	0	− 16	− 15.5
Water emissions (g)				
BOD	1	1	0	0
COD (chemical oxygen demand)	2	4	2	1.9
Total organic compounds	20	26	6	5.8
Solid waste (kg)	29.3	4.0	− 25.3	− 24.5

Source: Adapted from Arvanitoyannis and Bosnea (2001a,b).

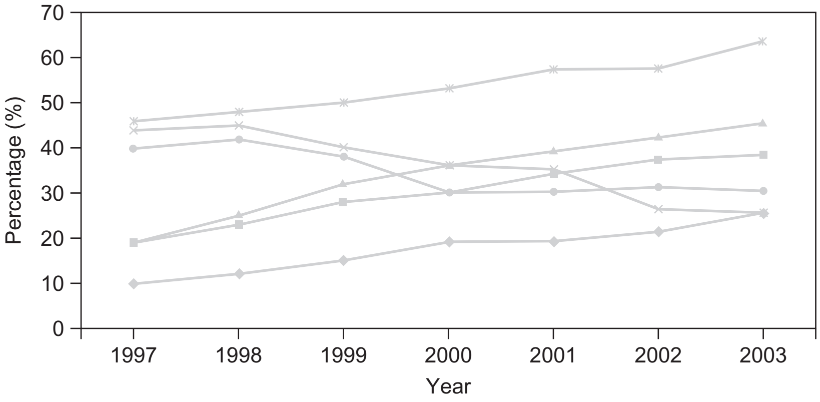

Figure 14.15 The percentage recycling of glass, aluminum, and PET in the European Union and the United States (♦ PET in European Union, ▲ aluminum in European Union, * glass in European Union, ■ PET in the United States, **X** aluminum in the United States, and ● glass in the United States). *Source: Adapted from http://container-recycling.org/aluminrate/gaphs.thm and http://europa.eu.int/lib/.*

Gravity and centrifugal techniques make use of the different densities (specific gravity) of the materials. Such a system is employed by Duales System, where the mixed plastics, after being cleaned, are suspended in water and enter the centrifuge as a suspension. Particles with a higher density than water precipitate down to the centrifuge bowl while the lighter particles float on the surface and are extracted. Sorting out specific types of plastic is feasible but the process has to be repeated with several centrifuges. Other methods employ rotating disks and inclined belts. The principles of plastic flotation show that it is more flexible than other techniques and could prove useful in separating mixtures of plastics, but more research needs to be carried out for its successful implementation in industry. Separation according to shape can be conducted manually. Optical methods are based on IR, UV, and visible spectroscopy; laser-induced plasma spectroscopy; X-ray spectroscopy; and fluorescence and NIR detectors. IR spectroscopy uses the way different materials respond to IR light for identification. Although IR spectroscopy is very selective and rapid, it is rather expensive and unsuitable for industrial applications, apart from special sorting installations, because only thin-film specimens can be scanned. The X-ray spectroscopic processes that are commonly used are fast, and reliable, but are appropriate only for PVC detection since they depend heavily on the layer thickness while sources of radiation are objective, comparatively expensive, and of limited applicability. This process is usually combined with IR spectroscopy. Some of the latest methods employ NIR systems, which have proved to be more advanced than IR because of its fast response and higher detectability. In this area, a tremendous amount of research has been carried out over the past few years. A system using NIR was developed by Buhler and launched in late 1993. The system, named NIRIKS, enormously increased the measuring speed and was designed as a pure industrial unit.

The system was flexible, rapid, and quite accurate. Another system using NIR was developed by Bayer and employs fluorescence spectroscopy (XFS, X-ray fluorescence spectroscopy) for identifying halogens and heavy metals. Short-wave NIR spectroscopy uses low-wavelength IR light for polymer identification. The technology is quite limited but the equipment is easy to use, compact, and portable. Fourier transform mid-infrared spectroscopy (MIR) uses the light reflected from a plastic for identification. The main systems available need a relatively smooth-surfaced plastic to be effective. MIR systems are accurate, but the polymer to be identified needs to be close to the sensor for at least a second and identification takes a few seconds more. Systems that use UV and visible spectroscopy are also used for polymer identification. Electrical charges vaporize the plastic's surface, and the analysis of the emissions gives an accurate identification regardless of the color or coating. Computer software is essential in these devices. Another technique is based on laser-induced plasma spectroscopy where lasers are used to vaporize the plastic's surface and the emissions are analyzed by a spectrometer. The device is highly accurate, additives can also be identified, and the method is quite rapid. Raman spectroscopy is a method under development that is expected to become one of the most reliable identification technologies. This system uses lasers to generate light from the sample that provides identification upon analysis. Laser impulse thermography is another identification technique that uses laser beams. A carbon dioxide laser generates two "spots" of energy onto a sample. The rise in temperature is measured, as is the cooling rate, which both differ based on materials. Although fast, it is still under development because of current limitations. Mass spectroscopy may also be used in identification. Finally, color images can be identified with special digital cameras to recognize different colors for sorting mixed plastics or removing contaminants. In addition, another system uses people to identify and sort items passing on a conveyor belt simply by their touching the image of selected items on a video screen.

Electrostatic techniques are based on the electrical properties of plastics. Plastics have a range of electrical properties and any differences can be used both to identify and separate them. The existing devices are portable and cheaper than many other systems. Unfortunately, they are only really effective at differentiating plastics with distinctly different characteristics, which is a limitation factor regarding their applicability. Any water in the system can also cause problems. A project funded in Germany called "optical recycling" aimed at developing a reasonably priced process in which a single compact device would detect the type of plastic by using NIR, the color with color cameras, the shape by using a 3-D measuring device, and any impurities and residues present in the package with an X-ray module. Strongly charged particles of plastics are deflected in free fall in a high-voltage field (120,000 V) toward the electrode and are separated. This method of sorting is based on electrostatic differences between polymers, and it is independent of density, size, or shape. The advantages of this technique are its effectiveness and the low energy required, but it is still on the pilot scale and the presence of additives makes the separation difficult.

Another technique is the use of tracers (i.e., fluorescent) for identification and sorting of plastics. A European project, set for the implementation of tracers on an industrial scale, concluded that it is a fast and reliable identification technique. Furthermore, marking by tracers can differentiate between grades of generic type plastics and also by destination, for example, one specific tracer used for plastics not to be recycled. The ultrasonic technique is based on the use of ultrasound attenuation measurements, which were developed for medical diagnostic analyzes by Langton. A specialized computer was designed for this specific application and patented by Hull and Langton in order to assist the classification and identification of polymer waste. The ultrasonic analysis offers a cheap, reliable technique able to be used both on- and off-line.

By air classification, it is quite easy to distinguish a thick-walled from a thin-walled polymer such as LDPE and HDPE. Any small and big fragments can be effectively identified by micronization. This method is usually applied to separate PET and PVC. The different specific densities of plastic are used in some sorting plants for developing automatic sorting techniques as long as the mixed plastics to be sorted are not too heavily contaminated. The hydrocyclone is an old technique using this property. In a hydrocyclone, the shredded and washed plastic fragments are separated in a centrifugal field according to their density, resulting in purity of more than 99%. Another device demonstrated recently is based on solubility of polymers. Using this technique, it is possible to separate six or more polymer categories by dissolving them all in a solvent system and taking advantage of the different temperature dissolving points (each polymer dissolves at a different temperature). This method has proved to be effective both in laboratory analysis and industrial applications. This is a very promising technique since modern packages usually employ several polymers in order to achieve the desired properties. Finally, molded-in codes can be used for identification and sorting of plastic waste. Molded bar codes appear to be the simplest, most cost-effective approach, but their main disadvantage resides in the possibility that any damage occurring to the label, which is likely to happen, would render the code illegible. The analysis on the composition and properties of plastic waste and the physical properties of plastics demonstrates that, although several separation technologies can be applied to separate mixed plastics, their applicability is still very limited (Brown, 1993; Eisenreich et al., 1995; Hull et al., 1994; Kenny, 1995; Lambert, 1995; Riess, 1995; Saetti and Peroni, 1995; Schudel and Koller, 1995; Soler, 1992).

The techniques used for separation of different kinds of plastics are based on differences in density, shape, color, physicochemical properties, and solubility. The solubility-based processes (SDP) include stages of dissolving a series of incompatible polymers in a common solvent at various temperatures or in different solvents, so that one polymer is separated each time. The method employed to recover the polymer after the dissolution stage varies. So far, the SDP have been successfully applied in a laboratory scale for the recycling of PP pipes, rigid PVC bottles, polystyrene (PS) waste foam, LDPE film from greenhouses, and HDPE bottles from agrochemical packaging (Pappa et al., 2001; Poulakis and Papaspyrides, 1995). The technique involves the following steps, shown graphically in Figure 14.16:

1. Cutting the waste into smaller pieces and, if necessary, washing with water.
2. Preliminary separation of the initial mixture to two or more mixtures by flotation in water or another liquid.
3. Addition of a solvent (S) that selectively dissolves only one of the polymers under certain conditions.
4. Filtration to remove the nondissolved polymers.
5. Addition of an antisolvent (AS) to precipitate the dissolved polymer.
6. Filtration and drying of the precipitated polymer.
7. Separation of the S/AS mixture by distillation for reuse.
8. Application of the same procedure for each polymer of the mixture.

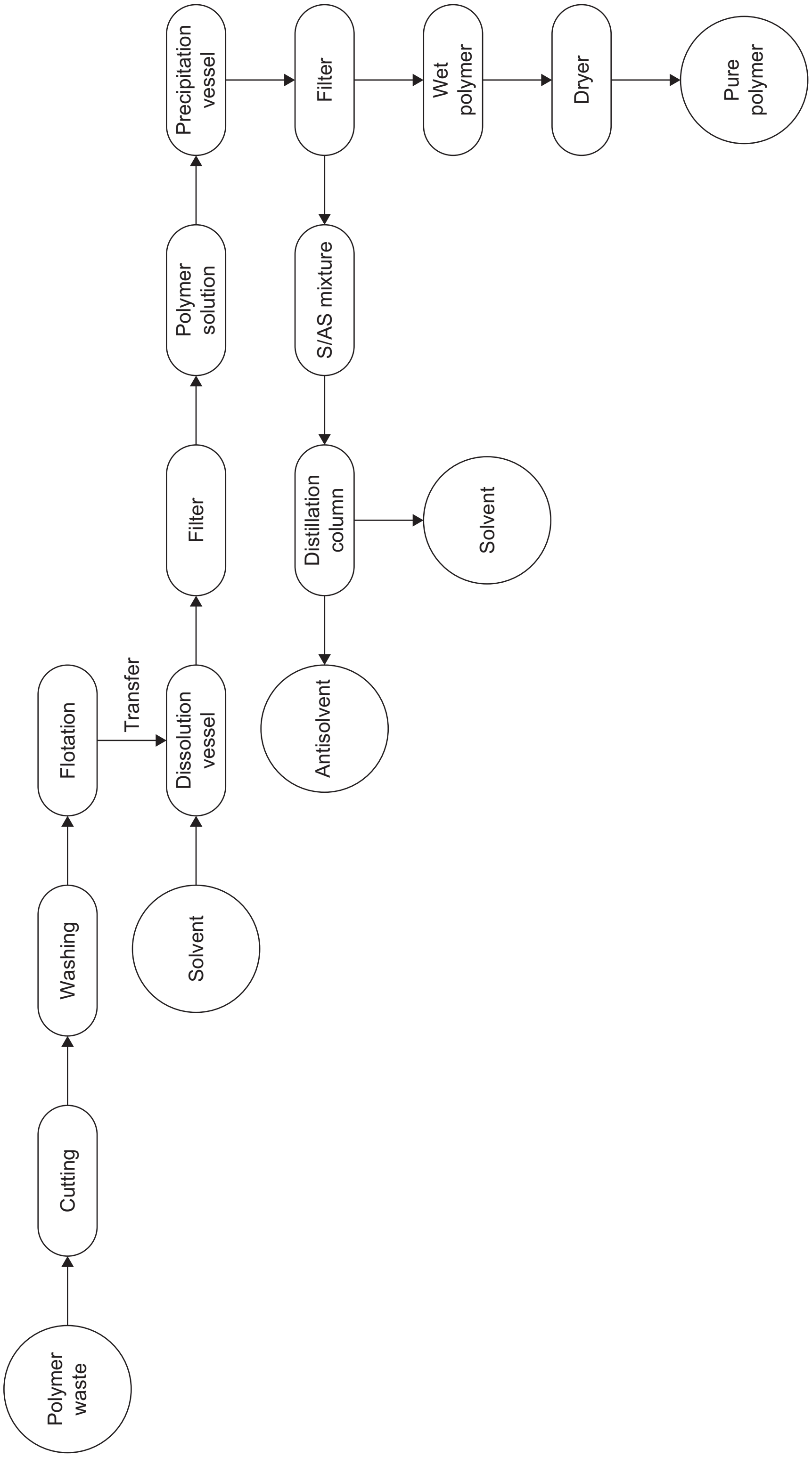

Figure 14.16 Flow diagram of the selective dissolution/precipitation method for the separation of polymer mixtures. *Source: Adapted from Pappa et al. (2001).*

In this study, the SDP method was applied to separate mixtures consisting of polyolefins—LDPE, HDPE, PP—at both laboratory and pilot scale. Excellent recoveries were achieved and the quality of the recycled polymers remained practically intact. The feasibility study of the method for a high-capacity unit, based on the scale up of the pilot one, showed that the cost of the recycled polymer is comparable to the commercial price of the virgin one.

Dodbiba et al. (2002) studied the separation of PET−PE and PET−PP mixtures in order to improve the grade of the raw input used in PET bottle recycling. First, PET bottles and their caps (made of PE or PP) were shredded and the floatability of each polymer was tested. Even with the addition of the wetting reagents, dodecylamine acetate (DAA) or PVA, the results did not suggest that the required 99.995% purity of PET plastic could not be achieved by flotation. Second, the mixtures were separated with a sink−float process using a drum separator. Finally, as the required purity of PET could not be obtained by either technique alone, a system utilizing a combination of the two processes was developed. This system easily achieved the desired PET grade. Finally, some sink−float experiments were performed in a magnesium sulfate medium (dense medium separation).

Shen and coworkers (2002) found that the floatability of all the plastics decreased with the addition of surfactant, but they are different in floatability and follow the order POM (polyoxymethylene) < PVC < poly(methyl methacrylate) (PMMA) < PET < polycarbonate (PC) < acrylonitrile butadiene styrene (ABS) < PS. From the separation test results of several plastic mixtures, it was shown that the Gamma flotation method not only can be used to separate plastics mixture with different densities, such as separation of POM and PVC from PC, POM and PVC from PS and ABS, PET and PMMA from PS and ABS, but also can be used to separate plastics mixtures with similar density, such as separation of PMMA from PC. Products with grade higher than 99% and recovery higher than 97% can be obtained for the separation of some plastic mixtures. It was found that the depressing effect of surfactant 15-S-7 on the plastics is mainly due to the reduced liquid surface tension, and flotation selectivity for the plastics with identical particle size is dominated by contact angle, particle density, and shape.

Over recent years, several experimental studies have been reported describing the separation of plastics by froth flotation. In principle, selective flotation separation of plastics can be achieved by the following methods:

1. gamma flotation using a liquid medium with a specific value of the surface tension,
2. chemical conditioning using adsorption of wetting agents,
3. physical conditioning, for example, plasma treatment or wet oxidation,
4. hydrophobic modification using a chemical conditioning agent such as a plasticizer, for example, diisodecylphthalate on PVC.

In general, all these methods emphasize the modification of the plastic surface or the flotation medium, and in many cases, this can be success with different plastics leading to high selectivity in separating mixtures. From the results, it was shown that plastics flotation is affected not only by surface chemical factors but also by gravity factors. It is suggested that plastics flotation should be carried out by a combination of froth flotation and gravity separation. According to this relation, the idea of particle control was first applied for the separation of plastics mixtures. From the separation results, it was deduced that this method can greatly increase the separation efficiency for flotation separation of plastics mixtures. The particles in cutting products are not uniform in size and shape. Cutting products of PMMA and POM have a relatively wide size distribution and contain a considerable number of particles of less than 1 mm in diameter, which are difficult to depress by wetting agents. PVC and PS give an intermediate size distribution with an intermediate left tail but a small right tail. Finally, ABS, PC, and PET gave a relatively narrow particle size distribution. Particle shape tends to be more irregular in the fine size fractions. The equation and the experimental results showed that particle size and shape control are important for plastics flotation. It is an effective way to improve the separation efficiency for plastics flotation (Shen et al., 2001).

The dry separation of a mixture of three plastics by combining air tabling and triboelectric separation has been described (Dodbiba et al., 2005). While air tabling is effective for particles of different density, the triboelectric separation can be used for separation of particles of similar density. Before commencing the separation tests, the effectiveness of the separating devices was evaluated by analyzing the effects of the particle size and the difference in density between components of the mixture. A two-stage process has been proposed for separating mixed plastics prior to recycling. PP, PET, and PVC were selected for investigation as they are widely used in the manufacture of everyday products. An air table was employed for the first stage of the process to collect a PP-rich low-density fraction and a PET/PVC high-density fraction. In the second stage, the PET/PVC fraction was separated by means of a triboelectric separator utilizing differences in surface charge. A mixture of PP, PET, and PVC was selected for investigation. Each component amounted to one-third of the total mass of the mixture. Thus, high-density plastics (i.e., PET and PVC) amounted to approximately 67% of the total. Before commencing the separation tests, the effectiveness of the techniques was evaluated by investigating the effects of the particle size and the difference in density between components of the mixture. The triboelectric separation was effective for separating materials of similar density. However, an upper limit of particle size was set after considering the magnitude of the surface potential attained by plastics and the maximum electric field strength that the triboelectric separator could create without causing electric breakdown. The air tabling was effective if the density difference between particles was at least 450 kg/m^3 and the feed was properly sized. A general schematic flow sheet of the dry process for separating mixtures of three plastics is shown in Figure 14.17.

The plastic waste samples (PET, HDPE, and PP) were taken from an MSW separating and composting plant (Araraquara, SP, Brazil). The PET consisted predominantly of carbonated soft drink bottles, plus a few water and vegetable oil bottles. The HDPE and PP were mainly packaging materials from cleaning, personal hygiene, utensils, food, and automotive mineral oil products. The polyolefins were mixed in a proportion 9:1 (HDPE:PP) according to a recent study on MSW composition (Mancini et al., 2000). Owing to the heterogeneity of contamination of these wastes, one lot (ca. 40 kg) for each of these materials (PET and polyolefins) was ground in a knife mill and then mixed and homogenized in an appropriate bag. Afterwards, three samples of about 3 kg each were taken from these lots and cleaned independently in order to achieve three typical samples of wastewater generated during the cleaning processes of these plastics (Santos et al., 2005). Since polyolefins and PET have different characteristics, the conditions used during the washing process also differed from each other. Specifically for PET, a step that carries out the separation of labels and caps residue by differences in density is necessary. Furthermore, the susceptibility of PET to adhesive residues during processing also requires more aggressive conditions in the washing step in order to maximize the adhesive removal (Sanko, 1999). Care was taken not to use high alkalinity content. As an alternative, increments in bath temperature are recommended. Ordinary tap water without addition of any chemical was used for the prewashing step. Caustic soda was then used in the washing step for both plastics, though surfactant was used only for PET. No significant differences in the effluent characteristics were found between the two types of plastic studied and between the prewashing and washing steps, except those differences intrinsic to the cleaning processes (temperature, surfactant, caustic soda concentration). Some specific unit differences are necessary depending on the type of plastic used due to extrapolation of emission limits of oil and grease in the polyolefins prewashing step and Pb excess in the PET washing step.

Cryo-comminution of plastic waste was recently introduced by Gente and coworkers (2004). Laboratory comminution tests were carried out under different conditions of temperature and sample preconditioning adopting CO_2 and liquid nitrogen as refrigerant agents. The temperature was monitored by thermocouples placed in the milling chamber. Moreover, different internal mill screens have been adopted. A proper procedure has been set up in order to obtain a selective comminution and a size reduction suitable for further separation treatment. Tests have been performed on plastics coming from medical plastic waste and from a plant for recycling spent lead batteries. Results coming from different mill devices have been compared taking into consideration different indexes for representative size distributions. The results of the performed tests showed cryo-comminution improves the effectiveness of size reduction of plastics, promotes liberation of constituents, and increases specific surface size of comminuted particles in comparison to a comminution process carried out at room temperature.

Flame treatment was effectively used to modify the surface of plastics to allow water-based coatings to be attached. The effect of the treatment was to

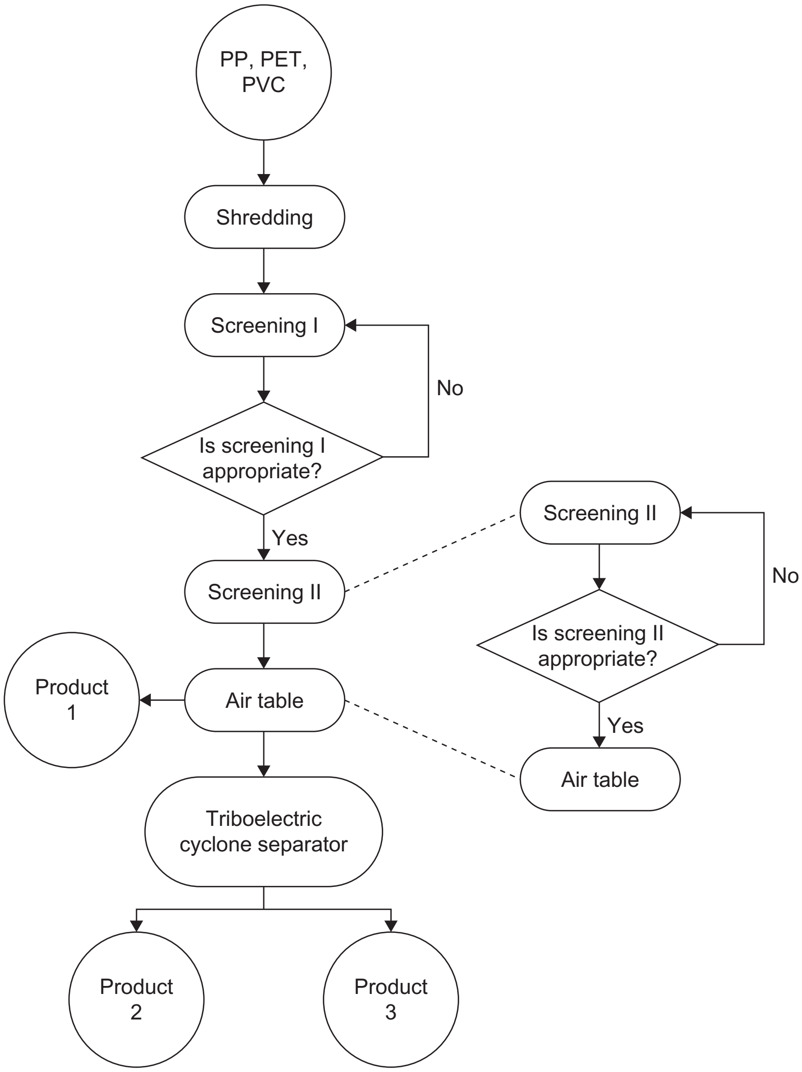

Figure 14.17 A general scheme flow sheet of the dry process for separating mixtures of three plastics. *Source: Adapted from Dodbiba et al. (2005).*

produce hydrophilic species on the surface of the plastic. The process is therefore potentially useful for the separation of plastics by froth flotation, provided that the production of the hydrophilic surface can be achieved selectively. PVC and PET were selected for investigation as they were found as a comingled product in the recovery of beverage containers (Pascoe and O'Connell, 2003). A simple, but effective, flame treatment method for flaked plastics was developed. The treatment involved the use of an acceleration chute that delivers the flakes through the flame of an angled burner. In experiments with virgin plastics, the PVC was found to be less susceptible to surface modification than PET, as indicated by contact-angle measurement. Separation of the treated virgin plastic by froth flotation was found to be possible, by careful control of added frother. The technique was then considered for the treatment of postconsumer plastic bottles. It was demonstrated that flame treatment was effective in rendering the surface of both plastics hydrophilic, although the process alone was not sufficiently selective. Hydrophobic recovery of the PVC, but not the PET, was achieved by raising the temperature of the material to 140°C for a period of 10 min. A two-stage flotation process was tested for the separation of the plastics. In the first stage, PET was floated away from the PVC capitalizing on differences in particle thickness and surface contamination. The float product was then subjected to flame treatment and hydrophobic recovery prior to the second stage of flotation. In this stage, the PVC was conveyed to the float product leaving a PET-rich sinks fraction.

Hearn and Ballard (2005) developed two sorting techniques using the electrostatic properties of materials to produce separate material streams for the purposes of recycling. Trials were undertaken using typical common items of waste packaging, giving encouraging results. Early results indicate reliable operation under a range of environmental conditions; however, the effects on sorting efficiency of extremes of surface contamination, moisture, temperature, and humidity have yet to be quantified. It is recognized that the presence of high levels of surface contamination on the waste items to be streamed may cause problems, particularly for the triboelectric sensor probe. Preliminary examination of material from an MRF (materials recycling facility), however, suggests that these materials are generally not heavily contaminated with anything other than moisture. The presence of surface water does significantly influence both charge generation and triboelectrification. MRFs and plants where these techniques are likely to be applied lend themselves to the application of driers or air curtains that could be installed upstream of the electrostatic sorting area. It is also recognized that this technique may not be appropriate for all polymer types but can be used in conjunction with other techniques. Such techniques may include an optical sensor to separate PVC from HDPE and Fourier transform IR spectroscopy (Hearn, 2003) to sort the stream containing PET/PETE and PS. Difficulties may be encountered with certain packaging geometries and the presence of labels and coatings with respect to all of these issues, the use of the small triboelectric probe is an advantage as it can be directed at an area of packaging that is most likely to constitute exposed polymer.

14.8.3 Preparation for Recycling

After the materials have been collected and sorted, they must be converted into a homogeneous pourable bulk material that is easy to transport and store and is suitable for recycling. The quality criteria are high bulk density, defined grain size, low chlorine content, and low dust content. These properties can usually be achieved within the frame of the agglomeration process. The agglomeration process is followed by the shredding and separating steps, thus reducing the mixed plastics to a grain size of less than 50 mm and producing a more or less homogeneous material. The target of agglomeration is to convert mixed plastics into a product with specific properties suitable for recycling. The final product should be pure and easily processable. In this process, the preshredded mixed plastics were fed into rotating blades and heated to 135−140°C. As a result, small pieces of film sheeting cake together and can then be processed into compact plastic granules. Moreover, inpelletizers are also employed so that plastics compacted by means of pressure are cut off by cutters and subsequently pelletized. However, agglomeration is considered a “young” technology requiring further research and development work (Pearson, 1996).

14.8.4 Mechanical Recycling

The purpose of mechanical recycling is to process postconsumer plastics and recover a secondary raw material for the production of new items (Pearson, 1996). Packaging material sorted into individual fractions is either melted down directly and molded into a new shape or melted after being shredded into flakes and processed into granules called regranulate. There are several mechanical recycling processes: extrusion and intrusion, injection molding, transfer molding process, and regranulation (http://www.eps.co.uk/mechanical.html). In the extrusion process, the regranulate is heated and melted into a plastic mass, which is then transferred to molds for simple products such as profile section or sheets. The only difference between extrusion and intrusion processes is that, in the latter, impurities such as glass fragments, sand, and wooden pieces can remain in the plastic melt. The extruder is designed in a way so that impurities are embedded in the plastic melt. The molten mass is pressed directly into molds such as honeycomb-type paving stones. Circulation of cold water speeds up the hardening process of the paving stones, which can be removed from the molds after a short time. The molten plastic mass, during the injection molding process, is injected into a mold under high pressure. Similar to the intrusion process, the machines are designed for processing mixed plastics containing impurities. The molten plastic is pushed by the piston into the mold for the article to be produced. The pressure on the piston remains constant until the tray has cooled down and can safely be removed from the mold (Pearson, 1996). During the molding process, mixed plastics are shaped into finished products by means of direct melting and molding, either without or after only coarse preshredding. Finally, in the regranulation process, the postconsumer plastics are sorted into different fractions, heated, and regranulated. The plastic produced in this way can be used in various sectors such as construction (frame sections, cable insulation, piping, insulating materials, etc.), packaging and logistics (film sheeting, hollow containers, transport containers, pallets), and industry (shaped parts for the car industry). Recycled films can be manufactured from used PE films. Films of recycled materials and virgin material can be permanently joined to produce frame sections of film sheeting by co-extrusion (http://www.environment97.org/). It is estimated that the recycling rate for foamed PS can reach 100%. The material is broken down to its components and either added to new foamed PS packaging or regranulated to produce the starting material PS that is utilized for the manufacture of injection-molded parts. In Germany, a recycling rate of 40% has already been achieved. However, it should be mentioned that current standards and regulations prevent secondary plastics from being used to an even greater extent. For instance, packaging for foodstuff may only be manufactured from virgin polymers. Similarly, the production of certain types of piping prohibits the use of regranulate. In principle, most of the 9.1 million tons of plastic utilized in packaging in Western Europe could be recycled by remelting and extrusion or molding into films.

Actually, in 1996, 53% of the plastic sales for packaging were recycled mechanically, and more than 90% has been recycled in Germany since 1997. Therefore, the mechanical recycling process is an important technique despite the problems that have been encountered in practice (Halle, 1994), including the high cost of collection and separation equipment, the lack of a substantial and reliable market for the recycled material, and limited applications (i.e., exemption of food packaging materials) for the recycled materials. The implications of mechanical recycling have partially influenced packaging design. The three predominant trends can be summarized as follows: an increased need for simple structures consisting of a single polymer or at least a single polymer type instead of complex multilayer structures, which are difficult to separate into individual materials. Recent predictions for the packaging film market suggest the replacement of PS and PVC with PP.

Therefore, the use of compatibilizers—chemical additives that assist the blending of various polymer types—helps to alleviate some of the problems of blended polymers. The addition of 5% of an ethylene-vinyl acetate (EVA) film grade polymer of 28% VA content substantially improved the properties of 85/15 LLDPE/PP mixtures (Teh et al., 1994). Furthermore, several new linear ethylene polymers have been successfully used to increase the recyclable content of postconsumer recycled polyolefins to high levels, while maintaining good film properties (Begley and Hollifield, 1993). Safety and contamination considerations and current legislative standards are the main obstacles for an extensive use of mechanically recycled polymers by the food packaging industry. Nevertheless, pack designers and polymer scientists can facilitate the recyclability of food packs so they can be easily used for other applications. The obvious dominance of the food sector within the overall packaging market suggests that a response of this kind by the food packaging industry is expected to have a key influence on the future of plastic recycling.

The increasing consumption of polymeric blends results in a great environmental impact because the used plastics are discarded in nature in a nonrational form. As a solution to all these problems, recycling becomes a powerful strategy regarding the reduction of the environmental impact caused by plastic waste. Polymeric blends were prepared with mechanical recycling and characterized. LDPE/Al residues from cartoned packaging were blended with recycled HDPE/LDPE and virgin PE resins. It was observed that processability, mechanical properties, chemical resistance, and water absorption are dependent on the blend compositions. Also, an aluminum film was found to remain as isolated particles in the polymeric matrix, and the mechanical behavior of the blend depends on the aluminum dispersion. Moreover, the blend water absorption depends on recycled material contamination, mainly PAs. Finally, the amount of recycled material added to the blends determines both chemical stability and thermal characteristics (Paula et al., 2005).

Recycling of mixed plastic wastes composed of LDPE matrix and PP was carried out by compounding using single-screw or twin-screw extruders.

Blends of virgin polymers were prepared to compare mechanical properties of both virgin and regenerated materials. First, a model composition of virgin LDPE/PP blend was prepared to study the effect of process parameters and that of different types of compatibilizers. Second, the results were applied to industrial postconsumer plastic waste. The mixture of plastic wastes was purified in a pilot plant by grinding, washing, and separating. The detailed treatment is shown in Figure 14.18. By adding compatibilizing agents such as ethylene-propylene-diene monomer, ethylene-propylene monomer, or PE-g-(2-methyl-1,3-butadiene) graft copolymer, elongation at break and impact strength were improved for all blends. The effect of these various copolymers was quite different and was in relation to their chemical structure. The recycled blends exhibited suitable properties leading to applications that require good mechanical properties (Bertin and Robin, 2002).

14.8.5 Feedstock Recycling

The main purpose of feedstock recycling is to convert prepared postconsumer plastics into their basic components, such as oil, gas, naphtha, and to use them as secondary feedstocks in refineries or petrochemical industries for the production of new plastics, paints, or adhesives. Post-consumer plastics may also be utilized as a substitute for valuable raw materials like oil. Plastics can be effectively applied in the production of steel. Currently, the carbon and hydrogen molecules bound in plastics are used for the reduction of iron oxide. A single industrial-scale plant for feedstock recycling has a capacity of 100,000 t of postconsumer plastic per year. The techniques employed consist of hydrogenation, BASF (Badische Anilin und Soda Fabrik) process, etc. and are of crucial importance in the recycling of plastics (Caluori, 1995).

Steel and iron have been overtaken after a period of 3000 years as the most used and most versatile materials by the different kinds of plastics, and this in a period of only 50 years. Feedstock recycling is one of the greatest challenges for the recycling of plastics, and various technologies have been successfully demonstrated and continue to be developed. Kaminsky and coworkers (2004) investigated different processes such as degradation of plastics to monomers, pyrolysis into monomers and oil, gasification into syngas. Pyrolysis of mixed plastic wastes and elastomers is a cost-effective process to recover feedstocks for the petrochemical industry. The Hamburg process, using an indirectly heated fluidized bed, can be varied to produce mainly monomers, aliphatic hydrocarbons, or aromatics. At temperatures of 450°C, PMMA is depolymerized to more than 98% of the monomer. However, the influence of fillers on the monomer yield has been studied. PS as feed gives up to 75% of styrene and 10% of oligomers. First demonstration plants are running for feedstock recycling of PMMA in a fluidized bed.

Schemes such as the Duales System Deutschland in Germany ("green dot") have addressed feed recycling, but there remains the high energy and process costs of the feedstock recycling technology. Thermal and catalytic cracking, although effective, require significant operating temperatures and are strongly endothermic, leading to large adiabatic temperature falls across reactors. Oxidation methods, energetically more favorable, are carried out at high temperature and have associated difficulties such as dangerous emissions, product quality, and expensive materials of construction. Hydro-cracking studies have been limited to date and merit further study since the process is exothermic and can be carried out at significantly lower temperatures (Garforth et al., 2004). Total plastic waste generated and recovered in Western Europe is given in Figure 14.19.

Feedstock recycling by catalytic cracking of a real plastic film waste from Almeria greenhouses (Spain) toward valuable hydrocarbon mixtures was studied over several acid catalysts (Serrano et al., 2004). The plastic film waste was mostly made up of ambient degraded LDPE and EVA copolymer, the vinyl acetate content being around 4 wt%. Nanocrystalline HZSM-5 zeolite (crystal size ~60 nm) was the only catalyst capable of degrading completely the refuse at 420°C despite using a very small amount of catalyst (plastic/catalyst mass ratio of 50). However, mesoporous catalysts (Al-SBA-15 and Al-MCM-41), unlike as occurred with virgin LDPE, showed fairly close conversions to that of thermal cracking. Nanocrystalline HZSM-5 zeolite led to 60 wt% selectivity toward C_1—C_5 hydrocarbons, mostly valuable C_3—C_5 olefins, that would improve the profitability of a future industrial recycling process. The remarkable performance of nanocrystalline HZSM-5 zeolite was ascribed to its high content of strong external acid sites due to its nanometer dimension, which are

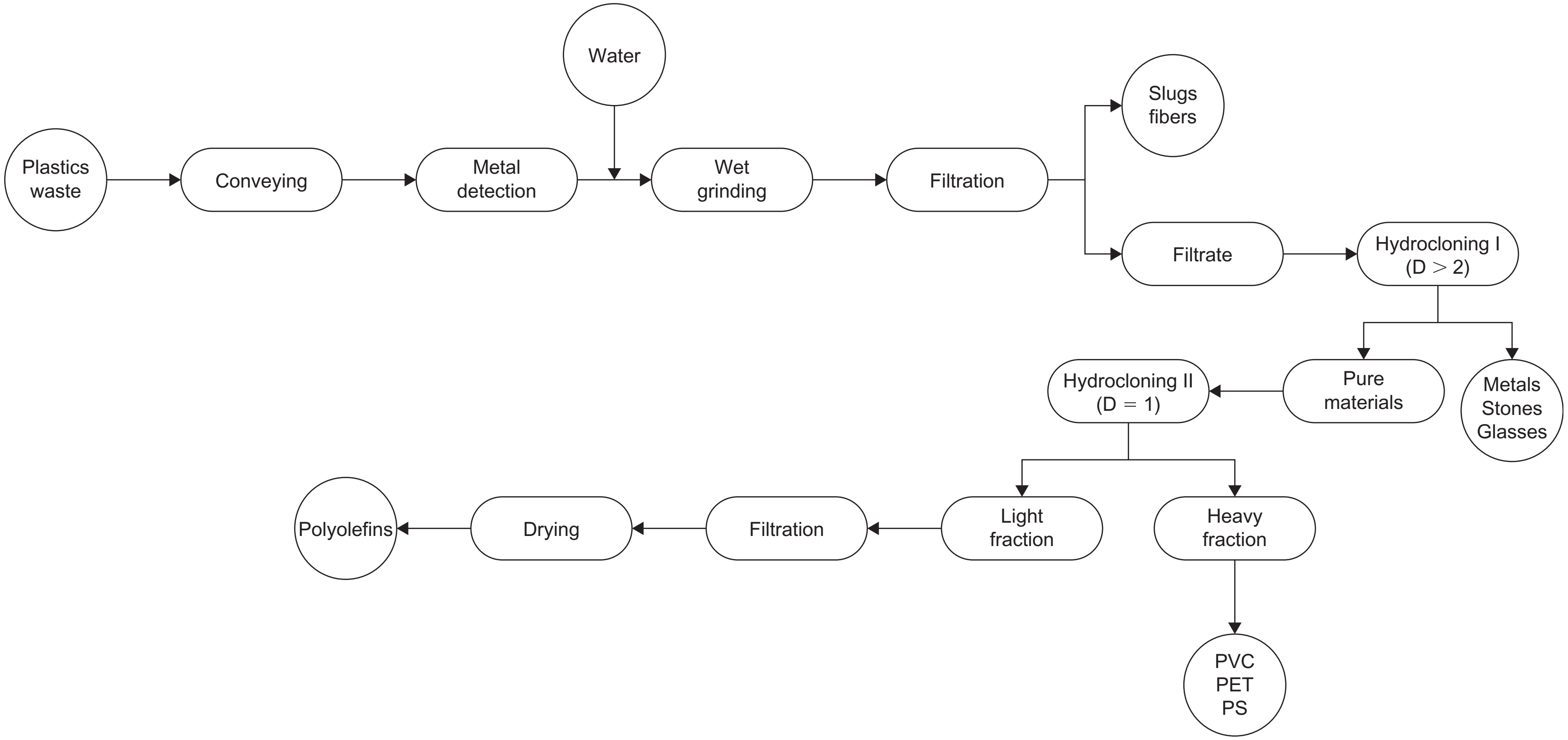

Figure 14.18 Flow sheet of the recycling pilot plant. *Source: Adapted from Bertin and Robin (2002).*

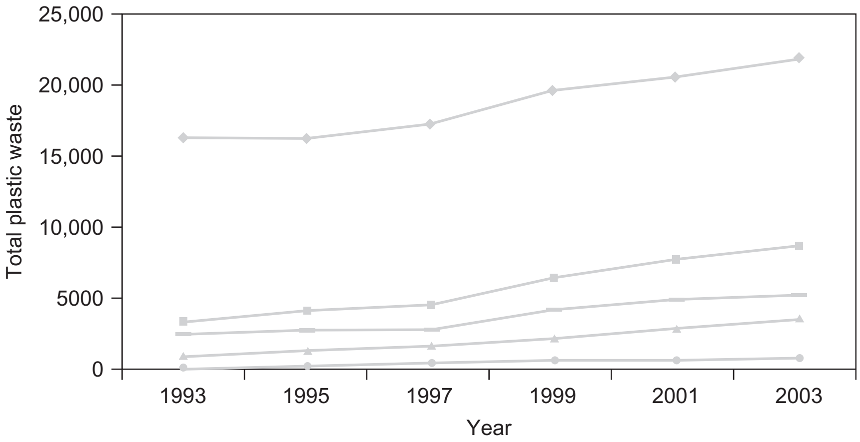

Figure 14.19 Total plastic waste generated and recovered in Western Europe (♦ total plastics waste, ■ total plastics waste recovered, – energy recovery, ▲ mechanical recycling, and ● feedstock recycling). *Source: Adapted from Garforth et al. (2004).*

very active for the cracking of bulky macromolecules. Hence, nanocrystalline HZSM-5 can be regarded as a promising catalyst for a feasible feedstock recycling process by catalytic cracking.

Hydrogenation in the Kohleol-Anlage Bottrop

The hydrogenation process in the Kohleol-Anlage Bottrop serves to recover synthetic crude oil and gases that can be used for industrial purposes. At the beginning of the twentieth century in Germany, work was initiated on the development of feedstock recycling techniques and technologies in order to enhance the recovery of energy and raw materials. Initially, the purpose of hydrogenation was to recover oil from coal. At the beginning of the 1950s, the utilization of this form of hydrogenation ceased because of its high cost. Only after the second oil crisis was interest in development work on hydrogenation techniques rekindled (Kohleol-Anlage, Bottrop). In the second half of the 1980s, industrial residue was processed to an increasing extent in Bottrop because of the detoxifying effect that hydrogenation has on various types of contaminated residue, such as oil containing chlorine. Since hydrogenation occurs at very high pressure, the plastics have to be liquefied first to make them suitable for pumping. The solid liquefaction of hydrocarbons is called depolymerization and is applied to the long polymeric chains resulting in fragmented short and mobile units. Cracking may occur when the plastics are heated for a longer period of time. After liquefaction, high-pressure pumps compress the mixture at a pressure of 15–250 bar. Finally, the liquid mass is heated to 440–480°C and is transferred to a high-pressure column reactor where the actual hydrogenation takes place. The carbon chains are cracked to an even greater extent and hydrogen is bound to the fragments. Hydrogenation occurs in three series of connected column reactors, and then the product is exposed to a lower pressure so that solid, nonusable components are removed. The final products consist of synthetic crude oil and gases (a mixture of methane, ethane, propane, butane, pentane, and hexane). A closed system is advantageous because there are no harmful emissions to the environment (Ball and Unsworth, 1995; Pearson, 1996).

Production of Gas

Several gasification techniques are used worldwide by companies such as Thermoselect, TEES, Texaco, BCU, etc. The plastics are converted into a gas mixture (mainly carbon monoxide and hydrogen) at 800°C or higher by adding oxygen and steam. Similar to hydrogenation, any chlorine-containing compounds present in the plastic waste (such as PVC) are decomposed by the high temperatures used in the process and are converted to a more useful product. Heavy metals and mineral substances are melted into a vitreous slag to be used in road construction work at later stages of the procedure. This process of binding heavy metals and minerals is known as vitrification. The obtained crude gas is cooled very abruptly in order to prevent the formation of harmful substances such as dioxins and furans. Tars and solids are first separated in a further step of the process, and then the liquid tars, consisting of carbon and hydrogen, can be converted into gas by employing a special gasifier for liquid products. The production of methanol from waste materials still remains of major importance worldwide (Pearson, 1996).

Coal can be replaced by a thermal equivalent of this gas in the rotary kiln or can be effectively used in gas engines. The mineral raw materials can probably be used for the production of a special cement. Several research groups have taken an interest due to the importance of this recycling method and the necessity for further research. Therefore, in BCU (Bundrer Cementwerke AG, Switzerland), various gasification processes are currently being studied, tested, and compared. Among others, for example, the fluidized-bed method was studied, by using air as a gasifying medium, for the thermoselect process that involves gasification with pure oxygen. This latter method, according to BCU, has numerous advantages, such as higher gasification temperature, much smaller volume of gas of very high quality, and clean slag that can be drawn off as fluid. Its only disadvantage resides in its high initial investment.

During the thermoselect process, the material is compressed to about one-tenth of its original volume without any prior treatment. The material is pressed into compact plugs that are fed into an airtight heated degassing duct. The organic components are driven off and converted into carbon by increasing the heat in the duct. The carbon forms a continuous renewed active carbon filter that absorbs any pollutant. After being mixed with inorganic components, such as metals and minerals, it is fed into a reactor where gasification occurs in the presence of oxygen at temperatures above 2000°C. At these temperatures, the metallic, mineral components and chlorinated hydrocarbons are completely decomposed. The reformation of dioxins and furans is prevented by rapid cooling of the hot gas. This gas, which represents about 10% of the amount of gas for a refuse incineration plant, undergoes thorough cleaning and can be utilized as an energy carrier. The liquefied slag components are fed into a second high-temperature reactor where the mineral components, with the addition of oxygen, gas, and propane at a temperature of 1800°C, are converted into raw materials. Metals are separated and made available to the metal industry (Caluori, 1995). In most gasification systems, environmental emission controls are significantly reduced since the volume of gas emitted is much smaller than in traditional incineration systems. Furthermore, these systems contain small amounts of dioxins, acid gases, and other pollutants because of the relatively high quality of the fuels combusted.

Another research study conducted by De Stefanis et al. (1995) under the supervision of ENEA (Italian National Agency for New Technology, Energy and the Environment) focused on the observation of plant operations, data collection, and extensive sampling of the produced gas. Several more studies have been conducted in this area over the past 10 years (Brunner and Frey, 1995: Calamius, 1998; Carlsson, 1995; Edlinger, 1995; Redepenning, 1995; Rijpkema, 1995; Seddon-Brown, 1995; Steiner, 1995).

BASF Process

BASF was quick to realize that mechanical recycling can only be a partial solution. The task of the BASF pilot plant was to convert used plastics into petrochemical products that can be used in the BASF plant network as raw materials. The agglomerates are delivered in silo trucks to BASF and pneumatically conveyed with nitrogen to the storage silos of the pilot plant. The agglomerates are then converted into petrochemicals by means of a three-stage process (Wanjek, 1995). Similar to hydrogenation, the BASF process also starts with liquefaction of the plastics at about 30°C in the absence of air, and simultaneously a dehydrochlorination of the PVC present in the plastic mixture occurs. The released hydrochloric acid is absorbed and reprocessed in the hydrochloric acid unit of the plant. In the second step, the liquefied plastics are cracked into petrochemical feedstocks without the addition of hydrogen. At temperatures above 400°C, the polymer chains are fragmented down to shorter length chains, and various oils and gases are formed. The gases are compressed and used as feedstock in a steamcracker. In the third step, the mixture is fractionated producing a sulfur-free product similar to crude oil (naphtha), short hydrocarbon molecules, and aromatic compounds. All these products can be used by the network of chemical plants available at BASF in Ludwingshafen.

For instance, gaseous molecules such as ethylene and propylene are recovered from naphtha in the steamcracker. After separation (distillation), these can be directly used for polymer production (PE, PP, etc.). The oils, which only boil at high temperatures, are gasified and processed into methanol. About 5% of residues is the maximum amount to be obtained. The process runs pressure-free in a closed system, thus generating practically no toxic emissions to the environment (Pearson, 1996; Wanjek, 1995).

Reduction Process

At Bremer Stahlwerke (steelworks in Bremer), plastic agglomerate is used as a substitute for heavy oil, one of the materials needed for operation of the blast furnace. During steel production in a blast furnace, the chemically bound oxygen must be separated from the iron fed into the furnace. Reduction, which is the removal of oxygen, is the reaction of carbon, carbon monoxide, or hydrogen with oxygen. These reactions require energy input to take place, whereas combustion releases heat. The gases are formed when plastic is injected into the furnace at 2000°C, melts at the bottom of the blast furnace, and undergoes abrupt gasification. Since plastic and oil have a very similar chemical composition, 1 kg of oil can be replaced by 1 kg of plastic in this process. As the gas migrates upward through the long blast furnace shaft, more than 80% of the reduction potential of the gas produced from the plastic is utilized. A mixture of slightly combustible gas, carbon monoxide, and steam, which is known as blast furnace gas, is obtained and used in the steelworks (Pearson, 1996).

14.8.6 Chemical Recycling

Chemical conversion processes can be used for recycling plastic waste, but chemical recycling of polymers requires plastics of almost uniform chemical composition and high purity. With regard to the potential cost, this type of recycling can be performed on an economical basis only with the more expensive engineering plastics, such as polyurethanes. The target of any chemical recycling process is to depolymerize polyurethane and recover those materials that can be reused. The processes that are widely applicable are the following: hydrolysis, hydrogenation, pyrolysis, aminolysis, glycolysis, hydroglycolysis, chemolysis, and ammonolysis. The processes differ greatly in terms of quality of the plastic feed, complexity of the process, and final products. The plastic, however, must be adapted to chemical recycling processes by liquefaction. A degradative extrusion has been suggested as a pretreating process for chemical recycling of plastic with satisfactory effects (Cassey et al., 1995; Lentz and Mormann, 1992; Marechal et al., 1995; Michaeli and Lackner, 1995; Seyfarth et al., 1995).

Chemical plastic recycling processes may find application in recycling of PVC/PET blend where sorting operations are either not possible or prohibitively expensive. The advantage of such a process is the possibility to "tailor" the end product to the application requirements. Since this approach is innovative, energy and material economics need further elaboration (Lusinchi et al., 1998). Ammonolysis of polyurethanes has been reported in only a few studies of which the oldest is a patent dating from 1955. Two more patents, assigned to the McDonnell Douglas Corporation, claim ammonia acts as co-reagent in the alcoholysis of polyurethanes. Another representative example is ammonolytic cleavage of urenane and urea bonds of a polyurethane elastomer and flexible foam based on methylenebis(phenyl isocyanate) (MDI) and polyetherpolyol under supercritical conditions producing polyols, amines, and substituted urea (Lentz and Mormann, 1992).

The glycolysis, is carried out by charging compacted pellets into a stirred batch reactor containing diethylene glycol (DEG). A catalyst is added and the reactor is heated to 200°C. The pellets dissolve within 1 h and the reaction finishes in 2 h. The stirrer of the reactor is stopped and the reaction mixture is allowed to separate into two layers. The top layer consists of DEG and flexible polyol with a small quantity of impurities. The bottom layer consists primarily of DEG and aromatic compounds derived from the isocyanate in the foam. The two layers are separated for further processing. The top layer is washed with more DEG either in the batch reactor or in a liquid/liquid extraction column. After the final wash, DEG is removed by vacuum stripping, yielding pure flexible polyol. Following purification, the obtained flexible polyol undergoes a split-phase glycolysis so it can be used to replace virgin polyol completely. Propylene oxide (PO) is added to the bottom layer to form an aromatic polyol rich in DEG. This mixture is heated under vacuum to react and distill off any residual PO. Excess of DEG is also removed and is suitable for reuse at any stage of the process (Cassey et al., 1995; Marechal et al., 1995).

A new recycling technique has been developed that utilizes a natural solvent, D-limonene, to shrink expanded polystyrene (EPS). The new recycling system consists of EPS shrinking equipment and a recycling plant for separating the limonene solution. There are two types of EPS shrinking equipment: a mobile (truck) and a static EPS shrinking apparatus. The final product is PS and not EPS because PS cannot be used to produce EPS by the thermal shrinking method (Noguchi et al., 1998a,b,c).

Chemical recycling refers to the decomposition of the macromolecular structure to generate low-molecular weight compounds. This is typically carried out at high temperature and in the presence of various types of catalysts. This approach consumes large amounts of energy and, in many cases, results in rather low value products. Probably the type of chemical recycling having the highest potential value involves depolymerization. In this case, the resulting monomer can then be utilized to regenerate more polymeric material (Burillo et al., 2002).

14.8.7 Radiation Technology

One technological barrier to polymer recycling is the incompatibility of different polymer types. When an attempt is made to mold a product using a polymer mixture, the materials typically form separate phases, resulting in poor properties. Another problem is degradation that may be present in the recycled material. Properties are affected by changes in molecular structure caused by environmental factors during use, including UV light, thermal-oxidative processes, attack by pollutant gases, chemical interaction with liquid contents, and others. Ionizing radiation offers unique possibilities in its application to the problem of recycling polymers (Clough, 2001), due to its ability to cause cross-linking or scission of a wide range of materials without dissolving the sample. Possibilities for using radiation in recycling include the following:

1. enhancing the mechanical properties of recovered materials or blends,
2. decomposition of polymers.

Radiation-included oxidation of PE prior to blending with recycled polyethyleneterephthalate (PET) was particularly beneficial; this enhanced the miscibility of the PE with the more polar PET (Burillo et al., 2000).

Recycling of butyl rubber from inner tubes, using irradiation of cryogenically ground rubber crumb, is a commercial process in China (Yang et al., 1998) that leaves few refining wastes. A limited amount of work has been reported on the use of radiation in chemical recycling (degradation) of polymers, yielding liquids of mixed composition for potential use in the petrochemical industry. Radiation can be useful in lowering the energy requirements for chemical recycling as well as providing a means of controlling the nature of the products (Zhao et al., 1996). Another study reported that when particles of radiation-cross-linked PE were incorporated as an additive into a melt of uncross-linked polyethylene, an enhancement of elasticity was obtained (Matusevich and Krul, 1999; Matusevich et al., 1999).

Radiation may potentially provide a major benefit either for material or chemical recycling. A success in material recycling could constitute a major breakthrough in demonstrating an energy-efficient and economically attractive recycling technology. Due to its ability to penetrate solids, including opaque materials, and to induce chemistry in the solid phase, radiation may be uniquely suited to this purpose. Since radiation can also result in the degradation of materials, depending on polymer type and environmental conditions, it may likewise be of utility in reducing energy costs by pretreatment of polymers to promote chemical recycling. Studies over the past two decades have established that irradiation can be very useful in the processing of polymer blends. Nearly all of this work has involved virgin (i.e., nonrecycled) samples.

Polyethylene and Polyamide

Mixtures of polyethylenes and PA-6 are normally immiscible. The use of PE (chemically functionalized by introduction of polar groups through irradiation) to prepare miscible blends with PA-6 has been reported by several workers. Spadaro et al. (1992, 1993, 1996) used this method to produce uniform blends of LDPE, HDPE, and linear low-density polyethylene (LLDPE) with PA-6. Blending of LDPE with PA-6 led to lower values of TS and higher values of Izod impact strength

(Valenza et al., 1992, 1993). The irradiated blends with stabilized morphology can then be conventionally processed, including conventional curing. These blends include NR/EPDM, SBF/EPDM (ethylene propylene diene monomer), and BRF/EPDM (NR, natural rubber; SbF, styrene-butadiene copolymer; BrF, polybutadiene). In another study, the processability of HMWPP/EPDM (HMWPP, high-molecular weight polypropylene) blends was found to improve on irradiation (van Gisbergen, 1989), and the radiation-induced cross-links stabilized the morphology of this blend during injection molding. Gamma irradiation under an inert atmosphere of mixed compositions of PET and PP, which had been coextruded, was reported to show modest improvement in properties at low dose (50 kGy) as a result of material cross-linking, though the data were not conclusive; significantly degraded properties were seen at higher doses (300 kGy) (Revyakin et al., 1999). The addition of agents that undergo cross-linking when exposed to radiation to compositions representing recovered waste materials has been investigated. Mixed materials containing HDPE, PP, and PS, with triallyl cyanurate (TAC) added, showed significant improvement in modulus at a dose of B200−350 kGy. Some positive effect was seen at 2% TAC; substantial improvement was found at 10% TAC (Fujii and Nomura, 1986). Czvikovszky and coworkers have reported a number of studies in which recycled, reinforced polymer systems were prepared using PP from reprocessed car bumpers (Czvikovszky et al., 1999; Czvikovszky and Hargitai, 1999).

Gamma irradiation of butadiene-containing polymers in the presence of oxygen caused the material to exhibit a decrease in the onset temperature for mass loss, compared to unirradiated material or material irradiated in the absence of oxygen, when the samples were subjected to thermogravimetric analysis (TGA) (Schnabel et al., 1999). There is a large and successful industry based on the radiation degradation of Teflon powder, which renders the material capable of being incorporated into inks, lubricants, and other formulations (Lunkwitz et al., 2000).

14.9 The Issue of Contamination on Recycling

After sorting and washing, the waste polymer is likely to contain polymeric, particulate, and chemical contaminants that might render the recycled material unsuitable for food applications. In general, recycled materials are not allowed to be used for food packaging applications. Food packaging in contaminated recycled materials is a serious problem and well understood scientifically (Allen and Blakistone, 1995; Blakistone, 1994; Devliegehere et al., 1998; Franz et al., 1994, 1997; Miltz et al., 1997). The main drawback with old plastics comes from mass transfer that takes place during its previous use (Feigenbaun et al., 1997; Yoda, 1999) and that old plastics, exhibiting potential contamination (by contact with harmful substances), cannot be in contact with the food (Perou et al., 1999). One of the most interesting approaches consists of reusing the wasted plastic as the core of the new material, a layer of virgin polymer being placed between the recycled material and the food (Feigenbaun et al., 1997). Based on data of hundreds of known chemicals, the Food and Drug Administration (FDA) considered the risk linked to the ingestion of an unknown chemical amounting to 10 ppb migrated substance (Bayer et al., 1995). Usage of the above-mentioned virgin polymer considerably retards the migration of the contaminant, which tends to be uniformly distributed through the bilayer packaging into the food. In view of the current state of the art, only a predictive approach can be of help in deciding whether recycled plastics, although possibly polluted, can be used safely (Harmati et al., 1995).

The marketing of unsafe materials is likely to be a barrier to more extensive exploitation of recycling of plastics. Exclusion of recycled materials from food packaging applications is likely to limit further advances in plastic recycling. Therefore, it is crucial for the industry to function within a frame of a clear and scientifically sound legislation. It has been suggested that the best strategy is to allocate virgin polymers to food contact uses and recycled materials to other applications. Many research groups are currently carrying out further investigation on this topic in order to ensure the veracity of such suggestions. Another proposal involves the use of multilayer PET according to which the recycled PET layer is "sandwiched" between two layers of virgin PET. This technique is supposed to be efficient both for the protection of food and the environment as well. Therefore, the difficult problem of isolating any possible contaminants present in the recycled PET film is reduced to

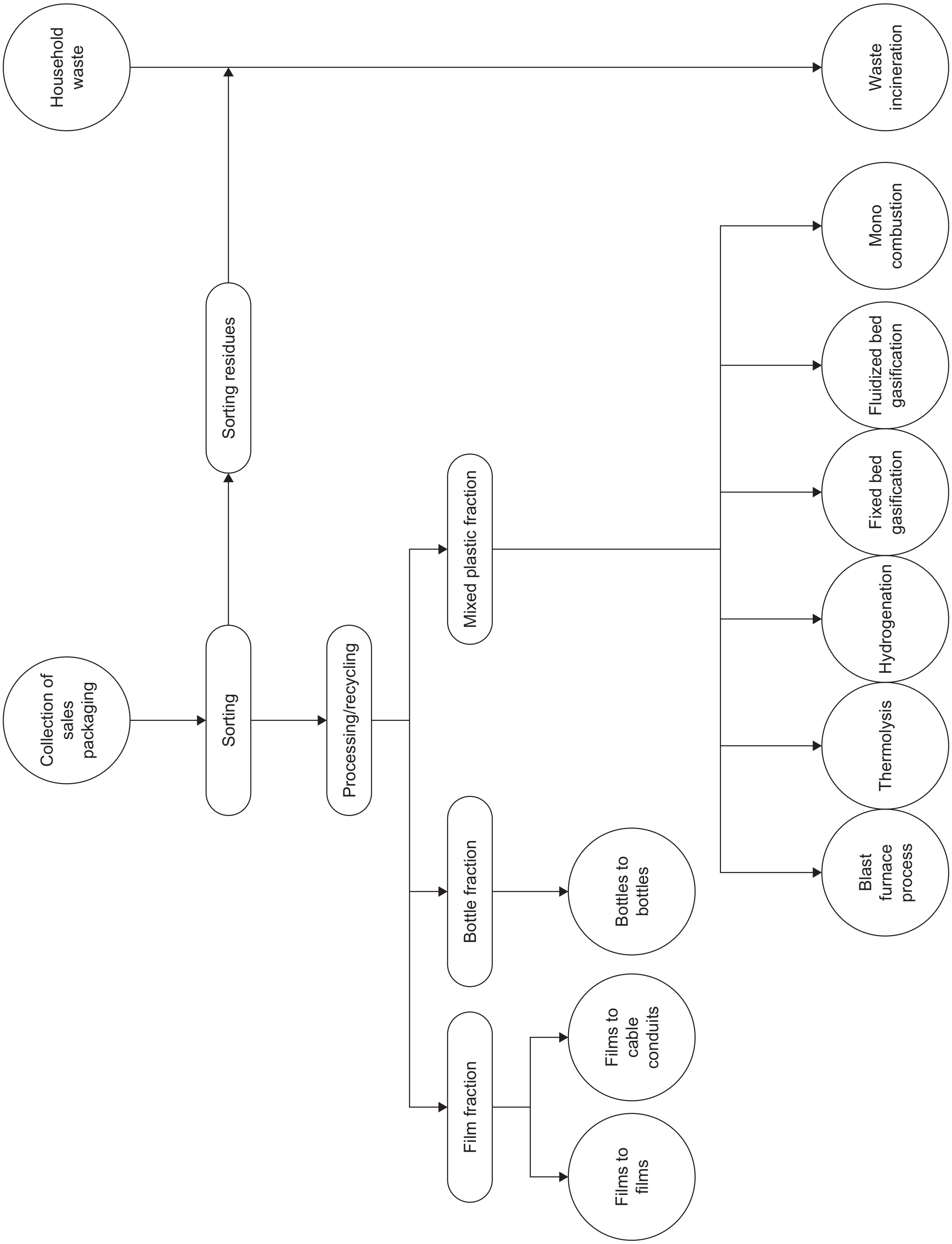

Figure 14.20 Scope of life cycle analysis for mechanical and feedstock recycling processes as well as energy recovery techniques.

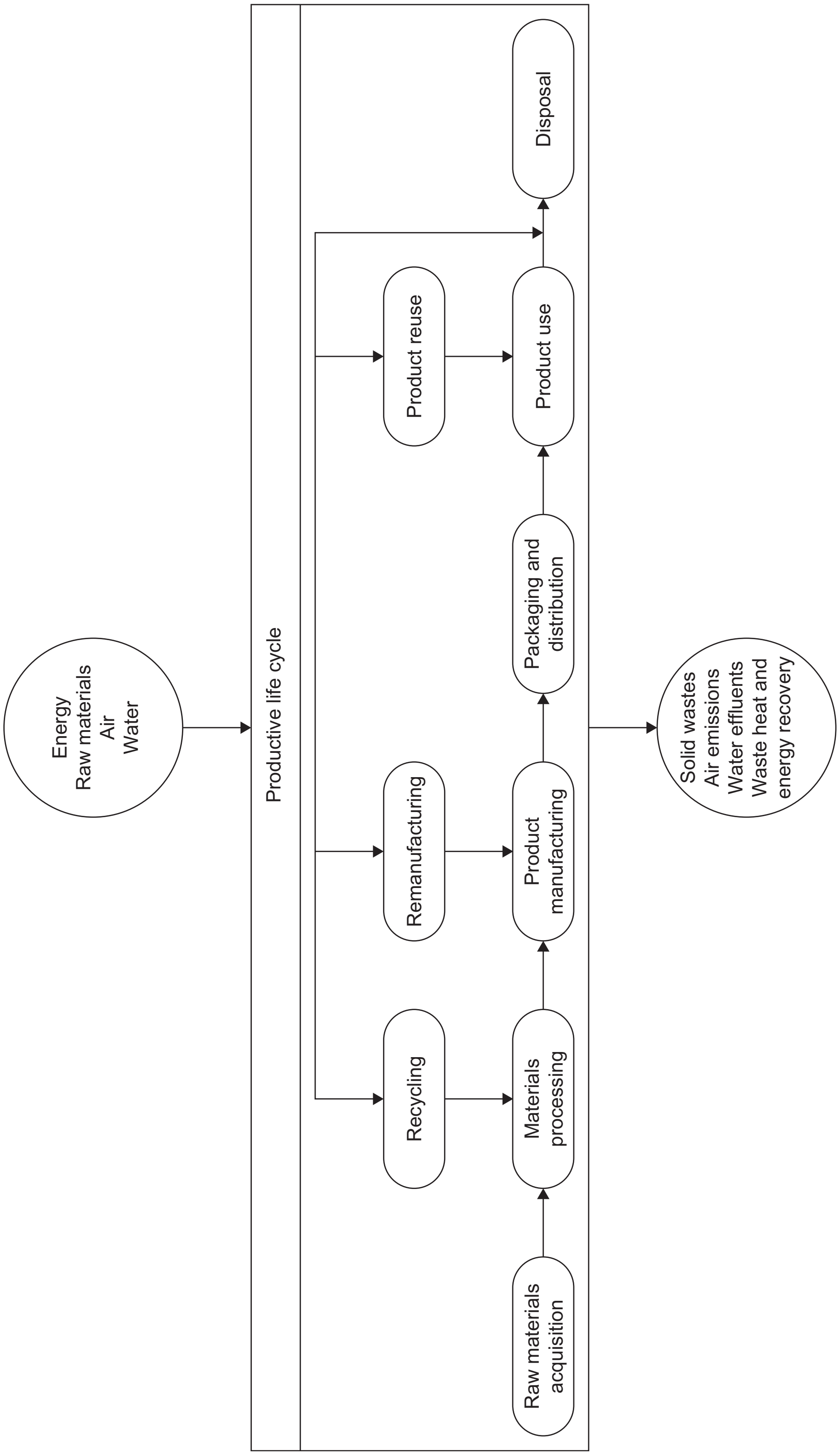

Figure 14.21 The life cycle of a product, including clarification of the terms “reuse” and “recycling.”

blocking the transport of the contaminants across the virgin layers.

The US and EU regulators have tried to harmonize worldwide regulations concerning the use of recycled materials in food packaging. The FDA in 1992 considered several suggested uses of recycled plastic for food packages and commented favorably on the use of recycled plastic in the following applications: expanded PS for foam egg cartons, HDPE for grocery bags, PE and PP for harvesting crates, PET for quart- and pint-size baskets for fruits, regenerated PET for soda beverage bottles. Several processes using recycled PET for food packaging applications have been approved by regulatory agencies outside the United States. In 1992, the UK Ministry of Agriculture, Fisheries, and Food (MAFF) approved the methanolysis process, and the same process was approved by the European Union as well. Japan, in 1992, also approved methanolysis as a recycling process for PET that is going to be used for soft drink bottles. In 1993, Australia approved the multilayer proposal and was followed in 1994 by New Zealand, Sweden, and Switzerland (Hope et al., 1992; Kaiser, 1995; Moser and Dudler, 1995; Van Rijwijk, 1995).

14.9.1 Environmental Impacts of Waste Management Processes

Any recycling operations wishing to be considered responsible have to meet both market and environmental requirements. Recycling seems to be the most popular option for reducing packaging waste. The EEC discussed a directive that should harmonize the different national regulations at the European level. Therefore, any assessment of plastic recycling processes has to take into account their environmental impacts and compatibility in addition to the actual recycling cost.

Consequently, life-cycle analysis is a system describing the environmental and resource impacts of a product over its entire life cycle. It is a research instrument for any environmental parameters with the background of technical and economical specifications. For that purpose, the raw material, energy, emissions, wastewater, and waste balances are carried out throughout the entire life cycle. An ecoprofile is based on the same theory as a life-cycle assessment (LCA) but it describes environmental and resource impact in a way which makes possible the ranking of different processes. The description of the system studied is the first step for preparing a life cycle analysis or an ecoprofile. The next step is an inventory of all emissions and resource consumption caused by the processes in the life cycle, and standardization of the emissions is the third step for a thorough LCA. Normalization of the equivalents is essential and is considered as a fourth step. The equivalents are normalized by dividing them by the average annual emission per inhabitant. For global effects, the equivalents are divided by the annual emission per inhabitant in the world and for regional effects the equivalents are divided by the annual emission per inhabitant in the region. The units of normalized equivalents are called person equivalents (PE). Only after normalization of the equivalents is it be possible to evaluate and speculate on the significance of the environmental contributions. LCA, sometimes, may include a fifth step, which is the improvement analysis.

In Germany, within the frame of “LCA of recycling and recovery of plastics waste packaging materials from households”, three research institutes have studied the various feedstock and mechanical recycling techniques with respect to their consumption of resources, greenhouse effects, pollution, and the production of municipal and hazardous waste. All steps involved in the recycling techniques and the fabrication of recycled products were thoroughly investigated. The most important conclusion reached in the LCA is that there is often more than one ecologically safe method for the recovery of plastics. Either feedstock recycling, mechanical recycling, or energy recovery techniques may be selected depending on the particular situation. From an ecological point of view, the best possible utilization of the chemical and physical properties and the energy content of the postconsumer plastics is the ultimate aim. All aspects of products should be taken into account so that there are no erroneous results. There have been many examples of published “eco-balance” studies of various packaging systems. The German Institute for Market Research on Packaging studied the impacts of replacing PVC with other plastics. It was concluded that the total tonnage of single-layered films would remain the same were PVC to be replaced. However, because of the PVC’s superior barrier properties compared to other plastics, the amount of composite films would increase by 25%. This would result in an increase of waste production (almost 10% by weight) because composites are difficult to recycle while PVC is molded.

A joint application of LCA and energy synthesis, named "energy life cycle assessment", is shown to provide information about input and output material flows as well as about the environmental support to the system, in order to facilitate choices and policy-making toward "zero-emission strategies and techniques". Results show that increasing the complexity of the system as well as the use of co-products help to achieve a better performance and an optimum use of available resources. The case study is only based on the performance comparison of two power plants, which does not entail all the possible ways for complexity increase. In fact, if a plant (or any other production system) is really integrated within the local productive structure, it is no longer just a point source of electricity, hot water, and released chemicals. Other cycles can be involved (water and wastewater, fuel from urban and biomass waste, use of sulfur from fuel purification, etc.) that could generate further nonnegligible economic and environmental advantages. In order to do this, the input of information needed may take the form of landscape planning and alternative option exploration and lead to the construction of infrastructures capable of linking all the possible partners involved in co-product/raw material exchange and use. This new framework for the evaluation of production activities, the so-called zero-emission strategy, was found to be in very good agreement with Lotka-Odum's maximum power principle in ecosystems. The two strategies/statements are, in principle, equivalent. Zero-emission technologies guide the way human-dominated systems can achieve maximum power output in times of scarce resources, as natural ecosystems have already learned to be over their evolutionary trajectories (Ulgiati et al., 2006).

The LCA approach was used to determine whether a recycle and reuse strategy for plastics-based packaging system that substantially reduces the quantity of waste to landfill would also reduce its overall environmental burden. The following conclusions were reached:

1. The life cycle impacts in all categories examined were less for the proposed EPS-high-impact polystyrene (HIPS)/PE shrink-wrap packaging than for a present EPS/PE packaging. This is due to its lighter weight and also to the innovative recycling/reuse strategy for the new packaging system.
2. The life cycle oil consumption for the proposed EPS−HIPS/PE shrink-wrap packaging is about one-third less than the present EPS/PE shrink-wrap packaging. However, for both packagings, the consumption of oil accounts for a relatively small proportion of the overall energy consumption.
3. Both packaging options contribute to photochemical oxidant problems in Sydney and Melbourne. However, the EPS/PE packaging contributes more nitrogen oxides and volatile hydrocarbon precursors than the proposed EPS−HIPS/PE packaging and will therefore have a greater marginal impact.
4. Recycling or, better still, reuse of plastic products can significantly reduce the energy required across the life cycle because the high energy inputs needed to process the requisite virgin materials greatly exceed the energy needs of the recycling or reuse process steps (Ross and Evans, 2003).

Therefore, if a product requires a large input of energy derived from fossil fuels during primary production, as is the case for plastic-based products derived from virgin materials, then recycling is likely to reduce its environmental burden (Patel et al., 2000). It was also found that the energy consumed during transportation is negligible when compared to the overall energy consumption of the system. This is true even with the additional transport needs of the recycling and reuse steps. This is important because transport emissions are often cited as a reason for not pursuing recycling possibilities (Pearce, 1997). The raw material, energy, emissions, wastewater, and waste balances are carried out throughout the total life cycle, as presented in Figures 14.20 and 14.21.

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15 Polymer Blending for Packaging Applications

Barry A. Morris
DuPont, Wilmington, DE, USA

15.1 Introduction

Blending of polymers is becoming increasingly important in packaging applications to enhance properties, improve processing or reduce cost. Tailoring surface properties, such as coefficient of friction (COF), adding color, promoting adhesion, increasing output, improving stability, and obtaining easy-opening features, are just a few of the attributes that can be achieved by blending.

The simplest blends can be made by mixing ingredients in the extruder that is used to convert the resin into a film or coating. For more complex blends, specialized screw designs or customized compounding equipment may be required to achieve the desired properties. These machines incorporate various mixing modes, such as flow rearrangement (distributive mixing) or high stress levels to break up particles (dispersive mixing). Complex shear and elongational flow fields may also be used to obtain optimum mixing.

The final blend properties will depend not only on the flow and stress history, which is process dependent, but also on the thermodynamics and the polymers' thermal and rheological properties. Most polymer blends are immiscible—the minor component forms a separate dispersed phase or domain within the major component, and the major component forms a continuous phase or matrix. The phase size and shape is known as the blend morphology. Blend morphology has a profound effect on final properties and is the subject of much study. Morphology is influenced by:

- interfacial tension (thermodynamics),
- dispersed to continuous phase viscosity ratio,
- elasticity of each phase,
- minor component concentration,
- mixing and melting order,
- and much more.

A basic understanding of the complex relationships between polymer properties and processing can aid in optimizing blends for a given application.

In this chapter, we will highlight some fundamentals of blending polymers for packaging applications. The literature is too broad for a detailed review of polymer blending and alloying. The goal is to familiarize the reader with those aspects of polymer blending that are important for in-line mixing of resins and other ingredients during film converting. Some blend requirements, however, are too demanding for in-line mixing and are best left to a resin manufacturer or compounder. Some of the technology that may be used to design and to produce such blends is also reviewed.

15.2 Why Blend?

Even with the flexibility of controlling properties by introducing specific layers within the film, blending can still be critical for the package function. Blending may be needed to make the polymer stable enough to extrude or have the right surface properties after extrusion. Blending may be a way to tailor specific properties into a layer, such as barrier or heat-seal performance. The resin manufacturer often adds polymer additives, such as antioxidants, catalyst killers, and various processing aids, to the polymer. But the film manufacturer may add these and other additives, such as slip, antiblock, antifog, antistatic agents, or processing aids such as fluoroelastomers for reducing sharkskin. Typically, these additives comprise less than 1% of the final composition. They are usually in the form of a powder or liquid. Because of this, and their low concentrations, they are typically first made into a masterbatch; a highly concentrated blend of the additive with a carrier resin. Masterbatches are typically produced by outside compounders using specialized compounding equipment. The film manufacturer blends the

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masterbatch into the resin at the extruder feed hopper used to make the film or sheet.

Pigments such as titanium dioxide (TiO_2) and various colorants are typically added as a masterbatch. Since the additive or pigment is well dispersed in the masterbatch, blending can be done in a single-screw extruder without special screw designs or compounding equipment.

Blending may be used to reduce the resin cost. For example, a metallocene polyethylene (m-PE) plastomer may be diluted with standard linear low-density polyethylene (LLDPE) or low-density polyethylene (LDPE) to lower cost. Recycle may be incorporated back into the film structure too. In-house scrap may be ground up and introduced into the extruder hopper as "regrind".

Blending may also help improve resin processability. Two material grades with differing flow properties (such as melt index) may be blended together to achieve the proper flow for a given process. This is an example of a miscible blend described in more detail later. LDPE is typically blended into LLDPE to reduce extruder pressure and torque and increase output. Other examples where blending improves processing include blending amorphous polyamide into polyamide 6 to increase extruder output, and adding amorphous polyamide or ionomer to ethylene vinyl alcohol (EVOH) to improve thermoformability (Fetel 1997a,b).

A polymer which is deficient in one property is often blended with another to enhance that property. Blending in cyclic polyolefins (e.g., cyclic olefin copolymers) can enhance LLDPE stiffness (Jester, 2002). Soft polymers are often blended into harder polymers to improve the toughness. Examples include blending ethylene vinyl acetate (EVA) into LLDPE, m-PE into LLDPE, and ethylene-propylene-diene-monomer rubber (EPDM) or m-PE into polypropylene (PP) (Qiu et al., 2003).

In the engineering polymer world, rubber is added to polyamide to improve low temperature toughness. Adding polyethylene terephthalate (PET) to polycarbonate (PC) lowers cost and improves chemical resistance and processability. Blends of PC and acrylonitrile-butadiene-styrene (ABS) copolymer have lower cost than PC and higher heat deflection temperature and toughness than ABS (Encyclopedia of Polymer Science and Technology, 1987).

Barrier properties may be enhanced by blending. High-density polyethylene (HDPE) is blended into LLDPE or LDPE to improve moisture barrier performance. Amorphous polyamide, such as DuPont's Selar® PA, is blended into polyamide 6 to improve the oxygen barrier at high relative humidity (DuPont, 2012). DuPont invented a laminar barrier technology where polyamide is blended into HDPE forming large platelets that impede the flow of species trying to migrate through. The laminar morphology is accomplished by choosing specific resins and processing conditions (Garmabi and Kamal, 1999; Huang et al., 2005; Kamal et al., 1995; Subramanian, 1985).

Adhesion may be promoted with several resins. Adding ethylene methyl acrylate (EMA) or EVA to PE can improve adhesion to certain inks. Anhydride modified polyolefins are blended with PE or EVA to improve adhesion to polyamide or EVOH in coextrusion. An acid-based additive has been developed for enhancing the adhesion of LDPE to aluminum foil in extrusion coating (Morris, 2004).

Additives may also help control adhesion during the heat-seal process. "Contaminants" are often blended into sealant resins to achieve easy openability. Examples include blending polybutene-1 (PB) into LDPE, LLDPE, EVA, or ionomers and EVA/ionomer blends (Hwo, 1987; Mergenhagen et al., 1996; Pirtle et al., 2004; Soutar, 1986). The blend morphology and phase compatibility is important for these applications. For example, in the blends containing PB, the PB is the minor phase. It forms spherical particles that are stretched into fibers and ribbons during the film fabrication process. The poor compatibility between the PB and matrix resin results in failure along these fibers and ribbons near the sealant interface, lowering the seal strength.

15.3 Blending Processes

Blending requires that the ingredients be brought together in the right proportions and then homogeneously mixed. In polymer blending, the former is important because there is little back-mixing in most continuous mixing devices used by the industry. This is particularly true of the single-screw extruder, which is the predominant device used by the film converting industry. For simple blends, such as those adding masterbatches, the pellets are premixed together and fed into the extruder hopper. In more sophisticated compounding devices, such as twin-screw extruders, ingredients can be added at various stages along the extruder.

Once the polymer enters the extruder or other mixing device, it is melted and the mixing mechanism depends on the specific device employed. We will focus on mixing in single-screw extruders, introduce some more sophisticated devices, and compare and contrast them to single-screw extruders. While specialty compounding devices, such as twin-screw extruders, kneaders and continuous mixers, have historically been used by the resin manufacturer or toll compounder and not by film converters, they are beginning to be used as in-line compounders for some large-scale film operations (Martin, 2002).

15.3.1 Pellet Premixing

Pellet mixers fit into two general types: off-line batch mixers and in-line feeders/mixers. Batch mixers can be as simple as a cement mixer. The ingredients are weighed and poured into the mixer, blended, and then transported to the extruder hopper. Batch mixers generally are less expensive and occupy less space than in-line mixers. They can be used to feed more than one extruder. Also, the ingredients' weight can be accurately measured, depending on the scale being used. On the other hand, they can be labor intensive, leave no automatic records, and open up the chance for human weighing errors and the possibility for pellet segregation during transport. Human weighing errors can be eliminated with automatic weighing that use either gravimetric or volumetric feed systems, as described here.

In-line mixers generally are positioned above the extruder hopper. Each ingredient is fed by individual feeders. Figure 15.1 shows a typical pellet blender. The ingredient feeders meter out a specific volume or mass over time, either by constant revolutions per minute (rpm) of an auger (volumetric feeders) or by an auger whose rpm is controlled by the feed hopper loss in weight (gravimetric feeder). Volumetric feeders are less expensive but need to be manually calibrated for each ingredient since differences in density, bulk density, and compressibility affect the feed rate. Gravimetric feeders have become the most commonly used feeders. Their calibration is usually much simpler than that of volumetric feeders. For example, the feeder may measure the weight loss in 30 s of operation at 10% of the maximum feeder speed to compute a feed factor that takes into account the variation due to bulk density, density, etc. The whole calibration process is usually done electronically and requires little operator interaction. Since the feed hopper weight is monitored by the computer control system, gravimetric feeders allow the individual feed rates to be recorded. Alarms can be set to ensure each ingredient is being fed to the extruder. Care must be taken when the feed hopper is refilled. Various control schemes, such as temporarily going into volumetric mode, are used to ensure feed continuity as the weigh cell is recalibrated. Understanding how the gravimetric feeder handles refilling is helpful in ensuring a trouble-free operation.

Figure 15.1 Pellet blender. *Source: Courtesy of Keith Larson, Colortronic North America.*

In-line mixers generally take up more space and are more expensive than batch mixers. They allow, however, for changing ingredient proportions during processing and can record the actual ingredient weights entering the extruder, which can be important for process control. They are also generally less labor intensive.

The ingredients in premixed pellet blends may segregate if they differ in density, size, or shape and are transported a long distance. Keeping the transport distance as short as possible and avoiding mixing powders with pellets can minimize segregation.

Using properly sized feeders and augers is important to ensure that ingredients are controlled to the correct proportions. An oversized feeder will likely have less precision and accuracy. There are also practical limits to pellet blending. A 1% pellet blend corresponds to blending one pellet in every 100. When possible, it is best to strive for ingredients of 10% or higher for greater control and accuracy.

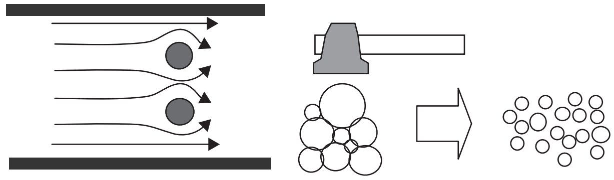
Care must be taken to clean the feeders, mixers, and transport lines thoroughly when changing over products. One wrong pellet in a product can cause gel problems and other quality issues.

The film producer incurs extra risk when blending since the blend properties cannot be directly measured or controlled, especially if the blend is a thin layer in a multilayer film. Premade blends from a resin manufacture or compounder can be tested for properties to ensure they meet specifications. The error associated with premixing is directly related to the precision and accuracy of the pellet premixing system, how well it is maintained, and procedures that have been adopted to ensure the ingredients never run dry. Gravimetric pellet mixers typically have precisions ranging from about 0.1% to 1%, depending on hopper, feeder, and auger size.

15.3.2 Melt Blending

Once the ingredients have been fed in the correct proportions into the mixing device hopper, typically an extruder, the polymers and/or additives must be homogeneously blended together. This requires that the polymers be in the molten state. The mixing device melts the polymers, provides a means for mixing, and generates pressure for subsequent operations such as making film when in-line mixing and pelletizing when compounding.

Mixing is described as either distributive or dispersive and is illustrated in Figure 15.2. In distributive mixing, the polymer is rearranged by deformation. Separation and rearrangement of flow and kneading are two examples of distributive mixing. In dispersive mixing, particles are broken up and dispersed within the polymer matrix. Shear stress is important for overcoming the yield stress of the material. Dispersing pigment particles in a masterbatch is an example of dispersive mixing.



Distributive Mixing—Flow is divided, separated, and redistributed.

Dispersive Mixing—Particles are broken up by application of stress.

Figure 15.2 Distributive and dispersive mixing.

The single-screw extruder is the most commonly used device for film production. It efficiently melts the polymer and generates pressure for extruding the polymer through a flat or annular die. It is suitable for many blending applications but has its limitations, many of which can be overcome by optimizing the screw design. Single-screw extruders rely on the difference in friction between the solid polymer pellets and the barrel and screw surfaces to propel the pellets forward. Slippery ingredients may impede the pellet flow and cause surging and other unwanted effects. Single-screw extruders are typically flood fed, meaning the throughput is determined by the extruder screw speed, not how fast the ingredients are fed to the feed hopper. In more sophisticated compounding devices, such as twin-screw extruders, the throughput is decoupled from the screw speed. The output in these devices is determined by the feed rate, and the screw speed can be increased or decreased to change the mixing intensity and energy input. Single-screw extruders are also generally not well equipped to handle powder (due to potential problems with segregation in the feed hopper and nonuniform melting) and liquid feeds.

The melting mechanism for pellet blends with different melt points in a single-screw extruder is not well understood. The standard melting model for uniformly melting pellets envisions a solid bed compressed against the trailing edge of the screw channel accompanied by an ever-lengthening melt pool that results from the frictional heat near the barrel surface (Maddock, 1959; Mount, 2005; Tadmor et al., 1967) (see Figure 15.23). Disruptions in the solid bed can result in poor melt quality; unmelted particles may exit the extruder, plugging screen packs or appearing in the final film as "gel" particles (Spalding and Hyun, 2003). A disruption in the solid bed can cause surging. Phase inversions and other aspects of blending of polymers that have different melt temperatures may cause disruptions in the solid bed and are not well documented in the literature. The low melting polymer may also act as a lubricant, impeding the melting of the high melting component since viscous heat generation from the friction between the polymer and barrel wall is one of the primary avenues for polymer melting.

In a standard screw, the polymer melt is subject to nonuniform temperature and flow histories. There are circulatory flow patterns in the metering section of the screw (Figure 15.3). These patterns aid distributive mixing and, as they are nonuniform, they may lead to uneven mixing. The shear stress and flow rates vary across the flow channel (Figure 15.4). As a consequence, the temperature varies across the flow channel. The temperature nonuniformity exiting the extruder can cause film thickness variability. Mixing elements incorporated into the screw design or at the extruder exit (such as static mixers) help homogenize the melt temperature for proper control of film thickness. These same mixing devices also help blend polymers. Mixing elements that have been utilized over the years include pins, restriction rings, and more specialized designs such as the pineapple, Dulmage, Saxton, and Maddock mixers (Rauwendaal, 1986).

Some mixing elements are characterized as distributive mixing elements—they achieve mixing by disrupting the flow. One of the easiest ways to do this is by inserting pins (Figure 15.5), blisters or other elements that impede the flow. Pins can cause problems, however, as stagnant flow zones are created behind the pins, setting up the potential for gel formation with some thermally sensitive polymers. More sophisticated designs, such as the Saxton mixer (Saxton) (Figure 15.6), eliminate the dead zones while dividing up the flow. Other elements are dispersive in nature, such as the well-known Maddock mixer (Figure 15.7). In this design, the

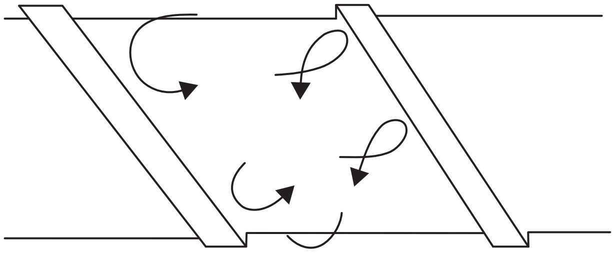


Figure 15.3 Illustration of circulatory flow patterns in the metering section of a single-screw extruder. *Source: Adapted from Middleman (1977).*

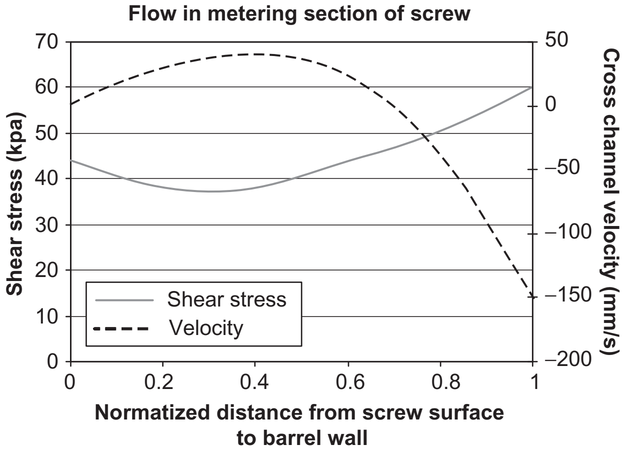


Figure 15.4 Example of stress and velocity distribution of PE in the cross-channel direction of the metering section of a single-screw extruder. Calculations were done using commercial software from Polydynamics, Inc.

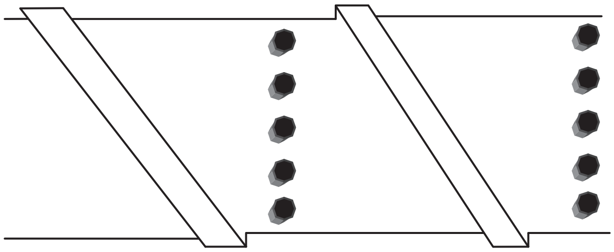


Figure 15.5 Pin mixing section.

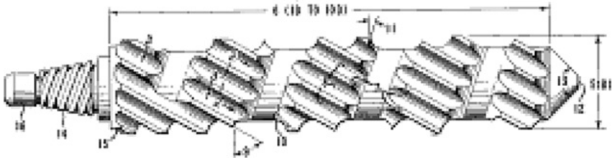


Figure 15.6 Saxton mixing section.

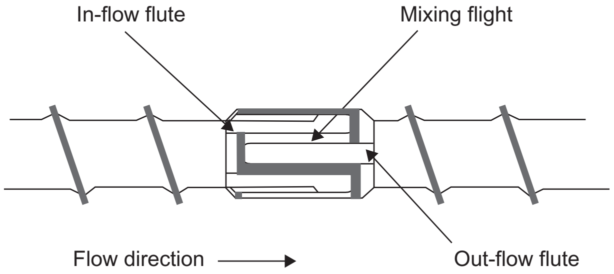


Figure 15.7 Maddock screw element. *Source: Adapted from Spalding and Hyun (2003). Courtesy of the Society of Plastics Engineers.*

polymer flows down a fluted section and over a small clearance between the screw and barrel, which introduces high shear stresses to break up agglomerates. Its actual effectiveness at dispersive mixing is suspect, particularly compared to specialized compounding devices, such as twin-screw extruders, but it is often used for multipurpose mixing.

In recent years, several new high-performance screw designs have been developed that try to improve the mixing efficiency while increasing output. These screws generally work by having the polymer flow through a series of relatively tight clearances. The solid material is both entrapped and given time to melt or subject to high shear or elongational flow fields that aid in melting and mixing (Rauwendaal, 1986; Schut, 1999). The high-performance section replaces the whole metering section of the screw. Some of the more commonly used high-performance screws include the energy transfer (Somers et al., 2002), variable barrier energy transfer (Hogan et al., 2003; Myers and Barr, 2002), double wave (Fan et al., 1998; Kruder and Calland, 1990), stratablend (Somers et al., 1998), unimix (Myers, 1994), and CRD (Rauwendaal and Ponzielli, 2004) screws. An example of a variable barrier energy transfer screw element is show in Figure 15.8.

Although optimizing the screw design allows many polymer blends to be made on single-screw extruders, in some cases, specialty compounding devices may be necessary. This is especially true when intensive dispersive mixing, reaction or devolatilization is required. There are several compounder designs on the market. For general purpose compounding, corotating twin-screw extruders are often employed (Curry, 1993; White, 1990). Kneaders provide good distributive mixing, easily allow the introduction of liquid feeds and minimize temperature buildup, which is important for thermally sensitive polymers. Counter-rotating twin-screw extruders are often used for reactive extrusion and devolatilization since they can have long L/Ds (length to diameter ratios). The Farrel continuous mixer operates like a continuous Banbury mixer and is useful for making masterbatches with high filler loadings. Planetary mixers and other multiscrew devices are also available for specialty applications.

Of the specialty compounding devices, the corotating twin-screw extruder is the most often used. Co-rotating twin-screw extruders offer considerable versatility in design and operation. As described earlier, feeding is independent of extruder rpm, which allows the mixing and energy intensity to be independently varied. Multiple feeding ports are common, and screw designs can be changed from job to job to tailor the process. The screws are built from individual elements, which can be changed to suit the application. These elements come in several geometries with different mixing intensities. They provide good distributive and dispersive mixing and impart both shear and elongational flow fields. Figure 15.9 shows some twin-screw modular elements. Some twin-screw extruders have screws that are self-wiping, which results in a narrow residence time distribution for better mixing control. One drawback is that they are poor melt pumps. Because of this, temperatures can be difficult to control at the extruder exit. Twin-screw extruders are not used alone for in-line compounding on a film line. They are adapted for better melt pumping

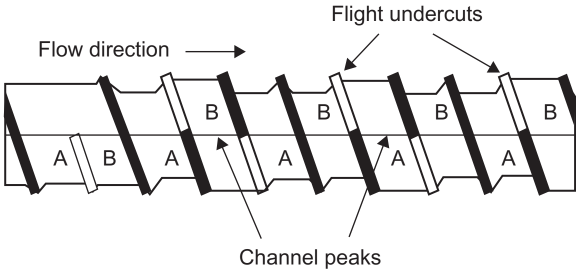


Figure 15.8 Illustration of a variable barrier energy transfer screw. *Source: Adapted from Hogan et al. (2003). Courtesy of the Society of Plastic Engineers.*

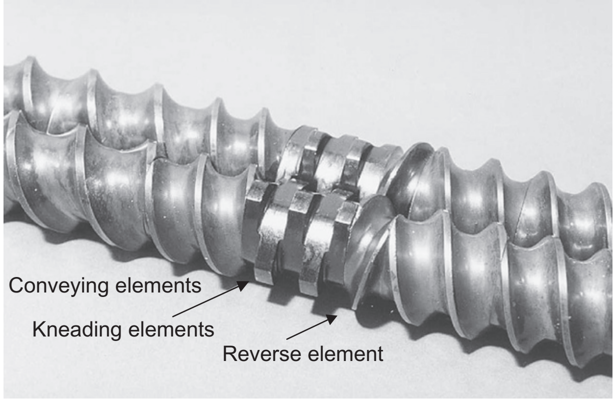


Figure 15.9 Twin-screw extruder modular elements.

by coupling the twin-screw extruder with a single-screw extruder or gear pump (Martin, 2002).

Twin-screw extruders and other specialty compounding devices are considerably more expensive than single-screw extruders.

15.4 Physics of Blending

The properties of a polymer blend are influenced by specific interactions between the molecules (thermodynamics) and their response to deformation (rheology). The thermodynamics determine whether the blend forms a single phase (miscible) or multiple phases (immiscible). Miscible blends typically follow the rule of mixtures, namely the blend properties are directly proportional to the component ratio. There are a few commercially important miscible polymer blends on the market today. One is Sabic Noryl® which is a polyphenylene oxide (PPO) and high-impact polystyrene (HIPS) blend.

How do we determine whether a blend is miscible? One method is to look at its transparency, either by microscopy or light scattering. An immiscible blend forms separate domains within the polymer matrix which may diffract light if they are large enough. Another technique is to measure the glass transition temperature (T_g) using differential scanning calorimetry (DSC) or other thermal analyses. A miscible blend will have a single T_g, typically between that of the components. Both techniques use a fairly large sample or probe size, which can at times be misleading. Sometimes blends appear to be miscible because the probe size is too large. Other techniques with smaller probe sizes are X-ray and neutron scattering and various spectroscopy techniques, such as infrared and nuclear magnetic resonance.

Occasionally, we use the word "compatibility" to describe the degree to which polymers interact. Miscibility is maximum compatibility. Compatibility is a subjective term and is not well defined. Miscibility has a specific definition—two polymers are miscible if they form a single phase over their entire composition range at a given temperature.

Immiscible blends, by definition, form multiple phases. In the simplest case, a two-component blend, the minor phase forms domains within a continuous major component matrix. The domain sizes, shapes, and distribution are known as the morphology. Figure 15.10 shows some immiscible blend morphologies. The morphology is influenced by the concentration, thermodynamics, component rheology, and the flow and stress history during mixing and processing.

The morphology is critically important to the final blend properties, which often do not follow the rule of mixtures (Figure 15.11). In many cases, blends are designed to create a specific morphology to achieve certain property gains. An example is super-tough polyamide, which is a polyamide 66/rubber blend. The rubber must achieve a certain domain size in order to stop cracks from propagating during impact. Another example is Selar® RB laminar technology developed by DuPont. Here, polyamide is dispersed in HDPE so that the polyamide phase forms platelets parallel to the surface. The platelets create a tortuous path for diffusion, resulting in improved barrier performance (Subramanian, 1985).

Once a specific morphology has formed, it may change with further processing. The domains may coalesce or be stretched through orientation (see Figure 15.10). Compatibilizers are frequently used to stabilize the blend morphology.

There is a third type of blend system, namely melt-miscible blends that are miscible in the melt state but phase separate in the solid state. An example is polyoxymethylene/polylactide (Ohme, et al., 2007). This phenomenon may be important for ease of processing in order to obtain a fine dispersion of one component into another during melt blending.

15.5 Thermodynamics

When two materials are brought together, there must be a decrease in the free energy for them to transform into a single material or miscible blend. This can be expressed mathematically as:

$$\Delta G_m < 0 \text{ for miscibility} \qquad (15.1)$$

where

ΔG_m = Gibbs free energy of mixing.

The free energy includes enthalpic and entropic contributions:

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (15.2)$$

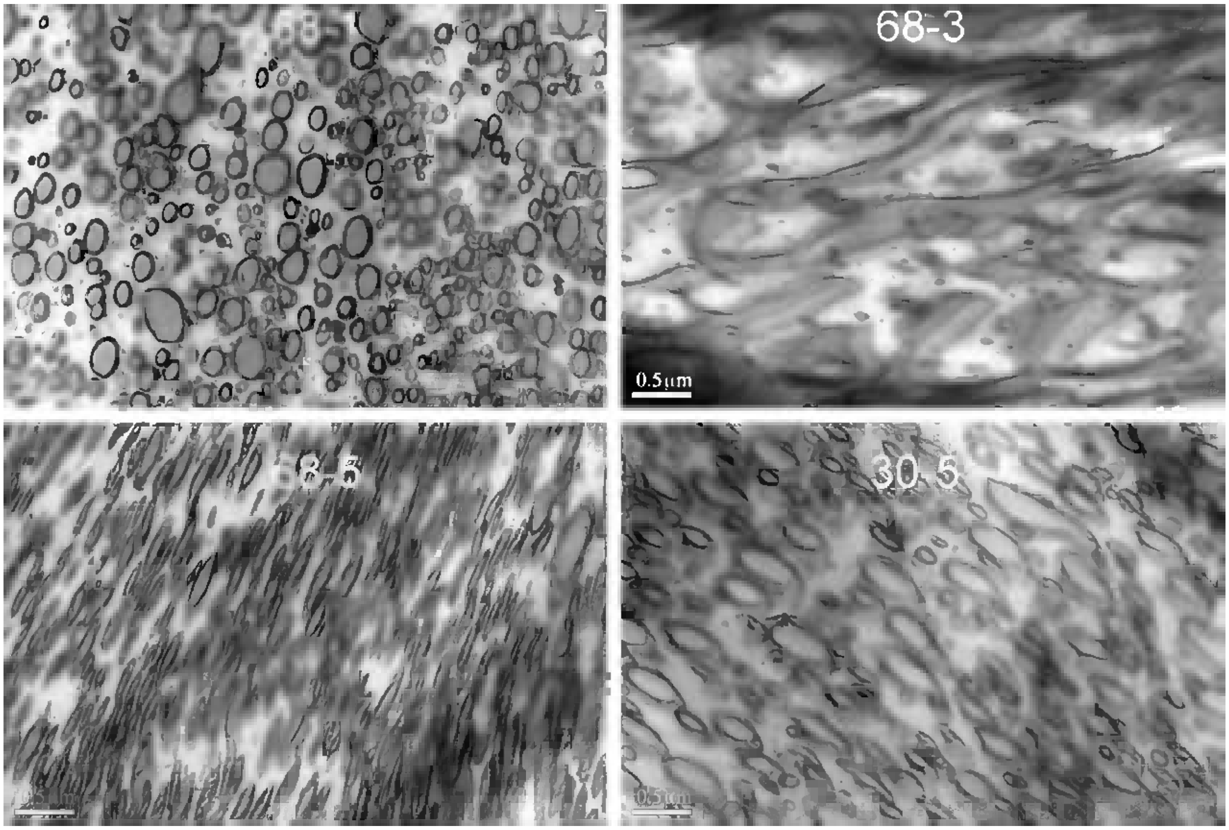


Figure 15.10 Transmission electron micrographs (TEMS) of immiscible PE–styrene polymer blends of varying chemistries. *Source: Courtesy of Barbara Wood and I-Hwa Lee, DuPont. Further examples of TEMS of immiscible blends can be found in Wood (1992, 2002).*

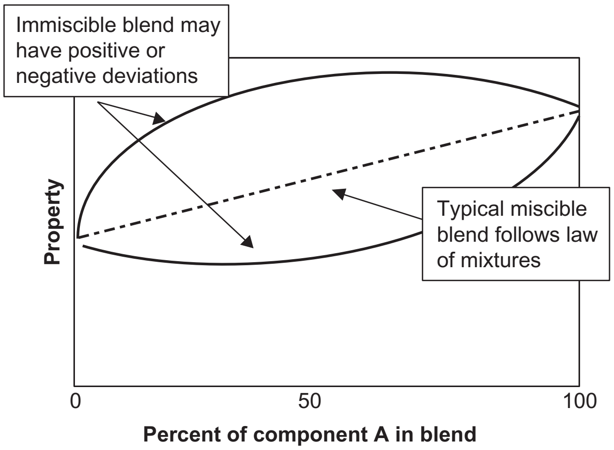


Figure 15.11 Properties versus percent A in polymer blends.

where

ΔH_m = enthalpy of mixing,

T = temperature,

ΔS_m = entropy of mixing.

For most polymer blends, ΔH_m is positive and ΔS_m is nearly zero. Thus, it is rare that polymer blends are miscible.

Coleman et al. (1991) derived the following relationship for ΔG_m based on the work of Flory and Huggins:

$$\frac{\Delta G_m}{RT} = \left[\frac{\Phi_A}{N_A}\ln\Phi_A + \frac{\Phi_B}{N_B}\ln\Phi_B\right] + \chi\Phi_A\Phi_B\left(\frac{\Delta G_H}{RT}\right) \tag{15.3}$$

where

ΔG_m = Gibbs free energy of mixing,

R = ideal gas constant,

T = temperature,

Φ_A = volume fraction of polymer A,

Φ_B = volume fraction of polymer B,

N_A = degree of polymerization of polymer A,

N_B = degree of polymerization of polymer B,
χ = interaction parameter,
ΔG_H = free energy of specific action between polymers, including hydrogen bonding.

The first term on the right side of Eq. (15.3) arises from combinatory entropy. Since N, which is related to molecular weight (MW), is large for polymers, this term is nearly zero. The second term also arises from entropy and is always positive. The interaction parameter, χ, is defined by:

$$\chi = \frac{V_{\text{ref}}}{RT}[\delta_A - \delta_B]^2 \tag{15.4}$$

where

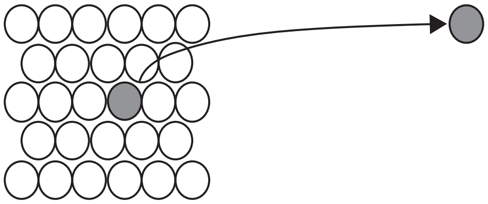
V_{ref} = reference volume,
δ_A = solubility parameter for polymer A,
δ_B = solubility parameter for polymer B.

The final term, $\Delta G_H/RT$, is negative when specific interactions are present.

From Eqs (15.3) and (15.4), we see that we can improve compatibility by matching solubility parameters and achieve miscibility only when we incorporate specific interactions. Nonpolar polymer blends, such as PP–PE blends, have no specific interactions beyond weak dispersive forces. As we shall see, even though their solubility parameters are nearly equal, they are not miscible.

In Eq. (15.4), we introduced the solubility parameter. We now discuss the origin of solubility parameters and how they can be helpful in understanding polymer blends. The energy per unit volume required to remove a molecule from a liquid or solid is known as the cohesive energy density. This is illustrated in Figure 15.12. The cohesive energy density is a function of the forces that hold the material together. The solubility parameter is the square root of the cohesive energy density. It contains contributions from both nonpolar (dispersive forces) and polar (dipole–dipole and hydrogen bonding) interactions.

Comparing solubility parameters is a way to quantify the "like dissolves like" principle of chemistry. For two polymers to be miscible, the difference in solubility parameters should be between 0.1 and 3 Hildebrands, depending on their interaction strength. Coleman et al. (1991) defined a critical solubility parameter difference, $\Delta\delta_c$, below which the polymers may be miscible. As shown in Table 15.1, the value of $\Delta\delta_c$ depends on what interactive forces are present.



Cohesive energy density is the energy needed to remove a molecule away from its environment and is the square of the solubilty parameter.

Figure 15.12 Illustration of cohesive energy density.

Table 15.2 lists solubility parameter values for some polymers used in packaging films. Returning to our PE–PP blend example, we see that the difference in their solubility parameters is less than 1 ($\Delta\delta < 1$). However, since only nonpolar dispersive forces are present, the critical solubility parameter difference ($\Delta\delta_c$) is less than 0.1. Thus, these polymers are not miscible.

It should be noted that there is some controversy around solubility parameters in the literature. They are exact for polymers with only physical interactions. There are errors associated with trying to extend the concept to polymer systems involving hydrogen bonding and other polar interactions and with the indirect methods used experimentally to measure them. These errors typically result in a range that is not very useful for predicting miscibility; hence matching solubility parameters is not a necessary and sufficient condition for the miscibility of polymers. However, they are useful guides for compatibility and, since most polymer blends are not miscible, this may be their greatest strength. The solubility parameter difference has been related to the interphase thickness between immiscible polymers. Immiscible polymers with a solubility parameter difference of about 0.5 Hildebrands or less may still build up enough strength at the interface for good mechanical properties (Walsh, personal communication).

Returning to our PP–PE blends example, PE is often used to modify the properties of PP. For example, ethylene–propylene rubber (EPR) is

Table 15.1 Critical Solubility Parameter Difference Upper Limit

Specific Interactions Involved	**Polymer Blend Examples**	$\Delta\delta_{critical}$ **Hildebrands**
Dispersive forces only	Polybutadiene–polyethylene (PBD–PE)	<0.1
Dipole–dipole	Polymethylmethacrylate–polyethylene oxide (PMMA–PEO)	0.5
Weak	Polyvinyl chloride–butadiene acrylonitrile copolymer (PVC–BAN)	1.0
Weak to moderate	PS acrylonitrile–polymethylmethacrylate (SAN–PMMA)	1.5
Moderate	PC–polyesters	2.0
Moderate to strong	Polyamide–polyethylene oxide (Polyamide–PEO)	2.5
Strong	Polyvinyl phenol–polyvinyl acetate (PVPh–PVAc)	3.0
Very strong	Polymethacrylic acid–polyethylene oxide (PMMA–PEO)	>3.0

Source: From Coleman et al. (1991).

Table 15.2 Solubility Parameters for Some Polymers Used in Packaging

Polymer	**Solubility Parameter ($cal^{1/2}/cm^{3/2}$) (Hildebrands)**	**Source**
PE (polyethylene)	7.7–8.4	Van Krevelen (1976)
PP (polypropylene)	8.2–9.2	Van Krevelen (1976)
PS (polystyrene)	8.5–9.3	Van Krevelen (1976)
PVC (polyvinyl chloride)	9.4–10.8	Van Krevelen (1976)
PVDC (polyvinylidene chloride)	9.9–12.2	Van Krevelen (1976)
PVOH (polyvinyl alcohol)	12.6–14.3	Van Krevelen (1976)
EVOH (44 mol% ethylene)	17	Kuraray literature
EVOH (32 mol% ethylene)	19	Kuraray literature
Polyamide 6	12.6	Kuraray literature
EVA(9%VA) (ethylene vinyl acetate)	8.1	DuPont calculation (McBride, 1993)
EVA(25%VA)	8.2	DuPont calculation
EMA(20%MA) (ethylene methyl acrylate)	8.3	DuPont calculation
PET (polyethylene terephthalate)	10.3	Wu (1982)

blended with PP to improve PP impact toughness. The EPR forms a phase with sufficient adhesion to the PP that the properties are enhanced, as would be predicted by their close solubility parameters.

LDPE–LLDPE blends are perhaps the most commercially important blends used in flexible packaging applications. A distinguishing difference between LDPE and LLDPE is long-chain branching

(LCB) in LDPE, which contributes to its relative processing ease. Typically, about 10–30% LDPE is added to LLDPE to improve melt strength, bubble stability, and other film production in general. Hussein et al. (2001, 2003, 2004) and Hameed and Hussein (2002) found that LDPE and LLDPE are not miscible over their entire composition range. Miscibility is favored for LLDPE-rich blends. The miscibility range increases by lowering the LLDPE MW and by increasing the short-chain branch length (replacing the butene comonomer with octene). At the same MW and branch content, a Zeigler–Natta LLDPE is more miscible with LDPE than metallocene LLDPE (m-LLDPE), which has a narrow MW and comonomer distribution. At the same molecular weight distribution (MWD) and MW, an m-LLDPE with higher branch content is more miscible with LDPE than an m-LLDPE with lower branch content. Comonomer type does not have an effect on miscibility of m-LLDPE with LDPE.

One can add specific interactions to promote miscibility. Coleman et al. (1991) have developed software that uses group contribution theory to predict solubility parameters of polymers that, in many cases, agree well with experimental results. This is illustrated in Figure 15.13. Here, vinyl acetate (VA) and styrene (St) contents are varied in an EVA copolymer–styrene vinyl phenol (EVA–StVPh) copolymer blend. Increasing the VA and the VPh content promotes polar interactions (ΔG_{H}) that drive ΔG_{m} below zero (Eq. (15.3)). The experimental data are represented by the open and closed circles: the open circles represent miscible blends and the closed circles immiscible blends. The line demarking the region of miscibility comes from Eq. (15.3), using the software to predict the solubility parameters with specific interactions. The miscibility region depends on the comonomer percent in each polymer.

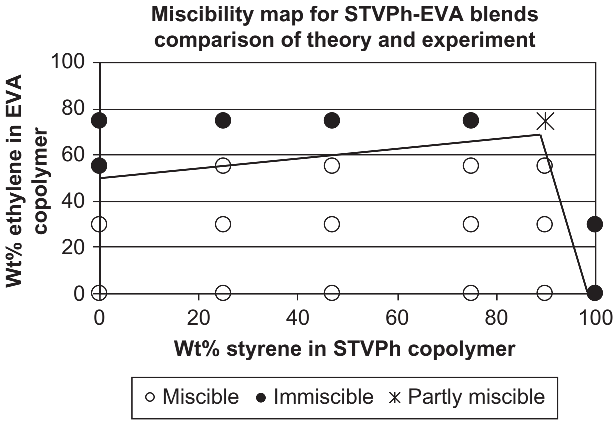


Figure 15.13 Example of using specific interactions between molecules to achieve miscible blends. . *Source: Taken from Coleman et al. (1991)*

A practical note about compatibility and miscibility concerns masterbatches. The carrier resin in the masterbatch should be compatible and, ideally miscible, in the resin in which it is being blended. This way, the carrier resin will not harm the let down resin properties. Poor compatibility can lead to poor optical properties, reduced barrier performance and, for sealants, poor seal performance. Benkreira and Britton (1994) found that better dispersion occurs when the carrier resin is lower in viscosity and has a lower melting point than the host polymer, for reasons that will become clearer in the next section.

Solubility parameters may also prove useful for predicting miscibility of low-MW additives in polymers.

15.6 Morphology Development in Immiscible Blends

To understand how morphology develops in a polymer blend, we will first look at how a single droplet suspended in a fluid is broken up during flow. The droplet is held together by interfacial tension, which arises from a nonuniform force distribution acting on the molecules at the interface (Figure 15.14). Inside a material, a molecule is

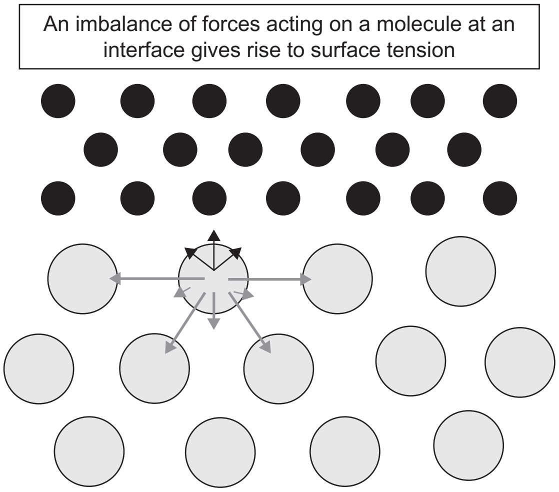


Figure 15.14 Illustration of the origins of interfacial tension.

bound to its neighbors by attractive forces related to the cohesive energy density. At an interface, however, molecules are only partly surrounded by their own kind. The material across the interface may exert different attractive forces. The difference in these attractive forces gives rise to the interfacial tension. The more alike the materials are, the lower the interfacial tension and the smaller the driving force holding the droplet together. If the droplet has a radius a, then this holding force, $F_{\text{interfacial}}$, is proportional to Γ/a, where Γ is the interfacial tension.

We can relate interfacial tension to solubility parameters as introduced earlier. Wu (1982) shows that the interfacial tension is related to the surface tensions of the two polymers:

$$\Gamma_{12} = \Gamma_1 + \Gamma_2 - 2\phi\sqrt{\Gamma_1 \cdot \Gamma_2} \qquad (15.5)$$

where

Γ_{12} = interfacial tension between polymers 1 and 2,

Γ_1 = surface tension of polymer 1,

Γ_2 = surface tension of polymer 2,

ϕ = interaction parameter.

This is known as the Good and Girifalco Equation. Wu (1982) tabulates the interaction parameter, ϕ, for several polymer combinations. They range from 0.79 to 0.98 for the polymers considered. The surface tension can be related to the solubility parameter:

$$\Gamma_1 = 0.2575 \cdot \frac{\delta_1}{\sqrt[3]{\rho_1}} \qquad (15.6)$$

where

Γ_1 = surface tension (dynes/cm),

ρ_1 = density of polymer 1 (g/ml),

δ_1 = polymer 1 solubility parameter $(\text{cal/ml})^{1/2}$.

Combining Eqs (15.5) and (15.6), recognizing polymer densities are around 1 g/ml and assuming $\phi = 1$, we find that the interfacial tension is directly proportional to the square of the difference in solubility parameters:

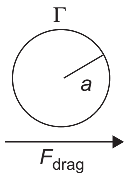


Figure 15.15 Balance of drag and interfacial forces on a spherical droplet in shear flow.

$$\Gamma_{12} \cong 0.26 \cdot (\delta_1 - \delta_2)^2 \qquad (15.7)$$

As shown in Figure 15.15, the flow field exerts a drag force that acts to breakup the droplet. For shear flow, the drag force is equal to the viscosity of the continuous phase, η_c, times the shear rate, γ', acting over the area of the particle ($\approx a^2$):

$$F_{\text{drag}} \sim \eta_c \cdot \dot{\gamma} \cdot a^2$$

We define the dimensionless capillary number, Ca, as the ratio of the drag force to the interfacial force:

$$Ca = \frac{F_{\text{drag}}}{F_{\text{interfacial}}} = \frac{\eta_c \cdot \dot{\gamma} \cdot D_d}{2\Gamma_{12}} \qquad (15.8)$$

where

D_d = droplet diameter ($=2a$).

When Ca exceeds a critical value, Ca_{critical}, the droplet breaks up because the drag force exceeds the force holding the droplet together. This hydrodynamic instability was first proposed by Taylor (1934). Taylor found that Ca_{critical} for a Newtonian droplet imbedded in a Newtonian fluid is a function of the viscosity ratio (the ratio of the droplet viscosity to the continuous phase viscosity): η_d/η_c. This has since been confirmed by other investigators and is illustrated in Figure 15.16. In a shear flow, Ca_{critical} reaches a minimum when the viscosity ratio is 1. When the viscosity ratio exceeds about 3.5, the droplet cannot be broken up in a shear flow, as indicated by the rapid rise in Ca_{critical}. The bottom curve in Figure 15.16 shows the relationship for Ca_{critical} in elongational flow. Elongational flow is more effective for breaking up droplets than shear flow; Ca_{critical} is lower and droplets can be broken up even at high viscosity ratios.

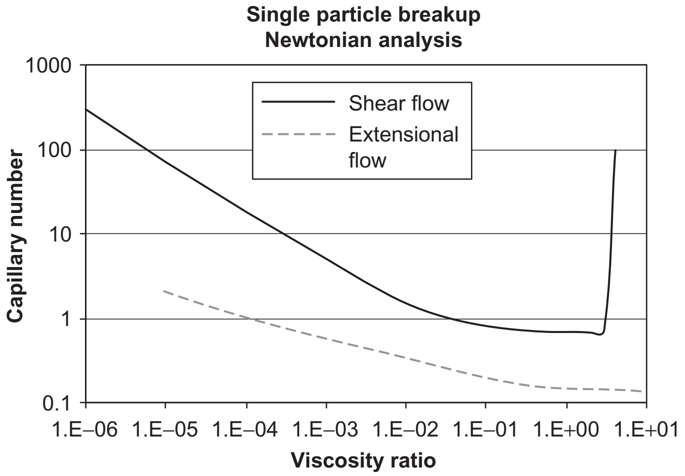


Figure 15.16 Critical capillary number for the breakup of a Newtonian droplet in shear and elongational flow. *Source: Data taken from Grace (1982)*

For transient flow, a different mechanism for drop breakup has been proposed by Tomotika (1935), based on Rayleigh's instability theory. Here, the droplet becomes an elongated ellipse or cylinder that, upon cessation of flow, breaks up into small droplets due to capillary disturbances, provided that the wavelength of these disturbances is greater than $2\pi a$ (Kang et al., 1995; Utracki and Shi, 1992).

The single droplet analysis gives us considerable insight into the dispersion of polymer blends (Figure 15.17). Typically, we want the minor component domain size (D_d) of the blend to be small. For example, for good clarity, the dispersed phase should be less than the wavelength of light, about 0.3 μm. For toughening, small soft rubber domains help prevent cracks from propagating. Equation (15.8) shows that we can decrease the droplet size by increasing the continuous phase viscosity and increasing the shear rate, or by decreasing the interfacial tension. We can further reduce the droplet size by matching the polymer viscosities (a good guideline is to choose a viscosity ratio between 0.01 and 2) and using a mixing device that imparts elongational flow. The interfacial tension can be minimized by reducing the difference in solubility parameters (Eq. (15.7)) or by introducing specific interactions.

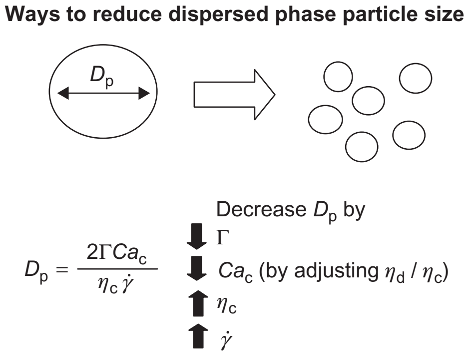


Figure 15.17 Learning from single droplet mechanics.

Compatibilizers are sometimes used to reduce the interfacial tension between polymers. Block or random copolymers often make good compatibilizers since they can be designed to contain two functionalities, each compatible with one of the polymers being blended. An example is using styrene–ethylene–butadiene–styrene (SEBS) copolymer to compatibilize HDPE and polystyrene (PS) blends (Bourry and Favis, 1995). Another approach is to add functional groups to the compatibilizer that reacts with one of the polymers. An example is using an ionomer to compatibilize polyamide and PE blends. The acid groups in the ionomer react with the polyamide amine end groups, and the ethylene backbone is compatible with PE.

While the breakup of a single Newtonian droplet in a Newtonian fluid is well understood, there are several difficulties in extending the analysis to polymer blends. The first is that polymer melts are typically non-Newtonian in their flow behavior (non-Newtonian fluids have viscosities that vary with shear rate and often exhibit elastic effects, such as normal stress differences and extrudate swell). Although several droplet breakup studies for non-Newtonian fluids have recently been published, this phenomenon is still not as well understood as the Newtonian case. Table 15.3 summarizes many of these studies. One aspect of non-Newtonian behavior is the polymer melt elasticity, characterized by the first and second normal stress differences. (Consult a rheology text such as Dealy and Wissbrun (1995) for a broader discussion of melt elasticity.) Some investigators have used the dynamic storage modulus, G', obtained from dynamic mechanical analysis (DMA), as a way to characterize elasticity. G' is proportional to the first normal stress difference, but only at low shear rates. At higher shear rates typical of polymer processing, G' may underestimate the polymer elasticity. In general, it has been found that when the droplet is more elastic than the continuous phase, it is more difficult to disperse. An elastic force aids in holding the droplet together, resulting in larger Ca_{critical} values and larger droplet sizes. Conversely, when the continuous phase is more elastic than the droplet, it is easier to break up the droplet because the matrix resin elasticity adds to the drag force on the droplet to break it up. Quantification and modeling of this behavior in flow regimes typical of polymer processing is still in its infancy.

Experimental studies with non-Newtonian fluids have also revealed different droplet breakup mechanisms. A Newtonian droplet immersed in a Newtonian fluid breaks up via Taylor (1934) and Tomotika (1935) instabilities (Figure 15.18). Under some conditions, non-Newtonian fluids also break up in this manner, but other mechanisms have also been observed. In some cases, the droplet flattens in the flow direction and becomes elongated perpendicular to the flow (Levitt et al., 1996; Mighri and Huneault, 2002). The ends of highly elongated particles find themselves in different planes with respect to flow and are torn apart by the velocity differences. At very high viscosity ratios, greater than the cut-off of 3.5 for Newtonian droplets, Mighri and Huneault (2002) observed breakup via attrition at the droplet surface.

As the droplet concentration increases, the breakup mechanism becomes more complex. Utracki and Shi (1992) and Macasko (2000) found that when the polymer concentration exceeds 0.5−1%, the droplet size after shearing was much greater than that predicted by the single drop experiments. As the concentration increases, the probability that droplets will collide and coalesce increases. The coalescence kinetics is not well understood and is thought to be critically important to the final blend morphology. Utracki and Shi (1992) observed that the same factors that enhance droplet breakup, namely high shear rates and reduced droplet viscosity, favor coalescence. Recently, several investigators (Macasko, 2000; Milner and Xi, 1996; Uttandaraman and Macosko, 1995) have proposed that compatibilizers act to inhibit coalescence by providing a protective shell around the droplet (Figure 15.19). The shell acts to repulse other droplets. Thus, dispersion stabilization may be more important to the droplet size than reducing interfacial tension. Indeed, Mighri and Huneault (2002) found that an EPR−PP droplet−matrix system with very low interfacial tension broke up in a similar manner as a PS−PE system with an order of magnitude greater than interfacial tension. They suggest that interfacial instabilities may not be required for non-Newtonian droplets to break apart.

As the minor component concentration is increased, the morphology may change. At high enough concentrations, the minor component becomes the continuous phase. Figure 15.20 shows the different morphologies possible for HDPE/PS blends studied by Bourry and Favis (1995). At low PS levels, the PS forms droplets in the HDPE matrix. As the PS concentration is increased, fibers are formed. At about 70% PS, the morphology becomes co-continuous—the HDPE and PS phases form an interpenetrating network structure where both phases are continuous. Higher PS levels result in HDPE droplets in a PS matrix. Note how the SEBS compatibilizer decreases the domain size.

Another concern in applying single-droplet studies directly to polymer blends is the uncertainties about the flow field in the mixing device and how to calculate the appropriate viscosity ratio. Polymer mixing devices, such as extruders, have complex flow fields involving both shear and elongational flow. The flow fields are typically nonuniform; the shear rate varies across the screw channel (see Figure 15.4). Further complicating matters are temperature changes along the extruder. Given these complexities, Lyngaae-Jorgensen (1993) proposes measuring the Ca_{critical} versus viscosity ratio curve for the given device.

Table 15.3 Viscoelastic Droplet Deformation in a Viscoelastic Matrix Under Shear or Elongational Flow Studies

Source	Expt or Theo	Droplet	Matrix	Flow	Result
Flumerfelt (1972)	Expt	Newtonian	Viscoelastic	Shear	Minimum droplet size and critical shear rate for breakup increases with matrix elasticity
Tavgac (1972)	Expt	Viscoelastic	Viscoelastic	Shear	Effect of elastic matrix depends on the viscosity ratio: when ratio is small, matrix elasticity stabilizes the droplet when ratio is high elasticity helps breakup the droplets
Gauthier et al. (1971)	Expt	Viscoelastic	Newtonian	Shear	Small viscosity ratio: similar to Newtonian drop in Newtonian matrix. High viscosity ratio: $Ca_c > Ca_{c\text{-Newtonian}}$
Parabodh and Stroeve (in Utracki and Shi, 1992)	Expt	Viscoelastic	Newtonian	Shear	For viscosity ratio <0.5, droplet viscoelasticity has a stabilizing effect
					For viscosity ratio >0.5, droplet viscoelasticity has a destabilizing effect
De Bruijn (1989)	Expt	Viscoelastic	Newtonian	Shear	Ca_{critical} for elastic droplet is slightly higher than for Newtonian droplet
Elmendorf and Maalcke (1985)	Expt	Viscoelastic	Viscoelastic	Shear	Viscoelastic drop deformation in Newtonian matrix decreases with increasing drop elasticity
					Newtonian drop deformation in viscoelastic matrix increases with increasing matrix elasticity
					Problems with quantifying the behavior due to fluid shear thinning
Varanasi et al. (1994)	Expt	Viscoelastic	Newtonian	Shear	At any viscosity ratio Ca_{critical} increases with increasing droplet elasticity
Levitt et al. (1996)	Expt	Viscoelastic	Viscoelastic	Shear	Studied PP droplets in PS matrix at different viscosity and elasticity ratios, shear flow at 1 s^{-1}. For high elastic matrix, the droplet widened in the direction perpendicular to flow. The width of the flattened drops depended on the differences in second normal stress differences between the phases

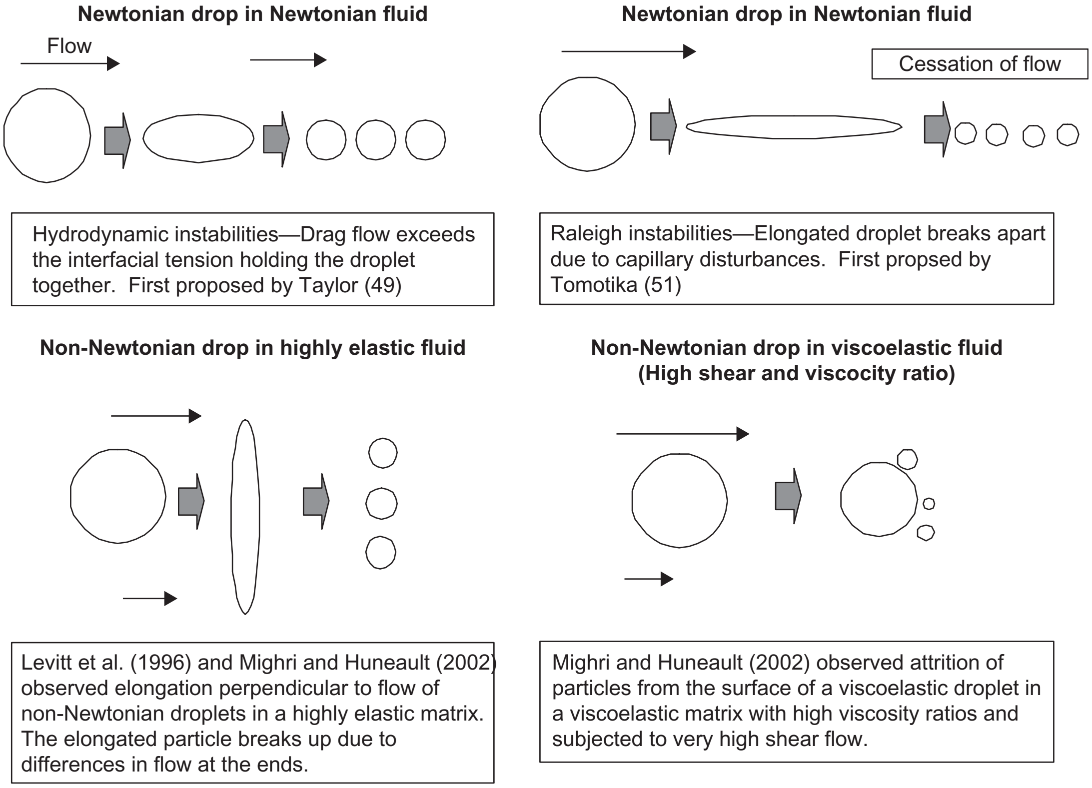
Han and Funatsu (1978)	Expt	Viscoelastic	Viscoelastic	Elong	Viscoelastic drops are more stable than Newtonian drops in both Newtonian and viscoelastic matrices
Milliken and Leal (1991)	Expt	Viscoelastic	Newtonian	Elong	Viscoelastic drops with viscosity ratios less than 1 have smaller deformation and Ca_{critical} than Newtonian drops. For viscosity ratio >1, the viscoelastic drop deformation behavior is similar to Newtonian drops
Delaby et al. (1994)	Expt	Viscoelastic	Viscoelastic	Elong	For negligible interfacial tension, viscoelastic drops deform less than the surrounding media when the viscosity ratio is less than 1 and more when the viscosity ratio is greater than 1
Meijer and Janssen (1993)	Expt	Not disclosed	Not disclosed	Elong	At small viscosity ratios, the droplet deformation in planar elongational flow resembles that for the matrix
Chin and Han (1979)	Expt	Viscoelastic	Viscoelastic	Elong	Higher droplet elasticity results in less deformation compared to the matrix
Shanker et al. (1996)	Expt	Viscoelastic	Viscoelastic	Elong	Higher droplet elasticity results in less deformation compared to the matrix
Mighri et al. (1997)	Expt	Viscoelastic	Viscoelastic	Elong	Used Boger fluids which have elasticity and nonshear thinning viscosity behavior
					For a given elastic matrix fluid, increasing the droplet elasticity decreased droplet deformation relative to the surrounding media. Droplet deformation increases with increasing matrix elasticity. Defined k' as first normal stress difference ratio divided by the viscosity ratio. When $k' < 0.2$, the matrix elasticity has a greater effect on deformation than the drop elasticity. The opposite is true with $k' > 0.2$. The study was conducted over a fairly narrow viscosity ratio range (0.5–1.1); shear rates were not disclosed

Mighri et al. (1998)	Expt	Viscoelastic	Viscoelastic	Shear	Used Boger fluids, which have elasticity and constant viscosity versus shear rate behavior
					Shear rates not disclosed; viscosity ratios ranged from 0.2 to 1.1. Defined k' as first normal stress difference ratio divided by the viscosity ratio For high matrix elasticity ($k' < 0.37$), the elastic drop deformation in an elastic matrix was higher than for the Newtonian case with same viscosity ratio and interfacial tension. In some cases, droplet widening in the direction perpendicular to flow was observed. For $k' > 0.37$, elastic drops deform less than the Newtonian case. The critical shear rate for droplet breakup increases with increasing k'. For $k' < 4$, $\mathrm{Ca}_{\mathrm{critical}}$ increases rapidly with k'; for $k' > 4$, $\mathrm{Ca}_{\mathrm{critical}}$ levels off at 1.75
Mighri and Huneault (2002)	Expt	Viscoelastic	Viscoelastic	Shear	Studied model systems and PS–PE system with viscosity ratio between 5 and 20 under relatively high shear rate ($1 - 20\ \mathrm{s} - {}^{1}$) in shear flow. In PS–PE system, the PS drop widened in the direction perpendicular to flow which contributed to droplet break up (the ends of the highly elongated droplet are in different flow planes). At high shear, a second breakup mechanism different from the Newtonian case was observed: attrition from the surface. An EPR–PP system had similar breakup mechanisms as the PS–PE system despite a 10 × difference in interfacial tension
Van Oene (1978)	Theo	Viscoelastic	Viscoelastic	Shear	Developed an expression for the dynamic interfacial energy to account for viscoelasticity:
					$\Gamma_{12} = \Gamma_{12}0 + D_p/12^{*}$ $[(N_{11} - N_{22})_d - (N_{11} - N_{22})_m]$
					where

					$\Gamma_{12}0$ = the interfacial tension in quiescent flow
					$(N_{11} - N_{22})$ = the first normal stress difference
					Droplet elasticity greater than the matrix stabilizes the droplet; matrix elasticity greater than the droplet destabilizes the droplet
Greco (2002)	Theo	Viscoelastic	Viscoelastic	Shear and Elong	Assumed the materials are simple second-order fluids, which includes elastic effects for slow flows. Used a perturbation method to analyze the first normal stress difference effect on droplet shape for small drop deformations
Maffettone and Greco (2004)	Theo	Viscoelastic	Viscoelastic	Shear and Elong	Developed a phenomenological model for the dynamics of a drop immersed in an immiscible fluid. Assume that the drop is ellipsoidal. Either or both fluids may have elasticity. Found that elastic drops deform less than Newtonian drops. Elastic drops in Newtonian matrix under shear are forbidden to break up at lower viscosity values than the Newtonian case. In elongational flow, the drop breakup is easier when the matrix is elastic and more difficult when the droplet is elastic
Lerdwijitjarud et al. (2004)	Expt	Viscoelastic	Newtonian	Shear	Studied deformation and breakup of viscoelastic drops (Boger fluids) in a nearly Newtonian matrix. Viscosity ratio controlled to around 1.0. Shear rates up to 5 s^{-1} used
					The deformation decreases for isolated drops at constant *Ca* as the drop elasticity increases. They did not observe droplet widening in the transverse to flow direction and suggest widening is influenced by factors other than first normal stress difference (such as second normal stress

					difference, shear thinning, or a shift of the critical condition to lower Ca when the matrix is elastic). Ca_{critical} increases with increasing droplet elasticity. For a 10% blend, the steady-state Ca is less than Ca_{critical} for an isolated drop (they suggest this may be due to flow differences in concentrated suspensions). The steady-state Ca was found to increase monotonically with the dispersed phase first normal stress difference

Expt, experimental; Theo, theoretical.



Newtonian drop in Newtonian fluid

Newtonian drop in Newtonian fluid

Hydrodynamic instabilities—Drag flow exceeds the interfacial tension holding the droplet together. First proposed by Taylor (49)

Raleigh instabilities—Elongated droplet breaks apart due to capillary disturbances. First propsed by Tomotika (51)

Non-Newtonian drop in highly elastic fluid

Non-Newtonian drop in viscoelastic fluid (High shear and viscocity ratio)

Levitt et al. (1996) and Mighri and Huneault (2002) observed elongation perpendicular to flow of non-Newtonian droplets in a highly elastic matrix. The elongated particle breaks up due to differences in flow at the ends.

Mighri and Huneault (2002) observed attrition of particles from the surface of a viscoelastic droplet in a viscoelastic matrix with high viscosity ratios and subjected to very high shear flow.

Figure 15.18 Single droplet breakup mechanisms in shear flow.

One must also consider the fact that the polymer melt viscosity varies with temperature and shear rate. Generally, there are two schools of thought on calculating the viscosity ratio. Some argue that the zero shear viscosities should be used. Others suggest using the viscosity at a representative shear rate for the process. However, it is stress, not shear rate that drives dispersion and droplet break up.

Stress is determined by the flow field and is continuous across an interface, whereas the shear rate is discontinuous. A better method is to plot the viscosity as a function of stress (stress is equal to the viscosity times the shear rate) and compare the blend components at a representative stress for the process. This is illustrated in Figure 15.21. Here, polymers A and B are the minor and major components, respectively. At a constant shear rate equal to 100 s^{-1}, the viscosity ratio is 1.6. But, at constant stress, the ratio is 2.6, very close to the 3.5 cut-off for shear flow.

The polymer temperature changes along the extruder as the polymer becomes molten and is conveyed to the exit. Huneault et al. (1995) showed that, for a PS–HDPE blend, the viscosity ratio varied by six orders of magnitude depending on the temperature (Figure 15.22). Computing the viscosity ratio just at the final extrusion temperature may be misleading. They found that, for this blend, the mixing was much better than what they would have expected just by looking at the viscosity ratio at the final temperature (200°C). Note that in Figure 15.22 the viscosity ratio is sometimes less than 1 and other times greater than 1. This indicates

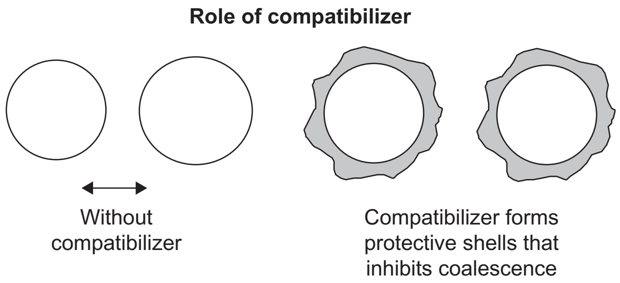
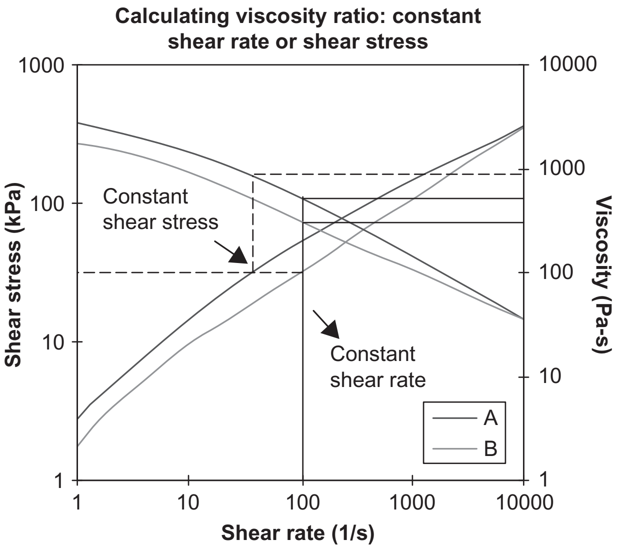


Figure 15.19 Role of compatibilizers in reducing coalescence in polymer blends.



	Viscosity A	(Pa-s) B	Ratio A/B
Constant shear rate	520	320	1.6
Constant shear stress	840	320	2.6

Figure 15.21 Calculating viscosity ratio.

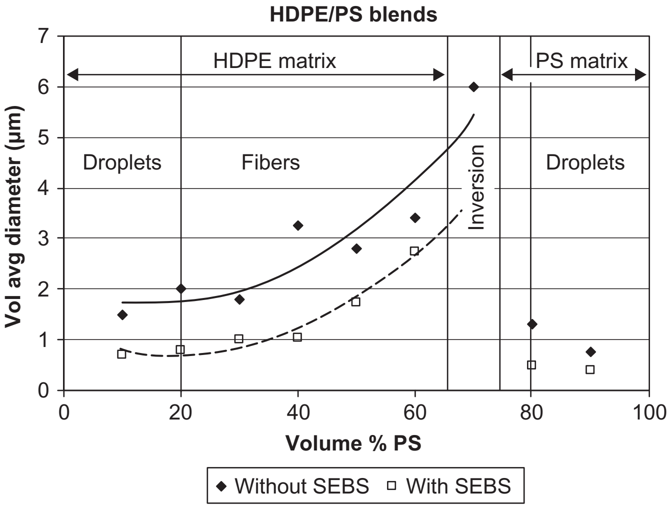


Figure 15.20 Blend morphology as a function of concentration. PS–HDPE blends from Bourry and Favis (1995).

that, for the two polymers, the viscosity temperature dependence is not the same, another complication in computing the viscosity ratio.

So far, we have assumed that both the polymers are molten at the time they are mixed. This is generally not the case, as mixing can begin during melting. Ghosh et al. (1991) studied the softening/mixing of two similar amorphous polymers and found that laminar sheets or striations form that subsequently break up into droplets. Lindt and Ghosh (1992) found that the striations come from the single-screw extruder melting process. A thin molten layer forms between the pellet solid bed and the barrel or screw surface caused by frictional heat and heat transferred from the barrel (see Figure 15.23 for the solid bed melting model). The high stress and deformation rates in this region transform the molten polymer into laminar morphologies as the pellets melt. The domain size decreases from a few millimeters (pellets) to about 50–100 μm due to the melting process. They made measurements as well as calculations that confirmed these striations and abrupt domain thickness changes for blends of both rheologically similar and dissimilar resins.

Benkreira et al. (1992) found that, when mixing a masterbatch into a host polymer, most of the mixing occurred during melting and little thereafter. They proposed a laminar mixing model where the striation stretching during melting leads to a reduction in dimensions. Scott and Macosko (1995) describe how component melting and softening in a batch mixer leads to the domain size reduction. They found sheets and ribbons are formed first, which become unstable due to flow and interfacial tension effects. Holes form, then a lace-like structure, followed by irregular-shaped particles, and finally spheres (Figure 15.24). Breakup is driven by interfacial instabilities. Burch and Scott (2001) found similar behavior for miscible polymers during the initial mixing stages and proposed instabilities due to dynamic interfacial tension as the cause. Willemse et al. (1999) found that sheets or striations were formed during single-screw extrusion and that the final droplet size depended on the striation dimensions at the start of breakup rather than the capillary number. The sheet to droplet breakup during shear is very effective at dispersing the minor phase, more so than the elongated droplet to subdroplet mechanism found in single drop experiments.

In a single-screw extruder, Tyagi and Ghosh (2002) followed a PP–EVA blend as it developed its morphology using freeze experiments pioneered by Maddock (1959). In these experiments, after the extruder has reached steady state, the screw is stopped and the polymer is quickly quenched. The screw is pulled and samples from the screw channels are analyzed. Tyagi and Ghosh (2002) found that striations formed in the feed zone. The dimensions quickly diminished along the channel length. In the compression zone, the shear and elongation increases, causing the striations to break up. The droplets that form are an order of magnitude smaller in size than the striation thickness prior to break up. The breakup into droplets requires a step-up in shear and stretching. They conclude that, for an extruder to be an effective mixer, periodic flow

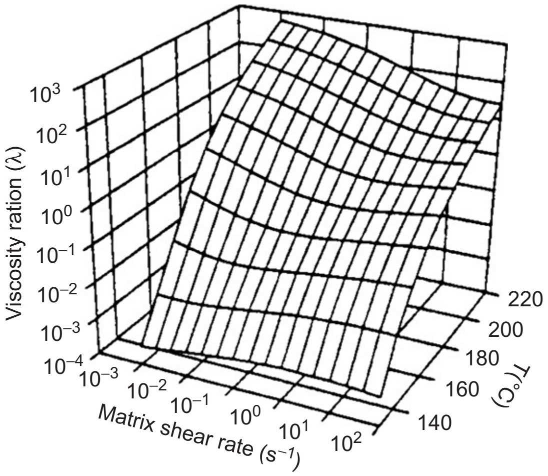


Figure 15.22 HDPE–PS blend viscosity ratio variation as a function of shear rate and temperature. *Source: Taken from Huneault et al. (1995). Courtesy of the Society of Plastics Engineers.*

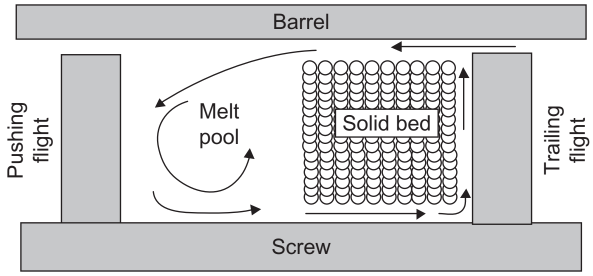


Figure 15.23 Single-screw extrusion solid bed melting model. Melting above and below the solid bed causes the minor component to form thin layers or striations in a two-component polymer blend. *Source: After Lindt and Ghosh (1992).*

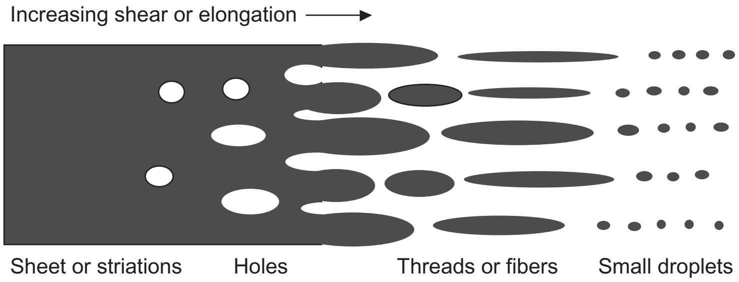


Figure 15.24 Morphology development during melting and subsequent shear in an extruder. Striations or sheets form during melting. Shear and stress cause holes to form, followed by threads and particle breakup. This process leads to large changes in the minor phase morphology.

reorientations should occur. This concept is used in high-performance screw designs where the polymers flow through tight clearances.

Li et al. (1999) found that the minor phase melts faster during mixing when a compatibilizer is present. They attribute this to faster heat transfer between the phases due to their intimate contact. Faster melting can affect the final blend morphology.

Shih et al. (1991) studied the solid−melt transition for many polymer blends in a batch mixer equipped with a glass window. They found that blends go through four stages from solid to melt:

- Elastic solid pellets: below the glass transition temperature (T_g) or melting point (T_m) the solid pellets were observed sliding in the mixer. Torque was low.
- Deformed solid pellets: as the temperature increased, some components began to soften and deform. The torque started to rise.
- Transition material: which took on several different forms including
    - a fluid with suspended solid particles,
    - fractured or semifluid material,
    - a dough-like material.

  This was the transition zone between solid and liquid. Different blends took on different transition phases. The temperature increased sharply and then remained constant near the polymer melt temperature (T_m) if it was crystalline. Torque rose sharply.
- Viscoelastic material: the typical liquid appearance was observed. Temperature rose to about 20−50°C above the matrix resin T_m or T_g and the torque decreased.

During the transition phase they observed several phase transitions that aided in the mixing process. Shih (1992) and others (Ratnagiri and Scott, 1996; Sundararaj et al., 1996) found that phase inversions are to be expected when the minor component melts first. The molten minor component surrounds the still solid major component. As the major component melts, it becomes the continuous phase. This inversion is accompanied by a spike in the mixer torque and dramatically reduces the minor component phase size. They also describe how phase inversion can explain some unique morphology, such as major component regions imbedded within the minor component domains.

The phase inversion onset is a function of the volume fraction ratio and viscosity ratio. A simple expression is given by (Bourry and Favis, 1995; Steinmann et al., 2001):

$$\frac{\eta_1}{\eta_2} \sim \frac{\Phi_1}{\Phi_2} \tag{15.9}$$

where

Φ = volume fraction.

Two polymers with the same viscosity will undergo a phase inversion when the minor component reaches about 50% of the blend composition. If the minor component viscosity is substantially less than the major component, the minor component can become the continuous phase. This is the case when the minor component melts first. As the major component melts and its viscosity decreases, then conditions no longer favor the minor component as the continuous phase and the phase inversion occurs.

15.7 Morphology Development in Blown Film

Several morphologies have been described for immiscible blends in blown film, including elongated particles such as fibrils and ribbons. Forming elongated morphologies is a two-step process:

- Sphere-like dispersed domains are formed during extrusion (in the absence of blowing or drawing). Shear flow fields in the extruder and die dominate the morphology. The domain size is a function of:
  - the dispersed phase concentration,
  - viscosity ratio,
  - interfacial tension,
  - continuous phase viscosity,
  - shear stress.
- Stretching and orienting the spherical particles in the elongational flow fields at the extruder exit (blowing and drawing) form elongated structures. The morphology is influenced by:
  - initial domain size,
  - polymer elasticity,
  - minor component percentage,
  - draw ratio.

Figure 15.25 shows the elongated morphology in a blown film. Here, PB has been added to a polyolefin to create a peelable sealant. Pirtle et al. (2004) suggest that too much PB phase orientation in a peel-seal blend can produce unwanted stringy seals. Thus, morphology control is important for packaging applications. We will now examine some factors that influence the morphology in more detail.

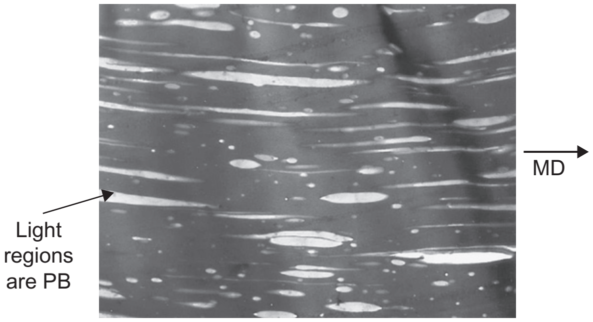


Figure 15.25 Elongated second phase (PB-1 in a polyolefin matrix) found in blown film. *Source: Photograph courtesy of DuPont.*

15.7.1 Viscosity Ratio

A viscosity ratio near 1 typically gives the smallest particle domains. These are difficult to elongate; the smaller the particle size the harder it is to deform the particle. David et al. (1991, 1992) and Getlichermann and David (1994) found that the dispersed phase viscosity has to be less than the matrix to obtain elongated morphologies. For viscosity ratios greater than 1, the dispersed phase cannot be deformed enough to create the elongated morphologies.

15.7.2 Interfacial Tension

As described by Eq. (15.8), the lower the interfacial tension, the smaller the particle diameter (in the extruder and die). Smaller particles are more difficult to elongate. Adding compatibilizers to the blend tends to reduce the particle size and makes elongated morphologies (such as laminar structures) more difficult to obtain (Lee and Kim, 1996; Ronzalez-Nunez et al., 1993).

15.7.3 Minor Phase Concentration in Blend

Increasing the dispersed phase volume fraction (ϕ_d) generally gives larger particle sizes, resulting in more fibril or laminar structures. The larger particle sizes may be due to coalescence, which becomes more significant as the concentration increases. David et al. (1991) found co-continuous fibrils formed as ϕ_d increased. This was determined experimentally by extracting films with a solvent that selectively dissolves the minor component. As the volume fraction was increased, more minor phase was extracted, suggesting co-continuous morphologies were forming.

David et al. (1991) and Getlichermann and David (1994) found that the onset of co-continuous fibril morphology occurred at a lower volume fraction than predicted by Eq. (15.9). They attribute this to elongational effects.

15.7.4 Polymer Elasticity (Non-Newtonian Behavior)

Getlichermann and David (1994) found that a viscosity ratio less than 1 was not sufficient to create elongated morphologies. If the dispersed phase was Newtonian in behavior, elongated morphologies were not observed after blowing and drawing.

The polymers of non-Newtonian (elastic) behavior help to stabilize the "threads" that form during elongation, allowing more elongation without the threads breaking up into small particles.

They suggested that dispersed phase tension thickening is one attribute that should help stabilize the thread and help create elongated morphologies. Tension thickening refers to elongational viscosity measurements, which are difficult to conduct. Linear polymers, such as LLDPE, have transient elongational viscosity that decreases with time (tension thinning), whereas polymers with LCB (such as LDPE) tend to increase with time (tension thickening).

15.7.5 Extruder RPM

Equation (15.8) predicts that, as extruder speed is increased, the increased shear rate should reduce the droplet size. As discussed previously, smaller particles formed in the extruder and die are more difficult to elongate after they exit the die. Lee and Kim (1996) found just the opposite for an LDPE–EVOH blend. They attributed this to the shorter extruder residence time at higher rpm. The EVOH, which melts at temperatures 50°C higher than the LDPE, has less time to melt fully and be dispersed. This gives rise to a larger particle size at the extruder exit and a greater tendency toward elongated laminar morphology.

15.7.6 Extruder Temperature

The extruder and die temperatures affect the morphology through their impact on the viscosity of both components. As the temperature is increased, η_c decreases. As described by Eq. (15.8), this allows less stress to be applied to breaking up the droplets, giving larger particle sizes. Also, the polymers' viscosity temperature dependence may differ, altering the viscosity ratio.

15.7.7 Shear Stress in Extruder, Adapter, and Die

During pressure-driven flow in an extruder, adapter tubes, and die, there is a shear stress distribution across the flow channel. The highest shear stresses occur at the wall. The wall also experiences the longest residence times since the flow rate at the wall is low. Thus, there may be a morphology distribution as a result of the stress differences. This was found to be true by Lee and Kim (1996) in LDPE–EVOH blends and it has also been documented for blends involving PB-1 and LDPE (Basell product literature).

15.7.8 Screw Design

For laminar morphologies, the literature teaches not to overmix the blend (Subramanian, 1985). Careful screw design may be needed to accomplish this.

15.7.9 Draw Ratio

Before drawing (or blowing) (see Figure 15.26 for blown film process description), the minor component morphology is typically spherical as it exits the extruder (David et al., 1991, 1992; Getlichermann and David, 1994; Lee and Kim, 1996; Ronzalez-Nunez et al., 1993). It is the elongational flow fields imposed by the drawing and blowing process that gives rise to the highly elongated structures. The degree of elongation depends on the process. David et al. (1991) found the convergence/divergence in a capillary geometry only gave rise to elongated ellipsoids. A flat die gave rise to fibrils in the machine direction (MD) and a blown film die gave fibrils and ribbons with two-dimensional orientation in the machine and transverse direction (TD) as well as co-continuous fibrils.

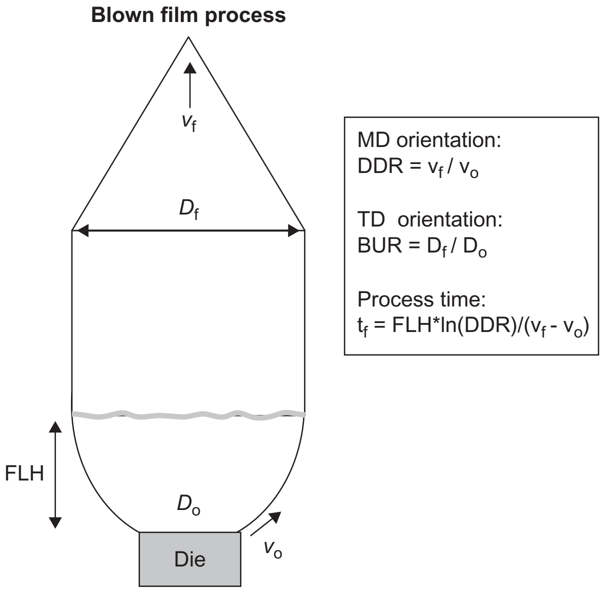


Figure 15.26 Blown film process.

The draw ratio in the MD is characterized by the draw-down ratio (DDR), which is defined as the haul-off speed divided by the polymer melt velocity as it exits the die. The blow-up ratio (BUR) characterizes the draw ratio in the TD or hoop dimension. BUR is defined as the final bubble diameter divided by the die diameter. The DDR is inversely proportional to BUR times the final film thickness divided by the die gap (Eq. (15.10)):

$$\mathrm{DDR} = \frac{V_\mathrm{f}}{V_0} \gg \frac{\mathrm{Die\ \ Gap}}{\mathrm{BUR} \times \mathrm{Film\ \ Thickness}} \qquad (15.10)$$

where

V_f = haul-off speed,

V_0 = velocity of polymer at die exit.

Thus, DDR decreases with increasing BUR and film thickness and decreasing die gap. (In Eq. (15.10), we have ignored the density change between solid and melt.)

David et al. (1991) found that the fibril diameter is not a straightforward function of draw ratio. Without any drawing, the particles were spherical with a diameter of 0.5 μm. At a DDR of 5 and 20, the fibril diameters were 0.1 and 0.2 μm, respectively.

15.7.10 Frost Line Height and Process Time

Process time in the blown film process is defined as the time it takes the polymer to begin to freeze once it has exited the die. It is proportional to the frost line height and inversely related to the haul-off speed (Eq. (15.11)):

$$t_\mathrm{f} = \frac{\mathrm{FLH}}{V_\mathrm{f} - V_0} \ln\left(\frac{V_\mathrm{f}}{V_0}\right) \qquad (15.11)$$

where

t_f = process time,

FLH = frost line height,

V_f = haul-off speed,

V_0 = velocity of polymer at die exit.

The effect of process time on the blend morphology has not been addressed in the literature. It is only within the last few years that this parameter has been accepted as an important scale-up parameter for blown film. It encompasses important aspects of the film blowing process, including the cooling and crystallization time. More important for this discussion is that the process time is inversely proportional to the elongation rate. Stress is related to the draw ratio and to the draw or elongation rate. Therefore, process time is inversely related to the stress imposed by the process (Morris, 1997).

15.8 Dispersion of Rigid Particles and Nanocomposites

Dispersing inorganic and other particles in polymers is not well studied. As White (1990) explains, this may be because breaking up agglomerates is hard to quantify, particularly since most fillers have a particle size distribution. Generally, it is thought that high stresses are needed to achieve dispersive mixing. Such stresses are typically not found in a single-screw extruder. Hence, most mineral-filled polymers are manufactured in specialized compounding equipment as described earlier. In packaging applications, blending fillers are generally limited to letting down masterbatches. Here, the filler, pigment or additive has been predispersed, and simple distributive mixing is all that is required.

One noteworthy aspect of dispersing rigid particles into polymers is particle attrition. Fillers, such as glass fibers, mica, and clay, may have long aspect ratios that are important for the blend properties. Too much dispersive mixing can reduce their aspect ratio, degrading the resultant performance. Filler abrading the mixing device surfaces can also cause excessive wear. Adding mineral filler in a downstream stage where the polymer is molten, rather than to the first stage with the solid pellets, can significantly reduce abrasion and attrition.

A key question when dealing with pigments is how do you know if good mixing has been achieved? One commonly used method is to compare a sample against a visual standard. Spectroscopic techniques have also been used, as well as microscopic image analyses (Benkreira et al., 1992). Various indices, such as striation thickness, variance in minor component concentration, and segregation scales, have been used, as discussed by McKelvy (1967). More recently, computer image analysis (red–green–blue correlations) has been used. Translating such color analysis to a quantitative distributive mixing index has been difficult. Recently, Alemaskin et al. (2004) and Alemaski et al. (2005) have made progress in developing such an index by employing Shannon entropy. They have used both computer simulation and experiments to verify the method. They simulated mixing two ABS colors in a conventional single-screw extruder metering section using a numerical particle tracer analysis. The results were compared with extrusion experiments under similar conditions. Here, the extruder was stopped, rapidly quenched, and the screw pulled to obtain samples along the extruder length. The color homogeneity evolution was measured using digital computer imaging. Color homogeneity indices based on entropic considerations were computed for both the simulations and digital images and they qualitatively agreed. Such an approach can potentially be used for scale-up, control, and process design optimization.

A polymer filled with nanocomposites is a special case. These blends are typically with inorganic particles that have nanometer dimensions. They have been found to be effective in improving:

- stiffness,
- mechanical strength,
- barrier,
- electrical conductivity, and
- flame retardance

at levels between 3 and 5 wt%. Still in its infancy, two nanofillers have received the most attention, carbon nanotubes and clay. Carbon nanotubes have been found to impart good electrical properties for shielding and other potential applications. Except for some specialty electronics applications, carbon nanotube composites are not suited for packaging applications.

Of greater interest are clay nanocomposites (Akkapeddi et al., 2003; Dahman, 2000; Krook and Hedenqvist, 2002; Leaversuch, 2001; Manias et al., 2001; Lan, 2007; Sherman, 2004). Most work to date has been done with montmorillonite clay, initially at Toyota. In its natural state, each montmorillonite particle is an agglomeration of many layers of nanosized platelets. The platelet length and width range from a few tenths of a micron to about 1.5 μm. Their thickness is only about 1 nm and is the reason they are considered nanomaterials. Their high aspect ratios give them their unique properties.

The platelets are hydrophilic and are held together at a distance of about 3.5 Å by attractive forces. Clay suppliers add surfactants to the clay to promote interplatelet expansion to about 20 Å. To obtain the best properties, the platelets must be completely separated from each other. This complete dispersion into the polymer matrix is known as exfoliation and is illustrated in Figure 15.27. There are two typical ways to accomplish this. One is to introduce the clay during the polymerization process. The monomer is absorbed into the spaces between platelets. As the monomer polymerizes the platelets separate. This process is only amenable to certain polymers where the clay can be introduced

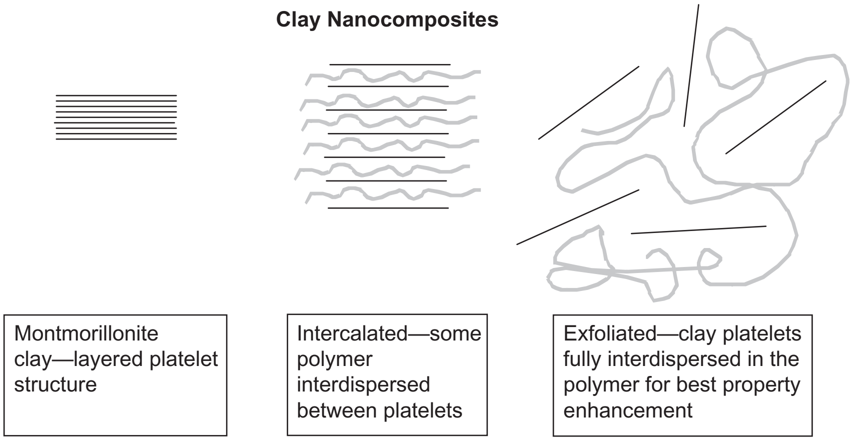


Figure 15.27 Illustration of states of clay nanocomposites.

during polymerization. Most often it has been applied to polyamide.

The second is to compound the clay particle with an already polymerized polymer and rely on the stress generated during mixing to separate the platelets. The surfactant selection is critically important; it must help turn the hydrophilic environment between the platelets into one that is compatible with the monomer or polymer. In some cases, compatibilizers are used to aid in the exfoliation. For example, in PP–montmorillonite nanocomposites, maleic anhydride–grafted PP is often added as a compatibilizer. Nevertheless, so far it has proven difficult fully to exfoliate montmorillonite in a compounding process and this process is the focus of continued R&D. The first approach of polymerizing in the presence of the clay has been more successful.

Adding nanosized particles to the polymer restrains the molecule's movement, more so than in conventional fillers because of the extremely high surface area that is generated. The restrained motion enhances stiffness and heat deflection temperature. Because the individual platelets are small, toughness and optical properties do not suffer. Of particular importance for packaging applications is the potential for increased barrier performance, especially oxygen barrier. The orientation of the platelets is flexible and their longer dimensions line up in the extrusion and orientation direction. The resulting platelet network structure creates a more tortuous path for gas molecules to diffuse through. Reductions in gas permeability of 60–80% for polyamide or EVOH nanocomposites have been reported (Akkapeddi et al., 2003; Lan, 2007).

15.9 Rheology of Polymer Blends

Utracki (1989) provides a good review of the rheology of polymer–polymer blends. Miscible blends are easier to characterize than immiscible ones. Often a log-mean rule is used to estimate the miscible blend viscosity, although there may be some positive deviation (Eq. (15.12)):

$$\log(\eta_{\text{blend}}) = X_{\text{A}}\log(\eta_{\text{A}}) + X_{\text{B}}\log(\eta_{\text{B}}) \qquad (15.12)$$

where

X_{A} = weight fraction of polymer A in the blend,

X_{B} = weight fraction of polymer B in the blend.

Equation (15.12) is useful for estimating the viscosity or melt-flow index (MI) for two grades of the same polymer. For example, a 70–30 wt%, LDPE1–LDPE2 blend where the LDPE1 MI is 4 g/10 min and LDPE2 MI is 12 g/10 min, yields:

$$\begin{aligned} \log(\text{MI}_{\text{blend}}) &= 0.7\log(4) + 0.3\log(12) \\ \text{MI}_{\text{blend}} &= 5.6\,\frac{g}{10\text{ min}} \end{aligned}$$

For immiscible blends, Lyngaae-Jorgensen (1993) points out that steady-state data, such as capillary rheometry data, look superficially like homogeneous polymers unless they have been compatibilized (Utracki, 1989); however, their behavior may be complex. They typically do not follow time–temperature superposition and mixing rules since the individual phases may behave differently. Their transient behavior and die swell may also be complicated. The immiscible blend morphology is the driving force for this complex behavior.

Reactive polymer blends are a special case. Typically, the reactive blend viscosity increases due to the formation of cross-links that effectively increase the polymer MW. An example is blending maleic anhydride–modified PE with polyamide. The polyamide viscosity can increase by an order of magnitude.

Some additives can cause gel formation and other problems when blended with a polymer. For example, the acid groups in acid copolymers and ionomers can react with a coupling agent used in some TiO_2 grades, producing gel and other problems. Adding wax, tackifiers, and other low-MW additives to polymers will reduce their viscosity.

The way that rigid fillers affect viscosity can also be complex. For very dilute solutions of rigid spheres in a Newtonian fluid, Albert Einstein derived the following result (Eq. (15.13)):

$$\eta = \eta_{\text{f}}(1 + 2.5\phi) \qquad (15.13)$$

where

η = viscosity of the suspension,

η_{f} = viscosity of the suspending fluid,

ϕ = volume fraction of the rigid spheres.

Many of the assumptions used to derive equation 15.13 do not apply to filled polymers: the filler loading is not typically dilute, the filler is not spherical and the polymer matrix is non-Newtonian. Dealy and Wissbrun (1995) describe the following complexities:

- non-Newtonian effects caused by particle concentration and aspect ratio,
- buoyancy effects,
- particle migration and agglomeration.

A number of equations have been proposed, including the following by Marion and Pierce (1956) (Eq. (15.14)):

$$\eta = \frac{\eta_f}{[1-(\phi/A)]^2} \tag{15.14}$$

Here, A is a constant that is a function of the filler. Dealy and Wissbrun (1995) propose that it can be thought of as the maximum filler packing fraction. For example, the value for A for spheres is 0.68, close to 0.637 which is the theoretical maximum packing fraction. The value for A decreases with the increasing filler aspect ratio (0.44 and 0.16 for L/Ds equal to 8 and 30, respectively). The value of A for a particle size distribution is greater than that for a uniform particle size. A nonuniform filler size distribution, therefore, can reduce the concentrated suspension viscosity.

There are other complications. One is the viscosity to choose when dealing with polymers, since η_f varies with shear rate. Dealy and Wissbrun (1995) point out that plotting the viscosity versus shear stress rather than shear rate, as noted earlier for polymer–polymer blends, gives the best results. At low shear rates, the filled polymer may exhibit a yield stress, below which the material behaves like a solid (and does not flow). The yield stress increases with filler concentration.

15.10 Conclusion

Blending is an important aspect of polymer/property design for many packaging applications. Achieving a consistent quality blend with the desired properties requires proper attention to both process and product design. The polymer blend properties are a complex function of the stress history imposed by the process and the rheological and thermodynamic properties of the components. Based on experience and science, we can propose several guidelines for reducing these complexities to practice:

- Careful control of the blend components fed to the mixing device feed hopper is important since most continuous mixers, such as extruders, do not have very good back-mixing.
- All things being equal, target 10% or more for the minor component for better accuracy and control.
- Single-screw extruders can be used for many blending applications where only simple distributive mixing is required. For more demanding applications, high-performance screws or ultimately specialty compounding devices, such as twin-screw extruders, may be required.
- When using a masterbatch concentrate, make sure the masterbatch carrier resin is compatible with the resin it is being blended into.
- Very few polymer blends are miscible. For miscible blends, the viscosity can be approximated using the log mean rule (Eq. (15.12)).
- The immiscible blend morphology influences the properties, which generally deviate from the mixing rule. Some examples include using small domains of a soft resin to improve toughness without detracting from optical clarity and laminar morphologies to help improve barrier performance.
- The immiscible blend morphology is influenced by:
  - the component concentrations,
  - stress history imposed by the compounding device,
  - the viscosity and mutual attractiveness (thermodynamics) of the components.
- The minor component domain size of an immiscible blend can be reduced by:
  - increasing the stress (by increasing the viscosity of the matrix phase and the shear rate or rate of elongation during mixing),
  - matching phase viscosities (a 0.01–2 viscosity ratio is preferred, particularly for shear flow),

  - lowering the interfacial tension by matching solubility parameters,
  - minimizing coalescence.
- Compatibilizers reduce interfacial stress and coalescence thus reducing domain size. They also reduce the minor phase melt time, which can affect domain size.
- Elongational flow is generally more efficient than shear flow for dispersing the minor component of an immiscible blend. The flow in single-screw extruders is typically dominated by shear flows unless special mixing elements are used. Both shear and elongational flow can be found in twin-screw extruders.
- Most mixing in a single-screw extruder occurs as the polymers melt, forming sheets or striations that break up into holes and droplets as the shear and elongation are increased along the extruder. Increased shear and stretching in the compression zone or high-performance metering zones (such as energy transfer screws) promote sheet break up.
- For immiscible blends, orientation during the blown film process often elongates the minor component domains within the matrix resin.
- Dispersive mixing may be required to break up agglomerates when blending mineral fillers or pigments with polymers. For this reason, these blends are often made as masterbatches using specialized compounding equipment and let down using a single-screw extruder by the film manufacturer.

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16 A Survey of Regulatory Aspects of Food Packaging

S. Ebnesajjad
President, FluoroConsultants Group, LLC

A variety of plastics in single and multilayer forms are used in packaging perishable and nonperishable foods. The use of plastics in the developed regions is regulated through a body of laws that are constantly updated. The Food and Drug Administration (FDA) issued the first guidance in the United States in 1949. Globalization and industrialization have lead to the consumption of packaged foods around the entire world.

Recognition of the impact of packaging material, in particular plastics, on the safety of foodstuffs has led to the promulgation of regulations in the developing countries. These regulatory efforts are at different stages of maturation depending on the country and region. For example, ASEAN countries have begun an effort to harmonize standards for food contact material (The 11th Meeting of ACCSQ−PFPWG in Manila, Philippines, 2010).

This chapter presents readers with an abbreviated discussion of aspects of regulations governing food packaging. A single chapter can in no way comprehensively address all the regulatory issues relevant to food packaging. Contact with regulatory agencies, study of the complete regulations, and most effectively legal advice (Catherine, 2012; Langhorn, 2011) are recommended for anyone who wishes to ascertain the regulatory status of actual packaging.

A survey of regulatory issues in the United States and European Union (EU) is presented in this chapter. To ensure accuracy, in many cases, the exact language and copy published by regulatory agencies has been republished. Alternatively, descriptions provided by specialists have been utilized in the presentation. The focus of this chapter is on the materials aspects of packaging, and no attention is paid to other aspects of foodstuffs, such as dietary and nutrition, health, impurities, etc.

16.1 Introduction

The first FDA advisory regarding the evaluation of chemical toxicity in food was issued in 1949. This event followed other milestones in the agency's successful enactments such as improving infant formula content, eliminating botulism in canned foods, and labeling products with possible food allergens. Since then, laws have been promulgated to regulate plastic and additives of food packaging and labeling materials, limits in irradiation of packages for terminal sterilization, and functionality of packaging materials.

These regulations have been critical for ensuring the safety of the food consumed by people and also to those companies that produce basic plastics and additives; convert the plastics into films, multilayer film structures, and containers; package food; and market and sell food packaging. Every player in the value chain has to be aware of the risks of actual or suspected contamination attributed to packaging materials. Such an occurrence is certain to attract public censure and potentially further regulatory activity. Examples of public concerns come to light from time to time. One such cautionary episode is the fate of bisphenol A (BPA).

16.1.1 Bisphenol A

The predicament of BPA is instructive in elucidating the impact of actual toxicological data and publicity on governmental action. New studies are conducted on old plastics and additives, the results of which can affect their regulatory status. New BPA studies turned up data indicating a review of the incumbent regulatory status of this chemical. These studies received widespread publicity in the media and the internet, which placed immense pressure on governmental agencies and the industry to take immediate action.

BPA is a chemical (or monomer) used in the production of polycarbonate plastic and epoxy resins. This monomer has been used safely in the manufacturing of these plastics for over 40 years and has played an important role in the development of numerous consumer products. Examples of BPA

Ebnesajjad: Plastic Films in Food Packaging. DOI: http://dx.doi.org/10.1016/B978-1-4557-3112-1.00015-6

applications include liner of cans, compact disks, impact-resistant eyeglass lenses, dental fillings, and food and beverage containers. Polycarbonate has other applications such as light globes, household appliances, components of electrical/electronic devices, automotive parts, telephones, safety and sports helmets, signs, windows, roofing structures, greenhouses, solar and construction glazing, skylights, and others.

Polycarbonate and BPA have undergone extensive safety testing because of their use in food packaging and medical devices. US Environmental Protection Agency (EPA) established an oral reference dose (RfD) of 50 μg/kg/day or 50 parts per billion (ppb) per day in 1998. This RfD is an "estimate of daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime". This RfD is much higher than actual exposure levels to BPA. The amount of BPA that migrates to food packaged in plastic containers or cans is extremely low and is much less than this RfD (Saulo, 2008).

In August 2008, FDA released a draft report finding that BPA remains safe in food contact materials. In October 2008, a subcommittee of FDA's science board raised questions about whether FDA's review had adequately considered the most recent scientific information available (Lang et al., 2008; Stahlhut et al., 2007). For example, an article in the September 2008 issue of the *Journal of American Medical Association* reported detrimental effects of BPA on adults (Lang et al., 2008). Other studies had reported subtle effects of low doses of BPA in laboratory animals (Richter et al., 2007). These newer studies have led federal health officials to express some concern about the safety of BPA. On January 15, 2010, the FDA issued an interim update on BPA complemented by a public information advisory by the US Department of Health and Human Services. The information indicated the presence of minute amounts of BPA in canned formula that could increase when heated. It also virtually advised avoidance of any baby bottles or feeding cups made with BPA-containing plastics. There has been some additional recent activity by FDA on BPA. FDA updated its opinion on BPA in late March 2012, http://www.fda.gov/newsevents/publichealthfocus/ucm064437.htm, and also, at the same time, rejected a petition filed by the NRDC to ban BPA: http://www.cnn.com/2012/03/30/health/bpa-ban-denial/index.html. Readers are encouraged to visit the FDA web site www.FDA.gov for new rulings.

The European Food Safety Authority's (EFSA) panel on food additives, flavorings, processing aids, and materials in contact with food (AFC) carried out a comprehensive risk assessment on BPA in 2006 and set a full tolerable daily intake (TDI) of 0.05 mg/kg body weight/day. EFSA received a request in September 2008 from the European Commission (EC) requesting an assessment of the implications to the hazard and risk assessment of BPA based on the JAMA study correlating urinary BPA concentrations with medical disorders in adults (Lang et al., 2008).

EFSA (2008) concluded that this single study (Lang et al., 2008) does not provide sufficient proof for a causal link between exposure to BPA and the health conditions mentioned in the study; i.e., heart disease, diabetes, and elevated liver enzyme activities. EFSA concluded there was no need to revise the TDI as derived by the panel in 2006.

Shortly after the JAMA article, since the beginning of 2009, all major US suppliers of baby bottles and infant feeding cups stopped manufacturing these products using BPA for the US market. On May 31, 2011 the European Union issued the following statement indicating a ban on BPA: "Baby bottles containing the substance BPA have to be removed from the shelves in stores across the European Union tomorrow, as a ban on the placing on the market and import into the EU of such products enters into force. The ban is foreseen in an EU directive (2011/8/EU) adopted in late January. The industry has been withdrawing voluntarily from the market baby bottles containing BPA. On March 1, the EU had banned the manufacture in the Union of baby bottles containing BPA."

There has been additional activity on BPA in the EU. EFSA made some additional statements regarding its investigation of BPA in February of 2012, as described here: http://www.efsa.europa.eu/en/topics/topic/bisphenol.htm.

16.2 Determining the Regulatory Status of Components of a Food Contact Material in the United States

The overall regulatory status of a food contact material is dictated by the regulatory status of each individual substance that comprises the article. The individual substance that is reasonably expected to migrate to food because of its intended use in the food contact material shall be covered by one of the following:

1. A regulation listed in Title 21 Code of Federal Regulations
2. A prior sanction letter
3. Meeting the criteria for generally recognized as safe (GRAS) status (including but not limited to a GRAS regulation or GRAS notice)
4. A threshold of regulation (TOR) exemption
5. An effective food contact notification (FCN)

Be aware that Section 409(h)(2)(C) of the Federal Food, Drug, and Cosmetic Act (the FD&C Act) states that an FCN is effective for the manufacturer, the food contact substance (FCS), and the conditions of use identified in the notification, and not effective for a similar or identical substance produced or prepared by a manufacturer other than the manufacturer identified in the notification. FCNs are proprietary to the manufacturer for whom the notification is effective; therefore, the FCS must be obtained from that manufacturer.

It is the responsibility of the manufacturer of a food contact material to ensure that its components comply with the specifications and limitations in all applicable authorizations. When reviewing your composite formulations to determine compliance, consider each authorization to be composed of three parts: the identity of the substance, specifications including purity or physical properties, and limitations on the use.

You may ask the manufacturer for a letter of assurance certifying that a particular product is acceptable for the intended food contact use. A key question is: how do you determine the compliance of the components of your food contact article with the requirements of the act? There are a number of ways that a component of your food contact article may comply with the act. The following list is designed to help the reader make that determination. It allows one to research each component for an appropriate authorization. Here are some possible approaches:

1. Consult 21 CFR 174–179 to see if the component is appropriately regulated as an indirect additive for the intended use.
2. Consult 21 CFR 182–186 to see if the use of the component is GRAS, or consult the list of GRAS notices.
3. Consult 21 CFR 181 to see if the use of the component is prior sanctioned.
4. Consult the listing of Threshold of Regulation Exemptions.
5. Consult the listing of Effective Food Contact Substance Notifications.

Another key question: what if one or more components of your food contact article are not covered by any of the categories above; what options do you have? Submit a Threshold of Regulation Exemption Request or:

1. Submit a Food Contact Substance Notification
2. Satisfy the criteria for GRAS status

To find out whether the component is appropriately regulated as an indirect additive for its intended use, consult 21 CFR 174–179 according to the following:

1. Adhesives and Components of Coatings (21 CFR Part 175)
2. Paper and Paperboard Components (21 CFR Part 176)
3. Polymers (21 CFR Part 177)
4. Adjuvants, Production Aids, and Sanitizers (21 CFR Part 178)
5. Irradiation in the Production, Processing, and Handling of Food (21 CFR Part 179)

The requirement for premarket approval in Section 409 of the FD&C Act in 1958 resulted in the development of a petition process by which a person could request approval of a food additive for an intended use. The approval resulted in a regulation listed in 21 CFR. Components of a food packaging material used in compliance with a regulation in 21 CFR (174–179) need no further FDA review. Most of the regulated indirect food additives can be found in CFSAN's "Indirect Additive" Database.

To find out whether the use of the component is listed as GRAS, consult 21 CFR 182–186 according to the following:

1. Substances GRAS in food (21 CFR Part 182)
2. Substances affirmed as GRAS in food (21 CFR Part 184)
3. Substances affirmed as GRAS for use in food packaging (21 CFR Part 186)
4. Not all substances that are GRAS are listed in FDA's regulations. FDA has instituted a procedure whereby someone may inform FDA of their own GRAS determination. A list of these GRAS notices, with FDA's response letter to the notifier, is also available at "Summary of all GRAS Notices".

16.2.1 Food Contact Formulation (FCF) Compliance Notification

Occasionally, individuals may wish to verify compliance of the components of a particular food contact material. In such instances, they may submit a notification for a FCS formulation. The purpose of a formulation notification is to verify that components of a food contact material may legally be used, and not to authorize a new FCS. Because these notifications are for the purpose of regulatory status and not safety assessments, notifications for formulations do not require resubmission of the information supporting the safety of the intended use of each FCS in the formulation. A notifier for a formulation need only to submit a completed FDA Form 347920 and any additional documentation required to establish that each of the components of the formulation is authorized for its intended use. In cases where the basis for compliance of an individual FCS in a formulation is an effective notification, a notifier of the formulation should establish that he or she can rely on the notification cited for the intended use of the FCS in the formulation.

16.3 Regulatory Report: FDA's FCS Notification Program

Among the responsibilities of the US FDA are the regulation of components of food contact materials, including packaging. Once known as indirect food additives, FDA now refers to these materials as food contact substances. In an effort to ensure the safe use of these substances, FDA has established a Food Contact Notification Program within the Center for Food Safety and Applied Nutrition's (CFSAN) Office of Food Additive Safety. This section describes how to submit an FCS notification to FDA and indicates how the food contact notification review process works. It also addresses the importance of participating in prenotification consultations, the role of threshold of regulation exemptions, and confidentiality concerns.

16.3.1 Definitions, History, and Scope

Definitions

Section 201(s) of the FD&C Act defines a "food additive" as any substance whose intended use results or may reasonably be expected to result, directly or indirectly, in its becoming a component or otherwise affecting the characteristic of any food (including any substance intended for use in producing, manufacturing, packing, processing, preparing, treating, packaging, transporting, or holding food, and including any source of radiation intended for any such use) and if such substance is not GRAS or sanctioned prior to 1958. (This is a shortened definition. The full definition found in the FD&C Act also provides for exclusions) Section 409 of the statute defines an FCS as any substance that is intended for use as a component of materials used in manufacturing, packing, packaging, transporting, or holding food, if such use of the substance is not intended to have any technical effect on that food. Common types of FCSs include coatings, plastics, paper, adhesives as well as colorants, antimicrobials, and antioxidants found in packaging.

History

In 1958, the FD&C Act was amended by adding Section 409, which requires FDA to approve new food additives before they can be used in foods. To meet this requirement, FDA established a process by which an individual can petition FDA to request approval of a food additive. All FCSs that are additives required approval. In 1997, the Food and Drug Administration Modernization Act (FDAMA) amended Section 409 of the FD&C Act establishing a food contact notification process that allows for faster review of FCSs that are food additives. The amendment did not alter the safety standard applied to all food additives, and notification for an FCS must contain sufficient scientific information demonstrating that the substance that is the subject of the notification is safe for the intended use. FDA's fiscal year 2000 budget contained an appropriation to fund the FCN program, and in October 1999 the Office of Food Additive Safety began converting approximately 120 in-house food additive petitions and threshold of regulation submissions for review under the new amended requirements. (Threshold of regulation for substances used in food contact articles can be found in 21 CFR 170.39.) On January 18, 2000, the Agency began accepting new food contact notifications, and in July 2000 FDA published proposed regulations for the program. The regulations were finalized in May 2002 and codified in 21 CFR Part 170.100−106.

Scope

Food contact notifications are required only for new uses of FCSs that are food additives. Although a notification is not required for a FCS that is GRAS or prior sanctioned for its intended use in contact with food, some companies do choose to notify the Agency in order to clarify the regulatory status of such substances. Manufacturers may also use FCNs to notify FDA of new uses of FCSs that are GRAS or prior sanctioned.

Unlike food additive regulations and threshold of regulation exemptions, approvals under the FCN process are proprietary. This is because Section 409 (h)(1)(C) of the FD&C Act states that an FCN is effective only for the manufacturer and substance identified in the notification. Thus, any person wishing to rely on an FCN needs to demonstrate that the FCS being marketed has been manufactured or supplied by the manufacturer identified in the FCN and is being used under the conditions that are the subject of the FCN. This may seem a trivial point, but it is important since the manufacturer for whom the FCN is effective does not need to be the actual manufacturer of the FCS but can also be a supplier who is purchasing the substance and distributing it for the intended use. If a notifier is not careful in defining the entities for which the FCN is effective, the proprietary approval received in a successful FCN may not be applied to the intended company.

16.3.2 The Notification Process

Anyone may submit a food contact notification to FDA. (Although the FD&C Act refers to manufacturers or suppliers submitting a notification, FDA interprets the term "supplier" broadly to include persons who could previously have requested authorization under the food additive petition process. This ensures that no one was unfairly excluded by the transition to the FCN process.) The FCN process is initiated when a submission, prepared by the notifier, arrives at the Office of Food Additive Safety. A notification control assistant logs the submission and assigns it a notification number. The submission is then distributed to a review team for assignment. The review team consists of a consumer safety officer, a chemist, a toxicologist, and an environmental scientist. During the initial month of the review period, FDA does not ordinarily contact the notifier; however, the notifier is free to contact the consumer safety officer in charge of the notification.

A "phase one" review meeting is held within the first 3 weeks after receipt of the FCN to ensure that the basic data and informational elements are present and that the submission meets the administrative requirements set forth in the FD&C Act and FDA's regulations. If the submission is complete, it is accepted and FDA sends the notifier an acknowledgment letter. The acknowledgment letter initiates formal communication between FDA and the notifier and gives the notifier an opportunity to comment on the Agency's understanding of the identity and intended use of the FCS that is the subject of the notification. Notifiers who disagree with FDA's description of the FCS should respond as quickly as possible to this acknowledgment letter. The acknowledgment letter also establishes the date of receipt of the notification, which indicates when the 120-day FCN review period began, and that the review team is entering into "phase two" review.

During "phase two", the team evaluates the safety of the FCS as it is proposed for use. If there are no concerns during the "phase two" review, the FCN automatically becomes effective on the 120-day date, and the consumer safety officer sends a letter to the notifier confirming the effective date. Information about the notification is then added to the Inventory of Effective Premarket Notifications for Food Contact Substances posted on CFSAN's web page.

If after "phase one" review the notification is deemed "not acceptable" and FDA must request additional information, the date of receipt of the additional information may be considered the date of receipt of the complete notification, and the 120-day review period would begin on that date. This determination is based on the nature of the additional information received, i.e. whether it is substantive or nonsubstantive in nature. Since the time for review of FCNs is short, requests for and receipt of additional information must be handled in a timely manner, as one of several scenarios may play out this point. If the requested information is not received within approximately 2 weeks and the notifier does not withdraw the submission, FDA may deem the notification incomplete and a nonacceptance letter may be issued to the notifier indicating termination of FDA's review. If FDA does receive the additional information within 2 weeks but still deems the notification to be incomplete, the notifier may be given the option of withdrawing the submission without prejudice before receiving a nonacceptance letter. (About one in four FCNs are withdrawn because of deficiencies.) If the information adequately completes the submission, it is accepted, an acknowledgment letter is sent, and the "phase two" review begins. Provided that there are no safety concerns during "phase two" review, a final letter is sent to the notifier confirming the FCN effective date, and the notification is added to the Inventory of Effective Premarket Notifications for Food Contact Substances posted on the internet.

What happens if there are safety concerns during the "phase two" review? If safety concerns emerge, the notifier is given the option of withdrawing the submission without prejudice to a future submission. If the notifier does not withdraw the notification, an objection letter is sent to the notifier.

Under 21 CFR 170.100 (c), FDA may also issue a nonacceptance letter for the following reasons: (1) FCS uses that increase the cumulative estimated daily intake (CEDI) of the FCS to a level equal to or greater than 3 mg per person per day for a substance that is not a biocide (e.g. it is intended to exert microbial toxicity), and 0.5 mg per person per day for a biocide; and/or (2) where a bioassay exists on the FCS, FDA has not reviewed the bioassay, and the bioassay is not clearly negative for carcinogenic effects.

Threshold of Regulation

Some FCNs are for uses that qualify for review under FDA's "threshold of regulation" process. The threshold of regulation process is an abbreviated review process for uses of indirect food additives that result in exposures below 1.5 μg per person per day. The threshold of regulation process can result in a faster approval; however, that approval is not proprietary.

Confidentiality

A common concern of many notifiers is the availability of information submitted in an FCN. The FD&C Act prohibits FDA from disclosing information in an FCN during the 120-day review period. In addition, FDA has issued regulations establishing that information in FCNs withdrawn before FDA issues an objection letter or before the FCN becomes effective will not be disclosed. FDA also considers information in an FCN that is "not accepted" to be confidential commercial information protected from disclosure.

Some notifiers seek to protect information by including it in a food additive master file. Such information is protected only if it is not used as the basis of an FDA safety decision or if it is not otherwise publicly available. In these scenarios, the information in the food master file is treated as if it was in the FCN. In short, information in an FCN is protected from disclosure during review, if the FCN is withdrawn, or if a nonacceptance letter is issued, but it is not protected from disclosure after an FCN becomes effective or if FDA objects to the FCN, unless it is trade secret or confidential information.

16.3.3 Increasing the Odds of Success

FDA encourages notifiers to participate in a prenotification consultation to facilitate the development of a complete FCN submission. Prenotification consultations are interactions between the Office of Food Additive Safety and industry prior to submission of an FCN, a food additive petition, or a threshold of regulation exemption request. They are particularly advisable in situations where current guidance is not completely applicable. There are three circumstances in which FDA specifically recommends a prenotification consultation. The first specific circumstance is when the notifier believes that an FCN is not sufficient and a food additive petition is required for the use of an FCS. Such a meeting may be used to verify that a petition is required and that an appropriate level of information is supplied in the petition. The second specific circumstance for which FDA recommends a prenotification consultation is when different interpretations of available data would result in different conclusions, which in turn could affect whether it is appropriate to submit a notification or a petition, e.g. if different interpretations of data in a bioassay could change the conclusion regarding the likely carcinogenicity of the substance. The third specific circumstance for which a prenotification consultation is recommended is when there are uncertainties about how specific data may be interpreted and those uncertainties are of such magnitude that they may affect the outcome of the overall safety determination; e.g. if the estimated daily intake (EDI) is close enough to the acceptable daily intake that different choices for the no-effect level may cause the resulting acceptable daily intake to be larger or smaller than the EDI. A prenotification consultation request may be sent via e-mail, facsimile, or letter and should be addressed to the notification control assistant.

16.3.4 FCS Formulations

Occasionally, individuals may wish to verify compliance of the components of a particular food contact material. In such instances, they may submit a notification for a FCS formulation. Such notifications are only meant to verify that components of a food contact material may legally be used and not to authorize a new FCS. Notifications for formulations do not require resubmission of the information supporting the safety of the intended use of each FCS in the formulation. A notifier for a formulation need only submit a completed FDA Form 3479 and any additional documentation required to establish that each of the components of the formulation is authorized for its intended use. In cases where the basis for compliance of an individual FCS in a formulation is an effective notification, a notifier of the formulation should establish that he can rely on the notification cited and that such notification is effective for the intended use in the formulation.

When checking compliance of components of a food contact material, remember that substances that are reasonably expected to migrate to food because of their intended use in contact with food should be one of the following: (1) approved indirect food additives used in compliance with 21 CFR Parts 174–179, (2) GRAS for use in or on contact with food, (3) substances whose use in contact with food are the subject of a prior sanction issued by FDA or USDA before 1958, used under a threshold of regulation exemption by FDA since October of 1999, or the subject of an effective FCN. If the substance does not fall into one of these categories, the FCN process or the threshold of regulation process are the preferred methods of providing for the safe use of the substance.

Individuals wishing to determine if FDA has a regulation for a specific food additive can view a list of food additives and their corresponding regulations at www.fda.gov. The individual regulations for food additives and GRAS substances listed for use in the United States are located in Title 21 CFR Parts 182–186 and can be accessed through CFSAN's web site. However, not all substances that are GRAS are listed in FDA's regulations. FDA has instituted a procedure whereby companies may inform FDA of their own GRAS determination (GRAS notification procedure). A list of these GRAS notices, with FDA's response letter to the notifier, can be found at www.fda.gov.

It is important to remember that the use of any chemicals to fabricate food contact articles is done with the understanding that it is the responsibility of the manufacturer to ensure that any resultant food contact articles comply with the specifications and limitations in all applicable regulations. When reviewing composite formulations to determine compliance, consider each regulation or notification to be composed of three parts: the identity of the substance; specifications, including purity or physical properties; and limitations on the conditions of use. In order for your products to be suitable for use in contact with food in the United States, each chemical component must comply with all three criteria.

16.4 Preservation of Foods by Irradiation

Food-borne diseases are a source of concern for every person who consumes food. These are the illnesses contracted from eating contaminated foods or beverages. The illnesses include food-borne intoxications and infections and are often incorrectly referred to as food poisoning (McKeen, 2012). There are more than 250 different food-borne diseases caused by viruses, bacteria, parasites, toxins, metals, and prions. According to the US Center for

Disease Control (CDC), 31 pathogens are known to cause 20% of the food-borne illnesses, with 80% being caused by unknown agents (Scallan et al., 2011).

Concern over food safety dates back thousands of years. Many techniques have been devised over the centuries to keep food safe, including drying, pickling, salting, sugaring, cold storage, smoking, canning, and blanching. Every one of these techniques has limitations such as preservation of freshness, applicability, scalability, and cost. Worldwide population growth and the demand for food grown in distant locations have resulted in a complex global distribution system, increasing the challenge of keeping foods safe. Ionizing irradiation has been recognized as a convenient technique for food preservation for over a century.

Present-day food processors prefer that food be prepackaged in its final packaging form before irradiation to prevent recontamination and to expedite shipment to market after irradiation. Prepackaged food could potentially be contaminated by the by-products formed if the packaging materials are degraded by irradiation. This may lead to a safety concern and, therefore, testing of packaging materials after exposure to irradiation is an integral part of the premarket safety assessment of packaging materials irradiated in contact with food (Packaging for Foods Treated with Ionizing Radiation, 2007). A partial preventive measure is to *limit* the radiation used to treat the packaged food (Table 16.1).

16.4.1 FDA Regulations for Treatment of Foods with Radiation

There are different reasons for the irradiation of foodstuff. Many foods are irradiated to kill bacteria and parasites that pose health risks to humans. This makes the food safer, and is comparable to pasteurizing milk. Irradiation at lower dose levels also extends shelf life and can be used to control insects. Food is also irradiated to destroy bacteria, fungi, or parasites that cause human disease or cause food to

Table 16.1 FDA Food Radiation Specifications (Packaging for Foods Treated with Ionizing Radiation, 2007)

Food Type	Purpose	Radiation Dose
Fresh, nonheated processed pork	Control of *Trichinella spiralis*	0.3 kGy minimum to 1 kGy maximum
Fresh food	Growth and maturation inhibition	1 kGy maximum
Foods	Arthropod disinfection	10 kGy maximum
Dry or dehydrated enzyme preparations	Microbial disinfection	1 kGy maximum
Dry or dehydrated spices/seasonings	Microbial disinfection	30 kGy maximum
Fresh or frozen, uncooked poultry products	Pathogen control	3 kGy maximum
Frozen packaged meats (solely used in the National Aeronautics and Space Administration (NASA) space flight programs)	Sterilization	44 kGy minimum
Refrigerated, uncooked meat products	Pathogen control	4.5 kGy maximum
Frozen, uncooked meat products	Pathogen control	7 kGy maximum
Fresh shell eggs	Control of *Salmonella*	3.0 kGy maximum
Seeds for sprouting		8.0 kGy maximum
Fresh or frozen molluscan shellfish (per FDA 2005)	Control of *Vibrio* species and other food-borne pathogens	5.5 kGy maximum

spoil. Irradiation kills harmful bacteria such as *Escherichia coli* O157:H7, *Salmonella, Listeria, Campylobacter*, and *Vibrio*, which are main contributors to the illnesses and deaths caused by foodborne poisoning (Feed Irradiation, 2012; Sommers and Fan, 2006). Moreover, parasites such as *Cryptosporidium* sp., *Cyclospora* sp., *Toxoplasma gondii*, and *Trichinella* are eliminated.

When used in this manner, irradiation is comparable to pasteurizing milk, in that the product is left fresh, but is much safer. Irradiation also extends the shelf life of food by retarding maturation in vegetables and reducing spoilage organisms that can even grow under refrigeration. Irradiated strawberries can last weeks in the refrigerator without developing mold. Irradiation can also be used in place of fumigants and other quarantine procedures to allow fruits and vegetables to be imported or exported without risking the introduction of harmful insects to the receiving country (Feed Irradiation, 2012).

The primary regulation that covers irradiation in the production, processing, and handling of food is 21 CFR 179. It is divided into subparts and sections and is summarized in Table 16.2. Subpart B of 21 CFR 179 describes the type of radiation and its sources; they include gamma ray, electron beam, and X-ray. The general provisions for food irradiation are described. Subpart B also describes other radiation methods such as radio-frequency radiation, ultraviolet, and pulsed light. Subpart C of 21 CFR 179 describes packaging materials for irradiated foods. The regulations listed in Part 179 are due to the approved food additive petitions via the codified process of 21 CFR 171. The actual content of each section in Table 16.2 has been described in this chapter.

16.4.2 Title 21 CFR 179. Subpart B: Radiation and Radiation Sources

Section 179.21: Sources of Radiation Used for Inspection of Food, for Inspection of Packaged Food, and for Controlling Food Processing

Sources of radiation for the purposes of inspection of foods, for inspection of packaged food, and for controlling food processing may be safely used under the following conditions:

a. The radiation source is one of the following:
   1. X-ray tubes producing X-radiation from operation of the tube source at a voltage of 500 kV peak or lower.
   2. Sealed units producing radiation at energy levels of not more than 2.2 million electron volts (MeV) from one of the following isotopes: americium-241, cesium-137, cobalt-60, iodine-125, krypton-85, radium-226, and strontium-90.

Table 16.2 Title 21, Part 179: Irradiation in the Production, Processing, and Handling of Food

Regulation Section	Regulation Coverage
Subpart B—radiation and radiation sources	
179.21	Sources of radiation used for inspection of food, for inspection of packaged food, and for controlling food processing
179.25	General provisions for food irradiation
179.26	Ionizing radiation for the treatment of food
179.30	Radio frequency radiation for the heating of food, including microwave frequencies
179.39	Ultraviolet radiation for the processing and treatment of food
179.41	Pulsed light for the treatment of food
Subpart C—packaging materials for irradiated foods	
179.45	Packaging materials for use during the irradiation of prepackaged foods

3. Sealed units producing neutron radiation from the isotope californium-252 (CAS Reg. No. 13981-17-4) to measure moisture in food.
4. Machine sources producing X-radiation at energies no greater than 10 MeV.
5. Monoenergetic neutron sources producing neutrons at energies not less than 1 MeV but no greater than 14 MeV.

b. To assure safe use of these radiation sources:
   1. The label of the sources shall bear, in addition to the other information required by the Act:
      i. appropriate and accurate information identifying the source of radiation
      ii. the maximum energy of radiation emitted by X-ray tube sources
      iii. the maximum energy of X-radiation emitted by machine source
      iv. the minimum and maximum energy of radiation emitted by neutron source
   2. The label or accompanying labeling shall bear:
      i. adequate directions for installation and use
      ii. a statement that no food shall be exposed to radiation sources listed in Paragraph (a) (1) and (2) of this section so as to receive an absorbed dose in excess of 10 Gy
      iii. a statement that no food shall be exposed to a radiation source listed in Paragraph (a)(3) of this section so as to receive an absorbed dose in excess of 2 mGy
      iv. a statement that no food shall be exposed to a radiation source listed in Paragraph (a)(4) of this section so as to receive a dose in excess of 0.5 Gy
      v. a statement that no food shall be exposed to a radiation source listed in Paragraph (a)(5) of this section so as to receive a dose in excess of 0.01 Gy

Section 179.25: General Provisions for Food Irradiation

For the purposes of 179.26, current good manufacturing practice is defined to include the following restrictions:

a. Any firm that treats foods with ionizing radiation shall comply with the requirements of Part 110 of this chapter and other applicable regulations.

b. Food treated with ionizing radiation shall receive the minimum radiation dose reasonably required to accomplish its intended technical effect and not more than the maximum dose specified by the applicable regulation for that use.

c. Packaging materials subjected to irradiation incidental to the radiation treatment and processing of prepackaged food shall be in compliance with 179.45, shall be the subject of an exemption for such use under 170.39 of this chapter, or shall be the subject of an effective premarket notification for a FCS for such use submitted under 170.100 of this chapter.

d. Radiation treatment of food shall conform to a scheduled process. A scheduled process for food irradiation is a written procedure that ensures that the radiation dose range selected by the food irradiation processor is adequate under commercial processing conditions (including atmosphere and temperature) for the radiation to achieve its intended effect on a specific product and in a specific facility. A food irradiation processor shall operate with a scheduled process established by qualified persons having expert knowledge in radiation processing requirements of food and specifically for that food and for that irradiation processor's treatment facility.

e. A food irradiation processor shall maintain records as specified in this section for a period of time that exceeds the shelf life of the irradiated food product by 1 year, or up to a maximum of 3 years, whichever period is shorter, and shall make these records available for inspection and copying by authorized employees of the FDA. Such records shall include the food treated, lot identification, scheduled process, evidence of compliance with the scheduled process, ionizing energy source, source calibration, dosimetry, dose distribution in the product, and the date of irradiation.

Section 179.26: Ionizing Radiation for the Treatment of Food

Ionizing radiation for treatment of foods may be safely used under the following conditions:

a. Energy sources. Ionizing radiation is limited to:
   1. Gamma rays from sealed units of the radionuclides cobalt-60 or cesium-137
   2. Electrons generated from machine sources at energies not to exceed 10 MeV
   3. X-rays generated from machine sources at energies not to exceed 5 MeV, except as permitted by Paragraph (a)(4) of this section
   4. X-rays generated from machine sources using tantalum or gold as the target material and using energies not to exceed 7.5 MeV

b. Limitations are listed in Table 16.3.

c. Labeling:
   1. The label and labeling of retail packages of foods irradiated in conformance with Paragraph (b) of this section shall bear the following logo:

along with either the statement “Treated with radiation” or the statement “Treated by irradiation” in addition to information required by other regulations. The logo shall be placed prominently and conspicuously in conjunction with the required statement. The radiation disclosure statement is not required to be more prominent than the declaration of ingredients required under 101.4 of this chapter. As used in this provision, the term “radiation disclosure statement” means the written statement that discloses that a food has been intentionally subject to irradiation.

   2. For irradiated foods not in packaged form, the required logo and phrase “Treated with radiation” or “Treated by irradiation” shall be displayed to the purchaser with either (i) the labeling of the bulk container plainly in view or (ii) a counter sign, card, or other appropriate device bearing the information that the product has been treated with radiation. As an alternative, each item of food may be individually labeled. In either case, the information must be prominently and conspicuously displayed to purchasers. The labeling requirement applies only to a food that has been irradiated, not to a food that merely contains an irradiated ingredient but that has not itself been irradiated.
   3. For a food, any portion of which is irradiated in conformance with Paragraph (b) of this section, the label and labeling and invoices or bills of lading shall bear either the statement “Treated with radiation—do not irradiate again” or the statement “Treated by irradiation—do not irradiate again” when shipped to a food manufacturer or processor for further processing, labeling, or packing.

Section 179.30: Radio-Frequency Radiation for the Heating of Food, Including Microwave Frequencies

Radio-frequency radiation, including microwave frequencies, may be safely used for heating food under the following conditions:

a. The radiation source consists of electronic equipment producing radio waves with specific frequencies for this purpose authorized by the Federal Communications Commission.

b. The radiation is used or intended for use in the production of heat in food wherever heat is necessary and effective in the treatment or processing of food.

Section 179.39: Ultraviolet Radiation for the Processing and Treatment of Food

Ultraviolet radiation for the processing and treatment of food may be safely used under the following conditions:

a. The radiation sources consist of low-pressure mercury lamps emitting 90% of the emission at a wavelength of 253.7 nm (2537 angstrom).

b. The ultraviolet radiation is used or intended for use as follows in Table 16.4.

Table 16.3 Food Permitted to be Irradiated and the Allowed Limitations

Use	Limitations
1. For control of *Trichinella spiralis* in pork carcasses or fresh, nonheat-processed cuts of pork carcasses	Minimum dose, 0.3 kGy (30 kilorad (krad)); maximum dose not to exceed 1 kGy (100 krad)
2. For growth and maturation inhibition of fresh foods	Not to exceed 1 kGy (100 krad)
3. For disinfestation of arthropod pests in food	Do.
1. For microbial disinfection of dry or dehydrated enzyme preparations (including immobilized enzymes)	Not to exceed 10 kGy (1 megarad (Mrad))
4. For microbial disinfection of the following dry or dehydrated aromatic vegetable substances when used as ingredients in small amounts solely for flavoring or aroma: culinary herbs, seeds, spices, vegetable seasonings that are used to impart flavor but that are not either represented as, or appear to be, a vegetable that is eaten for its own sake, and blends of these aromatic vegetable substances. Turmeric and paprika may also be irradiated when they are to be used as color additives. The blends may contain sodium chloride and minor amounts of dry food ingredients ordinarily used in such blends	Not to exceed 30 kGy (3 Mrad)
5. For control of food-borne pathogens in fresh or frozen, uncooked poultry products that are (1) whole carcasses or disjointed portions of such carcasses that are “ready-to-cook poultry” within the meaning of 9 CFR 381.1(b)(44) or (2) mechanically separated poultry product (a finely comminuted ingredient produced by the mechanical deboning of poultry carcasses or parts of carcasses)	Not to exceed 3 kGy (300 krad). Any packaging used shall not exclude oxygen
6. For the sterilization of frozen, packaged meats used solely in the NASA space flight programs	Minimum dose 44 kGy (4.4 Mrad). Packaging materials used need not comply with 179.25(c) provided that their use is otherwise permitted by applicable regulations in parts 174 through 186 of this chapter in the regulation
7.For control of food-borne pathogens in, and extension of the shelf life of, refrigerated or frozen, uncooked products that are meat within the meaning of 9 CFR 301.2(rr), meat by-products within the meaning of 9 CFR 301.2(tt), or meat food products within the meaning of 9 CFR 301.2 (uu), with or without nonfluid seasoning, that are otherwise composed solely of intact or ground meat, meat by-products, or both meat and meat by-products	Not to exceed 4.5 kGy maximum for refrigerated products, not to exceed 7.0 kGy maximum for frozen products
9. For control of *Salmonella* in fresh shell eggs	Not to exceed 3.0 kGy
10. For control of microbial pathogens on seeds	Not to exceed 8.0 kGy

Table 16.4 Ultraviolet Radiation for Treatment of Food

Irradiated Food	Limitations	Use
Food and food products	Without ozone production; high-fat-content food irradiated in vacuum or in an inert atmosphere; intensity of radiation, 1 W (of 2537 angstrom radiation) per 5−10 ft^2	Surface microorganism control
Potable water	Without ozone production; coefficient of absorption, 0.19 per cm or less; flow rate, 100 gal/h per watt of 2537 angstrom radiation; water depth, 1 cm or less; lamp-operating temperature, 36−46°C	Sterilization of water used in food production
Juice products	Turbulent flow through tubes with a minimum Reynolds number of 2200	Reduction of human pathogens and other microorganisms

Section 179.41: Pulsed Light for the Treatment of Food

Pulsed light may be safely used for treatment of foods under the following conditions:

a. The radiation sources consist of xenon flashlamps designed to emit broadband radiation consisting of wavelengths covering the range of 200−1100 nm and operated so that the pulse duration is no longer than 2 ms.

b. The treatment is used for surface microorganism control.

c. Foods treated with pulsed light shall receive the minimum treatment reasonably required to accomplish the intended technical effect.

d. The total cumulative treatment shall not exceed 12.0 J/cm^2.

16.4.3 Title 21 CFR 179. Subpart C: Packaging Materials for Irradiated Foods

Section 179.45: Packaging Materials for Use during the Irradiation of Prepackaged Foods

The packaging materials identified in this section may be safely subjected to irradiation incidental to the radiation treatment and processing of prepackaged foods, subject to the provisions of this section and to the requirement that no induced radioactivity is detectable in the packaging material itself:

a. The radiation of the food itself shall comply with regulations in this part.

b. The following packaging materials may be subjected to a dose of radiation, not to exceed 10 kGy, unless otherwise indicated, incidental to the use of gamma, electron beam, or X-radiation in the radiation treatment of prepackaged foods:
   1. Nitrocellulose-coated or vinylidene chloride copolymer-coated cellophane complying with 177.1200 of this chapter.
   2. Glassine paper complying with 176.170 of this chapter.
   3. Wax-coated paperboard complying with 176.170 of this chapter.
   4. Polyolefin film prepared from one or more of the basic olefin polymers complying with 177.1520 of this chapter. The finished film may contain:
      i. Adjuvant substances used in compliance with 178.3740 and 181.22 through 181.30 of this chapter, sodium citrate, sodium lauryl sulfate, polyvinyl chloride, and materials as listed in Paragraph (d)(2)(i) of this section.
      ii. Coatings comprising a vinylidene chloride copolymer containing a minimum of 85% vinylidene chloride with one or more of the following comonomers: acrylic acid, acrylonitrile, itaconic acid, methyl acrylate, and methyl methacrylate.
   5. Kraft paper prepared from unbleached sulfate pulp to which rosin, complying with

178.3870 of this chapter, and alum may be added. The kraft paper is used only as a container for flour and is irradiated with a dose not exceeding 500 Gy.

6. Polyethylene terephthalate (PET) film prepared from the basic polymer as described in 177.1630(e)(4)(i) and (ii) of this chapter. The finished film may contain the following:
    i. Adjuvant substances used in compliance with 178.3740 and 181.22 through 181.30 of this chapter, sodium citrate, sodium lauryl sulfate, polyvinyl chloride, and materials as listed in Paragraph (d)(2)(i) of this section.
    ii. Coatings comprising a vinylidene chloride copolymer containing a minimum of 85% vinylidene chloride with one or more of the following comonomers: acrylic acid, acrylonitrile, itaconic acid, methyl acrylate, and methyl methacrylate.
    iii. Coatings consisting of polyethylene conforming to 177.1520 of this chapter.
7. Polystyrene film prepared from styrene basic polymer. The finished film may contain adjuvant substances used in compliance with 178.3740 and 181.22 through 181.30 of this chapter.
8. Rubber hydrochloride film prepared from rubber hydrochloride basic polymer having a chlorine content of 30–32 weight percentage and having a maximum extractable fraction of 2 weight percentage when extracted with n-hexane at reflux temperature for 2 h. The finished film may contain adjuvant substances used in compliance with 178.3740 and 181.22 through 181.30 of this chapter.
9. Vinylidene chloride-vinyl chloride copolymer film prepared from vinylidene chloride-vinyl chloride basic copolymers containing not less than 70 weight percentage of vinylidene chloride and having a viscosity of 0.50–1.50 centipoises as determined by ASTM method D729-81, "Standard Specification for Vinylidene Chloride Molding Compounds", which is incorporated by reference. Copies may be obtained from the American Society for Testing Materials, 100 Barr Harbor Dr., West Conshohocken, Philadelphia, PA 19428-2959, or may be examined at the National Archives and Records Administration (NARA). For information on the availability of this material at NARA, call 202-741-6030, or go to http://www.archives.gov/federal_register/code_of_federal_regulations/ibr_locations.html. The finished film may contain adjuvant substances used in compliance with 178.3740 and 181.22 through 181.30 of this chapter.
10. Polyamide 11 conforming to 177.1500 of this chapter.

c. Ethylene-vinyl acetate copolymers complying with 177.1350 of this chapter. The ethylene-vinyl acetate packaging materials may be subjected to a dose of radiation, not to exceed 30 kGy (3 megarads), incidental to the use of gamma, electron beam, or X-radiation in the radiation treatment of packaged foods.

d. The following packaging materials may be subjected to a dose of radiation, not to exceed 60 kGy, incidental to the use of gamma, electron beam, or X-radiation in the radiation processing of prepackaged foods:
1. Vegetable parchments consisting of a cellulose material made from waterleaf paper (unsized) treated with concentrated sulfuric acid, neutralized, and thoroughly washed with distilled water.
2. Films prepared from basic polymers with or without adjuvants, and as follows:
    i. Polyethylene film prepared from the basic polymer as described in 177.1520 (a) of this chapter. The finished film may contain one or more of the following added substances:

Substances	**Limitations**
Amides of erucic, linoleic, oleic, palmitic, and stearic acid	Not to exceed 1 pct by weight of the polymer.
BHA as described in 172.110 of this chapter	Do.
BHT as described in 172.115 of this chapter	Do.

Calcium and sodium propionates	Do.
Petroleum wax as described in 178.3710 of this chapter	Do.
Polypropylene, noncrystalline, as described in 177.1520(c) of this chapter	Not to exceed 2 pct by weight of the polymer.
Stearates of aluminum, calcium, magnesium, potassium, and sodium as described in 172.863(a) of this chapter	Not to exceed 1 pct by weight of the polymer.
Triethylene glycol as described in 178.3740(b) of this chapter	Do.
Mineral oil as described in 178.3620 (a) or (b) of this chapter	Do.

16.5 Regulatory Aspects of Recycled Plastics—US FDA View

There is a great deal of interest in recycling plastics in today's society. The drivers include economic, environmental, and sustainability issues. The continuous increase in the cost of petroleum provides an economic incentive for the reuse of plastic parts and packaging materials beyond a threshold oil price. One of the largest applications of plastics is food packaging where there is opportunity for the consumption of recycled plastics.

FDA becomes involved when industry collects used polymeric materials (usually food containers) and proposes to recycle these materials to make new food containers. FDA's main safety concerns with the use of recycled plastic materials in food contact articles are as follows (from here forward, the regulation text is republished from FDA's web site):

1. That contaminants from the post-consumer material may appear in the final food contact product made from the recycled material
2. That recycled post-consumer material not regulated for food contact use may be incorporated into food contact packaging
3. That adjuvants in the recycled plastic may not comply with the regulations for food contact use

16.5.1 Introduction

Currently, to address these concerns, FDA considers each proposed use of recycled plastic on a case-by-case basis and issues informal advice as to whether the recycling process is expected to produce plastic suitable for food contact applications. FDA has prepared a document entitled "Guidance for Industry—Use of Recycled Plastics in Food Packaging: Chemistry Considerations" that is aimed to assist manufacturers of food packaging in evaluating processes for recycling plastic into food packaging. This guidance document represents the Food and Drug Administration's current thinking on this topic. This Guide is provided in the next section.

If a manufacturer would like FDA to consider the use of recycled plastic for a food contact application, the following information should to be submitted:

1. A complete description of the recycling process, including a description of the source of the recyclable plastic and a description of any source controls in place intended to ensure that only plastic that initially complied with the applicable regulations is recycled. Also necessary is a description of any steps that are taken to ensure that the recyclable plastic is not contaminated at some point, either before collection for recycling or during the recycling process.
2. The results of any tests performed to show that the recycling process removes possible contaminants. For use of the recycled material as a substitute for plastic made from virgin materials, it would be necessary to either show that there has been no possibility of contamination with substances other than food or to demonstrate, through surrogate contaminant testing and, if appropriate, additional migration testing, that your recycling process successfully removes possible contaminants. However, surrogate contaminant testing is no longer considered necessary to demonstrate that post-consumer-recycled (PCR) PET or polyethylene naphthalate

(PEN) produced by a tertiary recycling process is suitable for food contact use. Because FDA has determined that tertiary recycling processes produce PCR PET or PEN of suitable purity for food contact use, the Agency no longer sees a need to evaluate tertiary recycling processes for PET or PEN or to issue individual opinion letters for them.

3. A description of the proposed conditions of use of the plastic (e.g. information on intended temperature of use, type of food with which the plastic will come into contact, the duration of the contact, and whether the food contact plastic will be for repeated or single-use applications).

16.5.2 Use of Recycled Plastics in Food Packaging: Chemistry Considerations

Introduction

The purpose of this document is to highlight the chemistry issues that FDA recommends that a manufacturer of recycled plastic consider during the manufacturer's evaluation of a recycling process for producing material suitable for food-contact applications. This document supersedes the December 1992 "Points to Consider for the Use of Recycled Plastics in Food Packaging: Chemistry Considerations". The possibility that chemical contaminants in plastic materials intended for recycling may remain in the recycled material and could migrate into the food the material contacts is one of the major considerations for the safe use of recycled plastics for food-contact applications. Other aspects of plastics recycling, such as microbial contamination and structural integrity of the recycled plastic, are also important, but are not discussed in this document.

FDA's guidance documents, including this guidance, do not establish legally enforceable responsibilities. Instead, guidances describe the Agency's current thinking on a topic and should be viewed only as recommendations, unless specific regulatory or statutory requirements are cited. The use of the word *should* in Agency guidances means that something is suggested or recommended, but not required.

Background

Historically, glass, steel, aluminum, and paper have been recycled for food-contact use. Post-consumer use contamination has not been a major concern with glass and metals. These materials are generally impervious to contaminants and are readily cleaned at the temperatures used in their recycling. In addition, pulp from reclaimed fiber in paper and paperboard may be used for food-contact articles provided it meets the criteria in Title 21 of the Code of Federal Regulations, Section 176.260 (Pulp from reclaimed fiber).

Manufacturers of food-contact articles made from recycled plastic are responsible for ensuring that, like virgin material, recycled material is of suitable purity for its intended use and will meet all existing specifications for the virgin material. These requirements, which are described in 21 CFR, Parts 174 through 179, serve as the framework for the testing protocol and evaluation procedures outlined in this guidance document. In particular, §174.5 (General provisions applicable to indirect food additives), subparagraph (a)(2) states, "Any substance used as a component of articles that contact food shall be of a purity suitable for its intended use".

Several general methodologies exist by which plastic packaging can be recycled, and each presents distinct issues regarding the contaminant residues that may be present in post-consumer material. The agency presents below a preliminary discussion of the basic types of recycling and identifies specific concerns associated with each type. This guidance then describes a recommended approach for estimating the maximum level of a chemical contaminant in the recycled material that would result in an estimated daily intake (EDI) that does not exceed 1.5 μg/person/day (0.5 ppb dietary concentration (DC)), the level that FDA would generally consider to be of negligible risk for a contaminant migrating from recycled plastic. Finally, the guidance recommends a protocol for developing chemical data that would be useful for evaluating the adequacy of a recycling process to remove chemical contaminants. FDA notes that the testing protocol and evaluation procedures recommended in this guidance may change as new knowledge is acquired.

The following changes to the testing protocol and evaluation procedures that were previously recommended in the December 1992 “Points to Consider for the Use of Recycled Plastics in Food Packaging: Chemistry Considerations” are included in this document:

LOWERING FROM 1 PPB TO 0.5 PPB THE DC THAT FDA WOULD GENERALLY CONSIDER TO BE OF NEGLIGIBLE RISK FOR A CONTAMINANT MIGRATING FROM RECYCLED PLASTIC. THESE DC’S CORRESPOND TO EDIS OF 3 MICROGRAMS/PERSON/DAY AND 1.5 MICROGRAMS/PERSON/DAY, RESPECTIVELY.

INCREASING THE NUMBER OF RECOMMENDED OPTIONS FOR SURROGATE CONTAMINANTS FOR USE IN EVALUATING A RECYCLING PROCESS.

ELIMINATING THE RECOMMENDATION TO INCLUDE A HEAVY METAL CONTAMINANT IN THE SURROGATE TESTING OF RECYCLING PROCESSES FOR POLYETHYLENE TEREPHTHALATE (PET).

PROVIDING RECOMMENDATIONS TO ADDRESS SECONDARY RECYCLING OF PLASTICS FOR CASES IN WHICH PLASTIC CONTAINERS FROM NON-FOOD-CONTACT APPLICATIONS (THOSE THAT ORIGINALLY CONTAINED, E.G., HOUSEHOLD CLEANERS, SOAPS, SHAMPOOS, OR MOTOR OIL) ARE INCLUDED IN THE POST-CONSUMER FEEDSTOCK.

ELIMINATING ALL DATA RECOMMENDATIONS FOR TERTIARY RECYCLING PROCESSES FOR PET AND POLYETHYLENE NAPHTHALATE (PEN).

RECOMMENDING THE USE OF 0.05 AS THE DEFAULT CONSUMPTION FACTOR (CF) FOR ANY PLASTIC RECYCLED FOR FOOD-CONTACT USE.

Although not required by law or regulation, recyclers of plastics intended for the manufacture of food-contact articles are invited to submit information on their recycling process to FDA for evaluation and comment. Please send submissions to the Office of Food Additive Safety (OFAS) at the address given on the cover of this guidance.

Recycling Processes

In 1991, the Environmental Protection Agency (EPA) introduced a nomenclature that describes the three distinct approaches to the recycling of plastic packaging materials. Primary recycling (1°) refers to the use of pre-consumer industrial scrap and salvage to form new packaging, a common practice in industry. Secondary recycling (2°) refers to the physical reprocessing (e.g., grinding and melting) and reformation of post-consumer plastic packaging materials. Tertiary recycling (3°) involves subjecting post-consumer plastic packaging to chemical treatment whereby its components are isolated and reprocessed for use in manufacture.

EPA considers “recycling” to be the processing of waste to make new articles. Because bottles intended for reuse are not made to be discarded and become waste, reuse is not considered recycling by EPA. Rather, reuse is regarded simply as one form of source reduction, i.e., minimizing the amount of material entering the environment. In simple reuse, the package remains intact and is reused in its original form. In secondary and tertiary recycling, the original package is destroyed and new packaging is formed from the remains. This guidance focuses on the recycling of plastic packaging materials, and reuse will not be discussed further.

Pre-consumer Scrap: Primary Recycling

Primary recycling is the recycling of industrial scrap produced during the manufacture of food-contact articles and is not expected to pose a hazard to the consumer. The recycling of this scrap (“home scrap” as defined by the EPA in 56 FR 49992, Oct. 2, 1991) is acceptable, provided good manufacturing practices are followed. If the home scrap is collected from several different manufacturers, however, FDA recommends that the recycler consider whether the level and type of adjuvants in the recycled plastic would comply with existing approvals.

Physical Reprocessing: Secondary Recycling

Physical reprocessing involves grinding, melting, and reforming plastic packaging material. The basic polymer is not altered during the process. Prior to melting and reforming, the ground, flaked, or pelletized polymer is generally washed to remove contaminants. The size of the polymer flakes or pellets can influence the effectiveness of the washing. Smaller particles provide a greater surface area for enhancing the effectiveness of the wash. Different polymers may also undergo different reforming conditions, such as different processing temperatures, the use of vacuum stripping, or other procedures, that could influence contaminant levels. In some cases, during the grinding or melting phases, the reprocessed material may be blended with virgin polymer.

Recyclers must be able to demonstrate that contaminant levels in the reformed plastic have been reduced to sufficiently low levels to ensure that the resulting packaging is of a purity suitable for its intended use. To produce a polymer with the desired qualities, however, additional antioxidants, processing aids, or other adjuvants may need to be added to the recycled polymer. The type and total amount of these additives must comply with existing authorizations, and any adjuvants already in the plastic may not react during the recycling process to form substances whose safety has not been evaluated by the FDA. Use in the recycled polymer of a new additive or an amount of an approved additive in excess of what is currently authorized for the virgin polymer would require a food contact notification (FCN) or food additive petition (FAP) (Food Ingredients and Packaging Approval and Notifications Programs, 2012). This guidance has been prepared by the Division of Food Contact Notifications in the CFSAN at the US FDA.

A secondary recycling process presents some unique challenges that might cause it to be inappropriate for the production of food-contact articles, particularly if the recycler had little or no control over the waste stream entering the recycling facility (e.g., commingling of food-contact and nonfood-contact materials). Where effective source control or sorting procedures can be established, however, the potential for post-consumer food-contact materials to be recycled together with other post-consumer plastics will be minimized or eliminated. Nevertheless, even if all the incoming post-consumer polymer were comprised of food-contact materials, limitations on food type or conditions of use could be compromised in the finished recycled product. For example, an additive approved for use only in contact with aqueous food or only for refrigerated use could be incorporated into packaging intended for high-temperature use with fatty foods. The resulting food-contact article would not comply with existing approvals. This concern may be mitigated by development of sorting procedures that result in reprocessing of only a single characteristic container, e.g., a polyethylene terephthalate (PET) soda bottle.

Given the foregoing, FDA recommends that secondary recyclers address these concerns by, for example, implementing controls on the source of the post-consumer polymer, adequate sorting procedures for the incoming post-consumer material, use limitations on the finished recycled packaging (such as use at room temperature or below), or food-type restrictions (such as dry or aqueous foods only). In any submissions to FDA regarding 2° recycling processes, a discussion of these types of actions would be very helpful in FDA's evaluation of the processes.

Chemical Reprocessing: Tertiary Recycling

The primary goal of tertiary recycling is the regeneration of purified starting materials. Chemical reprocessing may involve depolymerization of the used packaging material with subsequent regeneration and purification of resulting monomers (or oligomers). The monomers are then repolymerized and the regenerated or reconstituted polymer is formed into new packaging. Regenerated monomer, polymer, or both may be blended with virgin materials. The regeneration process may involve a variety of monomer/polymer purification steps in addition to washings, such as distillation, crystallization, and additional chemical reaction.

Exposure to Chemical Contaminants

The FDA believes that acute consumer exposure to chemical contaminants from food containers produced from plastic that has been processed by 2° or 3° recycling will be extremely low because of the low concentrations of contaminant residues in the recycled polymers (see below). It is possible, however, that traces of a toxic substance could be carried through a 2° or 3° recycling process, become a part of the packaging, and migrate into food in contact with the packaging. Although subsequent recycling of the packaging will result in dilution of the toxin, a very low steady-state concentration of certain toxins could conceivably develop in the recycled material over the long term. Therefore, there is a potential for a consumer to be exposed to low concentrations of a particular toxin over a long period of time. In order to develop a recommendation for the maximum acceptable level(s) of residual contaminants in the recycled material, FDA has considered the question of risk in a probabilistic way rather than on a compound-by-compound basis.

To recommend a maximum acceptable level for chemical contaminants in recycled food-contact articles that can form the basis of Good Manufacturing Practice with respect to recycled material, FDA has determined the residual concentration of a contaminant that corresponds to an acceptable upper limit of dietary exposure. Using the scientific analysis supporting the Threshold of Regulation approach to evaluating indirect food additives as a basis (see 21 CFR 170.39), FDA believes that EDIs of contaminants from recycled food-contact articles on the order of 1.5 μg/person/day (0.5 ppb DC) or less are generally of negligible risk. The following exercise illustrates the calculation of the maximum acceptable level in the plastic of a contaminant in PET that would result in an EDI of no more than 1.5 μg/person/day.

In the case of PET, combining its density of 1.4 g/cm^3 with an assumed container thickness of 0.50 mm ($\sim$0.02 in.) gives a package with a mass-to-surface area ratio of 70 mg/cm^2 (450 mg/in.^{2}). FDA further assumed the following: individuals consume 3 kg of food per day, 10 g of food contacts one square inch of container, a consumption factor (CF) of 0.05 for recycled PET [FDA will assume a default CF of 0.05 for any recycled polymer. Previously, FDA used a CF for both virgin and recycled PET of 0.05. Based on recent market data that demonstrated that, since 1990, virgin PET has captured a dramatically larger share of the food packaging market, and FDA increased the CF for virgin PET to 0.16. Such an increase in market share has not been observed for recycled PET, so FDA uses a CF for recycled PET of 0.05. Since PET is recycled into food containers at a higher rate than any other polymer, it can be assumed that the CF for any other recycled polymer will not exceed 0.05], and a food-type distribution factor (f_T) of 1.0 for all food types (see "Preparation of Food Contact Notifications and Food Additive Petitions for Food Contact Substances: Chemistry Recommendations"). The relationships among EDI, DC, and the CF, f_T, and migration level from package to food are as follows:

$$\begin{aligned} \text{DC} &= \text{CF}\cdot <M> = \text{CF}\cdot\sum_{i=1}^{4}(M\cdot f_T)_i \\ \text{EDI} &= \text{DC}\cdot 3\ \text{kg food/person/day} \end{aligned}$$

where M is the concentration of migrant in a food simulant, i, where i represents the four simulated food types: aqueous, acidic, alcoholic, and fatty foods. Use of the parameters noted above leads to:

$$\text{DC} = 0.5\ \text{ppb} = 0.05\ <M>\ = 0.05(M)(1.0)$$

and

$$\begin{aligned} <M>\ &= (0.5\times 10^{-9}\ \text{g contaminant/g food})\div(0.05) \\ &= 1\times 10^{-8}\ \text{g contaminant/g food.} \end{aligned}$$

Then,

$$\begin{aligned} &(450\times 10^{-3}\ \text{g packaging/in.}^2)\div(10\ \text{g food/in.}^2) \\ &= 0.045\ \text{g packaging/g food} \\ &\quad (1\times 10^{-8}\ \text{g contaminant/g food}) \\ &\quad \div\left(0.045\ \text{g packaging/g food}\right) \\ &= 2.2\times 10^{-7}\ \text{g contaminant/g packaging} \end{aligned}$$

or 220 μg/kg of contaminant in the packaging material. In other words, if a contaminant were present at 220 μg/kg in the PET container made from the recycled material and if 100% migration of the contaminant into food were assumed (a conservative assumption for room-temperature applications of a high barrier material like PET), the DC of the contaminant would be 0.5 ppb (EDI: 1.5 μg/person/day).

The maximum acceptable level of a residual contaminant in a polymer (Table 16.5) that corresponds to an EDI equal to 1.5 μg/person/day will depend on the polymer density, polymer thickness, and CF. The table below reflects residue levels in several polymers that would result in an EDI of a contaminant of 1.5 μg/person/day. These calculations were done using a CF of 0.05 for each recycled polymer [FDA will assume a default CF of 0.05 for any recycled polymer. Previously, FDA used a CF for both virgin and recycled PET of 0.05. Based on recent market data that demonstrated that, since 1990, virgin PET has captured a dramatically larger share of the food packaging market, and FDA increased the CF for virgin PET to 0.16. Such an

Table 16.5 Maximum Acceptable Level of Residual Contaminant in a Polymer

Recycled Polymer	Density (g/cm^3)	Maximum Residue
PET	1.4	220 μg/kg
Polystyrene	1.05	300 μg/kg
PVC	1.58	200 μg/kg
Polyolefins	0.965	320 μg/kg

increase in market share has not been observed for recycled PET, so FDA uses a CF for recycled PET of 0.05. Since PET is recycled into food containers at a higher rate than any other polymer, it can be assumed that the CF for any other recycled polymer will not exceed 0.05.], a *container wall thickness of 0.50 mm (~0.02 in.)*, and the conservative assumptions that all food types are used with each polymer and that the finished article will consist of 100% recycled polymer.

Thus, to achieve EDIs below 1.5 μg/person/day for recycled containers of 0.50-mm thickness, individual chemical contaminants should not be present at levels greater than those given above. It must be emphasized that the calculated levels depend on the thickness of the packaging—the thicker the packaging, the lower the maximum residue levels must be to meet the 1.5 microgram/person/day EDI limit. If a specialized use for a recycled polymer can be documented, it may be possible to estimate a lower CF for use in calculating a maximum acceptable contaminant level. Finally, in cases in which recycled polymer is expected to be blended with virgin polymer, and thus, contaminants in the recycled polymer are diluted with virgin polymer, the maximum acceptable contaminant level calculated using the agency's recommended approach set out above may be divided by the fraction of recycled polymer in the blend.

16.5.3 Surrogate Contaminant Testing

How may the ability of a 2° or 3° recycling process to remove contaminants from plastic containers or packaging that has been subjected to consumer misuse or abuse (e.g., through storage of pesticides or automotive chemicals) be demonstrated? FDA recommends simulating consumer misuse by exposing virgin polymer (either in container form or as flake) to selected surrogate contaminants and then running the exposed or "challenged" polymer through the recycling process. Subsequent analysis of the processed polymer for the surrogate contaminants would provide a means to evaluate the efficacy of the recycling process.

Choice of Surrogates

The FDA recommends that recyclers use materials that have a variety of chemical and physical properties to simulate consumer misuse. In particular, FDA recommends that the surrogate contaminants represent "common" materials accessible to the consumer and include a volatile polar organic substance, a volatile nonpolar organic substance, a nonvolatile polar organic substance, a nonvolatile nonpolar organic substance, and a heavy metal salt (except for PET, see below). Examples of recommended surrogates are given below; FDA believes that one surrogate per category is sufficient for the testing.

Volatile Polar	**Nonvolatile Polar**
Chloroform	Benzophenone
Chlorobenzene	Methyl salicylate
1,1,1-Trichloroethane	
Diethyl ketone	**Nonvolatile nonpolar**
	Tetracosane
Volatile nonpolar	Lindane
Toluene	Methyl stearate
	Phenylcyclohexane
Heavy metal	1-Phenyldecane
Copper(II) 2-ethylhexanoate	2,4,6-Trichloroanisole

Chloroform and toluene are components of cleaning solvents; benzophenone is a suitable substitute for nonvolatile polar pesticides such as Diazinon; and tetracosane is a good representative of the long-chain hydrocarbons that comprise motor oil. A heavy metal salt such as copper(II) 2-ethylhexanoate, a substitute for the toxic salts commonly used in herbicides, would complete the range of properties noted. [Although FDA previously recommended testing with a polymer-specific surrogate, e.g. ortho-cresol, which is known to significantly swell PET, such data are no longer considered necessary because (1) the range of possible contaminant properties are already covered by the five surrogate categories selected, and (2) a consumer's storage of a polymer-specific solvent in a bottle would significantly degrade the bottle to the extent that it would be rejected during the sorting process.] OFAS is available to discuss the use of surrogates other than those listed in the table above.

In the case of PET, FDA does not recommend including a heavy metal salt in surrogate testing. In the PET recycling submissions reviewed over the past decade, migration of the heavy metal surrogate has never been detected in food simulants. FDA reviewed data for a number of heavy metal surrogates, including the metal salts calcium monomethylarsonate (an herbicide for crabgrass), copper acetoarsenite (Paris green), cadmium acetate, zinc stearate, and copper(II) 2-ethylhexanoate. The data show that, unlike small organic molecules, metal salts do not sorb as readily into PET and also that the salts are more easily washed out of PET, probably because they simply adsorb to the PET surface. In one case, the heavy metal surrogate was incorporated into the resin by blending and still was not detected in migration experiments. FDA believes that the metal-containing substances to which consumers have access are primarily in the salt form, and even if this were not the case, it is unlikely that nonionic organometallic species would behave any differently than the organic compounds represented by the four general surrogate categories.

To date, surrogate testing data for recycling processes for polymers other than PET are insufficient to support general conclusions about the behavior of heavy metals in those polymers. Therefore, FDA continues to recommend the use of a heavy metal surrogate in the testing of recycling processes for polymers other than PET.

Contamination of the Plastic

In order to test the recycling process, FDA recommends the following approach.

First, containers made of the virgin plastic of interest are contaminated or “challenged” by filling them with the surrogate contaminants, either “neat” or in “at use” concentrations, using a solvent such as hexane as a diluent. An alternative approach that would reduce the amount of potentially hazardous wastes would be to soak several kilograms of flaked virgin plastic of the type actually used in the recycling process in the selected contaminants at either “neat” or “at use” concentrations. A mixture, or “cocktail” of the contaminants could be used so long as the components of the “cocktail” do not react with each other. Agency recommendations for minimum concentrations of surrogates for a “cocktail” are shown in Table 16.6.

Table 16.6 Examples of Minimum Concentrations of Contaminants in a Surrogate Cocktail

Contaminant	Concentration
Chloroform (volatile polar)	10% v/v[a]
Toluene (volatile nonpolar)	10% v/v
Benzophenone (nonvolatile polar)	1% v/v
Tetracosane or Lindane (nonvolatile nonpolar)	1% w/w[b]
Copper(II) 2-ethylhexanoate (heavy metal)	1% w/w
Balance:	
2-Propanol (as solvent for Cu(II) 2-ethylhexanoate)	10% v/v
Hexane or Heptane (as overall solvent for cocktail)	68% v/v

[a] *v/v—volume of contaminant per unit volume of entire cocktail.*
[b] *w/w—mass of surrogate per unit mass of entire cocktail.*

Once the bottles are filled or after the contaminants are thoroughly mixed with the flakes, the bottles or flakes should be stored sealed for two weeks at 40°C with periodic agitation. After the contaminants are drained and the bottles or flakes are rinsed, the concentration of each surrogate should be determined in the polymer. The challenged polymer should then be subjected to the proposed recycling process, and regenerated components or packaging material formed from the reprocessed polymer should be analyzed for residual contaminants. This approach represents a worst-case scenario, i.e., all material entering the recycling stream is assumed to be contaminated.

Testing protocols may be submitted to OFAS for comment before any contamination studies are done. FDA recommends that all analyses be validated as discussed in the “Preparation of Food Contact Notifications and Food Additive Petitions for Food Contact Substances: Chemistry Recommendations”.

Other Considerations

If a proposed recycling process cannot be shown to remove contaminants to maximum acceptable levels under the scenario discussed above, then additional factors or limitations on use could justify a conclusion that the recycled package will not introduce contaminants into the diet at unacceptable levels. The following additional factors/limitations may result in an acceptable upper limit of dietary exposure: the use of a recycled/virgin blend, source controls, restricted uses, the fraction of contaminant that migrates into food or a food simulant, or the use of an effective barrier. FDA recommends that the effect of measured or mathematically modeled factors be supported by adequate documentation (e.g., studies on a specific source control program, studies on the actual extent of contaminated material entering the recycling stream, or information that demonstrates that the recycled polymer is separated from food contact by an effective barrier).

In cases where the post-consumer plastic feedstock is intended to consist of food containers only (i.e., containers that were used to package nonfood substances such as household cleaners are intentionally excluded), FDA would consider data submitted by recyclers that show the extent of contaminated material entering the recycling stream as a result of consumer misuse in order to demonstrate or allow a prediction of the actual incidence of chemical contamination of recycled articles. FDA believes that, due to the incidental nature of potential consumer misuse of a food container and subsequent introduction of that container into the recycling stream, this information (if properly validated) can be factored into the exposure calculations to obtain more realistic values.

16.5.4 Plastic Containers from Nonfood-Contact Applications as Feedstock

The 1992 "Points to Consider" was developed to address incidental contamination of food containers by consumers, following the original intended use of the containers. Containers with nonfood contents (e.g., household cleaners, furniture polish, shampoos, soaps, pesticides, or motor oil) were purposely not addressed.

The amount of custom PET containers (i.e., containers other than soda bottles that are used to package specialty foods as well as nonfood substances) collected via curbside programs has increased dramatically over the past several years [Of 280,000 tons of custom PET containers generated in 1993, 3.6% was recycled. Of 820,000 tons generated in 1999, 9.8% was recycled (see EPA, 1994; EPA, 1999) under the "other plastic containers" entries for PET.] and is predicted to continue to increase ("Plastics", 1996, and "Adding", 1996). In addition, the use of PET in nonfood containers is increasing ("PET", 1997, and Schumacher et al., 1997). These trends indicate that the contamination introduced into post-consumer PET feedstock via nonfood containers, as well as the probability that up to 100% of the post-consumer plastic feedstock might consist of nonfood containers, are likely to increase. Therefore, FDA recommends that worst-case contamination assumptions be made for nonfood containers entering the recycling stream (see below).

The FDA believes that the following two questions are relevant in determining the appropriateness of recycling nonfood containers into new food containers by 2° processes:

1. Are the non-food container plastic, its adjuvants, and the adjuvant levels in the plastic currently authorized for use in contact with food? FDA believes that it is highly unlikely that 2° recycling processes will remove unapproved adjuvants (such as colorants or antioxidants) because these substances are incorporated into the polymer matrix during manufacture.
2. Can the levels of chemical contaminants introduced into the post-consumer feedstock by non-food containers, which can sorb relatively large amounts of chemicals from their contents over very long shelf lives, be sufficiently reduced so that finished recycled containers are suitable for food-contact use? FDA believes that it is likely that 2° recycling processes could remove residual amounts of non-food substances such as household cleaning solutions from non-food containers because these substances are simply sorbed into the container's surface.

These questions have been addressed for PET:

1. The FDA has received information from the plastics industry that verifies that all PET resin used to manufacture containers in the U.S. is authorized for food-contact use, i.e., food-grade PET is used to manufacture both food and non-food containers (see, for example, Phoenix, 1998).
2. The FDA has used a mathematical model, based on Fick's law of diffusion, to predict the amount of a contaminant (represented by

> the surrogate contaminants described above) that will sorb into a PET bottle during a period of one year at 25°C, the shelf life and use temperature of a typical non-food substance packaged in PET (see appendix). Because the model tends to overpredict sorption (see appendix), FDA's experimental sorption results and data from the literature have also been used to calculate the sorption of several surrogates into PET under these use conditions (Begley et al., 2002, and Demertzis et al., 1997). The PET sorption values for several surrogates are summarized in Table 16.7 below.

FDA recommends that recyclers who wish to include nonfood PET containers in their feedstock establish that the concentrations of the surrogates in challenged PET flake, prior to its being run through their recycling process, are greater than or equal to the sorption values shown in Table 16.7. FDA does not recommend that this criterion be included in surrogate testing for a recycling process that uses only food containers as feedstock—simply exposing virgin flake or intact bottles to the surrogate cocktail for 2 weeks at 40°C is sufficient to model incidental misuse of containers by consumers.

In order to obtain the initial concentrations shown in Table 16.7, FDA recommends exposing PET flake rather than intact bottles to the surrogate solutions for at least 14 days at 40°C. The use of intact PET bottles in surrogate testing potentially can result in at least an order of magnitude less sorption of the surrogate contaminants than the values shown in Table 16.7, due to the lower surface area of a PET bottle compared to an equal mass of flake (Komolprasert and Lawson, 1995).

Table 16.7 Sorption of Surrogate Contaminants into PET after 365 Days at 25°C

Surrogate	**Sorption Value (mg/kg)**	**Reference**
Volatile, polar		
Chloroform	4860	Begley et al. (2002) (modeled value)
Chlorobenzene	1080	Demertzis et al. (1997)[a]
1,1,1-Trichloroethane	1050	Demertzis et al. (1997)[a]
Diethyl ketone	4860	Assumed to be the same as chloroform, based on similar molecular weights
Volatile, nonpolar		
Toluene	780	Begley et al. (2002)
Nonvolatile, Polar		
Benzophenone	49	Begley et al. (2002)
Methyl salicylate	200	Begley et al. (2002)
Nonvolatile, nonpolar		
Tetracosane	154	Begley et al. (2002) (modeled value)
Lindane	750	Begley et al. (2002)
Methyl stearate	150	Assumed to be the same as tetracosane, based on preliminary FDA experimental results
Phenylcyclohexane	390	Demertzis et al. (1997)[a]
1-Phenyldecane	170	Demertzis et al. (1997)[a]
2,4,6-Trichloroanisole	1100	Based on value for lindane with molecular-weight correction

[a] *These values were measured at 40°C.*

FDA also recommends that a surrogate cocktail contain, at a minimum, the concentrations of contaminants given in Table 16.6 above. Finally, FDA recommends that recyclers consider using higher concentrations of volatile surrogates such as chloroform in the cocktail to offset losses that could occur before the flake is analyzed.

FDA recommends that, in cases in which the starting concentrations are found to be lower than the values in Table 16.7, recyclers correct for the shortfall by multiplying the surrogate testing results by a simple factor. For example, if the actual starting concentration of toluene were 500 mg/kg, then the factor would be 1.6 ((780 mg/kg)/(500 mg/kg) = 1.6).

FDA recommends against analyzing actual batches of post-consumer plastics for potential chemical contaminants in order to refine exposure calculations because these analyses provide only a snapshot of the composition of curbside-collected plastic containers, and there is no guarantee that the composition of nonfood containers in curbside recycling programs will remain the same over time.

Recyclers who have already had their PET recycling processes evaluated by FDA should not assume, based on the conclusions in this guidance document that their letters from FDA apply to the use of nonfood PET containers as feedstock. If these recyclers desire FDA's opinion on their use of nonfood PET containers, they may ask FDA to reevaluate their surrogate testing data and issue a separate letter.

16.5.5 The Use of an Effective Barrier

The use of 2° or 3° recycled material as a nonfood-contact layer of a multilayer food package is a potential application for recycled plastics. FDA believes that this use would not present a concern about potential contaminant migration into food as long as the recycled polymer is separated from the food by an effective barrier made from virgin polymer or other appropriate material, e.g., an aluminum film. Based on experimental and mathematically modeled diffusion data obtained by the OFAS laboratory (and others) for three-layered coextruded PET films in which the center layer contained surrogate contaminants and the outer layers were comprised of virgin material (Piringer et al., 1998), FDA has determined that virgin PET is an effective barrier to contaminants that could potentially migrate from a recycled plastic inner layer under the following conditions:

1. at a thickness ≥ 25 μm (~0.001 in.) at room temperature and below, and
2. at a thickness ≥ 50 μm (~0.002 in.) at higher temperatures, including use as a dual-ovenable container for cooking food at 150°C for 30 min, provided that only food containers are used in the feedstock to manufacture the recycled layer.

In these cases, the presence of a virgin PET layer ensures that migration of a contaminant to food will result in an EDI no greater than 1.5 μg/person/day. The calculation assumes a consumption factor (CF) of 0.05 for recycled plastic packaging. [FDA will assume a default CF of 0.05 for any recycled polymer. Previously, FDA used a CF for both virgin and recycled PET of 0.05. Based on recent market data that demonstrated that, since 1990, virgin PET has captured a dramatically larger share of the food-packaging market, and FDA increased the CF for virgin PET to 0.16. Such an increase in market share has not been observed for recycled PET, so FDA uses a CF for recycled PET of 0.05. Since PET is recycled into food containers at a higher rate than any other polymer, it can be assumed that the CF for any other recycled polymer will not exceed 0.05.] [Note: Although an EDI ≤ 1.5 μg/person/day for a contaminant is generally of negligible safety concern, a substance intentionally used as a component of a food-contact article is still subject to the food additive definition and might require FDA premarket approval via a food contact notification (see Preparation of Food Contact Notifications: Administrative) or a Threshold of Regulation submission (see Submitting Requests Under 21 CFR 170.39 Threshold of Regulation of Substances Used in Food Contact Articles), even if the EDI of the substance is ≤ 1.5 μg/person/day.]

To demonstrate that a given thickness of a virgin polymer functions as an effective barrier to the migration of contaminants, FDA recommends that the recycler subject intentionally contaminated polymer to the recycling process and incorporate the recycled polymer into a nonfood-contact layer of a finished article, using virgin polymer as the barrier layer. FDA recommends that migration studies be performed with food simulants as described in the "Preparation of Food Contact Notifications and Food Additive Petitions for Food Contact Substances: Chemistry Recommendations". If migration studies show that the EDI of individual contaminants would not exceed 1.5 μg/person/day, FDA would consider the virgin layer of the specified thickness to be an effective barrier to contaminants migrating from the nonfood-contact layer of recycled material. If data from studies other than migration experiments establish that a given thickness of a particular polymer is sufficiently impermeable under anticipated time/temperature use conditions, those data could serve to replace migration experiments.

16.5.6 Elimination of Data Recommendations for 3° Recycling Processes for PET and PEN

Based on a comprehensive review of all surrogate testing data submitted over the past decade for 3° recycling processes for PET and polyethylene naphthalate (PEN), FDA concludes that 3° recycling of PET or PEN by methanolysis or glycolysis results in the production of monomers or oligomers that are readily purified to produce a finished polymer that is suitable for food-contact use. Both 3° processes will clean the polyester sufficiently to allow it to be considered of suitable purity, even assuming 100% migration of residual surrogate to food. This is a significant difference from the surrogate testing of 2° recycling processes. Secondary recycling processes often produce PET that is insufficiently cleaned to withstand 100% migration calculations for the residual surrogates. Under these circumstances, FDA recommends additional migration tests to demonstrate that the finished PET meets the 1.5 micrograms/person/day EDI limit.

Based on a determination that 3° recycling processes produce PET or PEN of suitable purity for food-contact use, FDA no longer recommends that such recyclers submit data for agency evaluation. Because 3° processes for polymers other than PET and PEN have not been the subject of FDA reviews, however, recyclers who wish to engage in 3° recycling of polymers other than PET and PEN are encouraged to submit data for evaluation.

16.6 EU Legislation on Food Contact Plastics

The situation in European Union is more complex than United States because of the existing national laws predating the formation of European Union. The EC began working on replacing the Plastics Directive with a regulation that would be directly applicable in all of the EU member states in 2004. This new regulation was enacted and published in the Journal of the European Union on January 15, 2011. The new regulation consolidates all previous directives and regulations on plastic food contact materials and implements some significant changes. This regulation, previously referred to as the Plastics Implementing Measure (PIM), and now commonly referred to as the Plastics Regulation, went into effect on February 4, 2011. As of May 1, 2011, the Plastics Regulation replaced the Plastics Directive (2002/72/EC) and its amendments as well as various directives on compliance (migration) testing. The Plastics Regulation became directly applicable in all of the EU member states as of May 1, 2011 (Langhorn, 2011).

16.6.1 EU Regulation No. 10/2011 on Plastic Materials Intended to Come into Contact with Food

This section presents an abridged version of the EU Regulation No. 10/2011. The readers can refer to the original document for complete information.

16.6.2 Consolidating Paragraphs

1. Regulation (EC) No 1935/2004 lays down the general principles for eliminating the differences between the laws of the Member States as regards food contact materials. Article 5(1) of that Regulation provides for the adoption of specific measures for groups of materials and articles and describes in detail the procedure for the authorization of substances at EU level when a specific measure provides for a list of authorized substances.
2. This Regulation is a specific measure within the meaning of Article 5(1) of Regulation (EC) No 1935/2004. This Regulation should establish the specific rules for plastic

materials and articles to be applied for their safe use and repeal Commission Directive 2002/72/EC of 6 August 2002 on plastic materials and articles intended to come into contact with foodstuffs.

3. Directive 2002/72/EC sets out basic rules for the manufacture of plastic materials and articles. The Directive has been substantially amended 6 times. For reasons of clarity the text should be consolidated and redundant and obsolete parts removed.
4. In the past Directive 2002/72/EC and its amendments have been transposed into national legislation without any major adaptation. For transposition into national law usually a time period of 12 months is necessary. In case of amending the lists of monomers and additives in order to authorize new substances this transposition time leads to a retardation of the authorization and thus slows down innovation. Therefore it seems appropriate to adopt rules on plastic materials and articles in form of a Regulation directly applicable in all Member States.
5. Directive 2002/72/EC applies to materials and articles purely made of plastics and to plastic gaskets in lids. In the past these were the main use of plastics on the market. However, in recent years, besides materials and articles purely made of plastics, plastics are also used in combination with other materials in so called multi-material multi-layers. Rules on the use of vinyl chloride monomer laid down in Council Directive 78/142/EEC of 30 January 1978 on the approximation of the laws of the Member States relating to materials and articles which contain vinyl chloride monomer and are intended to come into contact with foodstuffs (1).
6. OJ L 44, 15.2.1978, p. 15 already applies to all plastics. Therefore it seems appropriate to extend the scope of this Regulation to plastic layers in multi-material multi-layers.
7. Plastic materials and articles may be composed of different layers of plastics held together by adhesives. Plastic materials and articles may also be printed or coated with an organic or inorganic coating. Printed or coated plastic materials and articles as well as those held together by adhesives should be within the scope of the Regulation. Adhesives, coatings and printing inks are not necessarily composed of the same substances as plastics. Regulation (EC) No 1935/2004 foresees that for adhesives, coatings and printing inks specific measures can be adopted. Therefore plastic materials and articles that are printed, coated or held together by adhesives should be allowed to contain in the printing, coating or adhesive layer other substances than those authorized at EU level for plastics. Those layers may be subject to other EU or national rules.
8. Plastics as well as ion exchange resins, rubbers and silicones are macromolecular substances obtained by polymerization processes. Regulation (EC) No 1935/2004 foresees that for ion exchange resins, rubbers and silicones specific measures can be adopted. As those materials are composed of different substances than plastics and have different physico-chemical properties, specific rules for them need to apply and it should be made clear that they are not within the scope of this Regulation.
9. Plastics are made of monomers and other starting substances which are chemically reacted to form a macromolecular structure, the polymer, which forms the main structural component of the plastics. To the polymer additives are added to achieve defined technological effects. The polymer as such is an inert high molecular weight structure. As substances with a molecular weight above 1000 Da usually cannot be absorbed in the body the potential health risk from the polymer itself is minimal. Potential health risks may occur from non- or incompletely reacted monomers or other starting substances or from low molecular weight additives which are transferred into food via migration from the plastic food contact material. Therefore monomers, other starting substances and additives should be risk assessed and authorized before their use in the manufacture of plastic materials and articles.

10. The risk assessment of a substance to be performed by the European Food Safety Authority (hereinafter the Authority) should cover the substance itself, relevant impurities and foreseeable reaction and degradation products in the intended use. The risk assessment should cover the potential migration under worst foreseeable conditions of use and the toxicity. Based on the risk assessment the authorization should if necessary set out specifications for the substance and restrictions of use, quantitative restrictions or migration limits to ensure the safety of the final material or article.
11. No rules have yet been set out at EU level for the risk assessment and use of colorants in plastics. Therefore their use should remain subject to national law. That situation should be reassessed at a later stage.
12. Solvents used in the manufacture of plastics to create a suitable reaction environment are expected to be removed in the manufacturing process as they are usually volatile. No rules have yet been set out at EU level for the risk assessment and use of solvents in the manufacture of plastics. Therefore their use should remain subject to national law. That situation should be reassessed at a later stage.
13. Plastics can also be made of synthetic or naturally occurring macromolecular structures which are chemically reacted with other starting substances to create a modified macromolecule. Synthetic macromolecules used are often intermediate structures which are not fully polymerised. Potential health risk may occur from the migration of non- or incompletely reacted other starting substances used to modify the macromolecule or an incompletely reacted macromolecule. Therefore the other starting substances as well as the macromolecules used in the manufacture of modified macromolecules should be risk assessed and authorised before their use in the manufacture of plastic materials and articles.
14. Plastics can also be made by micro-organisms that create macromolecular structures out of starting substances by fermentation processes. The macromolecule is then either released to a medium or extracted. Potential health risk may occur from the migration of non- or incompletely reacted starting substances, intermediates or by-products of the fermentation process. In this case the final product should be risk assessed and authorized before its use in the manufacture of plastic materials and articles.
16. Directive 2002/72/EC contains different lists for monomers or other starting substances and for additives authorized for the manufacture of plastic materials and articles. For monomers, other starting substances and additives the Union list is now complete, this means that only substances authorized at EU level may be used. Therefore a separation of monomers or other starting substances and of additives in separate lists due to their authorization status is no longer necessary. As certain substances can be used both as monomer or other starting substances and as additive for reasons of clarity they should be published in one list of authorised substances indicating the authorized function.
16. Polymers can not only be used as main structural component of plastics but also as additives achieving defined technological effects in the plastic. If such a polymeric additive is identical to a polymer that can form the main structural component of a plastic material the risk from polymeric additive can be regarded as evaluated if the monomers have already been evaluated and authorized. In such a case it should not be necessary to authorize the polymeric additive but it could be used on the basis of the authorization of its monomers and other starting substances. If such a polymeric additive is not identical to a polymer that can form the main structural component of a plastic material then the risk of the polymeric additive cannot be regarded as evaluated by evaluation of the monomers. In such a case the polymeric additive should be risk assessed as regards its low molecular weight fraction below 1000 Da and authorized before its use in the manufacture of plastic materials and articles.

17. In the past no clear differentiation has been made between additives that have a function in the final polymer and polymer production aids (PPA) that only exhibit a function in the manufacturing process and are not intended to be present in the final article. Some substances acting as PPA had already been included in the incomplete list of additives in the past. These PPA should remain in the Union list of authorised substances. However, it should be made clear that the use of other PPA will remain possible, subject to national law. That situation should be reassessed at a later stage.
18. The Union list contains substances authorized to be used in the manufacture of plastics. Substances such as acids, alcohols and phenols can also occur in form of salts. As the salts usually are transformed in the stomach to acid, alcohol or phenol the use of salts with cations that have undergone a safety evaluation should in principle be authorized together with the acid, alcohol or phenol. In certain cases, where the safety assessment indicates concerns on the use of the free acids, only the salts should be authorized by indicating in the list the name as "... acid(s), salts."
19. Substances used in the manufacture of plastic materials or articles may contain impurities originating from their manufacturing or extraction process. These impurities are non-intentionally added together with the substance in the manufacture of the plastic material (non-intentionally added substance—NIAS). As far as they are relevant for the risk assessment the main impurities of a substance should be considered and if necessary be included in the specifications of a substance. However it is not possible to list and consider all impurities in the authorization. Therefore they may be present in the material or article but not included in the Union list.
20. In the manufacture of polymers substances are used to initiate the polymerization reaction such as catalysts and to control the polymerization reaction such as chain transfer, chain extending or chain stop reagents. These aids to polymerization are used in minute amounts and are not intended to remain in the final polymer. Therefore they should at this point of time not be subject to the authorization procedure at EU level. Any potential health risk in the final material or article arising from their use should be assessed by the manufacturer in accordance with internationally recognized scientific principles on risk assessment.
21. During the manufacture and use of plastic materials and articles reaction and degradation products can be formed. These reaction and degradation products are non-intentionally present in the plastic material (NIAS). As far as they are relevant for the risk assessment the main reaction and degradation products of the intended application of a substance should be considered and included in the restrictions of the substance. However it is not possible to list and consider all reaction and degradation products in the authorization. Therefore they should not be listed as single entries in the Union list. Any potential health risk in the final material or article arising from reaction and degradation products should be assessed by the manufacturer in accordance with internationally recognized scientific principles on risk assessment.
22. Prior to the establishment of the Union list of additives, other additives than those authorized at EU level could be used in the manufacture of plastics. For those additives which were permitted in the Member States, the time limit for the submission of data for their safety evaluation by the Authority with a view to their inclusion in the Union list expired on 31 December 2006. Additives for which a valid application was submitted within this time limit were listed in a provisional list. For certain additives on the provisional list a decision on their authorization at EU level has not yet been taken. For those additives, it should be possible to continue to be used in accordance with national law until their evaluation is completed and a decision is taken on their inclusion in the Union list.
23. When an additive included in the provisional list is inserted in the Union list or when it is decided not to include it in the

Union list, that additive should be removed from the provisional list of additives.

24. New technologies engineer substances in particle size that exhibit chemical and physical properties that significantly differ from those at a larger scale, for example, nanoparticles. These different properties may lead to different toxicological properties and therefore these substances should be assessed on a case-by-case basis by the Authority as regards their risk until more information is known about such new technology. Therefore it should be made clear that authorizations which are based on the risk assessment of the conventional particle size of a substance do not cover engineered nanoparticles.

25. Based on the risk assessment the authorization should if necessary set out specific migration limits to ensure the safety of the final material or article. If an additive that is authorized for the manufacture of plastic materials and articles is at the same time authorized as food additive or flavoring substance it should be ensured that the release of the substance does not change the composition of the food in an unacceptable way. Therefore the release of such a dual use additive or flavoring should not exhibit a technological function on the food unless such a function is intended and the food contact material complies with the requirements on active food contact materials set out in Regulation (EC) No 1935/2004 and Commission Regulation (EC) No 450/2009 of 29 May 2009 on active and intelligent materials and articles intended to come into contact with food. The requirements of Regulations (EC) No 1333/2008 of the European Parliament and of the Council of 16 December 2008 on food additives or (EC) No 1334/2008 of the European Parliament and of the Council of 16 December 2008 on flavourings and certain food ingredients with flavoring properties for use in and on foods and amending Council Regulation (EEC) No 1601/91, Regulations (EC) No 2232/96 and (EC) No 110/2008 and Directive 2000/13/EC(3) should be respected where applicable.

26. According to Article 3(1)(b) of Regulation (EC) No 1935/2004 the release of substances from food contact materials and articles should not bring about unacceptable changes in the composition of the food. According to good manufacturing practice it is feasible to manufacture plastic materials in such a way that they are not releasing more than 10 mg of substances per 1 dm^2 of surface area of the plastic material. If the risk assessment of an individual substance is not indicating a lower level, this level should be set as a generic limit for the inertness of a plastic material, the overall migration limit. In order to achieve comparable results in the verification of compliance with the overall migration limit, testing should be performed under standardised test conditions including testing time, temperature and test medium (food simulant) representing worst foreseeable conditions of use of the plastic material or article.

27. The overall migration limit of 10 mg per 1 dm^2 results for a cubic packaging containing 1 kg of food to a migration of 60 mg per kilogram food. For small packaging where the surface to volume ratio is higher the resulting migration into food is higher. For infants and small children which have a higher consumption of food per kilogram bodyweight than adults and do not yet have a diversified nutrition, special provisions should be set in order to limit the intake of substances migrating from food contact materials. In order to allow also for small volume packaging the same protection as for high volume packaging, the overall migration limit for food contact materials that are dedicated for packaging foods for infants and small children should be linked to the limit in food and not to the surface area of the packaging.

28. In recent years plastic food contact materials are being developed that do not only consist of one plastic but combine up to 15 different plastic layers to attain optimum functionality and protection of the food, while reducing packaging waste. In such a plastic multilayer material or article, layers may be separated from the food by a functional barrier. This

barrier is a layer within food contact materials or articles preventing the migration of substances from behind that barrier into the food. Behind a functional barrier, non-authorized substances may be used, provided below a given detection limit. Taking into account foods for infants and other particularly susceptible persons, as well as the large analytical tolerance of the migration analysis, a maximum level of 0.01 mg/kg in food should be established for the migration of a non-authorized substance through a functional barrier. Substances that are mutagenic, carcinogenic or toxic to reproduction should not be used in food contact materials or articles without previous authorisation and should therefore not be covered by the functional barrier concept. New technologies that engineer substances in particle size that exhibit chemical and physical properties that significantly differ from those at a larger scale, for example, nanoparticles, should be assessed on a case-by-case basis as regards their risk until more information is known about such new technology. Therefore, they should not be covered by the functional barrier concept.

29. In recent years food contact materials and articles are being developed that consist of a combination of several materials to achieve optimum functionality and protection of the food while reducing packaging waste. In these multi-material multilayer materials and articles plastic layers should comply with the same compositional requirements as plastic layers which are not combined with other materials. For plastic layers in a multi-material multilayer which are separated from the food by a functional barrier the functional barrier concept should apply. As other materials are combined with the plastic layers and for these other materials specific measures are not yet adopted at EU level it is not yet possible to set out requirements for the final multi-material multilayer materials and articles. Therefore specific migration limits and the overall migration limit should not be applicable except for vinyl chloride monomer for which such a restriction is already in place. In the absence of a specific measure at EU level covering the whole multi-material multilayer material or article Member States may maintain or adopt national provisions for these materials and articles provided they comply with the rules of the Treaty.

30. Article 16(1) of Regulation (EC) No 1935/2004 provides that materials and articles covered by specific measures be accompanied by a written declaration of compliance stating that they comply with the rules applicable to them. To strengthen the coordination and responsibility of the suppliers at each stage of manufacture, including that of the starting substances, the responsible persons should document the compliance with the relevant rules in a declaration of compliance which is made available to their customers.

31. Coatings, printing inks and adhesives are not yet covered by a specific EU legislation and therefore not subject to the requirement of a declaration of compliance. However, for coatings, printing inks and adhesives to be used in plastic materials and articles adequate information should be provided to the manufacturer of the final plastic article that would enable him to ensure compliance for substances for which migration limits have been established in this Regulation.

32. Article 17(1) of Regulation (EC) No 178/2002 of the European Parliament and of the Council of 28 January 2002 laying down the general principles and requirements of food law, establishing the European Food Safety Authority and laying down procedures in matters of food safety requires the food business operator to verify that foods are compliant with the rules applicable to them. To this end and subject to the requirement of confidentiality, food business operators should be given access to the relevant information to enable them to ensure that the migration from the materials and articles to food complies with the specifications and restrictions laid down in food legislation.

33. At each stage of manufacture, supporting documentation, substantiating the declaration of compliance, should be kept available

for the enforcement authorities. Such demonstration of compliance may be based on migration testing. As migration testing is complex, costly and time consuming it should be admissible that compliance can be demonstrated also by calculations, including modeling, other analysis, and scientific evidence or reasoning if these render results which are at least as severe as the migration testing. Test results should be regarded as valid as long as formulations and processing conditions remain constant as part of a quality assurance system.

34. When testing articles not yet in contact with food, for certain articles, such as films or lids, it is often not feasible to determine the surface area that is in contact with a defined volume of food. For these articles specific rules should be set out for verification of compliance.
35. The setting of migration limits takes into account a conventional assumption that 1 kg of food is consumed daily by a person of 60 kg bodyweight and that the food is packaged in a cubic container of 6 dm^2 surface area releasing the substance. For very small and very large containers the real surface area to volume of packaged food is varying a lot from the conventional assumption. Therefore, their surface area should be normalized before comparing testing results with migration limits. These rules should be reviewed when new data on food packaging uses become available.
36. The specific migration limit is a maximum permitted amount of a substance in food. This limit should ensure that the food contact material does not pose a risk to health. It should be ensured by the manufacturer that materials and articles not yet in contact with food will respect these limits when brought into contact with food under the worst foreseeable contact conditions. Therefore compliance of materials and articles not yet in contact with food should be assessed and the rules for this testing should be set out.
37. Food is a complex matrix and therefore the analysis of migrating substances in food may pose analytical difficulties. Therefore test media should be assigned that simulate the transfer of substances from the plastic material into food. They should represent the major physico-chemical properties exhibited by food. When using food simulants standard testing time and temperature should reproduce, as far as possible, the migration which may occur from the article into the food.
38. For determining the appropriate food simulant for certain foods the chemical composition and the physical properties of the food should be taken into account. Research results are available for certain representative foods comparing migration into food with migration into food simulants. On the basis of the results, food simulants should be assigned. In particular, for fat containing foods the result obtained with food simulant may in certain cases significantly overestimate migration into food. In these cases it should be foreseen that the result in food simulant is corrected by a reduction factor.
39. The exposure to substances migrating from food contact materials was based on the conventional assumption that a person consumes daily 1 kg of food. However, a person ingests at most 200 g of fat on a daily basis. For lipophilic substances that only migrate into fat this should be taken into consideration. Therefore a correction of the specific migration by a correction factor applicable to lipophilic substances in accordance with the opinion of the Scientific Committee on Food (SCF) and the opinion of the Authority should be foreseen.
40. Official control should establish testing strategies which allow the enforcement authorities to perform controls.
41. Basic rules on migration testing should be set out in this Regulation. As migration testing is a very complex issue, these basic rules can, however, not cover all foreseeable cases and details necessary for performing the testing. Therefore an EU guidance document should be established, dealing with more detailed aspects of the implementation of the basic migration testing rules.

42. The updated rules on food simulants and migration testing provided by this Regulation will supersede those in Directive 78/142/EEC and the Annex to Council Directive 82/711/EEC of 18 October 1982 laying down the basic rules necessary for testing migration of the constituents of plastic materials and articles intended to come into contact with foodstuffs(3).
43. Substances present in the plastic but not listed in Annex I to this Regulation have not necessarily been risk assessed as they had not been subject to an authorization procedure. Compliance with Article 3 of Regulation (EC) No 1935/2004 for these substances should be assessed by the relevant business operator in accordance with internationally recognized scientific principles taking into account exposure from food contact materials and other sources.
44. Recently additional monomers, other starting substances and additives have received a favorable scientific evaluation by the Authority and should now be added to the Union list.
45. As new substances are added to the Union list the Regulation should apply as soon as possible to allow for manufacturers to adapt to technical progress and allow for innovation.
46. Certain migration testing rules should be updated in view of new scientific knowledge. Enforcement authorities and industry need to adapt their current testing regime to these updated rules. To allow for this adaptation it seems appropriate that the updated rules only apply 2 years after the adoption of the Regulation.
47. Business operators are currently basing their declaration of compliance on supporting documentation following the requirements set out in Directive 2002/72/EC. Declaration of compliance need, in principle, only to be updated when substantial changes in the production bring about changes in the migration or when new scientific data are available. In order to limit the burden to business operators, materials which have been lawfully placed on the market based on the requirements set out in Directive 2002/72/EC should be able to be placed on the market with a declaration of compliance based on supporting documentation in accordance with Directive 2002/72/EC until 5 years after the adoption of the Regulation.
48. Analytical methods for testing migration and residual content of vinyl chloride monomer as described in Commission Directives 80/766/EEC of 8 July 1980 laying down the Community method of analysis for the official control of the vinyl chloride monomer level in materials and articles which are intended to come into contact with foodstuffs and 81/432/EEC of 29 April 1981 laying down the Community method of analysis for the official control of vinyl chloride released by materials and articles into foodstuffs are outdated. Analytical methods should comply with the criteria set out in Article 11 of Regulation (EC) No 882/2004 of the European Parliament and of the Council on official controls performed to ensure the verification of compliance with feed and food law, animal health and animal welfare rules. Therefore Directives 80/766/EEC and 81/432/EEC should be repealed.
49. The measures provided for in this Regulation are in accordance with the opinion of the Standing Committee on the Food Chain and Animal Health.

16.6.3 Chapter I: General Provisions

Article 1: Subject Matter

1. This Regulation is a specific measure within the meaning of Article 5 of Regulation (EC) No 1935/2004.
2. This Regulation establishes specific requirements for the manufacture and marketing of plastic materials and articles:
    a. intended to come into contact with food; or
    b. already in contact with food; or
    c. which can reasonably be expected to come into contact with food.

Article 2: Scope

1. This Regulation shall apply to materials and articles which are placed on the EU market and fall under the following categories:
    a. materials and articles and parts thereof consisting exclusively of plastics;
    b. plastic multi-layer materials and articles held together by adhesives or by other means;
    c. materials and articles referred to in points (a) or (b) that are printed and/or covered by a coating;
2. plastic layers or plastic coatings, forming gaskets in caps and closures, that together with those caps and closures compose a set of two or more layers of different types of materials;
3. plastic layers in multi-material multi-layer materials and articles.
4. This Regulation shall not apply to the following materials and articles which are placed on the EU market and are intended to be covered by other specific measures:
    a. ion exchange resins;
    b. rubber;
    c. silicones.
5. This Regulation shall be without prejudice to the EU or national provisions applicable to printing inks, adhesives or coatings.

Article 3: Definitions

For the purpose of this Regulation, the following definitions shall apply:

1. “plastic materials and articles” means:
    a. materials and articles referred to in points (a), (b) and (c) of Article 2(1); and
    b. plastic layers referred to in Article 2(1) (d) and (e);
2. “plastic” means polymer to which additives or other substances may have been added, which is capable of functioning as a main structural component of final materials and articles;
3. “polymer” means any macromolecular substance obtained by:
    a. a polymerization process such as polyaddition or polycondensation, or by any other similar process of monomers and other starting substances; or
    b. chemical modification of natural or synthetic macromolecules; or
    c. microbial fermentation;
4. “plastic multi-layer” means a material or article composed of two or more layers of plastic;
5. “multi-material multi-layer” means a material or article composed of two or more layers of different types of materials, at least one of them a plastic layer;
6. “monomer or other starting substance” means:
    a. a substance undergoing any type of polymerization process to manufacture polymers; or
    b. a natural or synthetic macromolecular substance used in the manufacture of modified macromolecules; or
    c. a substance used to modify existing natural or synthetic macromolecules;
7. “additive” means a substance which is intentionally added to plastics to achieve a physical or chemical effect during processing of the plastic or in the final material or article; it is intended to be present in the final material or article;
8. “polymer production aid” means any substance used to provide a suitable medium for polymer or plastic manufacturing; it may be present but is neither intended to be present in the final materials or articles nor has a physical or chemical effect in the final material or article;
9. “non-intentionally added substance” means an impurity in the substances used or a reaction intermediate formed during the production process or a decomposition or reaction product;
10. “aid to polymerization” means a substance which initiates polymerization and/or controls the formation of the macromolecular structure;
11. “overall migration limit” (OML) means the maximum permitted amount of non-volatile substances released from a material or article into food simulants;

12. "food simulant" means a test medium imitating food; in its behaviour the food simulant mimics migration from food contact materials;
13. "specific migration limit" (SML) means the maximum permitted amount of a given substance released from a material or article into food or food simulants;
14. "total specific migration limit" (SML(T)) means the maximum permitted sum of particular substances released in food or food simulants expressed as total of moiety of the substances indicated;
16. "functional barrier" means a barrier consisting of one or more layers of any type of material which ensures that the final material or article complies with Article 3 of Regulation (EC) No 1935/2004 and with the provisions of this Regulation;
16. "nonfatty food" means a food for which in migration testing only food simulants other than food simulants D1 or D2 are laid down in Table 2 in Annex V to this Regulation;
17. "restriction" means limitation of use of a substance or migration limit or limit of content of the substance in the material or article;
18. "specification" means composition of a substance, purity criteria for a substance, physico-chemical characteristics of a substance, details concerning the manufacturing process of a substance or further information concerning the expression of migration limits.

Article 4: Placing on the Market of Plastic Materials and Articles

Plastic materials and articles may only be placed on the market if they:

a. comply with the relevant requirements set out in Article 3 of Regulation (EC) No 1935/2004 under intended and foreseeable use; and
b. comply with the labeling requirements set out in Article 15 of Regulation (EC) No 1935/2004; and
c. comply with the traceability requirements set out in Article 17 of Regulation (EC) No 1935/2004; and
d. are manufactured according to good manufacturing practice as set out in Commission Regulation (EC) No 2023/2006; and
e. comply with the compositional and declaration requirements set out in Chapters II, III and IV of this Regulation.

16.6.4 Chapter II: Compositional Requirements

Section 1: Authorized Substances

Article 5: Union List of Authorized Substances

1. Only the substances included in the Union list of authorized substances (hereinafter referred to as the Union list) set out in Annex I may be intentionally used in the manufacture of plastic layers in plastic materials and articles.
2. The Union list shall contain:
   a. monomers or other starting substances;
   b. additives excluding colorants;
   c. polymer production aids excluding solvents;
   d. macromolecules obtained from microbial fermentation.
3. The Union list may be amended in accordance with the procedure established by Articles 8 to 12 of Regulation (EC) No 1935/2004.

Article 6: Derogations for Substances Not Included in the Union List

1. By way of derogation from Article 5, substances other than those included in the Union list may be used as polymer production aids in the manufacture of plastic layers in plastic materials and articles subject to national law.
2. By way of derogation from Article 5, colorants and solvents may be used in the manufacture of plastic layers in plastic materials and articles subject to national law.
3. The following substances not included in the Union list are authorized subject to the rules set out in Articles 8, 9, 10, 11 and 12:
   a. salts (including double salts and acid salts) of aluminum, ammonium, barium, calcium, cobalt, copper, iron, lithium,

magnesium, manganese, potassium, sodium, and zinc of authorized acids, phenols or alcohols;
   b. mixtures obtained by mixing authorized substances without a chemical reaction of the components;
   c. when used as additives, natural or synthetic polymeric substances of a molecular weight of at least 1000 Da, except macromolecules obtained from microbial fermentation, complying with the requirements of this Regulation, if they are capable of functioning as the main structural component of final materials or articles;
   d. when used as monomer or other starting substance, pre-polymers and natural or synthetic macromolecular substances, as well as their mixtures, except macromolecules obtained from microbial fermentation, if the monomers or starting substances required to synthesize them are included in the Union list.

4. The following substances not included in the Union list maybe present in the plastic layers of plastic materials or articles:
   a. unintentionally added substances;
   b. aids to polymerization.
5. By derogation from Article 5, additives not included in the Union list may continue to be used subject to national law after 1 January 2010 until a decision is taken to include or not to include them in the Union list provided they are included in the provisional list referred to in Article 7.

Article 7: Establishment and Management of the Provisional List

1. The provisional list of additives that are under evaluation by the European Food Safety Authority (hereinafter referred to as the Authority) that was made public by the Commission in 2008 shall be regularly updated.
2. An additive shall be removed from the provisional list:
   a. when it is included in the Union list set out in Annex I; or
   b. when a decision is taken by the Commission not to include it in the Union list; or
   c. if during the examination of the data, the Authority calls for supplementary information and that information is not submitted within the time limits specified by the Authority.

Section 2: General Requirements, Restrictions, and Specifications

Article 8: General Requirements on Substances

Substances used in the manufacture of plastic layers in plastic materials and articles shall be of a technical quality and a purity suitable for the intended and foreseeable use of the materials or articles. The composition shall be known to the manufacturer of the substance and made available to the competent authorities on request.

Article 9: Specific Requirements on Substances

1. Substances used in the manufacture of plastic layers in plastic materials and articles shall be subject to the following restrictions and specifications:
   a. the specific migration limit set out in Article 11;
   b. the overall migration limit set out in Article 12;
   c. the restrictions and specifications set out in column 10 of Table 1 of point 1 of Annex I;
   d. the detailed specifications set out in point 4 of Annex I.
2. Substances in nanoform shall only be used if explicitly authorized and mentioned in the specifications in Annex I.

Article 10: General Restrictions on Plastic Materials and Articles

General restrictions related to plastic materials and articles are laid down in Annex II.

Article 11: Specific Migration Limits

1. Plastic materials and articles shall not transfer their constituents to foods in quantities exceeding the specific migration limits (SML) set out in Annex I. Those specific migration limits (SML) are expressed in mg of substance per kg of food (mg/kg).
2. For substances for which no specific migration limit or other restrictions are provided in Annex I, a generic specific migration limit of 60 mg/kg shall apply.

3. By derogation from paragraphs 1 and 2, additives which are also authorized as food additives by Regulation (EC) No 1333/2008 or as flavorings by Regulation (EC) No 1334/2008 shall not migrate into foods in quantities having a technical effect in the final foods and shall not:
    a. exceed the restrictions provided for in Regulation (EC) No 1333/2008 or in Regulation (EC) No 1334/2008 or in Annex I to this Regulation for foods for which their use is authorized as food additive or flavoring substances; or
    b. exceed the restrictions set out in Annex I to this Regulation in foods for which their use is not authorized as food additive or flavoring substances.

Article 12: Overall Migration Limit

1. Plastic materials and articles shall not transfer their constituents to food simulants in quantities exceeding 10 mg of total constituents released per dm^2 of food contact surface (mg/dm^2).
2. By derogation from paragraph 1, plastic materials and articles intended to be brought into contact with food intended for infants and young children, as defined by Commission Directives 2006/141/EC(1), shall not transfer their constituents to food simulants in quantities exceeding 60 mg of total of constituents released per kg of food simulant.

16.6.5 Chapter III: Specific Provisions for Certain Materials and Articles

Article 13: Plastic Multi-layer Materials and Articles

1. In a plastic multi-layer material or article, the composition of each plastic layer shall comply with this Regulation.
2. By derogation from paragraph 1, a plastic layer which is not in direct contact with food and is separated from the food by a functional barrier, may:
    a. not comply with the restrictions and specifications set out in this Regulation except for vinyl chloride monomer as provided in Annex I; and/or
    b. be manufactured with substances not listed in the Union list or in the provisional list.
3. The migration of the substances under paragraph 2(b) into food or food simulant shall not be detectable measured with statistical certainty by a method of analysis set out in Article 11 of Regulation (EC) No 882/2004 with a limit of detection of 0.01 mg/kg. That limit shall always be expressed as concentration in foods or food simulants. That limit shall apply to a group of compounds, if they are structurally and toxicologically related, in particular isomers or compounds with the same relevant functional group, and shall include possible setoff transfer.
4. The substances not listed in the Union list or provisional list referred to in paragraph 2(b) shall not belong to either of the following categories:
    a. substances classified as “mutagenic”, “carcinogenic” or “toxic to reproduction” in accordance with the criteria set out in sections 3.5, 3.6. and 3.7 of Annex I to Regulation (EC) No 1272/2008 of the European Parliament and the Council 16 December 2008;
    b. substances in nanoform.
5. The final plastic multi-layer material or article shall comply with the specific migration limits set out in Article 11 and the overall migration limit set out in Article 12 of this Regulation.

Article 14: Multi-material Multi-layer Materials and Articles

1. In a multi-material multi-layer material or article, the composition of each plastic layer shall comply with this Regulation.
2. By derogation from paragraph 1, in a multi-material multi-layer material or article a plastic layer which is not in direct contact with food and is separated from the food by a functional barrier, may be manufactured with substances not listed in the Union list or the provisional list.
3. The substances not listed in the Union list or provisional list referred to in paragraph 2 shall not belong to either of the following categories:

   a. substances classified as "mutagenic", "carcinogenic" or "toxic to reproduction" in accordance with the criteria set out in sections 3.5, 3.6. and 3.7 of Annex I to Regulation (EC) No 1272/2008;
   b. substances in nanoform.

4. By derogation from paragraph 1, Articles 11 and 12 of this Regulation do not apply to plastic layers in multi-material multi-layer materials and articles.
5. The plastic layers in a multi-material multilayer material or article shall always comply with the restrictions for vinyl chloride monomer laid down in Annex I to this Regulation.
6. In a multi-material multi-layer material or article, specific and overall migration limits for plastic layers and for the final material or article may be established by national law.

16.6.6 Chapter IV: Declaration of Compliance and Documentation

Article 15: Declaration of Compliance

1. At the marketing stages other than at the retail stage, a written declaration in accordance with Article 16 of Regulation (EC) No 1935/2004 shall be available for plastic materials and articles, products from intermediate stages of their manufacturing as well as for the substances intended for the manufacturing of those materials and articles.
2. The written declaration referred to in paragraph 1 shall be issued by the business operator and shall contain the information laid down in Annex IV.
3. The written declaration shall permit an easy identification of the materials, articles or products from intermediate stages of manufacture or substances for which it is issued. It shall be renewed when substantial changes in the composition or production occur that bring about changes in the migration from the materials or articles or when new scientific data becomes available.

Article 16: Supporting Documents

1. Appropriate documentation to demonstrate that the materials and articles, products from intermediate stages of their manufacturing as well as the substances intended for the manufacturing of those materials and articles comply with the requirements of this Regulation shall be made available by the business operator to the national competent authorities on request.
2. That documentation shall contain the conditions and results of testing, calculations, including modeling, other analysis, and evidence on the safety or reasoning demonstrating compliance. Rules for experimental demonstration of compliance are set out in Chapter V.

16.6.7 Chapter V: Compliance

Article 17: Expression of Migration Test Results

1. To check the compliance, the specific migration values shall be expressed in mg/kg applying the real surface to volume ratio in actual or foreseen use.
2. By derogation from paragraph 1 for:
   a. containers and other articles, containing or intended to contain, less than 500 millilitres or grams or more than 10 litres,
   b. materials and articles for which, due to their form it is impracticable to estimate the relationship between the surface area of such materials or articles and the quantity of food in contact therewith,
   c. sheets and films that are not yet in contact with food,
   d. sheets and films containing less than 500 millilitres or grams or more than 10 litres, the value of migration shall be expressed in mg/kg applying a surface to volume ratio of 6 dm^2 per kg of food. This paragraph does not apply to plastic materials and articles intended to be brought into contact with or already in contact with food for infants and young children, as defined by Directives 2006/141/EC and 2006/125/EC.
3. By derogation from paragraph 1, for caps, gaskets, stoppers and similar sealing articles the specific migration value shall be expressed in:

   a. mg/kg using the actual content of the container for which the closure is intended or in mg/dm^2 applying the total contact surface of sealing article and sealed container if the intended use of the article is known, while taking into account the provisions of paragraph 2;
   b. mg/article if the intended use of the article is unknown.

4. For caps, gaskets, stoppers and similar sealing articles the overall migration value shall be expressed in:
   a. mg/dm^2 applying the total contact surface of sealing article and sealed container if the intended use of the article is known;
   b. mg/article if the intended use of the article is unknown.

Article 18: Rules for Assessing Compliance with Migration Limits

1. For materials and articles already in contact with food verification of compliance with specific migration limits shall be carried out in accordance with the rules set out in Chapter 1 of Annex V.
2. For materials and articles not yet in contact with food verification of compliance with specific migration limits shall be carried out in food or in food simulants set out in Annex III in accordance with the rules set out in Chapter 2, Section 2.1 of Annex V.
3. For materials and articles not yet in contact with food screening of compliance with the specific migration limit can be performed applying screening approaches in accordance with the rules set out in Chapter 2, Section 2.2 of Annex V. If a material or article fails to comply with the migration limits in the screening approach a conclusion of non-compliance has to be confirmed by verification of compliance in accordance with paragraph 2.
4. For materials and articles not yet in contact with food verification of compliance with the overall migration limit shall be carried out in food simulants A, B, C, D1, and D2 as set out in Annex III in accordance with the rules set out in Chapter 3, Section 3.1 of Annex V.
5. For materials and articles not yet in contact with food screening of compliance with the overall migration limit can be performed applying screening approaches in accordance with the rules set out in Chapter 3, Section 3.4 of Annex V. If a material or article fails to comply with the migration limit in the screening approach a conclusion of non-compliance has to be confirmed by verification of compliance in accordance with paragraph 4.
6. The results of specific migration testing obtained in food shall prevail over the results obtained in food simulant. The results of specific migration testing obtained in food simulant shall prevail over the results obtained by screening approaches.
7. Before comparing specific and overall migration test results with the migration limits the correction factors in Chapter 4 of Annex V shall be applied in accordance with the rules set out therein.

Article 19: Assessment of Substances Not Included in the Union List

Compliance with Article 3 of Regulation (EC) No 1935/2004 of substances referred to in Articles 6(1), 6(2), 6(4), 6(5) and 14(2) of this Regulation which are not covered by an inclusion in Annex I to this Regulation shall be assessed in accordance with internationally recognized scientific principles on risk assessment.

16.6.8 Chapter VI: Final Provisions

Article 20: Amendments of EU Acts

The Annex to Council Directive 85/572/EEC is replaced by the following:

"The food simulants to be used for testing migration of constituents of plastic materials and articles intended to come into contact with a single food or specific groups of foods are set out in point 3 of Annex III to Commission Regulation (EU) No 10/2011."

Article 21: Repeal of EU Acts

Directives 80/766/EEC, 81/432/EEC, and 2002/72/EC are hereby repealed with effect from 1 May 2011.

References to the repealed Directives shall be construed as references to this Regulation and shall be read in accordance with the correlation tables in Annex VI.

Article 22: Transitional Provisions

1. Until 31 December 2012 the supporting documents referred to in Article 16 shall be based on the basic rules for overall and specific migration testing set out in the Annex to Directive 82/711/EEC.
2. As from 1 January 2013 the supporting documents referred to in Article 16 for materials, articles and substances placed on the market until 31 December 2015, may be based on:
   a. the rules for migration testing set out in Article 18 of this Regulation; or
   b. the basic rules for overall and specific migration testing set out in the Annex to Directive 82/711/EEC.
3. As from 1 January 2016, the supporting documents referred to in Article 16 shall be based on the rules for migration testing set out in Article 18, without prejudice to paragraph 2 of this Article.
4. Until 31 December 2015 additives used in glass fiber sizing for glass fiber reinforced plastics which are not listed in Annex I have to comply with the risk assessment provisions set out in Article 19.
5. Materials and articles that have been lawfully placed on the market before 1 May 2011 may be placed on the market until 31 December 2012.

Article 23: Entry into Force and Application

This Regulation shall enter into force on the 20th day following its publication in the Official Journal of the European Union. It shall apply from 1 May 2011. The provision of Article 5 as regards the use of additives, others than plasticisers, shall apply for plastic layers or plastic coatings in caps and closures referred to in Article 2(1)(d), as from December 31, 2015. The provision of Article 5 as regards the use of additives used in glass fiber sizing for glass fiber reinforced plastics, shall apply from December 31, 2015. The provisions of Articles 18(2), 18(4) and 20 shall apply from December 31, 2012.

16.7 European Union Legislation for Recycled Plastics

European Commission has promulgated regulations governing the use of used and scrapped plastics. The entire legislation, Commission Regulation (EC) No 282/2008 of 27 March 2008, can be found in the Official Journal of the European Union (27 March 2008).

A helpful questions and answer document published by the Commission accompanies the recycled plastic regulations. The exact document has been provided in Section 16.8.

16.8 Questions and Answers on Recycled Plastics in Food Contact Materials

The European Commission adopted today (27 March 2008) a Regulation on recycled plastic that will ensure that food packaging made of recycled plastics is safe. The Regulation sets the conditions under which the manufacturers of food contact materials can use recycled plastics and promotes the objectives of the strategies on the sustainable use of natural resources and the prevention and recycling of waste. At the same time, the regulation is expected to achieve a high level of consumer protection. Here are some more details about the issue:

Question: What are food contact materials?

Food contact materials are all materials and articles coming into contact with foods. These include packaging materials but also cutlery, dishes, processing machines, containers etc. The term also includes materials and articles, which are in contact with water intended for human consumption but it does not cover fixed public or private water supply equipment.

Question: What has been the legal status for the use of recycled plastic in food contact materials in the EU market?

Recycled plastics in food contact have been covered by the general requirements on food contact materials laid down in Regulation (EC) No 1935/2004. Member States have adopted different national measures for recycled plastics. Some Member States prohibit the use of recycled plastic in food contact, some have established an authorization procedure, others have issued recommendations and there's also a group of EU countries that does not have any national rules in place.

Question: Why is the Commission introducing a Regulation for recycled plastics in food contact?

The main objective of this Regulation is to open a market opportunity for recycling of plastics for food contact. A single market will be created for the use of recycled plastics in food contact by laying down criteria, which ensure the safety of the food contact material without posing unnecessary burdens on the manufacturers and at the same time allowing for a competitive position as compared to virgin plastics and other materials.

Question: What are the main rules for recycled plastics in the Regulation?

The proposed Regulation seeks to create a clear centralized authorization system, which will allow a unified approach for authorization of food contact materials throughout the EU. The European Food Safety Authority (EFSA) will be responsible for carrying out the risk assessment on the processes used for recycling of plastic intended for food contact, while the Commission will manage the dossiers of each applicant, putting forward a proposal for the authorization of recycling processes, which are found to be safe. Individual recycling processes are based on specific know-how and technology, therefore the regulation provides for individual authorizations of each process. The authorization holders are responsible for the process being implemented in all recycling premises according to the authorization that has been granted. They have to notify to Member States the premises that apply in the recycling process. Member States are responsible for the control of the recycling premises in their territory.

Question: What are the requirements for a recycling process to be authorized for use in the manufacture of food contact materials in the EU?

For a recycling process to be authorized it needs to be demonstrated that an adequate control system is in place ensuring that the plastic being recycled originates only from plastic materials and articles that have been manufactured in accordance with Community legislation on plastic food contact materials and articles. It must be demonstrated that the process is able to either reduce any contamination in the plastic from previous use to a concentration that does not pose a risk to human health or to rule out a contamination of the plastic. Furthermore, it needs to be demonstrated that the quality of the recycled plastic is characterized and controlled by a quality assurance system. Authorization will only be granted for those applications for which safe use can be demonstrated.

Question: What are the labeling requirements for the use of recycled plastics?

Labeling of recycled plastics used in food contact is voluntary. However, if a manufacturer wants to label the use of recycled plastics he shall follow the rules of ISO 14021:1999 or equivalent.

Question: Will the legislation affect innovation in the sector?

The aim of the Regulation is to create a level playing field within the EU for virgin and recycled plastics and to encourage innovation in the area of recycled and sustainable packaging.

Question: How will the Regulation affect food contact materials containing recycled plastics from Third Countries?

The Regulation also covers recycled plastics from third countries. Also, these can only be used if the recycling process is authorized. The Commission has to notify about premises in third countries that use the authorized recycling processes. A level playing field is established for products from Third Countries and those originating from within the EU.

Question: Can Member States ban/approve recycled plastics for food contact independently of the EU?

As from the establishment of the first list of authorized recycling processes Member States cannot ban or approve independently of the EU recycled plastics for food contact.

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Appendix: Model of the Sorption of Surrogate Contaminants into Plastic

FDA recommends using the following equation from Crank (1975) to model the sorption, at a fixed temperature, of any substance (including surrogate contaminants) into plastic:

$$\frac{M_t}{M_\infty} = (1+\alpha)\left[1 - \exp\left(\frac{T}{\alpha^2}\right) erfc\left(\frac{T}{\alpha^2}\right)^{1/2}\right] \quad \text{(A.1)}$$

$$T = \frac{Dt}{l^2} \quad \text{(A.2)}$$

In this equation, M_t and M_∞ are, respectively, the sorption (g surrogate/g plastic) at time t and the sorption at equilibrium (or "infinite" time), α is the ratio of the volume of the surrogate solution to the volume of the plastic, D is the diffusion coefficient (cm^2/s) of the surrogate in the plastic at a given temperature, t is the time in seconds, and l is the thickness of the plastic (cm). The full thickness is used for a single-sided experiment (i.e., a plastic bottle filled with surrogate solution) while half the thickness is used for a double-sided experiment (i.e., a plastic strip soaked in a surrogate solution).

In order to solve Eq. (A.1) for M_t, a value for M_∞ is needed. In the absence of experimentally determined values, FDA recommends using the following equation derived from Crank (1975) to calculate M_∞:

$$M_\infty = \frac{a}{w} C_0 \frac{1}{1+\alpha} \quad \text{(A.3)}$$

In equation (3) a is the volume of the surrogate solution (ml), w is the mass of the polymer (g), and C_0 is the starting concentration of the surrogate in the solution (g/ml). FDA's version of this equation differs from Crank's in that the mass of the polymer is included in the denominator to obtain M_∞ in the units g surrogate/g plastic.

The following parameters were used for a typical non-food PET bottle: a 1-liter capacity, a mass of 38.26 g, a density of 1.37 g/cm^3, and a wall thickness of 0.03 cm. The bottle's mass was divided by its density to obtain the volume of PET in contact with the surrogate solution. A 10% w/w concentration of each surrogate in solution was assumed to represent the maximum concentration of any given component of a non-food substance packaged in PET. (A search of a database of ingredients in household products (www.happi.com) shows that liquid detergents, shampoos, and hand cleaners might contain up to 30% long-chain fatty acids; however, these compounds are not expected to sorb into PET to any greater extent than lower molecular weight compounds from 10% solutions.) The densities of the surrogate and the remainder of the surrogate solution (assumed to be 1 g/cm^3) were used to calculate °C. The diffusion coefficients in Table 16A.1 were used for several surrogates in PET.

Table 16A.1 Diffusion Coefficients for Several Surrogates in PET

Surrogate	**D (cm^2/s), 25°C**	**Reference**
Chloroform	9.1×10^{-14}	Calculated with Piringer model (Baner et al., 1996)
Toluene	4.3×10^{-15}	Sadler et al. (1996)
Benzophenone	4.8×10^{-14}	Calculated with Piringer model (Baner et al., 1996)
Lindane	1.6×10^{-14}	Calculated with Piringer model (Baner et al., 1996)
Tetracosane	1×10^{-16}	Sadler et al. (1996)

In order to validate the model, the modeled results were compared with experimental measurements of toluene sorption into a PET strip (i.e., a two-sided experiment) made by Demertzis et al. (1997) after 15 and 40 days at 40°C. Sadler's D value of 3.92×10^{-14} cm^2/s for toluene at 40°C, which has been well characterized, was used in the model (Sadler et al., 1996). Specifications for the PET strip and the surrogate solution as given in the Demertzis article were also used, the results of which are summarized in Table 16A.2.

The excellent agreement of the modeled results with experimental measurements indicates that the model adequately predicts surrogate sorption into PET over time. However, the model tends to overpredict sorption when experimentally determined D

Table 16A.2 Results of Model Validation for Sorption of Toluene

Time (Days) at 40°C	Modeled Toulene Sorption from 16.7% (w/w) Solution	Experimentally Measured Toulene Sorption from 16.7% (w/w) Solution (Demertzis et al., 1997)
15	3.1 mg/dm^2 of PET (750 mg/kg in PET)	3.5 mg/dm^2 of PET
40	5.1 mg/dm^2 of PET (1230 mg/kg in PET)	6.0 mg/dm^2 of PET

Table 16A.3 Modeled Sorption of Surrogates into 1-Liter PET Bottles Filled with 10% w/w Surrogate Solutions After 365 Days at 25°C

Surrogate	Modeled Sorption into PET (mg/kg)
Chloroform	4860
Toluene	1000
Benzophenone	3390
Lindane	1920
Tetracosane	154

or M_∞ values are not available and semi-empirical or theoretical values are used. The Piringer model, an empirical correlation based on the molecular weight of the migrant, was used to calculate D for chloroform, benzophenone, and lindane for input to the sorption model (see Baner et al., 1996). Comparisons of modeled D values with experimental measurements indicate that the Piringer model can overestimate D by several orders of magnitude (Baner et al., 1996). This discrepancy has been attributed to failure of the model to account for partitioning of the migrant between the solvent and polymer phases. Similarly, Eq. (A.3) will generally overpredict M_∞ because it does not take into account partitioning of the migrant between the solvent and polymer phases (Crank, 1975). Because the sorption model depends on D and M_∞, overestimates of these values will result in overestimates of sorption. Modeled results for a typical bottle are given in Table 16A.3.

FDA believes that the modeled sorption value for chloroform is probably reasonable because there is very little partitioning of chloroform between the solvent and polymer phases. However, the measured sorption values for benzophenone and lindane have shown the modeled values to be significant overestimates due to the need to rely on semi-empirical or theoretical D and M_∞ values (Begley et al., 2002).

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