Polymer Blends and Composites

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Polymer Blends and Composites

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Contents

Preface

The emerging area of polymer blends and composites allows choosing a suitable combination of polymers and tailoring them for a desired performance. Although polymer blends and composites are relatively independent, history has shown that the interplay of new methods and ideas results in advancements in the development of new materials via properties and multifunctional approaches.

As part of the significant progress of science, engineering, and technology, it is highly gratifying that polymer blends and composites continue to advance at such a rapid pace. Today, continuously changing environmental aspects and natural resources dictate what is not allowed in the manufacture of new polymeric materials. Hence, blends and composites provide a powerful means of expanding new product development as well as new concepts in applications.

Today's challenge for material scientists is to develop technologies that can produce blends and composite products with extended lifetime, increased safety and perhaps with little or no maintenance. Therefore a technical reference is needed to help address this challenge, with text that provides the necessary value-added information to the reader. Consequently, an important motivation behind this book was to provide information that ultimately leads to advances in blends and composites. This along with the structure-property relationships in blends and composites are presented in order to achieve a new level of understanding of the area, resulting in the synergistic outcome of new materials.

The main objectives of this book are to present state-of-the-art preparation of novel materials, and to discuss their performance and application potentials. The wide scope of material covered provides a high-level of knowledge on polymer blends and composites. At the same time, the book gives young scientists the opportunity to understand areas of blends and composites and to develop professionally as quickly as possible. In addition, this book will encourage scientific and technological investigators to expand their knowledge of commercially relevant blends and composites.

I thank Mrs. Himachala Ganga, Mr. Venkatasubramanian and Mr. Sailesh for providing the encouragement to get the job done and help bring this book to fruition. Special thanks also to Mr. Martin Scrivener, Ms. Jean Markovich and to my professors. Above all, I thank the almighty Nataraja for bringing me into this wonderful earth to complete this work.

Dr. Muralisrinivasan Natamai Subramanian
Madurai
January 1, 2017

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Muralisrinivasan Natamai Subramanian.

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Introduction

Polymers are considered as matrix materials in blends and composites. These polymers, which are a result of the mixing of two or more polymers, enable the production of blends and composites with required properties. As the performance requirements of polymers become more demanding, their physical properties through the use of blends and composites has become increasingly important.

Polymers have recently been used more frequently as blends and composites, resulting in good technological qualities of each of the components. Polymer blend processing has emerged as an inexpensive and versatile route to control the microstructural characteristics of polymers and enhance their properties [1–4].

Polymers are macromolecules and are insoluble material. The physical properties of the material dictate the complex structure of polymer by their ability to establish a structure-property relationship that predicts various physical properties. With the introduction of food packaging, the use of polymers has grown greatly, particularly the use of thermoplastic polymers such as high- and low-density polyethylene (HDPE and LDPE), polypropylene (PP), polyethylene terephtalate (PET), polyvinyl chloride (PVC), and polystyrene (PS). Polymers have been widely used as a route to develop a combination of desired properties by blending or by composites.

1.1 Polymer Blends

Polymer blends have become a broad field that aims to tailor polymer functionality. The blending of polymers is an inexpensive route to the modification of various polymer properties. It is a viable and versatile way to control the performance of polymeric materials with available polymers [5]. There has been a significant increase in the use of polymer blends to obtain new high-performance organic materials without any synthesis, resulting in a new polymeric material. Polymer blends are composed of two or more polymers with or without compatibilizer, depending on the composition and viscoelastic properties of individual components. They have complicated properties which display elasticity and viscosity at different strain rates and temperatures [6, 7].

Polymer blending is a relatively simple process and cheaper than polymer synthesis. The blending of conventional polymers has been extensively employed to develop new polymeric materials. Polymer blends have become a traditional method for producing new, high-performance polymeric materials. Mechanical, optical and electrical properties of polymer blends depend on their morphological characteristics [8]. They are produced in order to achieve improvements in properties such as thermal stability, mechanical properties or chemical resistance [9]. Many important polymer blends are incompatible polymers [4]. Due to its utility and simplicity, blending is currently a feasible method for improving polymer surface properties [10, 11]. Polymer blends and composites improve product performance by combining different polymers with specific properties in order to combine as one material.

1.2 Polymer Composites

Polymer matrix composite is a material with at least two phases, a continuous phase as polymer and a dispersed phase as filler or fiber. The continuous phase is responsible for filling the volume and transferring loads to the dispersed phase. The dispersed phase is responsible for enhancing one or more properties of the composite.

Polymer matrix composites, due to their outstanding mechanical properties, are widely used as special engineering materials in applications for aerospace, automotive and civil engineering structures. Therefore, it is of great interest to have knowledge of the durability of these materials [12, 13]. Polymer composites are controlled by the reinforcing material content present in them. Volume fraction and orientation of reinforcing material decides the properties such as stiffness, strength, thermal conductivity, and other properties of composites. Instead of synthesizing new polymers, composites have several features in comparison with metallic and other products.

Composites have been developed to meet several industrial requirements such as the need for easier processing and broadening of the range of properties, either by varying the type, relative amounts or morphology of each component. These materials can be prepared so as, for example, to combine their high mechanical strength to a better dimensional stability and thermal resistance. Sometimes a higher stiffness is also attained with the use of reinforcing fillers [14–16]. Most of the composites target an enhancement of mechanical properties such as stiffness and strength, but other properties may be of interest such as density, thermal properties, etc.

One of the key parameters in controlling the successful design of polymer matrix composites is the efficient control of the interface between the continuous phase (polymer) and the discontinuous phase (reinforcement). The greatest advantage of composite materials is that they offer the possibility of tailoring their properties by playing with the volume fraction of the discontinuous phase, dimension of the particles (particularly when in fiber form), and their orientation [17].

1.3 Blends and Composites – Advantages

Polymers have been widely used as routes to develop a combination of desired properties by blending or by composites. Polymer blends and composites with useful combinations have increased considerably and rapidly. There has been a long practice of tailoring specific processing and performance requirements which combine both physical and mechanical properties of the existing polymers depending on the composition and level of compatibility of the materials.

Blends and composites are relatively

- Low cost;
- Light weight, thereby easily transported;
- Easy to fabricate using extrusion, injection molding, compression molding, etc.;

- Durable against environmental degradation such as corrosion, rust and higher thermal stresses which are present in metallic products.

Therefore, polymer blends and composites can be converted into products or components. They have thermal-oxidative stability with mechanical properties. Apart from consumer products, polymer blends are widely used in industrial and engineering applications, all over the world [18]. However, their conversion is not easy because most polymers are generally not miscible [19, 20].

1.4 Summary

- Simple blends have poor mechanical properties and unstable morphologies.
- Polymer blends offer attractive opportunities for developing new materials with a useful combination of properties.
- Development of composites for replacement application is particularly demanding from a mechanical, chemical and functional point of view.
- Blends and composites of commercial products are normally much cheaper than the synthesis of a new class of polymers.

References

1. Olabisi, O., Robeson L.M., Shaw M.T., *Polymer-Polymer Miscibility*, Academic Press, New York, 1979.
2. Ehlers, W. and Markert, B., *Int. J. Plast.* 19, 961–976, 2003.
3. Prince, L.M., in: *Microemulsions: Theory and Practice*, Academic Press, New York, 1977.
4. Mansion, J.A. and Sperling, L.H., in: *Polymer Blends and Composites*, 51, Plenum Press, New York, 1970.
5. Vigild, M.E., *et al.*, *Macromolecules* 34, 951, 2001.
6. Haupt, P., Lion, A., and Backhaus, E., *Int. J. Solids Struct.* 37, 3633–3646, 2000.
7. Ehlers, W. and Markert, B., *Int. J. Plast.* 19, 961–976, 2003.
8. Xie, X.-M., Xiao, T.-J., Zhang, Z.-M., and Tanioka, A.J., *Colloid Interface Sci.* 206, 189, 1998.
9. Prince, L.M., in: *Microemulsions: Theory and Practice*, Academic Press, New York, 1977.

10. Xie, X.-M., Xiao, T.-J., Zhang, Z.-M., and Tanioka, A.J., *Colloid Interface Sci.* 206, 189, 1998.
11. Schroeder, K., Klee, D., Hocker, H., Leute, A., Benninghoven, A., and Mittermayer, C.J., *Appl. Polym. Sci.* 58, 699, 1995.
12. Al-Haik, M.S., Garmestani, H., and Savran, A., *Int. J. Plasticity* 20, 1875–1907, 2004.
13. Megnis, M. and Varna, J., *Compos. Sci. Technol.* 63, 19–31, 2003.
14. Saha, S., *Eur. Polym. J.*, 37(2), 399–410, 2001.
15. Ramesh, P., *J. Appl. Polym. Sci.* 50, 1369–1377, 1993.
16. Freire, E., *Polímeros: Ciênc. Tecnol.* 3, 25–26, 1994.
17. Evans, S.L. and Gregson, P.J., *Biomaterials* 19, 1329–1342, 1998.
18. Chen, Z.R. and Kornfield, J.A., *Polymer*, 39, 4679, 1998.
19. Tepe, T., Hajduk, D.A., Hillmyer, M.A., Weimann, P.A., Tirrell, M., Bates, F.S., Almdal, K., and Mortensen, K., *J. Rheol.* 41, 1147, 1997.
20. Wiesner, U., *Macromol. Chem. Phys.* 11, 3319, 1997.

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Polymers

Polymers are materials that are widely used in many important emerging technologies. They have a number of beneficial functions with excellent mechanical properties. Due to their chemical inertness and optical, barrier and mechanical properties, they are suitable for use in a variety of products and have a wide range of applications [1]. Polymers are long-chain molecules with properties different from those of metallic and ceramic materials. They are light, strong, easily molded and durable.

Cost, performance and durability are major product requirements. Therefore, polymers have the advantage of economic cost with great potential for part integration and play a very important role in our lives. Quantities of polymer materials are used in many conventional applications. High production can be achieved with polymers.

2.1 Macromolecules

Polymers are built up by linking together monomers in large numbers. Monomers are molecules with functional groups or elements which react with each other to form large molecules. The degree of polymerization determines the size of a polymer. The polymer size is the total number of structural units which includes the end groups and is also related to both chain length and molecular weight.

Polymers are macromolecules which are constructed by the covalent linking of simple molecular repeated units. The structure is implied in the phrase "poly," meaning many, and "mer," designating the nature of the repeating unit [2–4]. Polymers are modified to provide specific compatibility, durability or properties dictated by their expected use in industry and there has been expanded use of polymer blends and composites in industrial applications. Polymers from synthetic resources are mainly non-biodegradable materials. Polymers, the molecules of plastic, are predominantly derived from fossil-based feedstocks. They are remarkably lightweight, durable, protective, conductive, and self-healing, which are just a few of their many attributes.

Polymers play a vital role in human activities by contributing to the sophistication and comfort of society. They are insoluble materials [5] whose properties are modified by using fillers and fibers to suit the high strength/high modulus requirements.

2.2 Types of Polymers

Polymers are categorized as thermoplastics and thermosets. The category is based on the characteristics of the recycling nature of the end products. Polymers have attracted attention because their physical properties differ from the starting monomer material. Figure 2.1 illustrates thermoplastic polymers versus thermoset polymers.

Basically the difference between thermoplastic and thermoset materials (Table 2.1) is that thermoplastic materials are independent chains which will flow with heat whereas thermoset materials are chemically bonded crosslinked chains which will not flow with heat. Moreover, thermoplastics

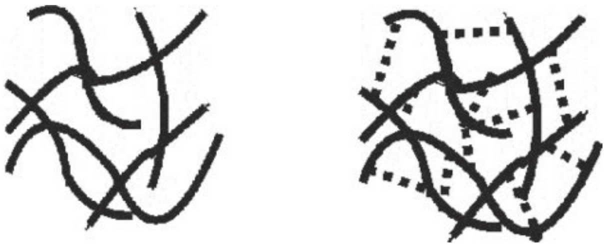


Figure 2.1 Thermoplastic polymers versus thermoset polymers.

Table 2.1 Thermoplastic polymers versus thermoset polymers.

Characteristics	Thermoplastic	Thermoset
Chains	Independent polymer chain	Chemically crosslinked chains
Flow	Will flow with heat	Will not flow with heat
Recycle	Possible	Not possible

are amenable to recycling. Thermosets, on the other hand, cannot be recycled. Thermoplastics can be relatively easy to process. Thermosetting polymers crosslink between separate polymer chains.

End use needs to be considered in terms of processing either thermoplastics or thermosets. Polymeric materials according to blends and composites fall into two categories, namely:

- Thermoplastic polymers – recycling ability
- Thermoset polymers – non-recycling ability but rigid

2.2.1 Thermoplastic Polymers

Thermoplastic polymers are linear chain polymers and are solid at room temperature. They may be melted and softened at an elevated temperature; and may be re-melted several times. They are simple chain which may differ in molecular weight, degree of branching with long or short chain, stereo structure or composition. Molecular weight distribution depends on polymerization kinetics, process conditions and mechanism. The polymerization must be carefully controlled and monitored to obtain the desired characteristics and processing ability.

Thermoplastic invariably requires a much higher processing temperature and has the following advantages:

- It is easy to process – It is highly viscous at its processing temperatures.
- It is less troublesome to recycle – Recycling of thermoplastic involves reversible physical change by heating the polymer above its processing temperature for shaping it and cools it to room temperature to obtain the desired recycled product.
- It is economical to refabricate.
- It even undergoes significant reduction in properties. However, it retains an acceptable fraction of properties from its original material [6].

Thermoplastic polymeric materials are thermal and electrical nonconductors. Thermoplastic polymers are used in a wide range of everyday applications such as in clothing, housing materials, medical applications, appliances, automotive and aerospace parts, and in communications.

2.2.2 Thermoset Polymers

Thermoset is a physical mixture consisting of base resin, reinforcement material, catalysts, colorants and lubricants subjected to a specific combination of heat, pressure and time. It undergoes an irreversible reaction referred to as polymerization. Upon complete polymerization, thermosets become infusible solids and will not soften when heated.

The polymerization of thermoset can be attained either by the initial application of heat or by the use of chemical accelerator. Upon processing and molding, these thermoset polymers become crosslinked and therefore remolding by heating will not be possible. Heating of thermosets in three-dimensional network must be broken either by cleavage of crosslinks or through the carbon-carbon linkage of the chain backbone, and finally into charred product.

In thermoset, polymer involves prepolymer upon curing whose molecules are capable of entering, through reactive groups, into further polymerization, thereby contributing more than one structural unit to at least one type of chain of the final polymer. It is not reliable or possible for recycling due to the crosslinking nature of the polymer.

2.3 Polymerization

Polymerization is the process in which the smaller monomers are linked together to form large molecules called polymers. The molecular weight of the polymer is a simple multiple of the molar mass of the original monomer. Many polymers involve two or more types of monomers, known as copolymerization. Figure 2.2 illustrates the conversion of simple monomer into polymer.

2.4 Polymerization Techniques

Polymers coincide with the molecular long-chain hypothesis, their strategic importance becoming evident during the Second World War through the innovation of artificial rubber. This led to the establishment of highly

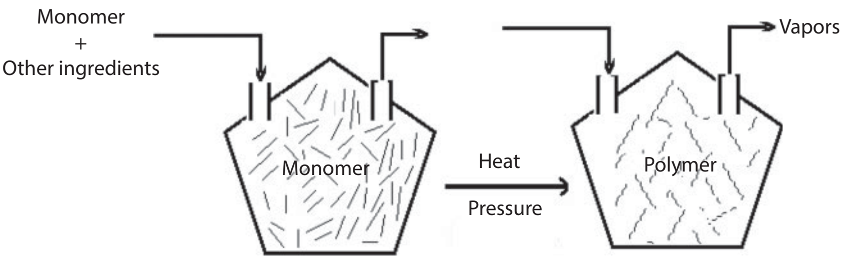


Figure 2.2 Schematic representation of the polymerization process.

productive applied polymer research groups in industry and academia [7]. The first attempt at polymer synthesis with modification was made in the middle of the nineteenth century. It could be said that celluloid was the first synthetic, or at least partly synthetic, plastic [8].

Polymerization techniques have been used to synthesize polymer at a large scale for commercial applications. Polymerization processes, such as bulk, suspension, solution and emulsion techniques, are used for conversion of monomers to polymers. Polymerization charge normally consists of monomer, monomer-soluble initiator, and a chain-transfer agent. Monomers combine in the field of polymerization, which allows accessing many advanced technical polymers.

The simplest direct method is bulk polymerization. The heat of reaction is very high, making it difficult to control polymerization, and normally high molecular weight polymer is formed. Heat transfer problems due to reactions are commonly encountered with bulk polymerization. It is also known as mass polymerization [9].

In suspension polymerization, the monomer in droplets is suspended in an inert, non-solvent liquid (almost water). Monomers used in suspension polymerization often have considerably different water solubilities. Relatively nonpolar monomers, such as styrene and butyl acrylate, tend not to be water insoluble, while polar monomers, such as vinyl acetate and methyl acrylate, are highly water soluble. Heat removal is facilitated by keeping the dimension of the reaction mass small. Heat can easily be soaked up by removal from the low-viscosity and inert suspension medium. Particle size, suspending agents, and agitation generally do not affect polymerization rate in batch polymerization [10, 11]. Suspension polymerization produces polymers, such as polyvinylchloride (PVC), in the form of powder with a complex morphology. The properties of the products depend on the composition of the PVC compound and on its processing conditions.

Suspension polymerization describes the process in which monomer(s) is relatively insoluble in water. With steric stabilizer, water is dispersed as liquid droplets with monomer(s). Vigorous stirring is maintained during polymerization to produce polymer particles as a dispersed solid phase. Initiators soluble in the liquid monomer are employed in this polymerization process. Pearl and bead polymerization are also used for the suspension polymerization process when particle porosity is not required.

The major aim is the formation of dispersion of monomer droplets as uniform as possible in aqueous phase with controlled coalescence of these droplets during polymerization. Interfacial tension, degree of agitation, and design of stirrer/reactor system govern the dispersion of monomer droplets. Many important commercial suspension polymers yield beads of relatively large particles. These particles are simply isolated by filtration and/or sedimentation [12].

The advantages that suspension polymerization has over other polymerization processes (bulk, solution and emulsion) is easy heat removal, low levels of impurities in the polymer product (compared with emulsion) and a final product in particle form. Important commercial polymers that are manufactured by suspension polymerization include polystyrene, styrene-acrylonitrile, poly(acrylonitrile-butadiene-styrene), poly(methylmethacrylate) and copolymers, poly(vinylacetate) and poly(vinylchloride) and copolymers [9].

Suspension polymerization is carried out in a batch reactor at constant temperature. The reaction is an exothermic polymerization reaction. Therefore, heat removal produced by the reaction is necessary. In large commercial polymerization reactors, the heat transfer area has a cooling jacket for heat removal. Poly(vinyl chloride) (PVC) is one of the major polymers that is commercially produced by suspension polymerization. The PVC particle properties, such as the particle size, porosity, and molecular weight of the polymer, and end-use properties are controlled by the temperature and heat transfer from the reactor.

Emulsion polymerization differs from suspension polymerization in two important respects. It produces higher molecular weight polymers at higher rates than bulk or suspension systems. The polymer particles produced are typically smaller than those from suspension polymerization.

Emulsion polymerization is a multiplicity of phases which vary widely in methods of chain initiation and termination in different systems. In this process, the continuous phase is aqueous and usually a water-soluble emulsifying agent is present. Considered in the process are:

- Nature of emulsifying agent, i.e., whether or not solubilizing micelles are present;
- Generation of initiating free radicals;
- Nature of chain transfer agent.

Based on the emulsifying agent and free radical initiation, the predominant locus of the polymerization may be in the micelles in true water solution (hydrogen peroxide ferrous ion catalyzed polymerization of acrylonitrile) or in the monomer phase (benzoyl peroxide catalyzed polymerization of methylmethacrylate in the absence of solubilizing micelles).

The emulsifiers mostly used are fatty acid soaps, fatty alcohol sulfates, and aliphatic sulfonates and aromatic alkylated sulfonates. Emulsion polymerization depends on the chain initiating and terminating factors. The oil and water solubilities of initiator and terminator ingredients are important in determining the polymerization point and molecular weight of the polymer.

Emulsion polymerizations occur in three stages and are composed of more than one phase. The monomer droplets act as monomer reservoir and the aqueous phase can act as a locus of polymerization as well as a species transport medium, and the polymer particle phase, the main locus of polymerization. Emulsion polymerization can occur by either micellar or homogenous nucleation. In the second stage, polymerization involves growth of the particles until the monomer droplets disappear. The third stage begins with the disappearance of monomer droplets and continues until the end of the reaction.

The polymer particles themselves, which contain dissolved monomer, become an important point for polymerizations initiating in micelles or aqueous solution. Even the oil-water interface may be a point for generating initiation free radicals and therefore should be considered for chain growth [13, 14].

Emulsion polymerization can be briefly described as follows:

- Initiation can be accomplished via a redox mechanism or via thermal decomposition of an initiator.
- The fate of radicals (initiator, monomeric, and oligomeric) in the water phase is propagation with dissolved monomers in the water phase, reaction with water-soluble impurities (WSI), termination in the water phase, possible recombination of initiator fragments, reaction with monomer droplets, desorption from polymer particles, reabsorption of desorbed radicals into polymer particles, capture by emulsifier micelles, and capture by polymer particles.
- The birth of particles can be accomplished by homogeneous (aqueous phase) nucleation, micellar nucleation, and particle coalescence. Once captured by particles (or micelles or droplets), the radicals may propagate, mutually terminate, react with monomer-soluble impurities (MSI), react

> with chain-transfer agent (CTA), undergo chain transfer to monomer, undergo chain transfer to polymer, and participate in internal and terminal double-bond polymerizations. The average number of radicals per particle is followed by accounting for entry/absorption of radicals from the water phase, radical-radical termination, radical-MSI termination, and desorption of radicals into the water phase. The partitioning of monomer, monomer-soluble impurities, and CTA into the various phases is another important factor.

All of the reaction steps in bulk, suspension and solution polymerizations proceed in a single phase. A reactor carrying out such polymerization would consist of a set of material balances giving rates of accumulation, inflow, outflow, and disappearance by reaction of various monomers, initiators, polymers, and other ingredients. Polymerization consisting of initiation, propagation, termination and chain transfer reactions occurs simultaneously through the full conversion range. It involves nucleation of polymer particles.

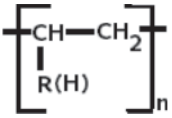
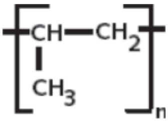
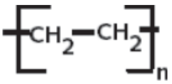
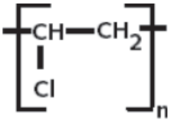
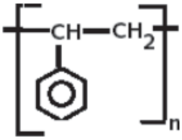
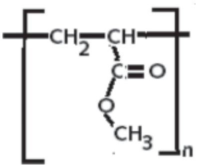
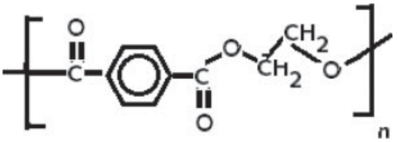
Solution polymerization alleviates many difficulties encountered in bulk polymerization. It reduces the tendency of auto acceleration. Also, the inert diluent adds its heat capacity without contributing to the evolution of heat. It also minimizes the viscosity of the reaction mass at any given conversion. The heat of polymerization may be conveniently removed by refluxing the solvent.

2.5 Synthetic Polymers

The term “synthetic polymer” is often associated with perdurability. However, there are cases where the polymer shows chemical and/or physical changes. These changes affect the initial characteristics and sustainability of the material in the long run [8, 9, 15]. Table 2.2 illustrates some of the polymers and their structures. There have been volumes of a series of commodity polymers, ranging from polyolefins to polyesters, commercialized for areas of technical development. Polymers with a highly commercial impact are limited not by component or system concepts but by the non-availability of reproducible, cost-effective materials to reduce the existing practices. They require high specific properties, reliability, good environmental and abuse resistance, high rate and economic fabrication cycles.

The advent of polymer blends and composites and their growth has been based on the ability to devise new materials. These materials offer the

Table 2.2 Some of the polymers and their structures.

Names	Structure	Names	Structure
Polyolefins		Polypropylene (PP)	
Polyethylene (PE)		Polyvinylchloride	
Polystyrene (PS)		Polymethylmethacrylate (PMMA)	
Polyethylene terephalate (PET)			

design advantages of light weight, corrosion resistance, abrasive resistance and a myriad of specific effects, which, allied to processing routes, allow finished component costs to be competitive based on the combined effects of material properties, costs, fabrication, elimination of assembly and finishing operations.

The two major classifications of the plastics industry are clearly thermoplastic and thermosetting polymers, and while it is natural to think of these simply in terms of their processing techniques, their use as blend and composite matrices has been equally dictated by fundamental polymer characteristics.

2.5.1 Thermoplastics

Thermoplastics have increasingly replaced wood, metal and glass due to their advantages of toughness, light weight, corrosion resistance, and easy processing. They aid in the manufacture of articles with various colors, complicated shapes and designs [16]. They are flexible and less susceptible to breakage, transparent and show acceptable mechanical, thermal, chemical and optical properties.

Thermoplastics exhibit a difference balance of properties and show a high level of toughness with useful stiffness. Thermoplastics coupled with the completion of rigorous chemistry at the polymer manufacturing stage and the characteristic ability to melt and reform, has led to the use of this class of polymer in high productivity molding applications. These van der Waals solids are formed of long, strong and highly flexible chains and have strength and toughness. This geometry and the associated important elastic anisotropy of intra- and intermolecular forces are at the origin of the unique visco-elastic and rubber-elastic response of polymeric materials [17, 18].

2.5.2 Polyolefins

Polyolefins are the most widely used low-cost, easy-to-process general polymeric materials. They have low polarity and low surface energy, which is a benefit for electric applications, packaging materials, and so on [18, 19]. Polyolefins are not inherently biodegradable [20].

Polyolefins are common polymer materials used in a wide range of applications because of their combination of adequate physical properties, low cost and simple processing [21]. They are a class of hydrophobic and inert polymer, and the compatibility between them and polar materials (such as inorganic fillers) is poor. Their compatibility is enhanced by inorganic fillers or engineering polymers.

Polyolefins are "mature" products. Polymerization is quickly progressing, and industrial production continues to grow exponentially. This has less to do with the opening of new markets than with the fact that polyolefins are taking over other large volume materials. They have led to precisely designed chain microstructures, and to polyolefin-based materials with better and fine-tuned physical and mechanical properties [22]. Thus, stiffened and toughened polyolefin materials are obtained. The life cycle of polyolefin materials is illustrated in Figure 2.3.

In thermoplastics, interbonds are hydrogen bonds. Stiffness is relatively low due to chains which are not aligned and more likely to act as a stiff hinge. Huge stress causes them to yield and yield will be limited at a certain point during their stress.

2.5.3 Polyethylene (PE)

Polyethylene (PE) is one of the most important commercial polyolefins. It is a versatile polymer with molecular weight ranging from low to very high. There are four established methods for producing polyethylene: gas phase,

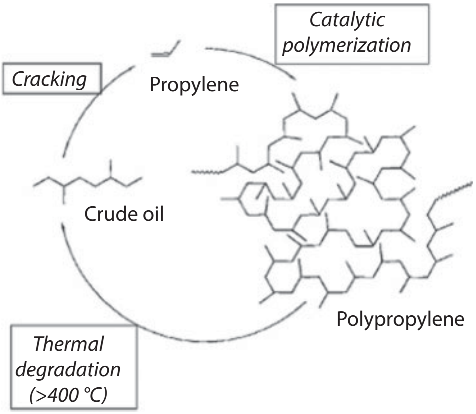


Figure 2.3 Life cycle of polyolefin materials. (Reprinted with permission from [23]; Copyright © 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. All rights reserved)

solution process, slurry emulsion technique and a high pressure method. Polyethylene is a simple hydrocarbon with repeating units of -[CH_2-CH_2]-.

Ethylene homopolymer has been manufactured with highly exothermic free-radical polymerization systems under high pressure, utilizing either tubular reactors or stirred autoclaves. In the tubular process, oxygen is primarily used as the initiator, whereas peroxides are added in the autoclave process. Amorphous polyethylene has a branched molecular structure and is characterized by low density (0.92–0.94 g/cm^3). Its branches prevent close packing of the main chains and the formation of crystallites.

Polyethylene is one of the most industrially relevant of the polyolefins, but because of its nonpolar nature, it finds limited use in emerging technologies. Polyethylene is relatively soft and its hardness increases as density increases. The chain configuration of polyethylene is shown in Figure 2.4. It has poor compatibility and adherence with other materials.

Polyethylene is available in four main classifications, namely low, medium, high and ultra-high, based on the density: low-density polyethylene (LDPE), high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), and polypropylene (PP) [24]. These are further categorized as linear or ultra-high molecular weights based on the requirement in the markets.

2.5.3.1 Physical Properties

Polyethylene is one of the most widely used polymer materials. Polyethylene has high toughness, and ductility. It also has high impact strength and flexibility with low cost. These combined properties make PE one of the highest

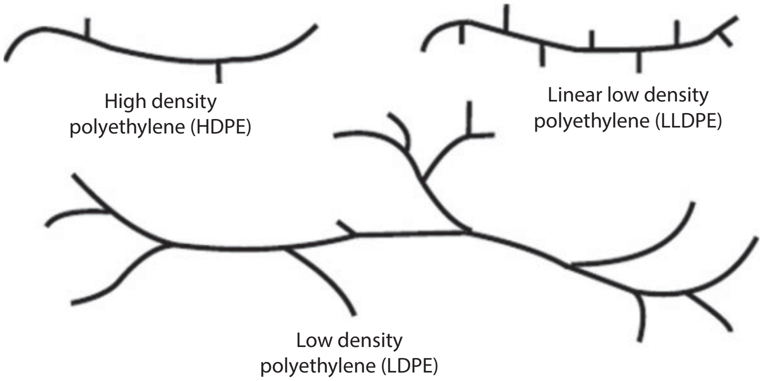


Figure 2.4 Chain configuration of different polyethylenes.

volume polymers in the world. Polyethylene is a microcrystalline polymer containing some amorphous material of smilar composition. Mechanical properties resemble that of nylon. Microcrystalline condition is strongly enhanced by temperature and persistence of crystalline structure up to about 113 °C. It is an important factor in the changes in certain physical properties with temperature.

Material reaches from crystalline to amorphous condition when heating from room temperature. Rate of change in certain properties with temperature also takes place while heating. Stiffness of polyethylene varies with temperature. The heat distortion temperature is indicative of the ability to withstand normal service temperatures under low load, and the low value for deformation under load is exceptionally good for a polymer which is not rigid. The toughness of polythene at low temperatures is unusual for a material of its stiffness. The brittleness temperature of polythene is consistently below −50 °C.

Polyethylene is semicrystalline with a melting temperature of approximately 130 °C and volume crystallinity X = 0.4–0.8 depending on the chain perfection. The crystals are flat lamellae embedded in amorphous phases forming stacks at higher crystallinities [25]. The origin of dielectric loss in PE is dipolar impurities, end groups, chain folds and branch points. The lower the concentration of these groups, the lower will be the dielectric loss. The surface of PE is chemically inert in nature. With low surface energy, PE is restricted to many practical applications [26, 27].

2.5.3.2 Chemical Properties

Polyethylene has good properties such as high chemical resistance due to its hydrophobic nature, excellent chemical resistance and low water vapor permeability. It is unusual in its insolubility and inertness to chemical reagents. Certain aliphatic and aromatic hydrocarbons have a more pronounced effect. For example, gasoline, lubricating oil, carbon tetrachloride, and trichlorobenzene show definite swelling action. The low moisture permeability and good water resistance indicate its suitability for the coating of cloth, paper, wood, brick, and concrete, for the fabrication of containers (for milk and other liquids), and for packaging in general. For packaging purposes the plastic can be employed either as sheeting or an impregnate for paper.

2.5.3.3 Low-Density Polyethylene (LDPE)

Low-density polyethylene (LDPE) was first produced [28, 29] which is highly branched form. LDPE is easier to process in terms of the amount of energy or power needed to fabricate articles and in many applications such as film blowing [30–32]. LDPE contains short-chain propyl- and butyl-branches as well as a few long-chain branches. However, LDPE has a large share of the market due to its great processing capability. Table 2.3 illustrates some of the properties of LDPE.

Low-density polyethylene (LDPE) is a commodity polymer used extensively in extrusion operations such as coating, blown film, blow molding, and foaming. Extrusion coating with polyethylene has been widely used commercially on substrates such as paper, other plastic films, cloth, and glass fiber. The advantages of coating with polyethylene include increased tear and crease resistance; a good barrier against moisture, grease, and oil; flexibility; nontoxicity; and low coating cost.

Table 2.3 Properties of low-density polyethylene (LDPE).

Properties	**Value**	**Unit**
Density	0.91–0.93	g/cm^3
Melt temperature (T_m)	115	°C
Glass transition temperature (T_g)	about –25	°C
Thermal conductivity	0.35	Wm^{-1}K^{-1}
Water absorption at saturation	<0.01	%
Elongation	50–800	%
Elastic modulus	0.1–0.3	GPa
Critical strain energy rate (G_c)	34	kJ/m^2
Heat of combustion	about 46.5	kJ g^{-1}
Thermal linear expansivity	5–25	10^{-5} K^{-1}

An important weight percentage of the polyolefins found in waste streams is represented by LDPE. However, this polymer alone is not really interesting for particular applications because it exhibits average mechanical properties, which are, moreover, influenced by the aging of the product. More frequently, LDPE wastes come from bags and pallet covers, and they are recycled as garbage bags, which limits its application. New outlets for these kinds of LDPE wastes can be developed if their low mechanical properties can be improved by adding other materials [33–35].

2.5.3.4 Linear Low-Density Polyethylene (LLDPE)

Linear low-density polyethylene (LLDPE) has commercial interest due to its superior mechanical strength compared to low-density polyethylene (LDPE) and high-density polyethylene (HDPE) [36]. It is used to manufacture film due the combination of processability, good mechanical properties and environmental stress cracking resistance [37–40].

LLDPE as an excellent material and contains short side chains. Addition of short-chain branches confers modification of polymer structure with specific properties to the resulting material. LLDPE resulting from polymerization contains only short-chain branches. However, LDPE contains both short- and long-chain branches. Typically LLDPEs have bivariate distributions. They are polydisperse in both molecular weight and comonomer content, i.e., branch content [41–45].

The physical properties of LLDPE (Table 2.4) lie between those of LDPE and HDPE and it is generally not used by itself but is compounded with LDPE high-pressure material. The molecular structures of LDPE and LLDPE differ in that LDPE has fewer but longer and widely branched side chains while LLDPE has more short side chains with no further branching.

Copolymerization of ethylene with a higher α-olefin, such as 1-butene, 1-hexene, 1-octene, or 4-methyl-1-pentene, produces LLDPE. The polymerization reaction takes place in the gas phase or in solution in

Table 2.4 Properties of linear low-density polyethylene (LLDPE).

Properties	**Value**	**Unit**
Density	0.91–0.94	g/cm^3
Glass Transition temperature (T_g)	about –25	°C
Water absorption at saturation	<0.01	%
Elastic modulus	0.05–0.1	GPa
Heat of combustion	about 46.5	$kJ\ g^{-1}$

the presence of a catalyst. Ziegler-Natta catalyst is commonly employed in the manufacture having more than one active site. This catalyst gives rise to a broad, often multimodal short-chain branching distribution [46]. However, LLDPE synthesized in the presence of Ziegler-Natta catalyst can be regarded as a blend of species differing from a number of short-chain branches on the polymer backbone.

2.5.3.5 High-Density Polyethylene (HDPE)

High-density polyethylene (HDPE) is an important polymer with high tonnage production due to its superior mechanical and physical properties shown in Table 2.5. However, its toughness, weather resistance, processability and environmental stress cracking resistance are not good enough, which have limited its application in many high-tech fields. One measure to improve the properties is to reinforce with some fillers to form a composite [47–52]. HDPE is one of the most commonly used polyolefins with a wide range of properties such as low density, good chemical resistance, good processability, toughness, flexibility, and low cost [53]. It is a versatile polymer of significance in the material substitution chain because of its low cost, availability, recyclability, and ease of processing. HDPE has a strong dependence on temperature, shear rate, molecular weight and molecular weight distribution. Properties such as environmental stress crack resistance (ESCR) and optics tend to be application-specific measures. Therefore, it is also applied in the frame construction of submerged cages in the sea [54, 55]. The thermal degradation problem is of great importance throughout PE processing

Table 2.5 Properties of high-density polyethylene (HDPE).

Properties	**Value**	**Unit**
Density	0.96–0.97	g/cm^3
Melt temperature (T_m)	137	°C
Glass transition temperature (T_g)	about −25	°C
Thermal conductivity	0.44	Wm^{-1}K^{-1}
Water absorption at saturation	<0.01	%
Elongation	15–130	%
Elastic modulus	0.4–0.7	GPa
Critical strain energy rate (G_c)	3.1	kJ/m^2
Heat of combustion	about 46.5	kJ g^{-1}
Thermal linear expansivity	13–20	10–5 K^{-1}

and usage [56–60]. Therefore, its use is restricted in many applications also because of its lower strength, photodegradation, and so on [61, 62].

High-density polyethylene requires enhancement of modulus and strength without loss of toughness. Toughness is generally related to energy dissipating events that occur in the vicinity of a sharp crack. Inorganic fillers and fibers can significantly increase modulus and yield strength through reinforcement [63–68].

2.5.3.6 Ultra-High Molecular Weight Polyethylene (UHMWPE)

Ultra-high molecular weight polyethylene (UHMWPE) is a group of PE that is composed of extremely long backbone chains forming entanglements. It acts as molecular defects and pseudo-crosslinks giving excellent toughness. Entanglements are believed to be the reason for its wear resistance and toughness. The material of choice for fabricating bearing surface is in various anthroplasties. The components have performed well in clinical use. However, there is concern about wear and the effect of wear particles on the longevity of the prosthesis.

2.5.4 Polypropylene (PP)

Polypropylene is a semicrystalline polymer. It shows many good properties such as excellent chemical and thermal resistance, high melting point, stiffness, chemical inertness and low density. Polypropylene has many desirable and beneficial properties such as a high melting point, a high tensile modulus, low density, excellent chemical resistance, and easy recyclability [69].

Polypropylene offers a very attractive combination of physical and mechanical properties at a relatively low cost with continuously increasing applications. Some of the characteristics of this material are suitable for common service conditions. Due to its high transition temperature and high crystallinity, PP exhibits poor low temperature impact resistance [69, 70].

Polypropylene forms very poor blends with other polymers. It has no chemical functionalities. Polypropylene is one of the most important commercial polymers, as shown in Table 2.6. It is a highly versatile material with an outstanding combination of cost performance and excellent physical properties. The property range of PP can be broadened by physically blending it with other polymers. It has a hydrophobic, low-free-energy, chemically inert surface. Polypropylene shows brittleness, low mechanical performance and low impact resistance at below or around glass transition temperature. It exhibits poor low-temperature, impact resistance because of its high transition temperature and high crystallinity [70, 71].

Table 2.6 Properties of polypropylene (PP).

Properties	Value	Unit
Density	0.90	g/cm^3
Melt temperature (T_m)	168–172	°C
Glass transition temperature (T_g)	−16	°C
Elongation	10–700	%
Heat of combustion	46.0	$kJ\ g^{-1}$
Thermal linear expansivity	6–10	$10^{-5}\ K^{-1}$
Specific heat capacity	1.93	$kJ\ kg^{-1}K^{-1}$
Solid heat capacity (Cp)	2.81	kJ/kg °C
Thermal conductivity	0.24	$Wm^{-1}K^{-1}$

Table 2.7 Properties of polyvinylchloride (PVC).

Properties	Value	Unit
Density	1.37–1.39	g/cm^3
Surface resistivity	10^{13}–10^{16}	$\Omega\ sq^{-1}$
Elongation	2–100	%
Heat of combustion	19.9	$kJ\ g^{-1}$
Thermal linear expansivity	5–25	$10^{-5}\ K^{-1}$
Critical strain energy rate (G_c)	1.4	kJ/m2
Specific heat capacity	1.05	$kJ\ kg^{-1}K^{-1}$
Thermal conductivity	0.15–0.16	$Wm^{-1}K^{-1}$
Elastic modulus	2.6–3.0	GPa

2.5.5 Polyvinylchloride (PVC)

Polyvinylchloride (PVC) is one of the most widely used polymers with properties as given in Table 2.7. This polymer is essentially linear, but a low number of short-chain branches may exist. PVC is a member of vinyl polymers and has the vinyl group (CH_2=CH-). The formula of the PVC's repeating unit is represented as $[CH_2CHCl]_n$. As a result of the removal of hydrogen chloride from the chain, PVC is self-extinguishing. Hence it has application in the field of wires and cables. It has excellent resistance to acids, bases, alcohol, oils and many other hydrocarbons. Therefore it finds application in chemical processing industries.

The thermal history must be carefully controlled to avoid decomposition. Thermal stabilizers are often added at addition cost to process PVC. However, PVC is thermally sensitive during processing. There are two basic forms of PVC, namely rigid and soft plasticized PVC. Rigid PVC exhibits high rigidity. PVC is modified with addition of low molecular weight plasticizers to soften and yield rubbery behavior.

Due to its low thermal stability, poly(vinyl chloride), commonly known as PVC, requires heat stabilizer along with lubricant and other additives to enhance the product physical and chemical properties [72].

Additives used in PVC are mainly plasticizers, stabilizers, lubricants, and fillers. Some of the additives can migrate to the surface during use. Stabilizers in PVC have a low mobility and can change their function by consumption or degradation. Usually fillers remain in their initial form and quantity [73]. With its inherent flame resistance, low cost and desirable physical and mechanical properties, PVC finds widespread use in these applications.

2.5.5.1 Rigid PVC

Polyvinylchloride (PVC) is linear and thermoplastic in nature. It is a substantially amorphous polymer that has huge commercial interest due to its properties [74]. Rigid PVC has been widely used in construction, transportation, and many other industries due to its high stiffness, flame retardancy, chemical resistance and low cost [75]. However, the disadvantages of rigid PVC, such as low notch impact strength and low heat resistance, have restricted its application. The characteristics of PVC are good strength, excellent weathering and chemical resistance, and excellent electrical insulation properties [76].

2.5.6 Polystyrene (PS)

Polystyrene (PS) is a rigid, amorphous polymer that is resistant to acids and bases and has the properties mentioned in Table 2.8. It can be processed at its glass transition temperature ($T_g \approx 100$ °C, with the exception of PS prepared by coordination polymerization) and is a good electrical insulator. It is a relatively low-cost thermoplastic material, having some excellent properties, and has a prominent limitation in its brittleness. For PS, stress increases with strain. The ultimate strain does not exceed a few percent, and PS undergoes brittle fracture. For PS, the impact strength is one of the most important mechanical characteristics. It can be improved by blending and has a low softening temperature. Polystyrene is widely used in packaging and building materials and for electrical and thermal insulation.

Table 2.8 Properties of polystyrene (PS).

Properties	Value	Unit
Density	1.05	g/cm^3
Glass transition temperature (T_g)	95–100	°C
Solid heat capacity (Cp)	1.43	kJ/kg °C
Heat of combustion	42.2	kJ g^{-1}
Thermal linear expansivity	6–8	10^{-5} K^{-1}
Specific heat capacity	1.2	kJ kg^{-1}K^{-1}
Thermal conductivity	0.16	Wm^{-1}K^{-1}
Elastic modulus	1.6–3.3	GPa
Critical strain energy rate (G_c)	0.6–0.8	kJ/m^2

2.5.7 Polyethylene Terephthalate (PET)

Poly(ethylene terephthalate) (PET) is a commercial polymer widely available and used in fiber and film. Both forms of PET are highly crystalline but crystallinity is induced by crystallization from the glassy state. It is further complicated by molecular and crystallite orientation. Although PET is a most important polymer with good mechanical and thermal properties, because of its high crystallinity and poor water absorptivity, it has a low electrical conductivity [77, 78]. It is widely used in various fields such as packaging materials, electrical and electronic parts, and automotive components because of its good mechanical and thermal properties. PET is inherently an electrical insulator [79].

Polyethylene terephthalate has good toughness and fatigue resistance at elevated temperatures. The fact that it can be (and is being) recycled is an advantage. However, its intrinsic low surface energy results in poor adhesion, wettability, and biocompatibility, making it an ideal candidate for chemical surface modification.

Although the main application of PET by far is in the textile industry, tremendous quantities of this material are consumed in the manufacture of DVDs, food packaging, and especially soft-drink bottles. It finds widespread uses in other engineering components. Because of its high melting temperature (T_m) and glass transition temperature (T_g), and in particular its moderate crystallization rate, a great variety of microstructures can be easily developed. Size, shape, and perfection of crystallites, volume fractions of different phases, and orientation of molecular chains all can be varied by changing process conditions of PET. Many researchers have investigated its crystalline phase, but less attention has been paid to its amorphous phase

Table 2.9 Properties of polyethylene terephthalate (PET).

Properties	**Value**	**Unit**
Density	1.34–1.39	g/cm^3
Melt temperature (T_m)	255	°C
Glass transition temperature (T_g)	75–80	°C
Crystalline melting temperature	270	°C
Heat of combustion	21.6	kJ g^{-1}
Thermal linear expansivity	10	10^{-5} K^{-1}
Specific heat capacity	1.01	kJ kg^{-1}K^{-1}
Thermal conductivity	0.14	Wm^{-1}K^{-1}
Elastic modulus	2.6–3.0	GPa
Elongation	50–300	%
Surface resistivity	1015–1016	Ω sq^{-1}

and many aspects have not yet been fully clarified [78, 80–83]. At temperatures below but close to the T_g, amorphous polymers are in thermodynamic nonequilibrium. Their physical properties, such as specific volume, enthalpy, and entropy, are greater than the equilibrium values.

Various industrial fields, such as bottles and moldings, also use PET. In the case of application as moldings, PET has the disadvantage of having a slow crystallization rate, which is sometimes controlled by the addition of crystal nucleation agents and/or plasticizers [84–86]. The crystallizability usually decreases with an increase in the irregularity of the molecular structure.

Poly(ethy1ene terephthalate) is a semicrystalline polymer with a T_g of 75 °C and a melting point of ca. 250 °C. Although PET has been a very important and versatile engineering polymer with properties as shown in Table 2.9, its relatively low T_g is a potential disadvantage. This may result in a significant decrease in modulus at temperatures between T_g and T_m, which limits its use in some applications. In addition, the fast crystallization kinetics is also a negative factor in such a process as PET bottle production [87].

2.6 Engineering Polymers

Engineering polymers consist of flexible chains with definite limits on their mechanical performance. They can improve the thermal and mechanical properties of the blend. Engineering polymers have bulk properties such as thermal stability, mechanical strength or solvent resistance. Toughness is a key parameter that determines whether a polymer can be used as an engineering material [88]. Engineering polymers are most frequently acrylonitrile-butadiene-styrene, polyamides, polycarbonate, and poly(methylmethacrylate), to name just a few.

For most engineering applications, polymers are considered to be competitive primarily with metals. Polymers have certain properties which are generally considered to be advantageous for engineering applications. They have better chemical and moisture resistance and are more resistant to shock and vibration than metals, and are also lighter in weight and usually either transparent or at least translucent in thin sections. They have the advantage of absorbing sound and vibration and some possess greater wear and abrasion resistance than metals. The use of polymeric materials has expanded from aerospace applications to consumer product industries. Many consumer products must be produced in large volume and at relatively low unit costs. The polymeric properties, such as stiffness and strength, and therefore the performance of the end products, are variable properties.

2.6.1 Acrylonitrile-Butadiene-Styrene (ABS)

Acrylonitrile-Butadiene-Styrene (ABS) is comprised of particulate rubber, usually polybutadiene or a butadiene copolymer, dispersed in a thermoplastic matrix of styrene and acrylonitrile copolymer (SAN). This is due to their attractive mechanical properties and convenient processing conditions. ABS ranks second only to nylon in their importance as engineering polymers [89, 90]. The polymers consist of an elastomeric component, usually butadiene, dispersed in a copolymer of styrene and acrylonitrile.

Because of their good balance of properties, ABS materials are used from the appliance to the car industries. These materials represent a valuable compromise in mechanical, aesthetic and processing properties. ABS is formed by a matrix of random SAN copolymer in which approximately spherical rubbery particles of polybutadiene are dispersed. The adhesion between the matrix and the second phase is provided by some graft SAN-PB copolymer at the interfaces. The presence of rubbery particles is the reason for the improved toughness of ABS. In fact, SAN is a quite brittle material [91].

The ABS terpolymers of commercial interest contain 15 to 35 wt% acrylonitrile and 10–40 wt% butadiene [92]. ABS polymers are based on three monomers: acrylonitrile, butadiene and styrene. High impact resistance, good dimensional stability, and good processability have made ABS terpolymers the material of choice in many engineering thermoplastic applications, particularly in the automotive industry and in electric

Table 2.10 Properties of acrylonitrile-styrene-butadiene (ABS).

Properties	Value	Unit
Density	1.04–1.07	
Heat deflection temperature	70–110	°C
Vicat softening temperature	85–125	°C
Rockwell hardness	80–115	
Melt temperature	218–268	°C
Elastic modulus	1.6–2.2	GPa
Critical strain energy rate (G_c)	47	kJ/m^2

household appliances. Specific processability properties are often required. Rheological properties of the viscoelastic behavior of ABS in the molten state are related to the fundamental principles which govern processability [93–99]. Because of its good balance of properties, toughness/strength/temperature resistance coupled with its ease of molding and high quality surface finish, ABS has a very wide range of applications. These include electrical and electronic equipment (EEE), as well as widespread applications in communication instruments and other commodities.

Acrylonitrile-butadiene-styrene has excellent low temperature impact strength and is very easy to process. The major disadvantage of ABS is its extremely poor solvent resistance, which tends to prohibit its application in areas involving contact with organic solvents. ABS is used for producing products that exhibit excellent toughness, good dimensional stability, and good chemical resistance.

Owing to its good mechanical and processing properties shown in Table 2.10, ABS copolymer is an engineering polymer that is widely used in industry. ABS is usually filled with rigid inorganic fillers, such as calcium carbonate ($CaCO_3$), talcum powder, kaolin and glass beads, in order to enhance its strength and stiffness and reduce the production cost. On the other hand, the rheological property is an important characteristic of material processability [100–102].

2.6.2 Polyamide (PA)

Polyamide (PA) is a large-volume commercial polymer with properties as shown in Table 2.11. Amorphous polyamides can possess a wide range of good mechanical properties, including high tensile and impact strength and high specific modulus, which are desirable for engineering applications. Also, it possesses good mechanical properties, exceptional chemical

Table 2.11 Properties of polyamide (PA).

Properties	Value	Unit
Density	1.13–1.15	
Melt temperature (T_m)	265	°C
Glass transition temperature (T_g)	50	°C
Heat of combustion	31.9	$kJ\ g^{-1}$
Melting point	265	°C
Water absorption at saturation	8.5	%
Thermal linear expansivity	9.0	$10^{-5}\ K^{-1}$
Specific heat capacity	1.7	$kJ\ kg^{-1}K^{-1}$
Thermal conductivity	0.25	$Wm^{-1}K^{-1}$
Elastic modulus	2.8	GPa
Critical strain energy rate (G_c)	5.0	kJ/m^2

and solvent resistance, and ease of fabrication and processing. The stereochemistry and rigidity of the constituent monomer structures will not only determine the bulk physical and mechanical properties of the polyamide, but also whether it is crystalline or amorphous.

Polyamides containing aromatic residues are normally very high melting, practically insoluble crystalline materials which are difficult to process. They easily absorb water, which deteriorates their mechanical properties and dimensional stability. PA is a strong polar polymer that has superior wear resistance compared with other polymers. Its friction coefficients are affected greatly by normal load, sliding speed and temperature.

There are types of polyamides, such as polyamide 6/6, which are semicrystalline polymers. They have a melting point near 265 °C. The physicochemical and mechanical properties have allowed their use in several types of industries, particularly the aeronautical and space industries [103, 104]. Impregnation of carbon fibers with synthesized polyamide 6/6 is used to obtain a good fiber/matrix interface, making the manufacture of thermoplastic composites with different arrangements of impregnated fibers and good mechanical properties viable.

2.6.3 Polycarbonate (PC)

Polycarbonate (PC) is one of the widely used engineering polymers. It has found wide applications in the electronics, automobile, optical material, and other fields. Polycarbonate can now be considered among the select

Table 2.12 Properties of polycarbonate (PC).

Properties	**Value**	**Unit**
Density	1.21	g/cm^3
Melt temperature (T_m)	230	°C
Glass transition temperature (T_g)	145	°C
Elongation	110–130	%
Heat of combustion	30.8	kJ g^{-1}
Elastic modulus	2.6	GPa
Critical strain energy rate (G_c)	4.8	kJ/m^2

group of aircraft transparent plastics and it has several key properties that make it attractive to the aircraft designer, particularly because of its impact resistance and good strength at elevated temperatures. It has the major advantages of having good heat resistance, exceptional toughness and impact resistance, and is formable to deep compound contour.

Polycarbonate is difficult to process due to its high melt viscosity [105]. Polycarbonates possess high impact strength, good optical clarity, and high heat distortion temperature. However, they suffer from the disadvantages of having poor chemical resistance, poor optical quality due to inherent limitations of the extrusion process, poor resistance to chemical attack; they may bubble at elevated temperature, their surface is degraded by outdoor weathering and they have low resistance to abrasion [106, 107].

Polycarbonate resin has excellent mechanical strength, particularly impact strength, good electrical properties and transparency (Table 2.12), and is widely utilized in a variety of fields such as office machinery, electric and electronic machinery, automobiles, architecture and the like. Many applications require that a polycarbonate composition be flame retardant and combine ease of processing with good optical properties.

Usually PC resin has been imparted with flame retardancy by being incorporated with a flame retardant and a flame retardant aid. The morphology and mechanical properties of the immiscible blend forms ductile PC with the brittle styrene-co-acrylonitrile copolymer (SAN) [108–112].

2.6.4 Poly(methylmethacrylate) (PMMA)

Poly(methylmethacrylate) (PMMA) is nontoxic. Therefore, it could be useful in dentures, medicine dispensers, food handling equipment, throat lamps and lenses. Due to the outstanding and promising mechanical and chemo-physical properties of PMMA, it has been utilized in many sectors such as aircraft glazing, signs, lighting, architecture, and transportation. PMMA embedded with inorganic or organically modified inorganic particles has been cast into films to yield enhanced functional properties such as electrical conductivity [113–119], photoconductivity [120], photoinduced charge transfer [121], nonlinear optical properties [122], photoluminescence [123–131], mechanical [126–132] and magnetic properties [133].

Poly(methyl methacrylate) (PMMA) is an unusual polymer with unique clarity. It has high softening temperature, high tensile and impact strength, good dielectric properties, low specific gravity, excellent light stability, and good UV transmission. It has outstanding properties and can be easily molded or cast into shapes and can be readily processed. It is softer than glass, therefore, more surface resistant than other polymer.

In fact, PMMA was the first implanted biomedical polymer [132] due to its resistance to the usual inorganic reagents and organic solvents. It has excellent resistance to weathering and electrical arcing. PMMA is a widely used material for biomedical implants, barriers, membranes, microlithography, and optical applications [134, 135]. High molecular weight and chain length of PMMA ensures molecular entanglement in order to increase mechanical properties and offer better resistance to moisture and a variety of industrial solvents. It has better toughness, better flexural and impact properties, and is not crosslinked and hence derives stiffness and strength from the inherent properties of monomers. However, it does not have any static properties or fatigue and inferior compress strength.

The transparency, strength, high softening temperature, specific gravity, and chemical resistance of PMMA (Table 2.13) make it an outstanding plastic material of either the cast or molded type. The unusual clarity of this resin permits its fabrication into delicately tinted shades. With the

Table 2.13 Properties of poly(methylmethacrylate) (PMMA).

Properties	**Value**	**Unit**
Density	1.19	g/cm^3
Glass transition temperature (T_g)	90–105	°C
Heat of combustion	26.2	$kJ\ g^{-1}$
Thermal linear expansivity	4.5	$10^{-5}\ K^{-1}$
Specific heat capacity	1.39	$kJ\ kg^{-1}K^{-1}$
Thermal conductivity	0.19	$Wm^{-1}K^{-1}$
Elastic modulus	2.4–3.1	GPa
Critical strain energy rate (G_c)	1.4	kJ/m^2

combined use of dyes and pigments, materials of varying degrees of color and transparency have been prepared. The value of this resin is greatly enhanced by the ease with which it can be worked, as described previously, engraved with unusual effects, and cemented to itself to give joints which for all practical purposes are as strong as the resin itself. Methyl methacrylate is readily molded in compression molds under the same conditions used for thermoplastic resins. Molding powders suitable for use in injection molding are being developed. The glass-like transparency of these resins suggests many uses as glass substitutes where strength, lightness, ultraviolet transmissibility, and ease of fabrication by molding are desired. Their substitution for glass in certain fields is facilitated by the remarkable chemical inertness of these resins.

The dielectric properties of methyl methacrylate resin make it of value in the electrical insulation and instrument field. Here again the transparency, nontracking qualities, inertness to ozone, high softening temperature, strength, water, oil, and chemical resistance, and the decrease of power factor with increase in temperature, combine to make this material of unusual interest.

2.6.5 Poly(ether ether ketone) (PEEK)

Poly(ether ether ketone) (PEEK) is an aromatic polymer. It is widely regarded as a high performance material with outstanding properties. These include excellent mechanical, thermal and chemical resistance properties, and permit unfilled PEEK to be used in many engineering applications, often in harsh environments [136].

Poly(ether ether ketone) is a semicrystalline thermoplastic polymer. It is well known for its excellent mechanical properties, good environmental resistance, and high continuous-use temperature, and is used in engineering applications [137–141]. It is especially suitable as matrix material for thermoplastic composites because of its good adhesion to glass and carbon fibers, ascribed to the formation of transcrystalline regions at the fiber surface [142–147].

Because PEEK is a high performance engineering thermoplastic with properties as shown in Table 2.14, it, has applications in the aeronautical and aerospace industries [135, 148]. Due to its outstanding properties, it has been employed as a component in blends with other polymers [149–151]. It also finds wide application in the reinforced form, containing either continuous or short fibers, and is a leading candidate among the thermoplastic composite group. PEEK is of interest in the study of structure/property relationships since the morphology can be controlled by simple thermal treatments. Thus,

Table 2.14 Properties of poly(ether ether ketone) (PEEK).

Properties	**Value**	**Unit**
Density	1.26–1.30	g/cm^3
Glass transition temperature (T$_g$)	145	°C
Melting point	340	kJ g^{-1}
Heat deflection temperature	156	°C
Specific heat capacity	2.16	kJ kg^{-1} °C^{-1}
Thermal conductivity	0.25	Wm^{-1} °C^{-1}

it can be quenched from the melt into a fully amorphous state or, alternatively, the degree of crystallinity can be developed to >40 wt% [152].

2.6.6 Poly(butylene terephthalate) (PBT)

Poly(butylene terephthalate) (PBT) is an important polymeric material for the electrical and electronic industries and automotive production. It has high heat resistance, good mechanical strength and toughness, good electrical insulation properties, lubricity, water resistance and good surface appearance. It is used, for example, in the production of lamp sockets, switches, relays, connectors, circuit breakers and motor casings, which require fire retardant properties. Neat PBT is highly combustible, so it is necessary to significantly improve its fire retardancy to meet fire safety requirements.

Poly(butylene terephthalate) is an important engineering thermoplastic with many useful properties; however, neat PBT materials fail in a brittle manner under certain loading conditions such as in notched Izod impact testing. The impact properties of PBT can be improved by simple melt blending with appropriate acrylonitrile-butadiene-styrene (ABS) materials [153–157]. These toughened materials, however, can only be produced within a limited processing range and have an unstable phase morphology; the ABS domains can coalesce during certain low shear conditions (particularly at high temperature when the PBT melt viscosity is low) in the melt, resulting in a reduction in mechanical properties.

2.7 Natural Polymers

Natural polymers can be agro- or animal-based materials. They are generally considered a renewable resource. Many of them are compatible, especially those derived from materials found in animal or human bodies. Natural polymers are biodegradable. They are abundantly available and environmentally friendly [158–164].

Agro-polymers, such as polysaccharides, are the first family of natural polymers. They are obtained from biomass by fractionation. Polymers of the third family are synthesized from monomers obtained from biomass such as polylactic acid (PLA). The fourth and last families are polyesters totally synthesized by petrochemical process from fossil resources such as polycaprolactone (PCL), polyesteramide (PEA), aliphatic or aromatic copolyesters.

Natural polymers are hydrophilic in nature. They are from renewable polymers and are utilized as mulch films, green packaging, and aid in transporting plants/seedlings [165]. Although they are not very economical, they are ecofriendly and natural. Materials are derived from renewable resources or their industrially processed wastes as well as by-products. Biomedical and biodegradable materials come from natural polymers hybridized with synthetic polymers. They serve as precursors for various kinds of polymers such as polyesters, epoxy, polyurethane, etc. [166, 167].

2.7.1 Cellulose

Cellulose is the most common organic polymer on earth. It is considered an almost inexhaustible source for raw materials that can be used in order to meet the increasing demand for environmentally friendly and biocompatible products [168, 169]. This macromolecule can be used for a great deal of important applications because of its supramolecular structure and its abundance on earth.

Cellulose is a natural polymer with high strength and stiffness per weight, and it is a building material with long fibrous cells. These cells can be found in the stems, leaves or seeds of plants. In general, the fiber consists of a wood core surrounded by a stem. Within the stem there are a number of fiber bundles which contain individual fiber cells or filaments. The filaments are made of cellulose and hemicellulose, bonded together by a matrix which can be lignin or pectin. The pectin surrounds the bundle, thus holding them on to the stem.

2.7.2 Wood

Wood is a natural product composed of a highly polymerized carbohydrate called cellulose in proportions of 50% to 60%. This mainly stands for its mechanical property. However, lignin constitutes about 25% and the rest of solid material, about 24%, is contained by water-soluble carbohydrates, gums, resins and so on, with 1% ash present in it. Among all the constituents of wood, cellulose is the most sensitive to radiation. Radiation creates sites on cellulose bone as free radicals that initiate the polymerization process. The elementary unit of cellulose macromolecule is a hydro-d-glucose, which contains three hydroxyl –OH groups. These hydroxyl groups form intramolecular hydrogen bonds inside the molecule and intermolecular hydrogen bonds with other cellulose molecules as well as hydroxyl groups of moist air. Wood is hydrophilic in nature and its moisture certainly reaches up to 12–13% [170]. The groupings of long-chain cellulose molecules in the cell wall contain crystalline and amorphous regions. In the crystalline regions, it is believed that –OH groups of adjacent cellulose molecules are mutually bonded or crosslinked. Therefore, there are no sites to hold water within the crystalline substance. However, within the amorphous or disordered regions the hydroxyl groups are accessible for absorption of water [171].

2.7.3 Starch

Starch is one of the most abundant natural polymers. It has been used as an adhesive in a wide range of products, including binders, sizing material, glues and pastes. More recently, the development of a starch-based wood adhesive for interior applications has been described [172, 173].

Starch macromolecules are composed of anhydroglucose units connected in amylose chains which are occasionally branched by connection through linkages. The starch molecules are arranged in a hierarchical structure to form starch granules with average diameter of 5–40 μ, depending on the particular plant species. Native starches, again depending on source, may also be partly modified with protein and lipids, and may be phosphorylated or have other functionality. There are two limiting forms of starch polymers that differ in molecular weight and the prevalence of branches [174, 175].

Starch as a filler in plastic materials has been of interest due to concern over the buildup of plastic wastes and possible shortages of petrochemicals. Two major technologies for starch addition to plastics have been developed. One is based on the use of gelatinized starch molecules as an integral part of the polymeric structure [176] and the other is based simply on the use of granular starch as filler [177].

2.7.4 Lignin

Lignin is an amorphous natural polymeric material that is based on phenylpropane derivates. Lignins are considered as three-dimensional natural polymers. They are invariably associated with cellulose and hemicelluloses. This association gives a major role to lignin in the case of new materials using lignocellulosic sources, since lignin is a macromolecular framework difficult to degrade even by microorganisms. Only lignolytic microorganisms can do it. It has many functions in wood, but its commercial utilization is relatively low. In biomass, lignin is present together with polysaccharides to the tune of 20–30% to 60–80% [178]. Various properties of lignin are designated for different technical purposes.

Wood, straw and twigs are composed largely of lignocellulose. The lignin component of these abundant natural products is a carbon-chain polymer containing aromatic rings, resembling the synthetic phenol-formaldehyde resins that are relatively resistant to biodegradation compared with pure cellulose [179]. Lignocellulose, like rubber, oxo-biodegrades slowly. Straw, however, is a particularly appropriate model for the biodegradation of synthetic polymers since it causes no problems when left on the fields or when included in compost, in spite of its slow rate of biodegradation. It may take up to 10 years for straw to be fully bioassimilated in biologically active soil [180].

2.7.5 Chitosan

Chitosan is a well-known type of polymer [181, 182] obtained by deacylating the biopolymer chitin, which is found in the skin or shell of anthropods. Chitosan is a promising natural cationic polymer with good biocompatibility, nontoxicity, and biodegradability. It is produced by alkaline N-deacetylation of chitin, the most abundant natural polymer after cellulose. Chitosan has been shown to be useful as a chelating agent, drug carrier, membrane, water treatment additive, biodegradable pressure-sensitive adhesive tape, wound healing agent, nerve repair agent, and in other important applications. However, such biomedical properties of chitosan must be improved for the adsorption of drugs and proteins and the adhesion of cells to biomedical materials.

2.7.6 Poly(lactic acid) (PLA)

Poly(lactic acid) (PLA) is of increasing commercial interest since it is completely made from renewable agriculture products with excellent properties comparable to many petroleum-based plastics and is readily biodegradable [183–185]. Even when burned, it produces no nitrogen oxide gases and only one-third the combustible heat generated by polyolefin, and does not damage the incinerator; thus, it provides significant energy savings.

Poly(lactic acid) is a promising polymer for various end-user applications [186], and currently there is increasing interest in using PLA for disposable degradable plastic articles [187]. However, some of the other properties, such as flexural properties, heat distortion temperature (HDT), gas permeability, impact factor, melt viscosity for further processing etc., are frequently not suitable for various end-user applications [188]. PLA has a D-content of 1.1–1.7% (T_g = 60 °C and T_m = 168 °C).

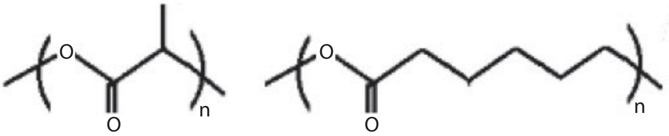
2.7.7 Poly(L-lactic acid) (PLLA)

Poly(L-lactic acid) (PLLA) is a renewable, biodegradable, and biocompatible thermoplastic polymer, which has found practical application in the medical, agricultural, and general-purpose plastics fields [182, 189–191]. However, its relatively poor mechanical properties, slow crystallization rate, and slow degradation rate have limited its further practical application. In order to overcome these disadvantages, polymer composites have been developed by copolymer synthesis, polymer blending, and reinforced composite [192–196].

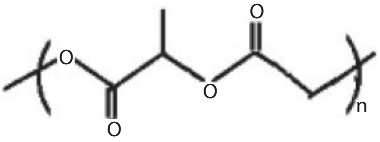
Among the biopolymers, corn, beets, or rice crop-based PLA is a promising material whose preparation encompasses a combination of biotechnology and classical chemical synthesis. Commercial PLA is a linear aliphatic polyester which is a random copolymer of poly(L-lactic acid) and poly(D-lactic acid). The relative abundance of the L-enantiomer and D-enantiomer is known to drastically affect the chain ordering in the material. Neat PLLA and PDLA are semicrystalline [197]. The resulting amorphous material has more desirable mechanical characteristics and is more easily degraded than PLLA [198], allowing its use in resorbable plating [199], artificial cartilage or bone [200], fixation of facial fractures [201], chemotherapeutic implants [202], and pharmaceutical devices like tablets for oral drugs administration [203], but its physical and mechanical properties were found to be poorly adapted for applications as membranes [204, 205].

2.8 Biodegradable Polymers

Biodegradation is the chemical breakdown of an organic material into simple chemicals that can be easily removed from the body or environment. The degradation can be hydrolytic, oxidative, enzymatic or bacteriological. Biodegradable polymers have the fundamental research as well as in the chemical industry. Biodegradable in this connection means hydrolyzable



Poly(lactic acid) Poly(caprolactone)



Poly(lactide glycolide)

Figure 2.5 Structures of common biodegradable polymers.

at temperatures up to 50 °C (e.g., in composting) over a period of several months to one year. Nontoxic degradation products have, of course, other important prerequisites for any potential application. The polyester and copolyesters of aliphatic polyesters possess these desirable properties. Some of the common biodegradable polymers are given in Figure 2.5.

2.8.1 Poly(lactic acid) (PLA)

Poly(lactic acid) (PLA) has proven to be the most attractive and useful class of biodegradable polyesters. There are several reasons for this prominent role. Lactic acid is easily obtained by a biotechnological process (usually based on the strain of a lactobacillus) from inexpensive raw materials. PLA is a high strength and high modulus thermoplastic, which can be easily processed by conventional processing techniques used for thermoplastics like injection molding, blow molding, thermoforming and extrusion. For large-scale production, the polymer must possess adequate thermal stability to prevent degradation and maintain molecular weight and properties. Its degradation is dependent on time, temperature, low-molecular weight impurities, and catalyst concentration.

The deficiencies that limit the use of PLA are its poor toughness and its low glass transition temperature (T_g), ~60 °C, compared to other commodity thermoplastics [206–208]. PLA with at least 85% L-lactide units is a semicrystalline polyester, but with a slow crystallization rate, and polymers with 15% D-lactic acid units are amorphous and optically clear [209]. Crystallinity increases the softening temperature of PLA and improves its mechanical properties above T_g, but the transparency decreases, which makes it unsuitable for packaging and coating applications [206–208]. The toughness of PLA can be improved by orientation [206], blending [210], and copolymerization [9], though none of these approaches are considered a commercially viable solution for applications of PLA requiring higher toughness than conventional resin. Predominantly hydrophobic polymers containing a modest amount (e.g., up to 15 mol%) of covalently bonded salt groups, such as metal carboxylates or sulfonates, are referred to as ionomers [211].

2.8.2 Polycaprolactone (PCL)

Polycaprolactone (PCL) forms miscible blends with numerous polymers and possesses considerable interaction with many more. It forms miscible blends with PC, PET, PVC, $PVCl_2$, SAN, nitrocellulose, and chlorinated PE, to name only a few [212]. Therefore, PP grafted with PCL would potentially be an extremely useful compatibilizer for many different polypropylene blend combinations. Poly(caprolactone) has a high flexibility, biocompatibility, and permeability to many compounds and is used as a matrix for controlled drug release [213] and in agriculture [214].

2.8.3 Poly(lactide-co-glycolide) (PLGA)

Poly(lactide-co-glycolide) (PLGA) is a biocompatible, biodegradable copolymer utilized for its degradation properties in drug delivery and as a tissue scaffold. PLGAs show low polarity surface characteristics, which will not promote bioadhesion. PLGA showed its characteristic bulk hydrolysis. It is a completely amorphous polymer largely used for medical and pharmaceutical applications. Because of its biocompatibility and biodegradability, it has been successfully used as base material to produce parenteral drug delivery systems (DDS).

2.8.4 Thermosets

Thermosets are polymers that consist of three-dimensional networks of atoms. Once formed, they cannot be recycled or reformed. They decompose upon further heating. Thermosets assume a permanent shape, or set, when heated. Some thermoset polymers set at room temperature. They begin as powders or liquids which react with a second material or polymerization by catalyst, resulting in a product. The resultant product properties differ from the starting material. Thermosets are crosslinked and the reaction is irreversible [215]. The cure mechanism and polymers kinetics depend on the composition of the thermoset polymers and exhibit a wide range of temperature dependence for different polymer formulations [216].

Thermosets play an important role in industry due to their high flexibility for tailoring the desired ultimate properties, leading to their high modulus, strength, durability, and thermal and chemical resistances as provided by their high crosslinking density. However, owing to their high crosslinking density, thermosetting resins are inherently of low impact resistance and cannot be reshaped after curing/polymerization [217–219].

Thermosetting materials, like rubbers, are crosslinked upon processing and molding, and therefore cannot be softened or remolded by heating again. Chemical additives (mostly in minor quantities) are generally incorporated into thermosets as stabilizers, flame retardants, colorants, plasticizers, etc., to optimize product properties and performance. Thermosetting materials are not easy broken down either through the cleavage of crosslinks, or through the carbon-carbon linkage of the chain backbone. The technology for recycling of thermoset polymers is complex, costly and less viable commercially [6]. Reprocessing of thermoset is difficult; still the use of reclaimed/reground thermoset resins in new polymer formulations is found to have some influence on flow and deformation characteristics during processing. Perhaps these are used as fillers.

Thermosetting polymer systems are characterized by an initial state of low viscosity, which upon curing leads to a crosslinked brittle matrix exhibiting low strain to failure, but high stiffness and yield strength. Resin systems alone have limited use as engineering polymer. They rely upon reinforcement by a variety of fibers for their mechanical performance. The ability to impregnate continuous fiber bundles relatively simply, and the high resin stiffness/yield behavior, are major attractions in their favor. It is this class of polymer, varying through polyesters, epoxies, polyimides and more recently bismaleimides, to which the polymer/continuous fiber composite industry owes its existence. The counterbalancing disadvantages are productivity, and in the case of the higher performance systems, elaborate cure operations. As the demands on composite materials increase, the resin performance remains a constraint.

2.8.5 Phenolic (Phenol Formaldehyde) Resins

Phenolic resins belong to one of the oldest classes of synthetic polymers still in common use [220–222]. Molding compounds undergo an irreversible chemical crosslinking reaction during curing, and a considerable increase in molecular weight occurs. This transformation is accompanied by strong changes in the viscoelastic properties of the material.

Phenolics are widely used in various applications, from commodity and construction materials to the needs of the high technology aerospace industry. Several desirable properties, such as good mechanical strength, dimensional stability, resistance against various solvents, flame retardance, are characteristics of phenolics. They are brittle, have poor shelf life, corrode processing equipment (due to the acid or base catalysts often used for resin preparation), and they release by-products (such as water, ammonia compounds during curing) which sometimes affect the properties of cured resins by forming microvoids. They have gained immense interest because they have the capability to exhibit the thermal and flame-retardance properties of phenolics along with mechanical performance and molecular design flexibility [223].

Phenolic resins especially exhibit outstanding properties at high temperatures and good chemical resistance against oil, fuel and coolant [224, 225]. Large quantities of low impact phenol formaldehyde materials are used commercially in various non-defense industries but this class of material has only a limited application to aircraft, as its low impact strength precludes its use in all applications where there is the slightest danger of accidental damage.

2.8.6 Epoxy Resins

Epoxy polymers are used in high performance composite materials due to their high dimensional stability. Cured epoxy resins exhibit low impact strength, poor resistance to crack propagation and low elongation at break. Epoxy polymers will set at room temperature by combining with a curing agent.

Because of these unique characteristics and useful properties of network polymer, such as high strength, very low creep, excellent corrosion and weather resistance, elevated temperature service capability and adequate electrical properties, epoxy resins are widely used in structural adhesives, surface coatings, engineering composites, electrical laminates, etc. [226–229]. They have static properties and fatigue and superior abrasion and dimensional characteristics. But they form crosslinked structure which is non-recyclable and non-biodegradable.

The major drawback of epoxy resins is that in the cured state they are brittle materials having fracture energies some two orders of magnitude lower than engineering thermoplastics and three orders lower than metal. This inherent brittleness causes the poor damage tolerance to impact of the composites made from epoxy resin and poor peeling and shear strength of epoxy-based adhesive.

Epoxy resins are compatible with many other synthetic resins. Because of the toughness and high adhesive properties of the epoxies, they are being used in increasing amounts as upgrading agents for coatings of all types of phenolics, polyesters, ureas, furanes, melamines, vinyls, fluorocarbons, asphaltic materials, polyurethanes, and silicone resins. On the other hand, many of these resins are used in epoxides to modify the properties of the cured system. Thus, phenolic resins may be used to increase heat distortion temperatures of some systems. Still other resins are used to impart flexibility, high impact strength, and greater thermal shock resistance. Lower priced synthetic resins may be used in fairly high percentages to reduce the overall cost of the epoxy resin system, etc.

Epoxy resins are widely used in many applications, from common adhesives and sealants to the matrix in high-performance composite materials, due to their many good performances such as high adhesive strength, high mechanical strength, high insulation and good processing property. However, these materials are rather brittle for the high-linked network, which limits their applications in some fields. So the toughening of epoxy resin has become a hotly studied area in recent years [230–235].

Epoxy resins are one of the most important classes of thermosetting polymers. The addition of additives or modifiers (catalysts, diluents, fillers, resinous modifiers, elastomeric modification, etc.) to the two main ingredients is frequently adopted to change the characteristics of the uncured resin (rheology, curing kinetics, etc.) or the properties of the final material (e.g., fracture behavior). Some formulations proposed in industry were found to contain small amounts of phenolic compounds mixed with the amine hardener component. The epoxy resins, also known as epoxides, have given outstanding performance to coatings, adhesives, and reinforced plastics. The copolymers are derived mainly from epichlorohydrin (EPI) and Bisphenol A, which produce excellent properties.

2.8.7 Polyurethanes

Polyurethanes are an interesting polymer group with widespread characteristics by molecular composition [236–240]. Increase of the hard segment content in polyurethane structures could give polymers with higher elastic modulus, and polyurethanes with modified properties could be produced by molecular weight and chemical structures of soft segments and the structure differences of chain extenders [241, 242]. Polyurethanes cured with excess isocyanate have several deficiencies, particularly in dynamic properties. In commercial processes, they are often difficult to handle. Peroxides were explored as replacements for the isocyanate usually used to cure these elastomers.

2.8.8 Silicone Resins

Combinations of silicone and epoxy resins offer considerable promise of unusual casting and coating materials. The epoxy resins possess good all-around electrical and mechanical properties together with ease of handling. Silicone polymers are usually very weak and soft mechanically, but they possess high thermal stability due to the presence of the silicone atom. Hence, a combination which couples the good properties of both should offer much in the way of improved high temperature electrical insulation [243].

2.8.9 Amino Resins

The raw materials of amino resins are urea and formaldehyde. The condensation polymerization produces a water molecule which is generally used to impregnate fillers. These resins have better tensile strength and hardness but their impact strength, heat and moisture resistance are low. Their distinct advantage is transparency. Almost 75% of all amino resins go into adhesives used for plywood and furniture.

2.8.10 Melamine Resins

Melamine resins are relatively new and are at present used only as thermosetting surface coatings where their permanent transparency is a distinct advantage. The major use of urea-formaldehyde resins in aircraft is as an adhesive, but they are also used in applications where a thermosetting material is needed and where light colors are essential, as phenol-formaldehyde resin has an inherent mahogany brown color which prevents its use in such applications.

2.8.11 Unsaturated Polyester Resins

Unsaturated polyester is formed by adding styrene (for crosslinking) to polyester having phthalic anhydride, propylene glycol and of maleic anhydride. This prepolymer is stabilized with hydroquinone. A final polymer is obtained by curing the prepolymer using a hydroperoxide initiator. The polymerization can be carried out at room temperature. The most important advantage of this resin is its ease of handling. Other benefits are rapid curing with no volatiles, light color, dimension stability, and good physical and electrical properties. When reinforced with fiber glass, the strong and rigid resin is used for boat hulls, auto parts, pipes, etc.

Thermosets based on unsaturated polyester are crosslinked materials resulting from free radical polymerization of unsaturated polyester chains with a crosslinker agent, usually styrene. To induce the production of free radicals, organic peroxides are used that can be decomposed by temperature or by chemical promoters. The curing process is characterized by both chemical reactions and physical changes, namely gelation and vitrification [244, 245].

2.8.12 Bismaleimide (BMI)

Bismaleimide (BMI) is a kind of high-performance matrix resin, which has been used in the aerospace industry [246–250]. Cured resin is extremely brittle due to its high crosslinking density. Bismaleimide resins, as a kind of high-performance material, have received more and more interest because of their good thermal stability, low water absorption and good retention of mechanical properties at high temperatures. However, due to their highly crosslinked structures, bismaleimide resins are extremely brittle and thus are often modified for application [251–254]. However, the cure mechanism of the blends of bismaleimide and dicyanate ester is highly controversial and sometimes conflicting, which is still not well established.

2.9 Trends

Polymers of different nature have their established position through diversified applications ranging from shopping bags to nuclear installations. Mixtures containing two or more chemically different kinds of polymers are of technological importance to basic polymers for modifying properties or cost. A very small amount of polymeric admixture can significantly improve end-use properties of polymeric material. Polymer properties can be modified using blend and composite techniques. Still, the search for continued improvement of the properties of polymers has led to the development of various blends and combinations generally composed of suitable chemicals and additives [229]. Polymers of natural or synthetic origin are indispensible to the modern world. They are used as commodity materials in industry and technology and it is hard to think of our present society without polymeric materials [255].

2.10 Summary

- Polymers are versatile materials that are essential to our quality of life and play a vital role in shaping a sophisticated and comfortable society.
- Polymers are insoluble materials.
- Apart from consumer products, polymers are widely used in industrial and engineering applications all over the world [256].
- Polymers are produced from man-made chemicals and are becoming more common place in industrial applications. The performance of polymers for industrial use is often dependent on their thermal stability, which is dependent on their molecular structure.
- Thermoplastic polymers are made of linear molecules. They deform under heat and pressure.
- Thermoplastics are replacing metals in many applications. They offer superior corrosion resistance, lower costs, lighter weight per item, and better flexibility in part design [257].
- Thermoset polymers have been, and are currently being, developed for improving the toughness of these materials.
- Renewable raw materials are natural substances which are used by mankind for purposes other than nutrition or foodstuffs [258] and can be agricultural, forestry, animal or microbial products.
- The utilization of biodegradable polymers [259] is due to their potential impact upon the complex issue of plastic waste management.

References

1. Beall, G. and Pinnavaia, T.P. (Eds.), *Polymer-Clay Nanocomposites*, Wiley & Sons: Chichester, U.K., 2000.
2. Staudinger, H., *From Organic Chemistry to Macromolecules*, Wiley-Interscience: New York, 1970.

3. Staudinger, H., *Chem. Ber.* 57, 1203, 1924.
4. Mark, H. and Whitby, G.S. (Eds.), *Collected Papers of Wallace Hume Carothers on High Polymeric Substances*, Wiley-Interscience: New York, 1940.
5. Chen, Z.R. and Kornfield, J.A., *Polymer* 39, 4679, 1998.
6. Throne, J.L., *Adv. Polym. Technol.* 7(4), 347, 1987.
7. Staudinger, M., *Die Hochmolekularen Organischen Berbindungen*, 1932.
8. Blank, S., *Stud. Conserv.* 35, 53–63, 1990.
9. Allen, N.S., Edge, M., and Horie, C.V. (Eds.), *Polymers in Conservation*, Royal Society of Chemistry, Cambridge, 1992.
10. Yuan, H.G., Kalfas, G., and Ray, W.H., Suspension polymerization. *J. Macromol. Sci. Rev. Macromol. Chem. Phys. C* 31(2–3), 215–299, 1991.
11. Kalfas, G., Yuan, H., and Ray, W.H., *Ind. Eng. Chem. Res.* 32, 1822–1838, 1993.
12. Dawkins, J.V., Aqueous suspension polymerizations. Chain polymerization. II, in: *Comprehensive Polymer Science: The Synthesis, Characterization & Applications of Polymers*, Geoffrey, A., Bevington, J.C. (Eds.), vol. 4, chap. 14, Pergamon Press: Oxford, Great Britain, 1989.
13. Quye, A. and Williamson, C. (Eds.), *Plastics: Collecting and Conserving*, NMS, Edinburgh, 1999.
14. Shashoua, Y., *Conservation of Plastics, Materials Science, Degradation and Preservation*, Butterworth Heinemann, Oxford, 2008.
15. Jois, Y. and Harrison, J., *Rev. Macromol. Chem. Phys. C.* 36(3), 433, 1996.
16. Khare, A. and Deshmukh, S., *J. Plast. Film Sheet.* 22, 193, 2006.
17. Michler, G.H., in: *Kunststoff-Mikromechanik*, Carl Hanser, Munich; Materials Science and Technology: A Comprehensive Treatment Series, 1993.
18. Cahn, R.W., Haasen, P. and Kramer, E.J. (Eds.), *Structure and Properties of Polymers*, vol. 12, Thomas, E.L. (vol. Ed.), Wiley, New York.
19. Yamashita, S., Kodama, K., Ikeda, Y., and Kohjiya, S.J., *Polym. Sci. A: Polym. Chem.* 31, 2437–2444, 1993.
20. Berlinnova, I.V., Amzil, A., and Panayotov, I.M.J., *Macromol. Sci. Pure Appl. Chem.* 29, 975–986, 1992.
21. Sung, W. and Zivko, L. Nikolov, *Ind. Eng. Chem. Res.* 31, 2332–2339, 1992.
22. Busico, V., *Macromol. Chem. Phys.* 208, 26–29, 2007.
23. Mülhaupt, R., *Macromol. Chem. Phys.* 204, 289–327, 2003.
24. Hanlon, J.F. and Kelsey, R.J., *Handbook of Package Engineering*, 3rd ed., Technomic Publishing Co., Inc., Lancaster, Pennsylvania, 1998.
25. Fawcett, E.W. and Gibson, R.O., *J. Chem. Soc.* 1934, 386, 1934.
26. Uchida, E. and Ikada, Y., *Curr. Trends Polym. Sci.* 1, 135, 1996.
27. Mergenthaler, D.B. and Pietralla, M., *Zeitschrift für Physik B.* 94, 461–468, 1994.
28. British Patent No. 471590, 1937.
29. Mendelson, R.A., *Trans. Soc. Rheol.* 9, 53, 1965.
30. Mendelson, R.A., Bowles, W.A., and Finger, F.L., *J. Polym. Sci. A2*, 8, 105, 1970.

31. Ghijsels, A., Ente, J.J.S.M., and Raadsen, J., *Int. Polym. Process.* 7, 44, 1992.
32. Muzsay, A., Gyimesi, G., and Felegyhazine, S.L., *Int. Polym. Sci. Technol.* 8(10), 7, 1981.
33. Buchert, M., Jenseit, W., and Wollny, V., *Kunstoffe* 83, 451, 1993.
34. De Groote, P. and Godard, A., Technical Report from APME, 1995.
35. La Mantia, F.P., *Polym. Degrad. Stab.* 37, 145, 1992.
36. Dulta, N.K. and Birely. A.W., *Plast. Rubber Process. Appl.* 3, 237, 1983.
37. La Mantia, F.P. and Acierno, D., *Eur. Polym. J.* 21, 811, 1985.
38. La Mantia, F.P., Valenza, A., and Acierno, D., *Eur. Polym. J.* 22, 647, 1986.
39. David, W., Fredriksson, J.C., and Decew, I.T., *Ocean Eng.* 34, 2124, 2007.
40. Ollick, A.M. and Al-Amir, A.M., *Alexandria Eng. J.* 42, 659, 2003.
41. Jog, P.K. and Chapman, W.G., *Macromolecules* 35, 1002–1011, 2002.
42. Behme, S., Sadowski, G., Song, Y.H., and Chen, C.C., *AIChE J.* 49, 258–268, 2003.
43. Koak, N. and Heidemann, R.A., *AIChE J.* 47, 1219–1225, 2001.
44. Ghosh, A., Ting, P.D., and Chapman, W.G., *Ind. Eng. Chem. Res.* 43, 6222–6230, 2004.
45. Dominik, A., Chapman, W.G., Swindoll, R.D., Eversdyk, D., Jog, P.K., and Srivastava, R., *Ind. Eng. Chem. Res.* 48, 4127–4135, 2009.
46. Karbashevski, E., Kale, L., Rudin, A., Tchir, W.J., Cook, D.G., and Pronovost, J.O., *J. Appl. Polym. Sci.* 44, 425–434, 1992.
47. Liu, Z.H., Kwok, K.W., Li, R.K., and Choy, C.L., *Polymer* 43, 2501, 2002.
48. Thongruang, W., Balik, C.M., and Spontak, R.J., *J. Polym. Sci. B: Polym. Phys.* 40, 1013, 2002.
49. Suwanprateeb, J., *J. Appl. Polym. Sci.* 75, 1503, 2000.
50. Privalko, V.P., Sukhorukov, D.I., Privalko, E.G., Walter, R., Friedrich, K., and Baltá Calleja, F.J., *J. Appl. Polym. Sci.* 73(6), 1041–1048, 1999.
51. Jeon, H.G., Jung, H.T., Lee, S.W., and Hudson, S.D., *Polym. Bull.* 41, 107, 1998.
52. Li, T., Liu, G., and Qi, K., *J. Appl. Polym. Sci.* 67, 1227, 1998.
53. Brydson, J.A., *Plastics Materials*, Butterworth, Heinemann: New York, 1999.
54. Suhey, J.D., Kim, N.H., and Niezrecki, C., *Aquacult. Eng.* 33, 285, 2005.
55. Zhou, D. and Xie, G., *Aging and Anti-aging of Plastics*, Beijing: China Light Industry Press, 1988.
56. Zhong, S. and Xu, Q., *Degradation and Stability of Polymers*, Beijing: Chemical Industry Press; 2002.
57. Lacoste, L. and Carlsson, D.I., *J. Polym. Sci. A: Polym. Chem.* 30, 493–500, 1992.
58. Gugumus, F., *Polym. Degrad. Stab.* 76(2), 329–340, 2002.
59. Gugumus, F., *Polym. Degrad. Stab.* 77(1), 147–155, 2002.
60. Sahebian, S., Zebarjad, S.M., Sajjadi, S.A., Sherafat, Z., and Lazzeri A., *J. Appl. Polym. Sci.* 104, 3688, 2007.
61. Ammala, A., Hill, A.J., Meakin, P., Pas, S.J., and Turney, T.W., J. Nanopart Res. 4, 167, 2002.

62. Vasile, C. and Seymour, R.B., *Handbook of Polyolefins*, Marcel Dekker: New York, 1993.
63. Hadal, R.S. and Misra, R.D.K., *Mater. Sci. Eng. A* 374, 374, 2004.
64. Hadal, R., Dasari, A., Rohrmann, J., and Misra, R.D.K., *Mater. Sci. Eng. A* 380, 326, 2004.
65. Trotigon, J.P., Verdu, J., de Boissard, R., and de Vallios, A., in: *Polymer Composites: Proceedings of Prague IUPAC Microsymposium on Macromolecules*, B. Sedlaucek (Ed.), p. 191, De Grugter, 1985.
66. Dasari, A., Sarang, S., and Misra, R.D.K., *Mater. Sci. Eng. A* 368, 191, 2004.
67. Dasari, A., Rohrmann, J., and Misra, R.D.K., *Mater. Sci. Eng. A* 364, 357, 2004.
68. Dasari, A. and Misra, R.D.K., *Acta Mater.* 52, 1683, 2004.
69. Rader, C.P., *Handbook of Thermoplastic Elastomers*, 2nd ed., chap. 4, Van Nostrand Reinhold: New York, 1988.
70. Thomas, D.A. and Sperling, L.K., Polymer Blends, vol. 2, Academic Press: New York, 1978.
71. Marvel, C.S. and Horning, E.C., *Organic Chemistry*, 2nd ed., Wiley, New York, 1943.
72. Herbst, H., Hoffman, K., Pfaendner, R., and Zweifel, H., in: *Frontiers in the Science and Technology of Polymer Recycling*, G. Akovali, C.A. Bernardo, J. Leidner, A.U. Leszek, Xanthos, M. (Eds.), pp. 75–76, Dordrecht: The Netherlands, Kluwer Academic Publishers, 1998.
73. Toshikazu, K., Barbara, A.W., Akio, T., and Hirokuni, O., *J. Electrostat.* 64, 377, 2006.
74. Andrady, A.L., Poly(vinyl chloride), in: *Polymer Data Handbook*, J.E. Mark (Ed.), pp 928–934, Oxford University Press: Oxford, 1998.
75. Titow, W.V., *PVC Technology*, London: Elsevier Applied Science Publisher Ltd, 1984.
76. Edenbaum, J., Polyvinyl chloride resins and flexible-compound formulating, in: *Plastics Additives and Modifiers Hand Book*, chap. 2, p. 50, Van Nostrand Reinhold: New York, 1992.
77. Jog, J.P., *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* C35, 531–553, 1995.
78. Schmidt-Rohr, K., Hu, W., and Zumbulyadis, N., *Science* 280, 714–717, 1998.
79. Jiang, W., An, L.-J., and Jiang, B.-Z., *Chinese J. Polym. Sci.* 21(2), 129, 2003.
80. Aref-Azar, A. and Hay, J.N., *Polymer* 23, 1129–1132, 1982.
81. Ito, E., Tajima, K., and Kobayashi, Y., *Polymer* 24, 877–882, 1983.
82. Bove, L., D'Aniello, C., Gorrasi, G., Guadagno, L., and Vittoria, V., *Polym. Bull. (Berlin)* 38, 579–585, 1997.
83. McGonigle, E.-A., Daly, J.H., Gallagher, S., Jenkins, S.D., Liggat, J.J., Olsson, I., and Pethrick, R.A., *Polymer* 40, 4977–4982, 1999.
84. Berghmans, G.H., Overbergh, N., and Smets, G.J., *Polym. Sci. Polym. Phys. Ed.* 12, 303, 1974.
85. Mercier, J.P., *Polym. Eng. Sci.* 30, 270, 1990.
86. Reinsch, V.E. and Rebenfelz, L.J., *Appl. Polym. Sci.* 52, 649, 1994.
87. Chen, H.-L., *Macromolecules* 28, 2845–2851, 1995.

88. Tullo, A.H., *Chem. Eng. News* 79, 15, 2001.
89. Kulich, D.M., Pace, J.E., Fritch, L.W. Jr., and Brisimitzakis, A., in: *Kirk-Othmer Encyclopedia of Chemical Technology*, J. Kroschkowitz (Ed.), vol. 1, 4th ed., p. 391, New York: Wiley, 1991.
90. Jenne, H., *Kunststoffe* 62, 616, 1982.
91. Cigna, G.J., *Appl. Polym. Sci.*, 14, 1781, 1970.
92. Beery, D., Kenig, S., Siegmann, A., and Narkis, M., *Polym. Eng. Sci.* 32, 14, 1992.
93. Lee, T.S., in: *Proceedings of the 5th International Congress on Rheology*, p. 421, 1970.
94. Han, C.D., Appl. Polym. Sci. 5, 2591, 1971.
95. Cogswell, F.N., *Appl. Polym. Symp.* 27, 1, 1975.
96. Kubota, H., *Appl. Polym. Sci.* 19. 2299, 1975.
97. Munstedt, H., in: *Proceedings of the 7th International Congress on Rheology*, p. 496, 1976.
98. Itoyama, K. and Soda, A., *Appl. Polym. Sci.* 23, 1723, 1979.
99. Tanaka, H. and White, J.L., *Polym. Eng. Rev.* 1, 89, 1981.
100. Gahleitner, M., *Prog. Polym. Sci.* 26, 895–944, 2001.
101. Brostow, W., Sterzynski, T., and Triouleyre, S., *Polymer* 37(9), 1561–1574, 1996.
102. Liang, J.Z. and Li, R.K.Y., *J. Appl. Polym. Sci.* 73, 1451–1456, 1999.
103. Liou, W.J., *J. Reinf. Plast. Compos.* 17(1), 39–50, 1998.
104. Ma, C.M. and Chang, F., in: *Proceedings of the 35th International SAMPE Symposium*, pp. 59–72, 1990.
105. Le Grand, D.G., Mechanical properties of polycarbonates, in: *Handbook of Polycarbonate Science and Technology*, D.G. Le Grand, J.T. Bendler (Eds.), p. 107, Marcel Dekker, Inc.: New York, 2000.
106. Wiser, G.L., *Aircraft Engineering*, 43, 18–20, 1971.
107. Capozzi, C.J. and Gerhardt, R.A., *Adv. Funct. Mater.* 17, 251, 2007.
108. Quintens, D., Groeninckx, G., Guest, M., and Aerts, L., *Polym. Eng. Sci.* 30, 1474, 1990.
109. Quintens, D., Groeninckx, G., Guest, M., and Aerts, L., *Polym. Eng. Sci.* 31, 1207, 1991.
110. Gregory, B.L., Siegmann, A., Im, J., and Bear, E., *J. Mater. Sci.* 22, 532, 1987.
111. Keitz, J.D., Barlow, J.W., and Paul, D.R., *J. Appl. Polym. Sci.* 29, 3131, 1984.
112. Maurer, F.H.J., Palmen, J.H.M., and Booij, H.C., *Rheol. Acta* 24, 243, 1985.
113. Thander, A. and Mallik, B., *Solid State Commun.* 12, 159, 2002.
114. Thander, A. and Mallik, B., *Chem. Phys. Lett.* 330, 521, 2000.
115. Lee, I., Niidome, Y., Matsuo, T., and Yamada, S., *Anal. Sci.* 13, 343, 1997.
116. Althues, H., Palkovits, R., Rumplecker, A., Simon, P., Sigle, W., Bredol, M., Kynast, U., and Kaskel, S., *Chem. Mater.* 18, 1068, 2006.
117. Althues, H., Simon, P., and Kaskel, S., *J. Mater. Chem.* 17, 758, 2007.
118. Li, S., Toprak, M.S., Jo, Y.S., Dobson, J., and Kim, D.K., *Adv. Mater.* 19, 4347, 2007.

119. Rawlins, K., Lees, A., Fuerniss, S., and Papathomas, K., *Chem. Mater.* 8, 1540, 1996.
120. Farmer, S.C. and Pattern, T.E., *Chem. Mater.* 13, 3920, 2001.
121. Li, Z., Zhang, J., Du, J., Mu, T., Liu, Z., Chen, J., and Han, B., *J. Appl. Polym. Sci.* 94, 1643, 2004.
122. Guo, L., Chen, S., and Chen, L., *Colloid Polym. Sci.* 285, 1593, 2007.
123. Gao, J., Lü, C., Lü, X., and Du, Y., *J. Mater. Chem.* 17, 4591, 2007.
124. Chen, L., Zhu, J., Li, Q., Chen, S., and Wang, Y., *Eur. Polym. J.* 43, 4593, 2007.
125. Ash, B.J., Rogers, D.F., Wiegand, C.J., Schadler, L.S., Siegel, R.W., and Benicewicz, B.C., *Polym. Compos.* 23, 1014, 2004.
126. Xi, Q., Zhao, C., Yuan, J., and Cheng, S., *J. Appl. Polym. Sci.* 91, 2739, 2004.
127. Ahmad, S., Ahmad, S., and Agnihotry, S.A., *Bull. Mater. Sci.* 3, 31, 2007.
128. Shen, J., Zheng, X., Ruan, H., Wu, L., Qiu, J., and Gao, C., *J. Membr. Sci.* 304, 118, 2007.
129. Avella, M., Errico, M.E., and Gentile, G., *Macromol. Symp.* 247, 140, 2007.
130. Palkovits, R., Althues, H., Rumplecker, A., Tesche, B., Dreier, A., Holle, U., Fink, G., Cheng, C.H., Shantz, D.F., and Kaskel, S., *Langmuir* 21, 6048, 2005.
131. Avella, M., Errico, M.E., and Martuscelli, E., *Nano Lett.* 1, 213, 2001.
132. Horikawa, A., Yamaguchi, K., Inoue, M., Fujii, T., and Arai, K., *Mater. Sci. Eng.* 217, 348, 1996.
133. Paul, D.R., *Polymer Blends*, New York: Academic Press, 1978. [Translated under the title *Polimernye smesi*, Moscow: Mir, 1981].
134. Nielsen, L.E., *Mechanical Properties of Polymers and Composites*, New York: Marcel Dekker, 1974. [Translated under the title *Mekhanicheskie svoistva polimerov I polimernykh kompositov*, Moscow: Khimiya, 1978].
135. Jones, D.P., Leach, D.C., and Moore, D.R., *Polymer* 26, 1385, 1985.
136. Cogswell, F.N., *Thermoplastic Aromatic Polymer Composites*, Butterworth-Heinemann, UK, 1992.
137. Wu, Z., Zheng, Y.B., Yu, H.X., Seki, M., and Yosomiya, R., *Angew. Makromol. Chem.* 164, 21, 1988.
138. Lustiger, A., *SAMPE J.* Sept/Oct, 13, 1984.
139. Seferis, J.C., *Polym. Comput.* 7, 158, 1986.
140. Song, S.S., White, J.L., and Cakmak, M., *Sen'i Gahkaishi* 45, 243, 1989.
141. Lee, Y. and Porter, R.S., *Polym. Eng. Sci.* 26, 633, 1986.
142. Hartness, J.T., *SAMPE J.* Sept/Oct, 26, 1984.
143. Luippold, D.A., *Proc. 30th Natl. SAMPE Symp.* 809, 1985.
144. Cogswell, F.N., *Proc. 28th Natl. SAMPE Symp.* 528, 1983.
145. Blundell, D.J., Crick, R.A., Fife, B., Peacock, J., Keller, A., and Waddon, A.J., in: *Proceedings of the Institute of Physics Conference*, Institute of Physics conference series, no. 89, 1987.
146. Hsiao, B.S. and Chen, E.J.H., *Mater. Res. Soc. Symp. Proc.*, 170, 117–123, 1989.
147. Gram, H., Person, H., and Skarendahi, A., *Natural Fibre Concrete*, (Falkoping: Gummessons Tryckeri AB), 1984.
148. Hergenrother, B.J., Jenson, B.L., and Havens, S.J., *Polymer* 29, 358, 1988.

149. Wang, S., Mo, Z., Zhang, H., Chen, T., and Feng, Z., *Eur. Polym. J.* 33, 949, 1997.
150. Zhang, Z. and Zeng, H., *Polymer* 34, 4032, 1993.
151. Zhang, Z. and Zeng, H., *Eur. Polym. J.* 29, 1647, 1993.
152. Medillin-Rodriguez, F. and Philips, P.J., in: *ANTEC 90*, p. 1264, Society of Plastics Engineers, 1990.
153. Hage, E., Hale, W., Keskkula, H., and Paul, D.R., Polymer 38, 3237, 1997.
154. Utracki, L.A., *Polym. Eng. Sci.* 35, 2, 1995.
155. van Berkel, R.W.M., van Hartingsveldt, E.A.A., and van der Sluijs, C.L., Polybutylene terephthalate, in: *Handbook of Thermoplastics*, O. Olabisi (Ed.), p. 465, New York: Marcel Dekker, 1997.
156. Cruz, C.A., Havriliak, S.J., and Slavin, S., in: *Proceedings of Additives '95: Advances in Additives and Modifiers for Polymers and Blends*, Executive Conference Management, Clearwater Beach, FL, 1995.
157. Hourston, D.J., Lane, S., and Zhang, H.X., *Polymer* 36. 3051, 1995.
158. Joseph, P.V., Kuruvilla, J.K., and Sabu, T., *Compos. Sci. Technol.* 59, 1625–1640, 1999.
159. Karnani, R., Krishnan, M., and Narayan, R., *Polym. Eng. Sci.* 37(2), 476–483, 1997.
160. Paul, A., Joseph, K., and Thomas, S., *Compos. Sci. Technol.* 57(1), 67–79, 1997.
161. Ansari, S.A., Gafur, R.B., Jones, K., Espada, L.A., and Polefka, T.G., *J. Appl. Polym. Sci.* 120(4), 2434–2439, 2011.
162. Jyothi, A.N., *Compos. Interfaces*, 17(2–3), 165–174, 2010.
163. Wang, J., Wang, Y., Tang, Q., Wang, Y., Chang, Y., Zhao, Q., and Xue, C., *J. Ocean Univ. Chin.* 9(1), 94–98, 2010.
164. Okada, M., *Prog. Polym. Sci.* 27, 87, 2002.
165. Weisz, P.B., *Phys. Today* 7, 47, 2004.
166. Ragauskas, A.J., Williams, C.K., Davison, B.H., Britovsek, G., Cairney, J., Eckert, C.A., Fredrick, W.J. Jr., Hallett, J.P., Leak, D.J., Liotta, C.L., Mielenz, J.R., Murphy, R., Templer, R., and Tschaplinski, T., *Science* 311, 484, 2006.
167. Imam, S.H., Mao, L., Chen, L., and Greene, R.V., *Starch/Stärke*, 51(6), 225–229, 1999.
168. Klemm, D., Schmauder, H.-P., and Heinze, T., in: *Biopolymers*, E. Vandamme, S. de Beats, A. Steinbüchel (Eds.), vol. 6, pp. 290–292, Wiley-VCH, Weinheim, 2002.
169. Kaplan, D.L., in: *Biopolymers from Renewable Resources*, D.L. Kaplan (Ed.), pp. 1–29, Springer, Berlin, 1998.
170. Uabolue, S.C.O., *Text. Inst.* 20(4), 1, 1990.
171. Hygreen, J.G. and Bowyer, J.L., *Forest Products and Wood Science: An Introduction*, 2nd ed., p. 155, Iowa State University Press/AME, 1989.
172. Yazaki, Y. and Collins, P.J., *Uses of Wattle Extract: Tannin Based Adhesives*, Rural Industries Research and Development Corporation. RIRDC Publication No. 97/72, Chap. 15, pp. 127–143, 1997.

173. Otey, F.H., Westhoff, R.P., and Russell, C.R., *Ind. Eng. Chem. Prod. Res. Dev.* 19, 592, 1977.
174. Perez, S., Baldwin, P.M., and Gallant, D.J., Structural features of starch granules I, in: *Starch Chemistry and Technology*, R.L. Whistler, J.N. BeMiller, E.F. Paschall (Eds.), 2nd ed., pp. 149–192, Orlando FL: Academic Press, 2009.
175. Jane, J.-L., Structural features of starch granules II, in: *Starch Chemistry and Technology*, R.L. Whistler, J.N. BeMiller, E.F. Paschall (Eds.) 2nd ed., pp. 193–236, Orlando FL: Academic Press, 2009.
176. Griffin, G.J.L., US Patent 4016117, 1977.
177. Glasser, W.G., Barnett, C.A., and Sano, Y., *J. Appl. Polym. Sci., Appl. Polym. Symp.* 37, 441, 1983.
178. Scott, G., Degradation and stabilisation of carbon-chain polymers, in: *Degradable Polymers: Principles and Applications*, G. Scott (Ed.), 2nd ed., chap. 3, Dordrecht: Kluwer Academic Publishers, 2002.
179. Janssen, L., The use of isotopes in soil organic matter studies, in: *Report of the EO/IAEA Technical Meeting, September*, Oxford: Pergamon Press, 1963.
180. Drumright, R.E., Gruber, P.R., and Henton, D.E., *Adv. Mater.* 12, 1841, 2000.
181. Pariser, E.R. and Lombardi, D.P., *Chitin Sourcebook: A Guide to the Research Literature*, John Wiley, New York, 1989.
182. Kovaly, K.A., *Chitin and Chitosan: Specialty Biopolymers for Foods, Medicine, and Industry,* Technical Insights, Inc. Fort Lee, NJ, 1989.
183. Martin, O. and Averous, L., *Polymer* 42, 6209, 2001.
184. Tsuji, H. and Ikada, Y., *J. Appl. Polym. Sci.* 67, 405, 1998.
185. Fang, Q. and Hanna, M.A., *Ind. Crops Prod.* 10, 47, 1999.
186. Gu, J.D., Gada, M., Kharas, G., Eberiel, D., McCarthy, S.P., and Gross, R.A., *Polym. Mater. Sci. Eng.* 67, 351, 1992.
187. Ogata, N., Jimenez, G., Kawai, H., and Ogihara, T., *J. Polym. Sci. B: Polym. Phys.* 35, 389, 1997.
188. Garlotta, D., *Polym. Environ.* 9, 63, 2001.
189. Bogaert, J. and Coszac, P., *Macromol. Symp.* 153, 287, 2000.
190. Ikada, Y. and Tsuji, H., *Macromol. Rapid Commun.* 21, 117, 2000.
191. Lu, J., Qiu, Z., and Yang, W., *Polymer* 48, 4196, 2007.
192. Wu, C. and Liao, H., *Polymer* 48, 4449, 2008.
193. Chang, J., An, Y., and Sur, G.J., *Polym. Sci. B: Polym. Phys.* 41, 94, 2003.
194. Fukuda, N. and Tsuji, H., *J. Appl. Polym. Sci.* 96, 190, 2005.
195. Thostenson, T., Ren, Z., and Chou, T., *Compos. Sci. Technol.* 61, 1899, 2001.
196. Cabedo, L., Feijoo, J.L., Villanueva, M.P., Lagaron, J.M., and Gimenez, E., *Macromol. Symp.* 233, 191, 2006.
197. Kister, G., Cassanas, G., Bengounhon, M., Hoarau, D., and Vert, M., *Polymer* 41, 925, 2000.
198. Moe, K.S. and Weisman, R.A., *Laryngoscope* 111, 1697, 2001.
199. Langer, R. and Vacanti, J.P., *Tissue Eng. Sci.* 260, 920, 1993.
200. Wittwer, G., Adeyemo, W.H., Voracek, M., Turhani, D., Ewer, R., Watzinger, F., and Enislidis, F., *Oral Maxillofac. Surg.* 100, 656, 2005.

201. Powell, H.M., Ayodeji, O., Summerfield, T.L., Powell, D.M., Kniss, D.A., Tomasko, D.L., and Lannutti, J.L., *Biomaterials* 28, 5562, 2007.
202. Steendam, R., van Steenberger, M.J., Hennink, W.E., Frijlink, H.W., and Lerk, C.F., *J. Control. Release* 70, 71, 2001.
203. Nieminen, T., Kallela, I., Keranen, J., Hiidenheimo, I., Kainulainen, H., Wuolijoki, E., and Rantala, I., *Int. J. Oral Maxillofac. Surg.* 35, 727, 2006.
204. Aslan, S., Calandrelli, L., Laurienzo, P., Malinconico, M., Migliaresi, C., *J. Mater. Sci.* 35, 1615, 2000.
205. Schindler, A., Jeffcoat, R., Kimmel, G.L., Pitt, C.G., Wall, M.E., and Zweidinger, R.A., in: *Contemporary Topics in Polymer Science*, E.M. Pearce, J.R. Schaefgen (Eds.), vol. 2, p. 251, Plenum Publishing Corp.: New York, 1977.
206. Sinclair, R.G., *J. Macromol. Sci. A: Pure Appl. Chem.* 33(5), 585–597, 1996.
207. Lipinsky, E.S. and Sinclair, R.G., *Chem. Eng. Prog.* 82, 26–32, 1986.
208. Mobley, D.P., *Plastics from Microbes: Microbial Synthesis of Polymers and Polymer Precursors*, Ohio: Hanser Gardner Publications, 1994.
209. Bigg, D.M., *Annu. Tech. Conf. Soc. Plast. Eng.* 54(2), 2028–2039, 1996.
210. Chen, X., Schiling, K., and Kelly, W., US Patent 5756651, 1998.
211. Tant, M.R., Mauritz, K.A., and Wilkes, G.L. (Eds.), *Ionomers: Synthesis, Structure, Properties and Applications*, London: Blackie Academic Press, 1997.
212. Koleske, J., Polycaprolactone blends, in: *Polymer Blends*, vol. 2, chap. 22, Academic Press: New York, 1978.
213. Potts, J.E., Clendinning, R.A., and Cohen, S., *Soc. Plast. Eng.* [*Tech. Pap.*] 21, 567, 1975.
214. Hull, D., *An Introduction to Composite Materials*, Cambridge: Cambridge University Press, 1981.
215. Ruiz, E. and Trochu, F., *Polym. Compos.* 26(2), 209, 2005.
216. Krawczak, P. and Pabiot, J., J. Compos. Mater. 29, 2230–2253, 1995.
217. Comas-Cardoona, S., Groenenboom, P., Binetruy, C., and Krawczak, P.A., *Compos. Part A* 36, 1004–1010, 2005.
218. Carfagna, C., Amendola, E., Giamberini, M., *Prog. Polym. Sci.* 22, 1607–1647, 1997.
219. Ghosh, N.N., Kiskan, B., and Yagci, Y., *Prog. Polym. Sci.* 32, 1344–1391, 2007.
220. Becker, G.W., Braun, D., and Wilbrand, W. (Eds.), Thermosets – *Kunststoff-Handbuch, Vol. 10 Duroplaste* [*Thermosets*], 2nd ed., Carl Hanser Verlag, 1988.
221. Gardziella, A., Pilato, L.A., and Knop, A., *Phenolic Resins: Chemistry, Applications, Standardization, Safety and Ecology*, 2nd ed., Springer, 1999.
222. Knop, A. and Pilato, L.A. (Eds.), *Phenolic Resins: Chemistry, Applications and Performance – Future Directions*, 2nd ed., Springer, 1985.
223. Potter, W.G., *Epoxide Resins*, Springer, New York, 1970.
224. Landi, V.R., Walters, L.A., and Mosko, J.C., *Plast. Eng.* 36(10), 24–26, 1980.
225. Landi, V.R., Mersereau, J.M., and Dorman, S.E., *Polym. Compos.* 7(3), 152–157, 1986.

226. May, C.A. and Tanka, G.Y., *Epoxy Resin Chemistry and Technology*, Marcell Dekker, New York, 1973.
227. Bouer, R.S., *Epoxy Resin Chemistry*, Advances in Chemistry Series 114, American Chemical Society, Washington, DC, 1979.
228. Hodd, K.A., *Rapra Rev. Rep.* 38, 4, 1990.
229. Chistyakova, A.A. and Kavina, V.A., *Tsvet. Metal.* 34(3), 67, 1961.
230. Xiong, Y. L., Wang, N.M., and Zheng, G., *China Adhesives* 14(7), 27–32, 2005.
231. Hao, D.M., Wang, X.L., and Tang, X.Z., *Polym. Mater. Sci. Eng.* 8(2), 541–547, 2002.
232. Wei, Y.B., Zhang, L., and Li, J., *China Adhesives*, 11(1), 76–81, 2001.
233. Iijima, T., Nishin, T., Fukuda, W., and Tomoi, M., *J. Appl. Polym. Sci.* 60, 37–45, 1996.
234. Xiao, K., *J. Polym. Eng. Sci.* 40(1), 70–81, 2000.
235. Harani, H., Fellahi, S., and Bakar, M., *J. Appl. Polym. Sci.* 70(13), 2603–2618, 1998.
236. Boretos, J.W., *Pure Appl. Chem.* 52, 1851, 1980.
237. Szycher, M. and Poirier, V.L., *Ind. Eng. Chem. Prod. Res. Dev.* 22, 588, 1983.
238. Yui, N., Kataoka, K., Yamada, A., Sakurai, Y., Sanui, K., and Ogata, N., *Macromol. Chem. Rapid Commun.* 7, 197, 1988.
239. Sharma, K., Knutson, K., and Kim, S.W., *J. Control. Release* 7, 197, 1988.
240. Kohjiya, S., Ikeda, Y., Takesako, S., and Yamashita, S., *React. Polym.* 15, 165, 1991.
241. Spathis, G., Niaounakis, M., Kontou, E., Apekis, L., Pissis, P., and Christodoulides, C., *J. Appl. Polym. Sci.* 54, 831, 1994.
242. Redman, R.P., in: *Developments in Polyurethanes*, J.M. Buist (Ed.), chap. 3, Applied Science Publishers, London, 1978.
243. Ku, P.L., *Adv. Polym. Tech.* 8(1), 81–91, 1988.
244. Prime, R.B., *Thermal Characterization of Polymeric Materials*, p. 1380, Academic Press, San Diego, 1997.
245. Muzamdar, S.V. and Lee, L.J., *Polym. Eng. Sci.* 31, 1647, 1991.
246. Glatz, F.P. and Mulhaupt, R., High Perform. Polym. 5, 297–305, 1993.
247. Stenzenberger, H.D. and Konig, P., *High Perform Polym.* 2, 133, 1989.
248. Mikroyannidis, J.A. and Melissaris, A.P., *J. Appl Polym Sci.* 37, 2587–2601, 1989.
249. Chaudhari, M., King, J., and Lee, B., in: *32nd International SAMPE Symposium*, p. 24, 1987.
250. Jin, S. and Yee, A.F., *J. Appl. Polym. Sci.* 43, 1849–1858, 1991.
251. Meng, J.R., Hu, X., Boey, F.Y.C., and Li, L., *Polymer* 46, 2766, 2005.
252. Meng, J. and Hu, X., *Polymer* 45, 9011, 2004.
253. Liu, Y.L. and Chen, Y.J., *Polymer* 45, 1797, 2004.
254. Jeng, R.J., Chang, C.C., Chen, C.P., Chen, C.T., and Su, W.C., *Polymer* 44, 143, 2003.

255. Mendell, J.F., Roberts, D.R., and McGarry, F.J., *Polym Eng Sci.* 23, 615–651, 1983.
256. Kobayashi, S. and Makino, A., *Chem. Rev.* 109, 5288–5353, 2009.
257. Theberge, J.E., *Polym.-Plast. Technol. Eng.* 16(1), 41, 1981.
258. Mann, S., *Nachwachsende Rohstoffe*, Ulmer Verlag: Stuttgart, 1998.
259. Lenz, R.W., *Adv. Polym. Sci.* 107, 1, 1993.

Polymer Blends and Composites: Chemistry and Technology.
Muralisrinivasan Natamai Subramanian.

3

Polymer Properties

Polymers are competitive with metal in several applications due to their flexibility, toughness, and ease of processing and fabrication. Polymers possess several characteristics, such as being flexible, electrically non-conductive, and thermal insulating, which make them useful materials. They may offer advantages such as transparency, self-lubrication, and economy in fabricating and decorating. These properties can be either advantageous or disadvantageous depending on the end use [1–4].

Polymers differ from monomers as starting material. They can be used to achieve high production due to their cost advantage and great potential for part integration. Polymer products are used around the world due to their physical and chemical properties. The majority of polymer products have suitable optical, barrier and mechanical properties for a wide range of applications due to their chemical inertness [5]. Polymers are light weight. They have a wide variety of useful combined effects, which has resulted in their dramatic emergence as one of the most important classes of materials on which modern society is built. The choice of polymer is governed by the particular application. In some cases the polymer is specifically selected for its physical and chemical characteristics.

3.1 Chemistry

The chemistry of chemicals has been connected to different molecular entities. It is possible for a router to connect two or more of the same or different molecular entities via a monomer. Therefore, it is possible to produce a product with properties which can be exploited in a variety of applications. In general, polymers belong to a very wide series of same and/or different monomers and also with different substrates. This confers to the monomer molecule typical basic properties such as the possibility of chains which are linear or branched or both.

Besides the behavior of the polymer, the functional groups present in the substrate and monomer also show peculiar properties which derive from their own structure. Of these, the possibility of monomer substitution by a functional group is an important aspect. It is noteworthy that several reactions of macromolecular chemistry involve monomers and their chemistry.

Polymers with flexible chain molecules can theoretically assume three diverse conformations in the molten state. Long chains may coil into balls, forming globular conformations in the molten state. They can either assume a completely irregular chaotic pattern, becoming interwoven with each other [6–14], or can gradually acquire a certain order by paralleling chain segments. The major uses of bulk polymers require that the material be in a rigid form, retaining its shape. In polymer, the stronger the interchain bond, the stiffer the polymer is.

3.2 Polymer Properties

The structure-property relationships are greatly significant industrially and scientifically, which accounts for the abundant research work. Polymers are long-chain molecules. They are composed of a main monomer unit that repeats throughout the structure. There are hundreds and even thousands of monomer units of polymer repeated to form one polymer chain. Polymer is a complex mixture of variable molecular weight present in distribution. Polymers are polydisperse to varying degrees in a variety of ways.

Many polymer properties depend on the type and parameters which come from the molecular structure shown in Figure 3.1. Chains of sufficient length may thus become entangled, which manifests itself in properties such as diffusion and melt viscosity. Many molecular properties influence the physical characteristics of polymers, including molecular weight and its distribution, short- and long-chain branching, branch length and

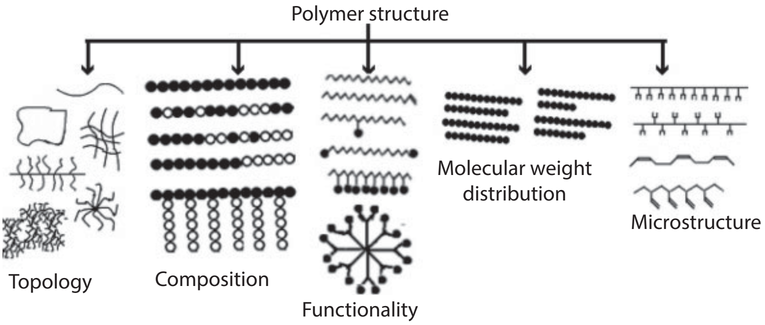


Figure 3.1 Parameters defining polymer structure.

frequency distribution. Excellent control over the molecular weight and its distribution has contributed to the fundamental understanding of long-chain branch [15, 16]. The properties of the polymers are also dependent on the nature of the substituent.

Suitable polymer at the molecular level is also responsible for mechanical properties such as strength, elasticity, etc. The chain may or may not contain a functional group, such as –NH or –OH bond, and may not contain any side groups which distort the linearity of the molecules. It is important to influence the interfacial activity of polymer chains to affect the polymer architecture and morphology of the properties of chains at penetrable and impenetrable interfaces.

Polyethylene and polypropylene are semicrystalline hydrocarbon polymers. Many polymers are completely amorphous, such as polystyrene and its copolymers and all thermosets. This should be satisfied to varying degrees by the glassy, amorphous, thermoset, and semicrystalline state of polymeric materials. The electrical, conductivity, solubility, mechanical and rheological properties are of equal theoretical and practical importance. The gap between molecular and macroscopic properties with intermediate processing history bridges the gap, as in Figure 3.2a. The tools and expertise required can be successfully used in the relation between the intrinsic behavior and the macroscopic response, as shown in Figure 3.2b [16].

The polymer chains are in a "network" structure. In the case of an amorphous polymer, the subchains of the network would be created by chain entanglements [17, 18]. However, in semicrystalline polymers, crystallites can also generate subchains [19]. Crosslinking is a broadly used method for the modification of polymer properties. This process involves the formation of tridimensional structures, gels, causing substantial changes in material properties [20]. Table 3.1 illustrates some of the physical properties versus molecular structure.

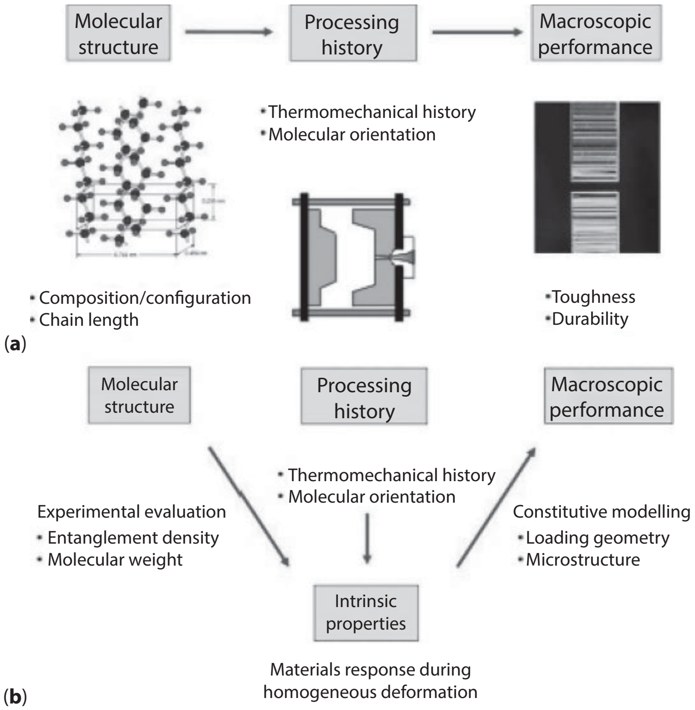


Figure 3.2 From molecular details to macroscopic response via the intermediate of the polymer's intrinsic deformation. (Reprinted with permission from [16]; Copyright © 2005 Elsevier Ltd. All rights reserved)

Table 3.1 Some of the physical properties versus molecular structure.

Physical property	Molecular structure requirement
Dimensional stability, resistance to solvent, and heat stability	Crosslinking
Melt fracture resistance	Long-chain branching
Stiffness/modulus	Polymer density, crystal morphology
Processing and melt strength	Long-chain branching and molecular weight distribution
Optical properties	Crystal morphology, density

3.2.1 Glass Transition Temperature (T_g)

The glass transition temperature is an important characterizing parameter for amorphous polymers. It is a kinetic rather than a thermodynamic transition and depends on cooling rates. During cooling, the temperature at transition point where the material forms glass from its equilibrium liquid state, molecular mobility decreases with decreasing temperature, which is known as the glass transition temperature [21, 22]. In thermoplastic polymers below glass transition temperature (T_g) the interchain bonds limit chain motion and above T_g the bonds of the polymer chains move freely and are of viscoelastic nature. Both polymers of thermosets and thermoplastics operating below T_g release stress, causing the molecular chain to spring back to its original position.

The T_g is affected depending on the extent of branching. With a low number of branches, T_g is reduced due to increased free volume. Higher branching density, as with side groups, restricts mobility and therefore results in higher T_g. Crosslinking tends to reduce the specific volume of the polymer. The free volume is reduced and the molecular motion becomes more difficult when T_g is raised in the case of reduction of specific volume. Some polymers are either partially crystalline or partially amorphous, giving them both a melting point and one or more glass transition temperaratures (T_g is the temperature above which the extent of localized molecular flexibility is substantially increased).

The relationship between the chemical structure and T_g of polymers is an important aid in the search for materials with specific physical properties in a given temperature range. The insertion of new chemical units into a polymer chain leads to a change in the T_g. As the temperature is lowered, the expansivity of all polymers, even in the absence of crystallinity, decreases from a value of about that of a normal liquid to a value near that of a normal crystalline solid. The structure as a function of the polymerization temperature has shown that the degree of stereospecificity and crystallinity increase as the polymerization temperature is lowered [23]. The T_g is determined by measuring the stiffness modulus versus temperature and mechanical loss versus temperature curves.

The T_g of a polymer to a large extent determines its processability, hardness, heat distortion temperature and other mechanical properties. Polymer structural variations, such as molecular weight, symmetry, polarity, pendant groups, hydrogen bonding, stereoregularity, etc., affect the T_g.

3.2.2 Crystallinity

The physical, chemical, and mechanical properties of crystalline polymers depend on the morphology, the crystalline structure, and the degree of crystallization. It takes a great deal of effort to control the rate of crystallization, degree of crystallinity and to obtain the desired morphology and properties [24–26]. Crystallization behavior optimizes process conditions and controls the properties of the final products. Increases in crystallinity lead to a decrease in the amplitude of the dielectric relaxation process [27].

The degree of crystallinity in polymers is an important property which needs to be taken into account when considering the manufacturing and applications of such materials. The degree of crystallinity (DC) diminishes with the increase of moisture absorption. The syndiotactic-isotactic ratio of this polymer, and consequently its crystallinity, depend on the polymerization conditions and on the thermal and mechanical history of the product [28].

Depending on the crystallization conditions, the amorphous component can be (1) located in the interlamellar zone between the crystalline lamellae, (2) excluded from the interlamellar zone but contained within the spherulite, and/or (3) rejected either partially or completely from the spherulite, resulting in the formation of a matrix in which the spherulites are embedded [29].

Changes in the crystallinity of thermoplastics result in significant changes in the mechanical behavior of composites containing them, particularly those that are matrix dominant such as buckling, compression or creep. For this reason, the ability to precisely characterize the polymer crystallinity in thermoplastic composites becomes an important requirement. Owing to the heterogeneous nature of the composite, determination of the crystallinity becomes more complicated [30]. Linear polymers which crystallize show a variation of thermodynamic properties such as heat content and specific volume. Semicrystalline polymers exhibit short-range as well as long-range ordering of macromolecular chains. Both types of ordering contribute towards the degree of crystallinity of the polymer.

Crystallization behavior is very important for determining the final properties of semicrystalline polymer blends. Crystallization behavior, such as spherulite structure, crystallization kinetics, crystallinity and melting temperature, is influenced by molecular structure [31–34]. The crystallization behavior of polymer is a basic problem in polymer physics. The filler in a polymer will especially affect the crystallization behavior of the polymer-based composites very much [35–37] because the filler may adsorb the polymer molecules and act as crystal nuclei.

Morphological characteristics of crystalline lamellae are important for macroscopic properties of polymer-based composites as well as filler orientation. The effect of crystallization on the properties of composite systems under various processing conditions, including elongation, injection, and extrusion, induce macromolecules to preferentially align parallel to the processing direction [38, 39].

3.2.3 Tacticity

Tacticity is defined as molecules requiring a longer sequence of stereoregular structure before discrete reflections can be observed. The stereoregularity of polymer molecules is a microstructural feature of great importance which determines, to a large extent, the bulk properties and hence the commercial value of many polymeric materials.

Subtle variations in chain tacticity may lead to a significant impact on the related properties such as crystallizability, thermal stability, and mechanical strength. Atactic polystyrene exhibits noncrystalline nature, however, both isotactic and syndiotactic polystyrene show crystallizable behavior; the crystallization rate is about one order faster for syndiotactic polystyrene than that for isotactic polystyrene at a given super cooling degree [39–41].

For vinyl polymers such as polypropylene (PP) and poly(methyl methacrylate) (PMMA), the tacticity has an effect on chain conformations [42–44] and molecular-dynamic simulation [45–47]. Stereoregularity in the polymers affects the local conformation, which, in turn, affects specific group interactions with other constituent polymers and hence the miscibility is varying tacticity with similar thermal behavior (i.e., T_g) in order to distinguish the effect of tacticity on conformation and intermolecular interaction from that on more local segmental mobility (related to T_g). Tacticity can have an effect on the phase diagram of a binary mixture [48]. Conformational differences between polymers of differing tacticities can have an impact on blend phase behavior.

3.2.4 Intermolecular Forces

Polymer chains are long and their interchain forces are amplified far beyond the attractions between conventional molecules. Different side groups on the polymer can tend to have ionic bonding or hydrogen bonding between their own chains. Stronger force results in higher tensile strength and higher crystalline melting points.

Polymers, such as polyethylene and polypropylene, can form hydrogen bonds as intermolecular force between adjacent chains. Therefore, it can result in high tensile strength and melting point of the polymers. In many polymers the functional group within the polymer chains can have dipole-dipole interactions. However, these are not as strong as hydrogen bonding. The melting point of such polymers will be lower than hydrogen-bonded polymers but the dipole-bonded polymers will have greater flexibility. Therefore, the attractive forces between polymer chains play a large part in determining polymer properties.

The behavior of solutes in polymers is important for many industrial applications. A wide variety of additives are incorporated with intermolecular forces in polymers, including plasticizers, antiplasticizers, processing aids, lubricants and heat stabilizers [49]. Large molecules will exhibit a substantial change in diffusion coefficient at T_g because the size of the solute dictates that intermolecular force is coupled with the cooperative relaxation associated with the glass transition [50].

3.2.4.1 Dipole Moment

Dipoles in the monomer units can affect the intermolecular forces in polymers. The dielectric constant and power factor remain constant over a wide range of frequencies, and the dielectric constant changes little with temperature. Its electrical properties are practically unaffected by changes in humidity or by immersion in water.

Olefin molecules have no permanent dipole. The force of attractions between polyolefin chains arise from weak van der Waals forces. As polymer chains approach each other, their electron clouds repel one another. This has the effect of lowering the electron density on one side of a polymer chain and in the other side it creates a slight positive dipole. It is enough to attract the polymer chain. Since van der Waals forces are weak, polyolefins can have a lower melting temperature compared to other polymers such as nylon, polycarbonate, etc. [51–53].

3.2.4.2 Phase Behavior

Polymer phase behavior inputs are critical for process development, process design, and process operation activities related to their production. These properties are strongly influenced by the phase behavior or the interactions between the polymer chains. The effects that occur at the phase boundary are of great importance. Introduction of a polymer into the polymer changes the kinetics and thermodynamics of its crystallization. Most mixtures of polymers can be considered to be a special kind of heterogeneous colloidal systems. As blends and composites, the adhesion improvements between the phases have some effects which occur at boundary phase [54–58]. Mixtures of polymers differ from the classical colloidal systems in the transient layer between their components [59].

Polymer-polymer phase behavior can be deceptively complex. Many molecular properties influence physical characteristics of polymers, including molecular weight and its distribution, short- and long-chain branching, branch length and frequency distribution. Excellent control over the molecular weight and its distribution has contributed to the fundamental understanding of long-chain branch [15, 60]. Also, the properties of the polymers are dependent on the nature of the substituent.

3.3 Surface Properties

Chemistry at polymer surfaces and interfaces is central to many polymer materials applications [61]. Surface property, i.e., surface energy, is expected to be influenced by changes in the bulk, including an increase/decrease of the extent of phase separation and the degree of compatibility; these are known to be reflected strongly in various mechanical properties as well. In fact, the dynamic behavior of polymer surfaces and the environmental dependence of polymer surface properties are already recognized [62, 63].

Polymer surfaces can be chemically modified by preparing substrates with controllable surface chemical structures and can rationally address the control of macroscopic surface properties (adsorption, adhesion, wettability, and friction). Polymer surfaces can be modified by using a number of different methods, each with certain advantages and disadvantages. Polymer surfaces and surface properties are important for many of the properties of a material. It is desirable for the properties at the surface of a polymer to be distinctly different from the bulk properties. Surfaces to promote adhesion, wettability, biocompatibility, chemical resistance, and hydrophobicity are all sought after for numerous applications, and the introduction of such properties is often achieved via a costly post-processing procedure [64].

In nonpolar polymers, applications have been restricted and many chemical and physical methods have been used to modify the surface properties of polymer materials. Therefore, polar functional groups are introduced directly onto the surface. Surface composition of a multi-component polymer system is usually different from that of a bulk polymer system [65] in that the surface segregation of one component in the polymer blends can be expected. This effect is believed to relate to the polymer surface region that is only several or several tens of angstroms thick.

The great challenge of the design of various bulk or surface properties is connected with the use of a non-changing polymeric backbone. This can be realized by the exchange of attached side chains to receive the desired characteristic features of such polymeric materials [66].

3.3.1 Viscoelastic Properties

The behavior of plastic materials under the action of stresses is very complex because elastic and viscous deformations take place simultaneously. A substance showing such behavior may be referred to as a viscoelastic material. In complex, overall deformation is usually divided into the following types:

- Deformation that is reached almost immediately upon application of the load and is completely recoverable upon release of the load.
- Deformation that is developed in the material at a continuously decreasing rate. Most of this deformation is recoverable. However, it may take from a few seconds to months or years to reach the complete delayed elastic deformation, depending on the temperature and the properties of the material.
- Viscous deformation (or flow), which is developed in a material at a rate proportional to the applied stress and will continue until the specimen is ruptured or the test conditions are altered. This type of deformation is irrecoverable.

The phenomenon is very complex for most materials due to the fact that apparently many delayed elastic processes or mechanisms differing in response or relaxation time are superimposed upon each other. At high temperatures some plastic materials show almost pure viscous flow.

Most plastic materials, however, show a mixture of viscous and “elastic” deformations even at high temperatures. Delayed elastic processes may become simple enough at high temperatures to be amenable to analysis, usually since many of the complicating processes, important at low temperatures, become negligible or disappear altogether. The fatigue behavior of polymeric materials is closely related to the nonlinear viscoelasticity being accompanied by irreversible structural change, which is very important to industrial applications. This nonlinear viscoelastic behavior accompanying irreversible structural changes in crystalline polymers appears even at small strain or stress level [67–71].

Viscoelastic behavior of concentrated systems of high polymers, such as polymer melt, has revealed that the entanglement couplings between molecular chains constitute one of the most significant factors which determine the rheological properties. Theoretical treatments of the entanglement couplings in the concentrated systems cannot satisfactorily describe very strong interactions between molecular chains or segments. Rheological properties of various high polymers, such as polyethylene, polypropylene, polystyrene, poly(methy1 methacrylate), and poly(vinyl acetate), in the molten state generalize the effect of entanglement couplings. The rheological properties of concentrated polymer systems are strongly affected by the molecular weight and its distribution, especially in the terminal and rubbery zones. In the bulk of the rubbery region, viscoelastic response is only slightly affected by the presence of the filler. The adsorption of polymer segments on the reinforced filler surface cannot cause a major loss in segmental mobility [72].

In branched polymers, the effects of branching are well characterized with respect to number and length of branches as well as molecular weight distribution. Molecular weight and its distribution have an effect on the viscoelastic and rheological properties of amorphous polymers. It is highly important to measure not only the viscous but also the elastic properties in the rubbery flow or terminal zones [73]. Typical viscoelastic materials and their behavior depend strongly upon time scale and temperature. The effect of branching on viscoelastic properties is also difficult to separate from that of molecular weight distribution [74]. In blends and composites, the viscoelastic and mechanical properties of polymeric materials are strongly affected by structure, conformation, and molar mass of the chain. The polymer molar mass directly influences the topological properties of polymer melts, which regulate the onset and the dynamics of the entangled regime, usually modeled by using the reptation concept [75].

3.3.2 Mechanical Properties

The testing of mechanical properties is an important measure of product quality. Strength refers to the ability of a structure to resist loads without failure. The mechanical properties are important to its practical use. The equilibrium and dynamic properties of polymers must ultimately be related to a number of characteristic molecular parameters.

3.3.3 Tensile Properties

Tensile properties are important for several reasons. They are used in selecting materials for engineering applications. Tensile properties include the resistance of materials to pulling or stretching forces. They ensure quality of new materials and processes so that different materials and processes can be compared. Tensile properties are used to predict the behavior of a material under forms of loading other than uniaxial tension. The strength of a material often is the primary concern. The strength of interest may be measured in terms of either the stress necessary to cause appreciable plastic deformation or the maximum stress that the material can withstand. These measures of strength are used with appropriate safety factors in engineering design.

The amount of force required to break a material and the amount it extends before breaking are important properties. For most materials, the initial resistance to force or modulus, and the point of permanent deformation, is obtained from plots of force against elongation. The material ductility is a measure of deformation before polymer gets fractures [76–78].

3.3.4 Electrical Properties

The electrical properties of polymers depend on the dielectric constant and the loss factor on the temperature and frequency, and the electrical conductivity in direct current and its dependence on the temperature and other factors. In regard to concepts of the interdependence of electrical parameters and changes due to polymerization, observations of the behavior of the dissipation factor during cure are useful tools in reaching an understanding of these important processes. Dielectric strength is a relationship between the breakdown voltage and the sample thickness, representing the maximum field which the materials can withstand. Many existing factors influence the AC dielectric strength of polymers [79, 80]: environmental conditions (temperature, moisture), applied voltage frequency, electrode conditions, and the polymers themselves with regard to their morphology, additives, defects and so on.

3.3.5 Thermal Properties

Differences in thermal properties, from low temperature through the glass transition temperature and into the liquid temperature regimes, emphasize the effect of stereoregularity upon the molecular motion in the glassy state, the change in specific heat at the glass transition temperature, and the entropy of the polymer liquid [81]. Improving thermal properties of polymer networks at a lower cost is of great interest, especially if it can be ensured that other properties, such as mechanical or electrical properties, are not affected by the increase in the glass-transition temperature.

3.3.6 Magnetic Properties

In molecules with magnetic behavior, usually only a diamagnetic contribution is expected. Magnetism in molecules arises from the intrinsic spin of unpaired electrons. The molecules are designed in such a way that they satisfy a conjugated but non-Kekulé and non-disjoint connectivity among the nonbonding molecular orbitals of the unpaired electrons. The spins within one conjugated polymer chain couple ferromagnetically, which results in a high-spin (polymer) molecule [82–84].

A mutual magnetic interaction between these spins aligns them parallel or antiparallel, affording magnetic order. In organic molecular ferromagnetism, unpaired electrons with the same spin orientation in the same molecule are required. Spins are deliberately introduced on the development of (conjugated) materials efforts to introduce magnetism in organic (polymer) materials.

3.3.7 Barrier Properties

Barrier properties in polymer have many uses in packaging due to their light weight, strength, transparent nature, and easy processing. Single polymer have high level of permeation of gas and solvents. Polymers exhibit poor barrier properties for solvents and gases. However, it has good moisture barrier properties. The dispersed polymer in the polymer blends improves barrier properties in laminates. The barrier properties of a polymer blend depend not only on the intrinsic barrier property of each polymer component but also on the end blend morphology. The blend morphology is generally decided by many factors, such as composition, blend mixing, interfacial tension and rheological properties. During processing, shear flow is less important than extensional flow in the deformation of dispersed phase on diffusion through arrays of spheres, cylinders, and ellipsoids [78, 79].

3.3.8 Rheological Properties

Rheological properties are used to monitor the degradation and crosslinking processes in polymers [85–88]. The viscosity is a rheological property that is most frequently used for characterization [89].

Like other rheological properties, viscosity depends on the flow conditions (shear rate, temperature and pressure) and polymer composition (chemical structure, molecular weight distribution and additives) [90, 91].

3.3.9 Elastic Properties

Improvement of elastics properties in the molten state, such as the strain-hardening in the elongational viscosity, normal stress difference, and swell ratio, is one of the most important areas of linear polymers. It would result in the availability of numerous conventional polymers for various processing operations that require the extension of molten materials with a free surface, such as blow molding, film processing, thermoformng and foaming [92–94].

The production of thermoplastic polymer specimens of high degrees of chain orientation by mechanical deformation requires deformation to take place at a temperature and rate where the mechanical response of the polymer can be described as rubbery [95]. This implies that the polymer chains are present in a "network" structure. In the case of an amorphous polymer, the subchains of the network would be created by chain entanglements [17, 96]. However, in semicrystalline polymers, crystallites can also generate subchains.

3.3.10 Thermodynamic Properties

Glass transition temperature (T_g) is the temperature at which polymer matrix undergoes a change in thermodynamic properties. Reinforcing agents (inorganic filler or fiber) or crosslinking agent does not experience discontinuities in its thermodynamic properties over that temperature range. Therefore, glass transition temperature depends on the adhesive strength of the reinforcing agent/matrix interface, and for crosslinked materials, it is directly related to mechanical reinforcement [97]. Local (segment scale) interactions are governed by both enthalpic and entropic factors.

Polyolefins present a particularly challenging set of materials since the enthalpic driving force or demixing is quite weak, thus amplifying non-ideal contributions to the overall mixing free energy [98]. They are characterized by opacity, multiple thermal transitions, etc., and their mechanical properties may be poor. Thermodynamically miscible polymer mixture is characterized by a single thermal transition as well as a single amorphous phase. These mixtures result in physical property compromises on balance, and may be superior to those of the individual constituent polymer. They could result in a new set of products without the usual significant capital investment [99, 100]. The majority of polymer mixtures are immiscible [101].

3.4 Catalysis

Catalysis plays a critical role in enhancing the rate of chemical reactions. It also controls the reaction of interest relative to other competing reactions. For fine synthesis, high chemo, region, and stereoseletivities, and particularly enantioselectivities, can compensate the rate [102]. Catalyst residue is often left in the final material due to the difficulty or added cost of separating these impurities from the resultant polymer. The selectivity for ideal polymer synthesis includes that which has control over the molecular weight, molecular weight distribution, the nature and number of polymer end groups, the architecture, stereochemistry, and topology of the macromolecules (linear, branched, cyclic), degree of crosslinking and the functionality and sequence of monomers in the chain [103].

3.5 Factors Affecting Polymer Properties

Polymer properties are influenced not only by their chemical structure (constitution, molar mass, configuration, microconformation), but also by their physical structure. These structures may range from totally irregular arrangements of chain segments over shorter or longer parallelizations of chains, to voids and other defects in otherwise highly organized assemblies of polymer molecules. Two possible ideal structures exist in the solid state: perfect crystals and totally amorphous polymers [104–106].

During polymerization, the degree of conversion is increased with some structural changes occuring in the polymer [107]. The main structural factors which affect the physical properties are stereoregularity, molecular mass, and polydispersity, mostly through their influence on crystallinity. In the polymerization stage, tailoring polymer properties requires a profound insight into the relationships between catalyst, chain microstructure, crystalline properties, and final product properties [108].

In polymer materials, there are additional problems such as molecular chain backbone and the overall part-wise morphology. Hence, bulk properties of polymer are classified as molten, semicrystalline, glassy and thermoset states. Understanding the interrelations between processing, properties and structure forms is the cornerstone of modern materials science. General properties of synthetic and natural polymers are given in Table 3.2.

Table 3.2 Typical properties of polymers.

	Synthetic polymers		
Properties	**Thermoplastics**	**Thermosets**	**Natural polymers**
Mechanical	Good	Good	Poor
Wather affinity	Hydrophobic	Hydrophobic	Hydrophilic
Processing	Easy	Difficult	Difficult
Biodegradation	No	No	Yes
Barrier	Good	Bad	Bad
Overall	Yes	Yes	No

3.6 Summary

- Polymers provide a viable route and highly promising approach for performance end products with blends and composites.
- They are greatly influenced by properties and result from required specific properties.
- Fastest growing areas of polymers have been developed on the basis of specific performance.
- Proper balance of properties is to be achieved by the control of phase morphology.
- Phase geometry and morphology parameters play an important role in determining properties of blends and composites [109].

References

1. Meenakshi, P., Noorjahan, S.E., Rajini, R., Venkateswarlu, U., Rose, and C., Sastry, T.P., *Bull. Mater. Sci.* 25(1), 25–29, 2002.
2. Fang, J. and Fowler, P., *Food Agric. Environ.* 1(3–4), 82–84, 2003.
3. Seymour, R.B., *Additives for Polymers: Introduction to Polymer Chemistry*, chap. 11, pp. 268–271, New York: McGraw-Hill Book Company, 1971.
4. Orhan, Y., Hrenovic, J., and Buyukgungor, H., Acta Chim. Slov. 51, 579–588, 2004.
5. Beall, G., Pinnavaia, T.P. (Eds.), *Polymer-Clay Nanocomposites*, Wiley & Sons: Chichester, U.K., 2000.
6. Gopalakrishnan, T.R. and Beiner, M., *J. Phys.: Conf. Ser.* 40, 67, 2006.
7. Beiner, M., Schröter, K., Hempel, E., Reissig, S., and Donth, E., *Macromolecules* 32 6278, 1999.
8. Arrighi, V., Triolo, A., McEwen, I.J., Holmes, P., Triolo, R., and Amenitsch, H., *Macromolecules* 33, 4989, 2000.
9. Arrighi, V., McEwen, I.J., and Holmes, P.F., *Macromolecules* 37, 6210, 2004.
10. Stepanyan, R., Subbotin, A.V., Knaapila, M., Ikkala, O., and Brinke, G.T., *Macromolecules* 36, 3758, 2003.
11. Fox, J.J. and Martin, A.E., *Proc. Roy. Soc. (London)*, A175, 208, 1940.
12. Smith, D.C., *Ind. Eng. Chem.* 48, 1161, 1956.
13. Cho, S. and Choi, W., Solid-phase photocatalytic degradation of PVC–TiO2 polymer composites. *J. Photochem. Photobiol. A: Chem.* 143, 221–228, 2001.
14. Hamid, S.H., *Handbook of Polymer Degradation*, 2nd ed., CRC Press: Florida, 2000.

15. Lohse, D.J., Milner, S.T., Fetters, L.J., Xenidou, M., Hadjichristidis, N., Mendelson, R.A., Garcia-Franco, C.A., and Lyon, M.K., *Macromolecules* 35, 3066, 2002.
16. Meijer, H.E.H. and Govaert, L.E., *Prog. Polym. Sci.* 30, 915–938, 2005.
17. Porter, R.S. and Johnson, J.F., *Chem. Rev.* 66, 1, 1966.
18. Gressley, W.W., *Adv. Polym. Sci.* 16, 1, 1974.
19. Mills, P.J., Hay, J.N., and Haward, R.N., *J. Mater. Sci.* 20, 501, 1985.
20. Chodak, I., *Prog. Polym. Sci.* 23, 1409, 1998.
21. McKenna, G.B. and Simon, S.L., *Handbook of Thermal Analysis and Calorimetry: Applications to Polymers and Plastics*, S.Z.D. Cheng (Ed.), vol. 3, pp. 49–109, Elsevier Science, 2002.
22. Plazek, D.J. and Ngai, K.L., *Physical Properties of Polymers Handbook*, J.E. Mark (Ed.), pp. 139–159, AIP Publishing: Woodbury, NY, 1996.
23. Fordham, J.W.L., Burleigh, P.H., and Sturm, C.L., *J. Polymer Sci.* 41, 73, 1959.
24. Choudhury, A., *Mater. Sci. Eng. A* 491, 492, 2008.
25. Run, M.T., Wu, S.Z., Zhang, D.Y., and Wu, G., *Polymer* 46, 5308, 2005.
26. Di Lonrenzo, M.L. and Silvestre, C., *Prog. Polym. Sci.* 24, 917, 1999.
27. Ishida, Y., Matsuo, M., Togami, S., Yamafuji, K., and Takahanagi, M., *Kolloid Z.* 183, 74, 1962.
28. Carrega, M., *Pure Appl. Chem.* 49 569, 1977.
29. Hudson, S.D., Davis, D.D., and Lovinger, A.J., *Macromolecules* 25, 1759, 1992.
30. Lee, T.H., Boey, F.Y.C., and Khor, K.A., *Compos. Sci. Technol.* 53, 259–274, 1995.
31. Martuscelli, E., Silvestre, C., and Abate, G., *Polymer* 23, 229, 1982.
32. Martuscelli, E., *Polym. Eng. Sci.* 24, 563, 1984.
33. D'Orazio, L., Mancarella, C., Martuscelli, E., and Sucott, G., *J. Mater. Sci.* 26, 4033, 1991.
34. Martuscelli, E., Silvestre, C., and Btanchi, L., *Polymer* 24, 1458, 1983.
35. Xu, W.B., Ge, M.L., and He, P.S., *J. Polym. Sci. B: Polym. Phys. Ed.* 40, 408, 2002.
36. Xu, W., Ge, M., and He, P., *J. Appl. Polym. Sci.* 82, 2281, 2001.
37. Zheng, Q.A., Peng, M., and Yi, X.S., *Mater. Lett.* 40, 91, 1999.
38. Jouault, N., Vallat, P., Dalmas, F., Said, S., Jestin, J., and Boue, F., *Macromolecules* 42, 2031, 2009.
39. Chen, W.C., Lai, S.M., and Chen, C.M., *Polym. Int.* 57, 515, 2008.
40. Cimmino, S., Pace, E.D., Martuscelli, E., and Silvestre, C., *Polymer* 32, 1080, 1991.
41. Wang, C., Lin, C.C., and Tseng, L.C., *Polymer* 47, 390, 2006.
42. Fuchs, K., Friedrich, C., and Weese, J., *Macromolecules* 29, 589, 1996.
43. Jones, T.D., Chaffin, K.A., Bates, F.S., Annis, B.K., Hagaman, E.W., Kim, M.H., Wignall, G.D., Fan, W., and Waymouth, R., *Macromolecules* 35, 5061, 2002.
44. Liu, C., Yu, J., He, J., Liu, W., Sun, C., and Jing, Z., *Macromolecules* 37, 9279, 2004.

45. Antoniadis, S.J., Samara, C.T., and Theodorou, D.N., Macromolecules 32, 8635, 1999.
46. Madkour, T.M. and Soldera, A., *Eur. Polym. J.* 37, 1105, 2001.
47. Arrighi, V., Batt-Coutrot, D., Zhang, C., Telling, M.T.F., and Triolo, A., *J. Chem. Phys.* 119, 1271, 2003.
48. Schurer, J.W., de Boer, A., and Challa, G., *Polymer* 16, 201, 1975.
49. Sears, J.K. and Darby, J.R., *The Technology of Plasticizers*, John Wiley: New York, 1982.
50. Fujita, H., in: *Diffusion in Polymers*, J. Crank, G.S. Park (Eds.), chap. 3, Academic Press, 1968.
51. Carraher, C.E. Jr., *Polymer Chemistry*, 6th ed., Marcel Dekker Inc.: New York, 2003.
52. Jones, R.W. and Simon, R.H.M., Synthetic plastics, in: *Riegel's Handbook of Industrial Chemistry*, J.A. Kent (Ed.), 8th ed., chap. 10, Van Nostrand Reinhold: New York, 1983.
53. Lokensgard, E., *Industrial Plastics: Theory and Applications*, Delmar Cengage Learning: Clifton Park, New York, 2010.
54. Bly, J.H., Brandt, E.S., and Burgess, R.G., *Radiat. Phys. Chem.* 14, 931–935, 1979.
55. Carstens, T.J. Jr., PVC the versatile plastic, in: *Proceedings of the 1998 Regional Technical Meeting for Society of Plastics Engineers*, SPE: Detroit, MI, USA, 1998.
56. Hirschler, M.M., in: *Developments in Polymer Stabilization*, G. Scott (Ed.), vol. 5, pp. 107–153, Applied Science Publisher: London, 1982.
57. Tkac, A., in: *Developments in Polymer Stabilization*, G. Scott (Ed.), vol. 5, pp. 170–189, London: Applied Science Publisher, 1982.
58. Rothon, R.N. and Hornsby, P.R., *Polym. Degrad. Stab.* 54, 383–385, 1996.
59. Carty, P. and White, S., *Polym. Degrad. Stab.* 43(3), 471–473, 1994.
60. Carella, J.M., Gotro, J.T., and Graessley, W.W., *Macromolecules* 19, 659, 1986.
61. Weidisch, R., Stamm, M., Michler, G.H., Fischer, H., and Jérôme, R., *Macromolecules* 32, 742–750, 1999.
62. Garbassi, F., Mona, M., and Occhiello, E., *Polymer Surfaces: From Physics to Technology*, John Wiley and Sons: UK, 1996.
63. Mansfield, K.F. and Theodorou, D.N., *Macromolecules* 24, 6283, 1991.
64. Narrainen, A.P., Hutchings, L.R., Ansari, I., Thompson, R.L., and Clarke, N., *Macromolecules* 40, 1969–1980, 2007.
65. Thomas, H. and O'Malley, J.J., *Macromolecules* 14, 1316, 1981.
66. Appelhans, D., Wang, Z.-G, Zschoche, S., Zhuang, R.-C., Haüssler, L., Friedel, P., Simon, F., Jehnichen, D., Grundke, K., Eichhorn, K.-J., Komber, H., and Brigitte Voit, B., *Macromolecules* 38, 1655–1664, 2005.
67. Catsiff, E., Alfrey, T., and O'Shaughnessy, M.T., *Tex. Res. J.* 23, 808, 1953.
68. Bauwens, J.C., *Colloid Polym Sci.* 270, 537, 1990.
69. Tieghi, G., Levi, M., Fallini, A., and Danusso, F., *Polymer* 32, 39, 1991.
70. Litt, M.H. and Torp, S., *J. Appl. Phys.* 44, 4282, 1973.

71. Rahaman, M.N. and Scanlan, J., *Polymer* 22, 673, 1981.
72. Kraus, G., Rollmann, K.W., and Gruver, J.T., *Macromolecules* 3, 92, 1970.
73. Onogi, S., Masuda, T., and Kitagawa, K., *Macromolecules* 3, 109, 1970.
74. Fujimoto, T., Narukawa, H., and Nagasawa, M., *Macromolecules* 3, 57, 1970.
75. Doi, M. and Edwards, S.F., *The Theory of Polymer Dynamics*, Oxford University Press: Oxford, 1986.
76. Gandhe, G.V., Lorenzo, L., and Noritake, Y., Design development of energy absorbing ribs for meeting FMVSS201 extended head impact, SAE Technical Paper, SAE-970161, 1997.
77. Lorenzo, J.M., FMVSS201 A: Pillar impact simulation and verification study, SAE Technical Paper, SAE-1999-01-0433, 1999.
78. Xiao, X., Plastic material modeling for FMVSS201 simulation, SAE Technical Paper, SAE-2002-01-0385, 2002.
79. Miyairi, K.F., *Jpn. J. Appl. Phys.* 40, 1297–1299, 2001.
80. Miyairi, K.F., *Jpn. J. Appl. Phys.* 42, 5153–5157, 2003.
81. O'Reilly, J.M., Bair, H.E., and Karasd, F.E., *Macromolecules* 15, 1083–1088, 1982.
82. Lahti, P.M. (Ed.), *Magnetic Properties of Organic Materials*, Marcel Dekker: New York, 1999.
83. Wasserman, E., Murray, R.W., Yager, W.A., Trozzolo, A.M., and Smolynsky, G.J., *J. Am. Chem. Soc.* 89, 5067, 1967.
84. Teki, Y., Takui, T., Itoh, K., Iwamura, H., and Kobayashi, K., *J. Am. Chem. Soc.* 108, 2147, 1986.
85. Murakami, K. and Ono, K., *Chemorheology of Polymers*, Elsevier: New York, 1979.
86. Komblowski, Z. and Turzecki, J., *Rheol. Acta* 22, 34–40, 1983.
87. Worhtsch, R., Schnabel, R., and Reher, E.O., *Plast. Kautsch* 38, 41–45, 1991.
88. Grajewski, F. and Sunder, J., *Kautsch. Gummi Kunstst.* [in German] 42, 604–609, 1989.
89. Dealy, J.M. and Wissbrun, K.F., *Melt Rheology and its Role in Plastics Processing*, Van Nostrand Reinhold: New York, 1990.
90. Kumar, N.G., *J. Polym. Sci. Rev.* 15, 255–325, 1980;
91. Saini, D.R. and Shenoy, A.V., *J. Elast. Plast.* 17, 189–217, 1985.
92. Malberg, A., Kokko, E., Lehmus, P., Löfgren, B., and Seppällä, J.V., *Macromolecules* 31, 8448, 1998.
93. Kolodka, E., Wang, W., Zhu, S., and Hamielec, A.E., Macromolecules 35, 10062, 2002.
94. Sperber, O. and Kaminsky, W., *Macromolecules* 36, 9014, 2003.
95. Ward, I.M., in: *Mechanical Properties of Solid Polymers*, p. 79, Wiley: New York, 1983.
96. Graessley, W.W., *Adv. Polym. Sci.* 16, 1, 1974.
97. Droste, D.H. and Dibenedetto, A.T., *J. Appl. Polym. Sci.* 13, 2149, 1969.
98. Maheshwari, S., Tsapatsis, M., and Bates, F.S., *Macromolecules* 40, 6638–6646, 2007.

99. Olabisi, O., Robeson, L.M., and Shaw, M.T., *Polymer-Polymer Miscibility*, Academic Press: New York, NY, 1979.
100. Olabisi, O., *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed., Wiley-Interscience: NY, 1982.
101. Krause, S., *J. Macromol. Sci. Rev. Macromol. Chem.* 7(21), 251, 1972.
102. Bertelsen, S. and Jørgensen, K.A., *Chem. Soc. Rev.* 38, 2178–2189, 2009.
103. Ober, C.K., Cheng, S.Z.D., Hammond, P.T., Muthukumar, M., Reichmanis, E., Wooley, K.L., and Lodge, T.P., *Macromolecules* 42, 465–471, 2009.
104. van Krevelen, D.W., *Properties of Polymers*, 3rd ed., chap. 7, Elsevier: New York, 1990.
105. Bicerano, J., *Prediction of Polymer Properties*, 2nd ed., chap. 5, Marcel Dekker: New York, 1996.
106. Porter, D., *Group Interaction Modeling of Polymer Properties*, Marcel Dekker: New York, 1995.
107. Turska, E. and Oblój-Muzaj, M., *Acta Polymerica* 32, 295–299, 1981.
108. De Rosa, C. and Auriemma, F., *J. Am. Chem. Soc.* 128, 11024–11025, 2006.
109. Dickie, R.A., Cheung, M.-F., and Newman, S., J. Appl. Polym. Sci. 17, 65–78, 1973.

Polymer Blends and Composites: Chemistry and Technology.
Muralisrinivasan Natamai Subramanian.

4

Additives

Additives are chemicals and modifiers which are essential ingredients in almost all polymer blends and composites for products and fabricated articles. They are used in blends and composites made up of homopolymers and/or copolymer combinations to modify behavior, appearance, mechanical properties, etc. They help processing in the industry to have better optimum properties [1, 2]. Additives enable polymers to meet the range of requirements and specialized applications. They also enhance processability, versatility, product appearance, and cost effectiveness.

4.1 Polymer Additives

Additives are introduced to confer specific properties, such as long-term light and oxidative stability, fire retardancy, plastification, processability, and toughness, upon the final plastic products. The addition of one polymer to mix with other polymers or additives is a very common practice in the manufacturing of blends and composites.

Additives in polymers are generally compounded with a wide variety of chemically diverse additive types. Thousands of additives are commercially available, ranging from pure compounds to oligomers components.

- Many additives are labile.
- In commercial formulation, complex mixtures of additives will normally be present.
- Levels of additives in a commercial polymer may be quite low and variable compared to the base polymer and its associated fillers.

The general trend calls for the use of fewer polymer additives, however, better-performing and ecologically acceptable additives.

4.2 Additives Influencing Blends and Composites

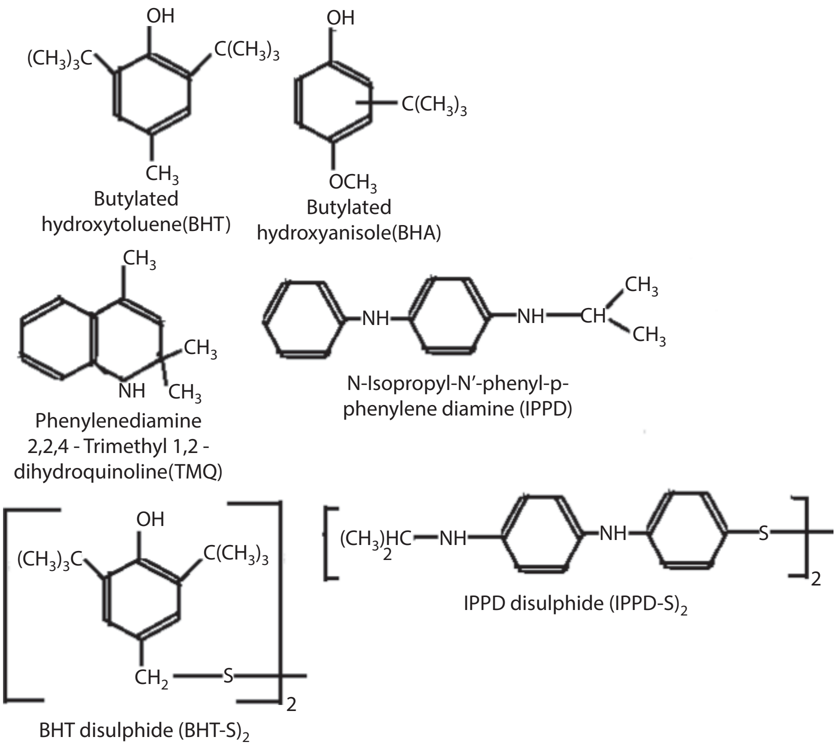
Additives have very specific behavior in the presence of other components in polymer. Their function can vary from being independent of the other ingredients in terms of their chemical or physical nature, to those whose function is vitally dependent. Many additives are multipurpose in nature. Therefore, the key to formulation is to understand the function of additive.

4.2.1 Antioxidants

An antioxidant is added to prevent thermal degradation during processing and under atmospheric aging. These antioxidants can retard the free radical reactions occurring during Autoxidation reactions [3]. Utility properties of polymers, such as polyolefins and polyamides, irreversibly degenerate under environmental effects. During processing, the thermal oxidation processes that take part lead to degradation of properties. The photoinduced processes contribute to the entire degradation mainly in atmospheric aging. Therefore, oxidation results in physical and dielectric failure of the polymer during thermal and photoinduced processes. Hence, the use of antioxidants is essential to control processing and long-term stabilities of such polymers.

Phenolic antioxidants hold an important position in polymer stabilization. Some of the antioxidants are given in Figure 4.1.

Chemical transformations of antioxidants are much higher in chemical, thermal and/or photochemical reactivities in comparison with that of the polymers to be protected. Therefore, properties of antioxidants are



Butylated hydroxytoluene(BHT)

Butylated hydroxyanisole(BHA)

Phenylenediamine 2,2,4 - Trimethyl 1,2 - dihydroquinoline(TMQ)

N-Isopropyl-N′-phenyl-p-phenylene diamine (IPPD)

BHT disulphide $(\text{BHT-S})_2$

IPPD disulphide $(\text{IPPD-S})_2$

Figure 4.1 Some of the antioxidants useful in polymer processes.

important factors involved in the stabilization processes. Their deviations are caused by changes in the severity of the environmental attack and optimization of the molecular structure of antioxidants.

Photooxidation is practically stopped by the addition of fine particle size carbon blacks [4]. Carbon blacks act as mild thermal antioxidants. Organic inhibitors, which are stronger high temperature antioxidants than carbon blacks, are customarily added to polymer to provide additional thermal protection during processing and subsequent exposure. In many instances carbon black and a conventional amine or phenol antioxidant are added together to protect polymers against both thermal- and photooxidation. Though it effectively protects against photooxidation, carbon black reduces the activity of many thermal antioxidants, rendering several completely ineffective.

The antioxidants, mainly the hindered phenols, such as butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA), and other antioxidants depend on their ability to trap peroxy and hydroperoxy radicals. Their catalytic action in hydroperoxide decomposition is basically compatible with the antioxidant of polymers [5]. The combination of antioxidants may lead to a positive or negative effect on the efficiency. Synergistic effects have a special importance from both a practical and economic point of view [6].

Alkyl and aryl phosphites are normally considered as weak antioxidants and are used in combination with hindered phenols for melt stabilization and for minimizing color development during processing of polymers such as polyethylene, polypropylene, etc. It is very important to limit antioxidant loss by extraction or volatilization [7].

4.2.2 Light Stabilizers

Light stabilizers are a stabilizing system for polymeric materials, especially for outdoor use. An efficient light stabilizer absorbs the UV part of solar radiation, thus slowing down the aging process. The use of these absorbers is very important for polymers susceptible to UV degradation [8]. Polymers are progressively modified by chain scission or crosslinking without light stabilizers. This results in crack formation on the surface zone. Therefore, there is a decrease in mechanical performance while polymer undergoes photooxidation [9–12].

Light stabilizers, such as hydroxybenzophenones and hydroxybenzotriazoles, are important groups of light stabilizers/absorbers, since they act by strongly absorbing part of the ultraviolet radiation and thus reduce its effect on the polymer. Light stabilizers absorb UV radiation, but light absorption by stabilizing additives alone in many cases cannot ensure a marked retardation of photolytic processes in the UV region [13–16]. Hindered amine light stabilizers, commonly referred to as HALS, represent significant progress in the stabilization of polyolefins. The efficiency of HALS is superior to that of other light stabilizers for polyolefins and even to carbon black [17].

4.2.3 Heat Stabilizers

The stabilization effect is most commonly interpreted as a physical mechanism based on the formation of a barrier to stabilize the polymer. It also prevents the diffusion of oxygen into the material and, on the other hand, the evaporation of volatile reaction products originating during thermal degradation. Polymers contain stabilizers that must protect the polymer during melt processing. They also contribute to the service lifetime of the finished article upon exposure to light and heat. Stabilizers are partially consumed during the processing and exposure of the polymer products, thus they must be replaced.

Polyvinylchloride (PVC) is a less stable polymer than many others. It is degraded by the impact of heat, light and mechanical energy. In the presence of oxygen, PVC causes formation of colloidal carbon, peroxides, hydroperoxides, carbonyl, and ester groups due to dehydrochlorination [18] and liberates hydrogen chloride. Liberation of hydrogen chloride creates many problems [19]. Thermal degradation of PVC is the result of a process called "zipper dehydrochlorination," which generates polyene sequences in polymer chains that may produce an undesirable color in the material [20]. This affects not only the color, but also the mechanical properties.

Heat stabilizers, such as tribasic lead sulfate and dibasic lead stearate, and metal soaps, such as lead stearate [21], are the most useful substitutes for the tertiary or allylic chlorine atoms and stop dehydrochlorination in PVC [22–24]. Basic lead and organo tin compounds have also been used [25–29]. The most important stabilizers of PVC are different metal soaps (e.g., lead, cadmium, barium, calcium and zinc carboxylates) and some monoalkyltin compounds (e.g., carboxylates and mercaptides) having higher stabilizing efficiency.

Thermal stabilizers based on tin and lead metals are most effective and are substituted by calcium-zinc stabilizers which are nontoxic. With zinc stearate, PVC can promote a sudden dehydrochlorination. Calcium and zinc carboxylates have no Lewis acidity. Therefore, they are able to scavenge hydrogen chloride with labile chlorine atoms [27, 30–33].

4.2.4 Plasticizers

Plasticizers are important additives to polymers to improve processing properties and product properties such as flexibility and toughness of the polymer. Ideal plasticizers are miscible and compatible in all proportions with plastic components. However, the more compatible and efficient a plasticizer is, the more rapidly it can diffuse out of the polymer [34]. Plasticizers present in polymer make it widely accepted for use in flexible products.

Plasticizers are low molecular mass organic compounds added to soften rigid polymers [35]. They act by reducing the glass transition temperature of polymers, reducing their crystallinity or their melting temperature [36]. Plasticizers dissolve in the polymer by reducing frictional forces between polymer chains from each other and thus facilitating molecular movement as internal lubricants [37]. Plasticizers may cause dramatic changes in mechanical properties of polymers [34, 38]. They are applied to increase workability, flexibility, and extensibility of polymers [39].

Branched plasticizers are more permanent than the equivalent but linear plasticizers, since branching tends to hinder movement or entangle the plasticizer within the polymer matrix, making it more difficult to migrate or be removed by volatilization or extraction. Although linear structures provide less permanence, they yield better low temperature properties.

Plasticizers cover a wide range of chemical compounds, including esters, hydrocarbons, water, alcohols, glycols, phenols, ketones, and ethers [34, 37]. The most widely used low molecular weight plasticizer is dioctyl phthalate (DOP) [40]. However, the low molecular weight plasticizers may migrate from materials, leading to a rigid character of the material, thus becoming unable to serve. Most important plasticizers are diesters of phthalic acid. The typical alkoxy groups in these esters are butylates and octylates (e.g., n-octylates, iso-octylates, 2-ethylhexylates). The most important plasticizer is di-2-ethyl hexyl phthalate (also designated as di octyl phthalate, DOP). Other types of plasticizer are epoxidized vegetable oils, phosphates and polymeric plasticizers. Generally plasticizers are low molecular weight liquids, and only seldom are they low or high molecular weight solids [41]. Plasticizer is used in PVC for increasing its processing nature, flexibility and low temperature properties [42, 43].

The migration of plasticizers limits the usage of material applications, especially in the pharmaceutical, medical and food packaging fields [44, 45]. Migration of plasticizer can be reduced by using polymeric plasticizers (high molecular weight plasticizers). Polymeric plasticizers are often flexible macromolecules with correspondingly low glass transition temperature (T_g) [46, 47]. Polymeric plasticizers present low volatility, high resistance to extraction and low migration at high temperatures [48].

The commonly used polymeric plasticizers are saturated polyesters obtained from the reaction between dicarboxylic acid and a diol [49, 50]. The dicarboxylic acids include phthalic, succinic, glutaric, adipic and sebacic acid. Diols include ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, and so on. Long-chain aliphatic dicarboxylic acids (the number of carbon atom is larger than 12) and diols have been used to synthesize long-chain linear polyester [51].

Low molecular weight plasticizer is one of the major additives used in PVC compounding. The addition of plasticizers to a PVC formulation decreases many mechanical properties of the PVC product (hardness, tensile strength, modulus, etc.); however, low-temperature flexibility, elongation, and ease of processing are all improved. The most widely used low molecular weight plasticizer is di-2-ethylhexyl phthalate (DOP) [52].

Plasticizers are mainly used for the modification of polyvinyl chloride (PVC) in different applications. Generally, plasticizing agents are essential to overcome the brittleness of biopolymeric films. Brittleness is an inherent quality attributed to the complex/branched primary structure and weak intermolecular forces of natural polymers. By reducing intermolecular forces, plasticizers soften the rigidity of the film structure and increase the mobility of the biopolymeric chains, thus improving the mechanical properties [53].

4.2.5 Lubricants

Lubricants are used in a wide range of polymers. They are added to polymer formulations where they gradually tend to bloom to the surface, imparting useful properties, including lubrication, to reduce polymer adhesion to metal surfaces during processing. Fatty acid amides are used in a variety of plastics such as polyolefins, polystyrene and polyvinyl chloride. The effects of various lubricants are described below.

- Paraffinic hydrocarbons, polyethylene, carboxylic acids, an ethylene Bis-mide, montan ester wax, etc., are expected to have a predominant effect at the molten plastic-metal interface during processing.
- Glycerol monostearate, epoxidized soybean oil, a paraffin-naphthene hydrocarbon fraction and the higher molecular weight primary alcohols C_{18} and C_{20} have interface and external action during processing.
- Lower molecular weight (C_{12}-C_{16}) alcohols, fatty acid esters and phthalates, and, above all, the alkyl hydroxyl and epoxy stearates have a predominant plasticizing effect rather than external lubricant properties.

Lubricants of a more polar nature yield more internal lubricating effects, while nonpolar lubricants migrate to a boundary layer, providing external lubrication [54, 55]. Lubricants for PVC are generally described as internal or external depending on whether their action is primarily to reduce intermolecular friction within the polymeric mass by plasticization of polymer segments or to function at the molten plastic-metal interface during processing. Internal lubricants are defined as those having an affinity for or compatibility with the polymer. They can drastically improve the processibility of rigid polyvinyl chloride (RPVC). Some of the more commonly used lubricants are shown in Table 4.1.

Lubricants reduce the internal friction of the polymer molecules. Therefore PVC is prevented from permanently adhering to the metal surface

Table 4.1 Some commonly used lubricants.

No.	Product	Melting point, °C
1	Calcium stearate	140–145
2	Barium stearate	162–167
3	Stearic acid	65
4	Stearyl stearate	50
5	Hydroxy stearic acid	78
6	Montonic ester	82
7	N,N′-ethylene bis stearamide	149
8	Polyethylene wax	113–126
9	Oxidized polyethylene wax	100

of the processing equipment, thereby improving the external appearance of the extrudate. External lubricants have little compatibility with the resin and thus show little effect on the fusion behavior of the resin. They act primarily at the interface between the resin and the equipment surface to reduce adhesion. They may also coat large aggregates of the polymer molecules and reduce the internal friction between the polymer aggregates. Internal lubricants have a substantial compatibility with the resin and can diffuse into the polymer aggregates, acting somewhat as a plasticizer. Thus, they promote the fusion of the resin and reduce the internal friction of the polymer molecules. Intermediate lubricants are those which exhibit both of these functions to a significant degree [55–57].

The choice of lubricants proved to be more critical for homopolymers than for copolymers. In compounds intended for either food or non-food contact uses the balance between internal and external lubrication was of paramount importance [58]. Guanidine stearate will function as a lubricant for melamine/formaldehyde resins (and guanamine/formaldehyde resins), and glyceryl monostearate can improve the mechanical properties of the former [59].

4.2.6 Silp Additives

Slip additives reduce the coefficient of friction at the surface of a polymer such as polyethylene [60]. Fatty acid amides are used as slip additives. These additives may cause discoloration via the absorption of atmospheric phenolics [61]. During processing, slip additives have an adverse effect on the properties and can cause poor thermal stability to become ineffective due to the formation of odorus and colored compounds [62–64].

4.2.7 Antiblocking Additives

Antiblocking additives reduce the phenomenon of blocking, which is the tendency of adjacent layers of film to adhere together causing an impediment to easy operation. Erucamide is generally considered and sometimes may cause blocking, particularly in films with low-density polyethylene [65]. The occurrence of blocking may be reduced with silica as antiblock agent [66]. However, the problem of antiblock is not fully eliminated. Antiblocking agents can have a number of adverse effects on both processing of film and its ultimate service life. An increased level of silica can increase the coefficient of friction with increased level of haze and reduce the gloss [67].

4.3 Processing Aids

The high melt viscosity of polymer presents problems, particularly with melt fracture, when it is processed on processing equipment. Processing aids with high dispersibility and thermal stability can produce polymer products with assurance of good quality control. Processing aids do not cause static problems. They do not lead to die lip build-up [68]. Processing aids [69] are generally understood to be a class of polymeric additives that are used at low concentrations to facilitate the melt processing of polymers.

Without processing aid, PVC results in poor processability. Slow fusion during processing reflects as poor melt strength, poor extensibility, and severe melt fracture. Therefore, the melt rheology during PVC processing can be improved by the addition of a small amount of processing aid. Acrylic processing aids in PVC can be classified as:

- Fusion promotion;
- Melt rheology modification;
- Lubrication.

To some extent the performance depends either on only one or two, or even all three of these functions, depending on the processing aids. It is important to recognize the selected processing aid for PVC compounding.

Polymer-processing additives (PPA) are widely used in extrusion of linear polyolefins to prevent sharkskin and melt fracture. In typical industrial usage, fluoropolymers are added to the polymer in small amounts (less than 0.5% of mass fraction of PPA in polymer). To be effective, the PPA must coat the die wall, particularly the die exit, and induce slippage between the polymer melt and the die wall. As a result of this slippage, the shear stress is reduced, and consequently the power requirements are lowered while keeping high production efficiency and high product quality [70].

The processing aid helps in reducing the head pressures in the equipment, power or torque, and melt temperatures. It eliminates defects such as melt fracture. Cost-effective, multifunctional processing aid permits increased productivity before limiting processing parameters of torque and pressure are reached. Output during processing is significantly increased through conventional narrow die gap extrusion equipment. Process economy obtained by processing aid is dependent upon evaluating the possibilities of increased production rates, improved properties and utilization of equipment.

4.3.1 Viscosity Modifiers

The variation of viscosity with temperature is an important property. Addition of viscosity modifiers controls the flow and sagging of prepolymers with improvement in their viscosity/temperature characteristics; thereby enabling the resulting lubricants to be thin enough at low temperature for easy starting while remaining thick enough at high temperature to provide good lubrication. Ethoxylated fatty acids are useful as viscosity improvers in prepolymers such as epoxy polymer.

Epoxy resins can contain reactive diluents that are based on derivatives of glycidyl ether. Butyl glycidyl ether is often used because a maximum viscosity reduction is achieved with a minimum amount of diluent. Reactive diluents are incorporated into the matrix and can decrease mechanical properties. Nonreactive diluents contain no reactive groups and function primarily as viscosity modifiers and plasticizers. The first requirement of such modifiers is that they must be miscible in the resin. Pine oil, dibutyl phthalate and glycol ethers have been used sparingly because of their adverse effects on the cured resin properties.

4.3.2 Accelerators

Accelerators are of great economic importance to the polymer industry. They not only reduce curing times from hours to minutes, but they also have important effects on the physical characteristics of the thermoset in which they are used. These influences on physical properties are important in relation to the final use of the thermoset products. Accelerators are additives which control the rate or nature of cure of polymer. The most important characteristic of an accelerator in composite is the stability of its properties. The curing of the compositions can be identified from the dependence of the viscosity of prepolymer with accelerators in a small amount on storage time. Composites with higher content are used for greater viscosity. During storage, their viscosity increases and the rate of curing is proportional to the accelerator content. The occurrence of chemical reactions with accelerator may indicate the storage conditions. Composites containing a small amount of accelerator possess more stable properties during curing. The choice of the accelerator in the process determines the kind of network structure, and consequently, leads to the specific material properties. Zinc oxide, stearic acid, dithiobisbenzothiazole, and dialkyldithio-carbamate are some of the commonly used accelerators.

Activators known as secondary accelerators may be used to potentiate accelerators. Useful activators include metal oxides (usually zinc oxide), fatty acids, and nitrogen-containing bases. Retarders and prevulcanization inhibitors are added to obtain longer processing times by avoiding premature vulcanization (scorch). Retarders include acidic compounds (phthalic anhydride, salicylic and benzoic acids) and nitroso compounds (N-nitrosodiphenylamine). The most widely used prevulcanization inhibitor is N-cyclohexylthiophthalimide (CTP).

4.3.3 Mold Release Agents

Mold release agents are substances that help separate the cured part during thermoset processing from the tool. Examples of internal release agents include zinc and aluminum stearate, which are used in low temperature molding. Compatible mold release agent can be used to assist in removing the sheet from the mold. Incompatible release agents can attack the sheet, causing crazing.

Formulations during molding exhibit shrinkage rates that are much slower than that of the incumbent materials. These reduced shrinkage rates can cause mold release difficulties, especially when mechanical ejection is not employed and/or the molded parts possess undercuts, which is often the case for these applications. Mold release agents prevent adhesion between two surfaces such as sticking of polymer and metal mold. Derivatives of fatty acids, montan wax, silicones, diethylene glycol monostearate, and ethylene bis(stearamide) are used as mold release agents in polymer molding.

4.3.4 Coupling Agents

Coupling agents are chemicals that improve the adhesion between two phases and are often used in composites and adhesives. Organosilanes are perhaps the most important coupling agents, although zirconates and titantes can be used to treat fillers. There is a wide selection of organosilanes to choose from. Typically, the head contains a trimethoxy silane that can react with surface hydroxyls. The tail consists of a short alkyl chain with the appropriate functional group at its end (to react with the thermosetting resin). γ-Aminopropyl silanes are common coupling agents for epoxy glass interfaces. Coupling agents are often used to improve the strength of interfaces in hot, humid environments.

4.3.5 Fillers

Fillers are simple or complex substances of organic or inorganic, metallic or nonmetallic, animal or vegetable origin, used for both changes of polymer properties or cost reduction. At low levels, filler may reduce crack formation and deformation in polymer products. It may improve the surface characteristics, abrasion, temperature and humidity resistance and flow properties under cold conditions. It may also increase dimensional stability and reduce molding pressure and processing temperature [71–73].

Fillers induce between polymers three types of interactions with viscoelastic behavior:

1. Polymer, attraction, relative movement and elastic recovery;
2. Filler particles and polymer;
3. Filler particles themselves.

The interaction between polymers is mainly determined by the (chemical) nature of the molecule, its regularity, mobility of its segments, degree of steric hindrance and the presence of stable or transient crosslinks and entanglements and loose ends in the curing. The presence of fillers alters the relative segmental mobility of the polymer only slightly.

Fillers are a rather simple and widely applied method to improve the mechanical performance and reduce the cost of polymeric materials. Several properties of materials have changed with the inclusion of fillers, including modulus, strength, impact resistance, thermal expansion, creep resistance, and so forth. Impact resistance is one of the important mechanical properties that enable the usage of materials in service [74–76]. The incorporation of fillers into polymers has enabled them to be employed in various engineering applications.

Filler acts as a heterogeneous nucleating agent. Its nucleating effect is controlled by the filler concentration, by the size and shape of the filler particles, the chemical composition of the filler and also by the distribution of the filler particles in the polymer matrix. It is also affected by the process of addition of filler into the polymer, modification of the filler surface and the mutual interaction of the polymer and the filler [77].

Fillers can be added to thermosetting polymers to increase toughness, strength, stiffness, dimensional stability, viscosity, thermal conductivity and electrical conductivity. Fillers can also be added to reduce mold shrinkage, coefficient of thermal expansion (CTE), vapor transport, and in some cases, cost. To improve such mechanical properties a wide range of fillers with a unique set of attributes are incorporated, such as inorganic fillers, including talc, glass fiber, calcium carbonate ($CaCO_3$) barium sulfate ($BaSO_4$), etc.

Calcium carbonate ($CaCO_3$) is the cheapest commercially available inorganic filler material. It has been extensively used as a particulate filler in polymer. However, the incompatibility of its high energetic hydrophilic surface with the low surface energy of hydrophobic polymers is a problem. It is necessary to solve this problem before it can be used as functional filler. The surface is often rendered organophilic by a variety of surface modifiers such as silane coupling agents [78, 79], titanate coupling agents [80], phosphate coupling agents [81, 82] or stearic acid [83]. Therefore, a monolayer of hydrophobic organic molecule is attached to the mineral surface.

Barium sulfate ($BaSO_4$) is used as filler owing to its excellent temperature and acid and alkali resistance. It improves properties such as impact resistance, chemical resistance, heat resistance, dimensional stability and strength, etc. Polymer composites with $BaSO_4$ have low density, high mechanical properties and thermal conductivity and are opaque to X-rays [84]. The polymer composites made with the incorporation of BN can decrease thermal expansion and increase thermal conductivity while enhancing the electrical insulation properties [85, 86].

A small addition of BN might enhance extrusion properties by increasing their flowability [87]. Carbon black-filled polymers have many interesting scientific and applied aspects. The numerous applications of these materials include antistatic materials with moderate conductivity and/or low cost [88]; and also in semiconducting materials for the cable industry [89].

Filler in polymer also has the opposite effects of reinforcement and nucleation. The reinforcement results in an increase in bulk crystallinity and modulus, whereas the nucleating ability of calcium carbonate decreases the spherulite size and has a negative impact on yield stress, neutralizing the positive influence of the increase in percentage of crystallinity.

The influence of fillers on the polymer structure, kinetics of crystallization, and ultimate properties of composite polymer materials is a complex problem due to a number of factors concerning the filler as well as the polymer [90]. Therefore, the degree of improvement depends on the judicious choice of reinforcement, particle size and shape, volume fraction, and the surface treatment that promotes interaction between the polymer matrix and filler [91, 92].

4.3.6 Flame Retardants

Flame retardants are additives that interfere with the chemistry and physics of the combustion process. Flame retardant with aromatic and aliphatic groups can give rise to hydrophobic and hydrophilic moieties. With flame retardant, the compatibility and miscibility with the polymer is important. Flame retardance requires the disruption of the burning process at one or more stages so that the process is terminated within an acceptable period of time, and various mechanisms are employed.

An important factor in the flame formation and burning of polymers are thermo-oxidative reactions which proceed simultaneously in the gas phase, condensed phase, and on the surface of the interface boundary. In addition to the acceleration of the degradation, the retardants also affect the release rate of products during degradation [93, 94].

The major basic chemical elements in most commercial flame retardants are chlorine, phosphorus, and bromine. Most flame retardants contain one or more of these elements, often in addition to such other elements as nitrogen and antimony. The presence of nitrogen and/or antimony enhances the effectiveness of the basic elements in certain combinations (formulations). Molecular structures of some of the flame retardants are given in Figure 4.2 [95].

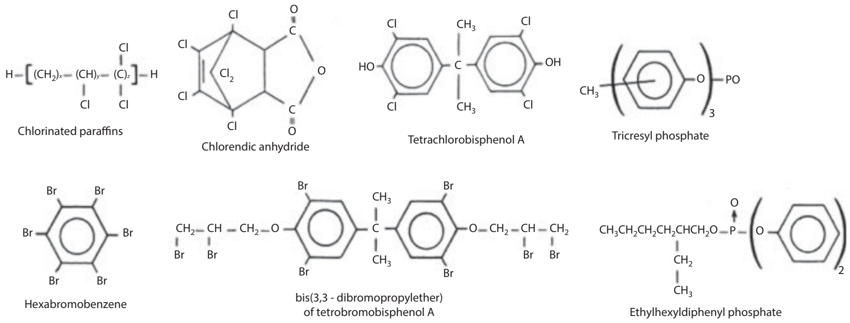


Figure 4.2 Molecular structures of some flame retardants.

The flammability of polymer can be considered from three viewpoints [96]:

1. Fire hazard, or the extent to which the material represents a danger to life and property;
2. Fire damage, or the extent to which the behavior of the material in a fire contributes to financial loss;
3. Fire protection, or the extent to which the material reduces the hazard and damage to other materials in the system.

Alumina trihydrate, mixtures of halogenated organics, and antimony oxide are the most commonly used flame retardants in polymers. Traditionally, halogen-containing compounds, alone or in conjunction with antimony trioxide, are the main flame retardants. Metal hydroxides, mainly aluminium hydroxide and magnesium hydroxide, are commonly used as flame retardants in polymers due to their nontoxicity and low cost. Ammonium polyphosphate (APP) is an effective intumescent fire retardant for polymer-based materials [97–99].

4.3.7 Antistatic Agents

Antistatic agents are used as additives in polymer to dissipate electrostatic surface charge on polymer surfaces due to incompatibility with polymer. The additive migrates to the surface of the polymer, building uniform layer. The hydrophilic end of the additive takes over the static charge leaving lipophilic end as anchors in the polymer. The protruding hydrophilic end absorbs moisture from the surrounding air and builds up a conductive path, reducing the surface resistivity. Antistatic agents can act by building up a conductive path to bring charged particles into contact and as lubricant or mold-release agents during processing.

The rate of migration is dependent on a number of factors such as compatibility between the antistatic additives and polymer, polymer crystallinity, total amount of polymer additives, concentration of antistatic, and temperature [100].

Quaternary ammonium compounds, long-chain derivatives of glycols and polyhydric compounds, and N,N-bis(2-hydroxy-ethyl)alkylamine are used as antistatic agents in polymer. However, glyceryl monostearate (GMS) is one of the most common antistatic additives used in polymer. Glyceryl monobehenate (GMB) and mixtures of GMB and GMS are more effective antistats in polymer than GMS alone.

Antistatic plastic materials are frequently made by compounding a thermoplastic with a conductive filler such as carbon black, carbon fibers or metal fibers [101]. Virtually all migration of internal antistatic additives to a polymer surface apparently takes place during processing [102].

4.3.8 Colorants

Useful colorants are formed through covalent coupling with polymers. They form agglomerates with polymer because most of them are polar species. Expensive organic pigments are the most vulnerable to the agglomeration problem. Colorants are normally used with carrier resins. These carrier resins promote good and uniform dispersion by:

- Wetting of the pigment surface, preventing agglomeration;
- Breaking down agglomerates or formation of agglomeration.

Pigments in conventional form have a nucleating effect on polymer. They cause an unpredictable and inconsistent effect on the physical properties with highly variable dimension, which are common problems in polymer products. Colorants do not nucleate and hence do not have an effect on physical properties. Therefore, colorants improve the appearance of polymers and mask discoloration due to processing. Some of the most common and cost-effective colorants are carbon black, titanium dioxide, and azo-type dyes.

4.3.9 Antimicrobial Agents (Biocides)

Antimicrobial properties, particularly mildew resistance, are in commercial polymer compositions containing low concentrations of physically incorporated antimicrobial agents such as chlorinated aromatics, organometallic compounds, etc. Antimicrobial agents are a major component of immunity that are lethal to a broad spectrum of pathogens, such as Gram-positive and Gram-negative bacteria, fungi and protozoa, but nontoxic to mammalian cells [103, 104].

A chemically bonded system might lead to a variety of industrial, medical, and consumer products having improved resistance to microbial attack. Heavy metals with broad-spectrum biocidal effects are the most commonly used inorganic antimicrobials. Ionic silver is known to have the largest antimicrobial capacity, with long-term biocidal properties, low volatility and low toxicity to eukaryotic cells. Thus, silver-based antimicrobial fillers in polymer matrices base their antimicrobial activity on a sustained release of silver ions [105–107].

Antimicrobials are integrated into polymer matrix materials wherever the microbial growth is detrimental to the products. Metallic silver is relatively nonreactive, but in aqueous environments, silver ions are released, and the antimicrobial activity depends on the intracellular accumulation of low concentrations of silver ions [108–110].

Use of polymeric materials with antimicrobial properties has been gaining increasing interest in blends and composites. Polymers can act as matrix of the materials holding the antimicrobial agents. The characteristics of the polymer, such as its hydrophilicity or its molecular weight, have a great influence on the final antimicrobial activity concerning aspects from the rate of biocide release to even conferring synergistic activities. Copper 8-hydroxyquinolate and n-(trichloromethylthio) phthalate are used to reduce growth of microbes on polymer surfaces.

4.3.10 Crosslinking Agents

Crosslinking agents tie together carbon atoms from different chains of the polymer, transforming what were once viscous linear segments into an insoluble gel network that no longer melts or flows like a typical thermoplastic. The degree of crosslinking that occurs is determined by the percentage of polymer chains that are interconnected in this network, or in other words, the density of the gel component. Higher crosslink density is the result of more linkages per length of polymer chain, resulting in larger property changes.

Crosslinking is a very useful technique for the modification of polymers. It can be initiated by heat, chemical agents, irradiation, or a combination of these [111]. Theoretically, any linear polymer can be converted into a crosslinked polymer with some modification in the molecule [112, 113]. Crosslinking is a method for improving the dimensional stability at higher temperatures and increasing resistance to mechanical stresses which produce deformation. Crosslinking is an effective way to improve its quality [114].

Molecules have two or more groups capable of reacting with the functional groups of polymer chains, where such a reaction connects or links the chains 2-mercaptobenzothiazole, benzoyl peroxide, dicumyl peroxide, sulfur, and toluene diisocyanate. Crosslinking of a thermoplastic is normally a two-step procedure. First, compounding and forming are performed under conditions which should not activate the crosslinking reactions. The latter is instead performed in a second step, often at somewhat increased temperature.

The rate of a thermally activated crosslinking reaction, e.g., a nucleophilic substitution, should thus be as high as possible. The reactivity should, on the other hand, not be high enough to prematurely cause molecular enlargement or even crosslinking. Wherever a branch radical combines with another branch radical, it forms a crosslink between the two macromolecules involved. Wherever the number of crosslinks thus formed exceeds a certain critical fraction of the number of chains, usually an infinite molecular weight crosslinked insoluble network may result.

Crosslinking is a rather general term in composite chemistry. Crosslinking is used as a more general term to include curing, which stands for crosslinking by chemicals. Crosslinking is a process of forming a three-dimensional network structure from a linear polymer by a chemical or physical method. Chemical methods produce covalently bonded networks, i.e., chemical gels. The formation of network structure is one of the essential conditions for generating the physical properties. Crosslinking agents have no effect within the crystalline regions of a polymer. Chemical crosslinking is another method that has been used commercially for crosslinking polymers such as polyethylene.

With no accelerators, the crosslinking reaction takes several hours and is no longer of commercial importance. With the use of accelerators, optimum curing can be accomplished. However, curing can be achieved with increased crosslinking using a number of different chemical functionalities, including amides, anhydrides and amines.

The crosslinking agents will introduce a network that improves heat and chemical resistance, stress cracking, and shrinkage. The most important method is the peroxide-induced crosslinking.

Normally dicumyl peroxide is applied as the crosslinking agent and stabilizers are needed towards thermo-oxidative degradation. Epoxy resins have recently been toughened using low T_g materials such as macromonomers of poly(n-butyl acrylate) [115].

4.3.11 Peroxides

Peroxides are used as curing agents to initiate the reactions in thermoset polymers. Organic peroxide agents are the most common agents used to initiate free radicals and thus controlled crosslinking in polymer. The polymer from a polymerization initiated by the peroxide has a molecular weight much lower than that of a polymer from a polymerization performed under similar conditions and proceeding at the same rate but initiated by azobisisobutyronitrile [116].

Benzoyl peroxide (BPO) and other peroxides have been used extensively as reaction initiators and/or crosslinking agents [117–119]. Ketone peroxides and bisazoisobutyronitrile degraded the polymer. Dicumyl peroxide, the most effective curing agent, was followed by tert-butyl cumyl peroxide, cymyl cumyl peroxide, and methyl cumyl peroxide. Similar in curing action was l-isobutoxy-1-cumyl peroxyethane. Benzoyl peroxide and lauroyl peroxide were more active at lower temperatures, while tert-butyl perbenzoate showed an intermediate behavior. Di-tert-butyl peroxide was much less active than the cumyl peroxides but similar in its thermal response. Tert-butyl hydroperoxide alone contributed to tensile or modulus enhancement in a polyurethane stock. Cumene hydroperoxide, p-methane hydroperoxide, and tert-butyl isopropylbenzene hydroperoxide are presumed to exert a quasi-curing action from reduced extensibility and increased recovery from tensile set by stocks in which they had been incorporated. Methyl ethyl ketone peroxide, dicyclohexanone peroxide, and methyl amyl ketone peroxide degraded the polymer. The main types of polymeric peroxides are [118–124]:

- Vinyl polyperoxides, obtained by the oxidative polymerization of vinyl monomers;
- Acid polyperoxides, obtained by the condensation of organic dibasic acids with sodium peroxide.

Vinyl polyperoxides are of interest due to their potential applications such as special initiators and curatives.

4.3.12 Foaming Agents

A foaming agent can be any substance or combination of substances capable of producing cellular structure within a polymer matrix. During processing, it forms gas that facilitates the expansion of the polymer. Two types of substances, namely physical and chemical foaming agents, are persistent. Nitrogen is a physical blowing agent which expands when pressure is released, resulting in the formation of cellular structure. The thermal and physical properties of mixtures of polymer and blowing agents together with knowledge of characteristics of these components are the basis of polymeric foams. The properties which improve while using foaming in polymeric materials are:

- Reduces weight, which reduces raw material costs;
- Enhances properties such as insulation against heat or noise and electrical properties;
- Relieves internal stresses that cause warpage or sink marks in the molded parts.

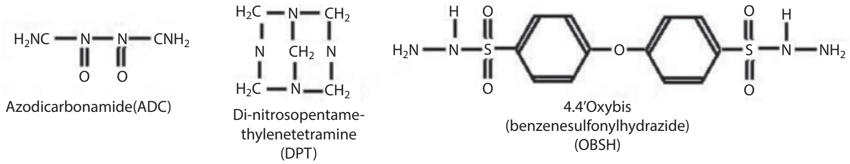

Azodicarbonamide(ADC)
Di-nitrosopentame-thylenetetramine (DPT)
4.4'Oxybis (benzenesulfonylhydrazide) (OBSH)

Figure 4.3 Some of the organic foaming agents.

Foaming agents are classified into two major categories:

- Inorganic blowing agents: Sodium bicarbonate, ammonium bicarbonate, sodium boron hydride, silicon oxy-hydride, etc. They generate gas rather slowly and generation is difficult to control.
- Organic blowing agents: Azodicarbonamide (ADC), dinitrosopentamethylene tetramine (DPT), 4,4′-oxybis(benzenesulfonyl hydrazide) (OBSH), etc. Gas generation at an appropriate rate by heating and decomposition temperature can be easily controlled with blowing activators. In Figure 4.3 some of the structures of organic foaming agents are given.

There are two types of chemical foaming agents, namely endothermic and exothermic foaming agents. A foaming agent is used to increase rigidity in many thermoplastic polymers. Endothermic foaming agents absorb and exothermically release heat during cellular structure formation. Foaming agents are used in polymer processing methods such as extrusion, injection, compression and rotational molding. Foaming agents should have the following characteristics:

- Gas formation must take place in a temperature range close to the processing temperature of the polymer;
- They should be easily dispersible within the polymer;
- Decomposition products should be compatible with the polymer;
- They should not have any detrimental influence on the polymer's properties;
- They should be color neutral, and not be corrosive in nature.

4.3.13 Coupling/Dispersing Agents

Coupling agents such as silane, titanate, etc., are used to improve the composite properties. They convert the hydrophilic surfaces of reinforcing

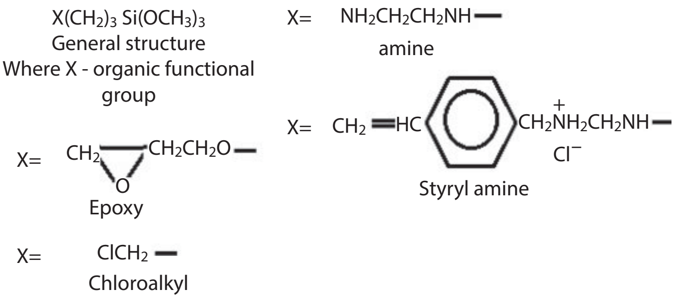


Figure 4.4 Structures of silane coupling agents.

agents, such as fillers of calcium carbonate and natural fibers, to hydrophobic ones in order to disperse them in the polymer. Therefore, the polymer and reinforcing agents are effective enough to have the interfacial adhesion properties of each other.

Aminosilane is promoted for the interaction between fiber and polymer as adhesion promoter [125]. It helps to improve the tensile strength of the composites. Other treatments with dichlorodiethylsilane, phthalic anhydride and maleated polypropylene in wood fiber with some polymers were found to be ineffective [126]. Molecular structures of silane coupling agents are shown in Figure 4.4.

4.3.14 Comonomers

Comonomers incorporate into one or both polymers of a miscible blend can cause change in the phase behavior. The temperature at which the blends phase separate on heating changes dramatically with the content and type of comonomer. Polymer-polymer miscibility has been balanced between an unfavorable free volume term and a favorable interaction term [127].

4.3.15 Impact Modifiers

Impact modifiers aid in improving both impact properties and weld strength; the weld strength depends on impact modifier effects that do not necessarily apply or correlate to the more familiar case of impact in the extruded profile [128]. The impact improvement of polymer is that the presence of an elastomeric second phase is essential to absorb the mechanical energy of the impact stress in various polymer matrices. For modifiers having similar impact efficiency, the contribution to improved strength is maximized through optimization of the viscosity and blend morphology.

Butadiene-based modifiers, such as methyl methacrylate-butadiene-styrene (MBS), acrylonitrile-butadiene-styrene (ABS), and poly(butyl acrylate), have been used for improving impact strength. Styrene ethylene/butylenes styrene copolymers (SEBS), ungrafted or grafted, have been found to be effective impact modifiers in polyolefin blends [129–131]. Some of the acrylic processing aids may also act as impact modifiers depending upon their molecular weight, which ranges from low to high.

4.3.16 Natural Fibers

Natural fibers are largely divided into two categories depending on their origin [132–136]:

- Plant-based natural fibers (e.g., flax, jute, sisal and kenaf) are utilized more frequently due to their natural abundance, cost effectiveness, world annual production and a wide range of properties depending on the plant source. They are composed of cellulose, hemicellulose and lignin and are lignocellulosic in nature [137].
- Animal-based natural fibers (e.g., silk and wool) are rarely used in biocomposite material.

Natural fibers are attractive reinforcement materials due to their advantages over other materials [137]. Thermal treatment leads to a variety of physical and chemical changes during processing with polymers [138]. Short-fiber reinforcement composites are highly dependent on degree of interfacial adhesion. However, modulus of the material is controlled by the orientation of the fiber present in the end products [139].

Short-fiber reinforcement materials and their properties depend on the following factors [140]:

- Ratio of the fibers present;
- Critical length of the fiber is required to influence fracture properties;
- Impregnation of fibers with polymers compatible with the polymer matrix to achieve combatibility;
- Chemical modification of both cellulose and grafted polymer results in copolymer and therefore displays the characteristic properties of fibers [141].

Natural fibers such as cotton stalk, rice straw, bagasse and banana fiber are used as reinforcement material. Without modification natural fibers result in poor bonding with polymer and therefore they require compatibilizer to have better polymer-fiber bond [142]. They have disadvantages such as [143]:

- Presence of absorbed water;
- Hydroxyl groups;
- Poor adhesion to nonpolar polymer matrices.

4.3.17 Copolymers as Additives

Copolymers are used as additives to improve the properties of polymer blends [144–152]. The copolymers are normally chosen due to their miscibility with one or the other of the homopolymers. Therefore, the reduction of interfacial tension is ensured and the adhesion between homopolymers is improved.

Copolymer molecules that reside at the biphasic interface in a phase-separated blend can couple the two phases together. This brings improved morphology with finer dispersion, mechanical properties, phase behavior, and interfacial adhesion in the blend [153–156]. Reinforcement of the interface is primarily accomplished by the copolymer crossing the interface and entangling with both homopolymers, forming stitches [157]. Coupling of the two phases results in stress transfer. Copolymer is able to compatibilize polymers in blend.

Copolymer possesses two different blocks. They are identical to or miscible with the two components to be blended.

4.3.17.1 Compatibilizers

Compatibilizers are either a pre-synthesized copolymer or are used via reactive processing to control the interfacial properties generally in heterogenous blends. They stabilize the morphology of blend polymer matrix against coalescence and, thus, affect the equilibrium degree of dispersion [158–161].

Compatibilizer can be generated during blending via copolymerization or exchange reactions. These reactions must generate sufficient copolymer in order to optimize the morphology and the blend performance. The reactions occur across phase boundaries. Therefore, high stresses must be applied to enlarge the interfacial area and ensure high reaction rates. Compatibilizers are often necessary in order to have the advantages of blend components in most of the immiscible blends. Compatibilization can be achieved following two strategies. The blends can be compatibilized reactively, by coupling of reactive groups on each of the immiscible polymers [162]. The second way is the addition of premade block or graft copolymers [163]. Therefore, an effective compatibilizing agent is expected to form an "interphase" between two homopolymers, thus significantly improving mechanical properties or adhesion.

Reactive compatibilization has been widely used as a means of controlling the morphology and material properties of immiscible polymer blends. Many polymers have been found in reactive blends, primarily through changes in blend morphology in the presence of reaction during reactive blending [152, 164, 165]. Morphology development during mixing of nonreactive polymers forms reactive blends that are more complex [166–168]. Reactive blending affects rates of copolymer formation and thus blend morphology.

Compatibilizer can reduce the size of the dispersed phase, produce a uniform distribution of the dispersed phase and stabilize the morphology of the blend [127, 169–175]. The effect of compatibilizer is found to be temperature dependent. Therefore, the miscibility of polymers is temperature dependent.

There are a number of methods available to compatibilize the immiscible blends, namely:

- Addition of preformed block or graft copolymers [155, 176, 177];
- Use of random copolymers, where the compatibility can be controlled by the copolymer composition [178–180];
- Introduction of reactive groups to afford interfacial grafting [181].

4.3.18 Interfacial Agents

Copolymers are practical strengthening interfacial agents. They should synthesize easily and at low cost. Copolymers strengthen the interface between phase-separated homopolymers and segregate to the region of the interface. A lot of chemicals and methods have been developed for the incorporation of interface modifiers which generally improve the compatibility of the wood-polymer composites (WPC). There are different treatments for polymer matrices (e.g., graft copolymerization or grafting fiber) [182, 183], coupling agents (e.g., silanes and isocyanates) [184–186] and interface compatibilizer (e.g., maleic anhydride grafted polyolefin or elastomer) [186, 187–189]. The use of organic carboxylic acids (e.g., stearic acid, acetic anhydride, maleic anhydride, and phthalic anhydride) [190–192] has been considered due to their effectiveness in improving adhesion between natural fiber and polymer matrix.

4.3.18.1 Block Copolymers

Block copolymers and, as a rule, multiphase polymers, are materials of great interest because the general behavior of the corresponding homopolymers is maintained along with the added benefit of some new properties in relation to the phase morphology. At the interface, they will promote the interfacial interaction and reduce the interface tension of the immiscible components to improve the interfacial bonding. The compatibility of block copolymer depends on its molecular architecture. To have sufficient cohesive forces at the interface, the segments of the block copolymer should be long enough to penetrate into the domains of the homopolymers [161, 193].

As a copolymer becomes more random and alternating, a pancake-type structure is attained, which covers a substantial area of the interface. The number of times these copolymers cross the interface and are able to entangle with the homopolymer is less clear than for blocky structures such as diblock and multiblock copolymers.

The possible conformations of several blocky copolymers are illustrated in Figure 4.5, which diagrammatically depicts the possible conformations of several blocky copolymers. As the number of blocks increases, the number of interface crosslinkings also increases.

Block copolymers are composed of segments having different surface energies. They are useful additives for the surface modification of bulk polymers [195, 196]. Surfaces of block copolymers are substantially enriched in the component of lower surface energy [195–197]. To understand the effect of a block copolymer on the adhesion between immiscible polymers, a block of copolymer of known thickness is placed between the

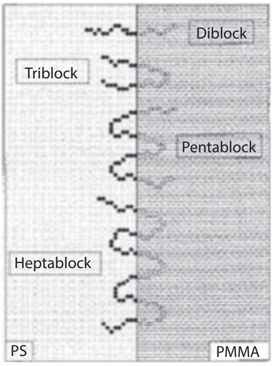


Figure 4.5 Illustration of the probable alignment of block copolymers at an interface. (Reprinted with permission from [194]; 2002 © American Chemical Society. All rights reserved)

homopolyers and joined by heating at elevated temperature for a fixed period of time [157, 198, 199].

The presence of a block copolymer in blends is beneficial in two ways. Block copolymer molecules [201–203]:

- Accumulate at the interface to act as bridges binding the two homopolymer phases. Therefore, they mechanically enhance the adhesion between the two.
- Help in making the average size of the dispersed phases small.

The precise mechanism for achieving particle size reduction in block copolymer is, however, not yet completely understood; one or more of the following factors may contribute:

- During shear mixing of incompatible polymer melts the reduced interfacial tension may help break up the dispersed phases into smaller particles. Particle diameter of the dispersed phases is obtained directly proportional to the interfacial tension [204].
- Subsequent to phase separation or to forced mechanical dispersion, the dispersed particles coalesce and grow in size with time. This tendency is reduced when the interfacial tension is lower. The growth of the dispersed particle volume is directly proportional to the interfacial tension according to the condensation-evaporation mechanism [205].
- The stable droplet phases, protected by the block copolymer accumulated at the interface, might exist as thermodynamic equilibrium phenomenon. The radius of such stable droplets is determined by the balance between the elastic rigidity and the spontaneous radium of curvature of the interfacial film [206, 207].

Block copolymers do not meet some of the criteria for being preferred interfacial agents. They are relatively expensive to synthesize in commercial quantities. They may also form low-energy states in blends such as micelles. The ability of block copolymers depends on their diffusion to interfaces in sufficient quantity for strengthening the blends [208, 209].

–M–M–M–M–M–M—N–N–N–N–N–N Block copolymers are composed of two chemically distinct macromolecules covalently joined at one end. Micro-phase separates into spherical, cylindrical, lamellar and gyroid morphologies which depends on the volume fraction of the blocks. The size of the domain is dictated by the molecular weight of the block copolymer. These self-assembled structures serve as ideal templates and scaffolds that find use for the generation of low dielectric constant materials, sectored floating gates in flash memory, ultrahigh-density magnetic storage media, and photovoltaic devices [210–213].

4.3.18.2 Random Copolymers

Random copolymer is believed to cross the interface multiple times, although the exact number is not known. It should be emphasized that the microstructure of the copolymer can dramatically affect the configuration of a copolymer at the interface. The more times a copolymer molecule crosses the interface, the more effective the copolymer interfacial modifier would be [214, 215]. The logic is that there exist more joints or stitches sewing the two phases together, which must be broken or pulled out to allow fracture.

Random copolymers are relatively inexpensive to synthesize and offer a great extent of design flexibility. Also, they do not form micelles in blends. Currently the strengthening abilities of random copolymers are not as well understood as those of their blocky counterparts, as fracture toughness experiments involving random copolymers at homopolymer joints currently provide inconclusive results [216].

The reactive polymer employed is a random copolymer and the resulting structure (block, graft, or crosslink) of the copolymer formed at the interface could also be influenced by parameters such as the amount of reactive groups per chain, arrangement of the reactive groups along the chain, and annealing temperature and time.

Random copolymers are usually prepared by free radical polymerization. Depending on the copolymerization parameters and the starting monomer feed ratio, it is possible that the chains formed at low conversion may have a considerably different composition to those formed in a later stage of the polymerization. The composition along a single chain is, however, approximately the same:

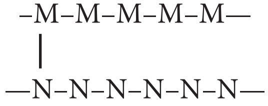
–M–N–N–N–M–M—M–N–N–N–M–N–N–

Alternating copolymer:

–M–N–M–N–M–N—M–N–M–N–M–N–

4.3.18.3 Graft Copolymers

Graft copolymers can be prepared either by a grafting from or onto a backbone, or by (co)polymerization of macromonomers. In the first case, the amount of homopolymer and the copolymer as well as the number and length of the grafts have to be determined. In the second case, the length of the grafts is determined by the length of the macromonomer. The main questions here concern the amount of unreacted macromonomer, the length of the backbone, and the number and distance of the grafts.



$$\begin{array}{l} \quad -\mathrm{M}-\mathrm{M}-\mathrm{M}-\mathrm{M}-\mathrm{M}- \\ \qquad | \\ -\mathrm{N}-\mathrm{N}-\mathrm{N}-\mathrm{N}-\mathrm{N}-\mathrm{N}- \end{array}$$

Segmented copolymer:

–M–M–M–M–M–N–N–N–M–M–M–M–M—

Graft polymers are believed to function as compatibilizers by a mechanism similar to that of block polymers. However, there is very little consistent, complete, and convincing evidence about the synthesis, structure, effectiveness, and location of the graft polymers in a blend.

4.4 Summary

- Additives are continuously developed to improve the appearance, performance, and processability of polymers.
- Environmentally friendlier additives are safer. However, the availability of the additives is very limited in comparison with the demand.
- Different physical processes occur, such as the diffusion of additives up to the surface and transport through the interface.
- The loss of additives from polymer material from the surface into the surrounding medium is a complex process and even occurs during polymer material thermal degradation.

References

1. Snyder, M.R., *Composites Technology* 14(1), 40–42, 2008.
2. Sim, F., in: *Proceedings of Vinyltec 2004: Processing the Perfect Polymer – PVC*, Paper 21, p. 16, SPE: Brookfield, CT, 2004.
3. Pospisil, J., *Adv. Polym. Sci.* 36, 67, 1980.
4. Wallder, V.T., Clarke, W.J., DeCoste, J.B., and Howard, J.B., *Ind. Eng. Chem.* 42, 2320, 1950.

5. Shlyapnikov, L.A., Kiriuskin, S.G., and Maŕin, A.P., *Antiokislitelnaia Stabilizatiia Polimerov* [in Russian] Moscow: Ed Himiia, 1986.
6. Pospísíl, J. and Klemchuk, O.P., in: *Oxidation Inhibition in Organic Materials*, vol. 1, CRC Press, 1990.
7. Pobedimiskii, D.G., Mukmeneva, N.A., and Kirpichnikov, P.A., in: *Developments in Polymer Stabilisation*, Scott, G., vol. 2, chap. 4, Applied Science Publishers, 1980.
8. author missing, *Mod. Plast. Int.* 50(9), 65, 1973.
9. Herbst, H., Hoffmann, K., and Pfaendner, R., Durable goods from recyclates for outdoor applications: The role of light stabilizers. Ciba Additive GmbH, R '97 International Congress, Geneva, Switzerland, 1997.
10. Carlsson, D., Garton, A., and Wiles, D., The photo-stabilization of polyolefins, in: *Developments in Polymer Stabilization*, G. Scott (Ed.), vol. 1, chap. 7, p. 219, Applied Science Publishers: London, 1979.
11. Gugumus, F., Developments in the U.V.: Stabilization of polymers, in: Developments in Polymer Stabilization, G. Scott (Ed.), vol. 1, chap. 8, p. 261, Applied Science Publishers: London, 1979.
12. Kartalis, C.N., Papaspyrides, C.D., Faendner, R.P., Hoffmann, K., and Herbst, H., *J. Appl. Polym. Sci.* 77, 1118–1127, 2000.
13. Gordon, G.Ya., *Stabilizatsiya sinteticheskikh polimerov* [*Stabilization of Synthetic Polymers*], Goskhimizdat, Moscow, 1963.
14. Schmitt, R. and Hirt, R., *J. Appl. Sci.* 7, 1565, 1963.
15. Hiller, H.J., *Eur. Polym. J. Suppl.* p. 105, 1969.
16. Carlson, D.J. and Wiles, D.M., *J. Polym. Sci. Polym. Chem. Ed.* 12, 2217, 1970.
17. Gugumus, F. and Linhart, H., *Chemicke Vlakna*, 32(2), 94, 1982.
18. Nagotomi, R., Yasuhari, S., and Rewiev, A., *Jpn. Plast. Age* 5, 1, 1967.
19. Otani, S., *Carbon* 3, 31, 1965.
20. González-Ortiz, L.J., Arellano, M., Sánchez-Peña, M.J., and Mendizábal, E., *Polym. Degrad. Stab.* 91, 2715–2722, 2006.
21. Moghri, M., Garmabi, H., and Akbarian, M., *J. Vinyl Addit. Technol.* 14, 73–78, 2008.
22. Frye, A.H. and Horst, R.W., *J. Polym. Sci.* XL, 413, 1959.
23. Frye, A.H. and Horst, R.W., *J. Polym. Sci.* XLV, 1, 1960.
24. Martinez, G. and Millan, J., *Angew Makromol. Chem.* 75, 215, 1979.
25. Hawkins, W.L., *Polymer Stabilization*, p. 132, Wiley-Interscience: New York, 1972.
26. Onozuka, M. and Asahina, M., *J. Macromol. Sci.* C3, 235, 1968.
27. Suzuki, M., Tsuge, S., and Takeuchi, T., *J. Polym. Sci.* 10, 1051, 1972.
28. Manzoor, W., Youssef, S.M., and Ahmed, Z., *Polym. Degrad. Stab.* 51, 295, 1996.
29. Vymazal, Z., Mastny, L., and Vymazalová, Z., *Eur. Polym. J.* 25, 1069, 1989.
30. Gökçel, H.İ., Balköse, D., and Köktürk, U., *Eur. Polym. J.* 35(8), 1501–1508, 1999.

31. Balköse, D., Gökçel, H.İ., and Göktepe, S.E., *Eur. Polym. J.* 37(6), 1191–1197, 2001.
32. Lévai, G., Ocskay, G., Nyitrai, Z., and Meszlényi, G., *Polym. Degrad. Stab.* 25(1), 61–72, 1989.
33. Lévai, G., Ocskay, G., and Nyitrai, Z., *Polym. Degrad. Stab.* 26(1), 11–20, 1989.
34. Chatfield, H.W., *Varnish Constituents*, Leonard Hill: London, UK, 1953.
35. Ward, I.M. and Hadley, D.W., *An Introduction to the Mechanical Properties of Solid Polymers*, Wiley: New York, 1993.
36. Sperling, L.H., *Introduction to Physical Polymer Science*, 2nd ed., pp 16, 314, 358–359, Wiley: New York, 1992.
37. Briston, J.H. and Katan, L.L., *Plastics in Contact with Food*, chap. 4 & 5, Food Trade Press: London, UK, 1974.
38. Roos, Y.H., Food components and polymers, in: *Phase Transitions in Foods*, pp. 109–156, Academic Press: San Diego, CA, 1995.
39. Ferry, J.D., Concentrated solutions, plasticized polymers, and gels, in: *Viscoelastic Properties of Polymers*, 3rd ed., pp. 486–598, Wiley: New York, 1980.
40. Ma, X., Sauer, J.A., and Hara, M., *Polymer* 38(17), 4425–4431, 1997.
41. Groote, P.D., Devaux, J., and Godard, P., *J. Polym. Sci. Polym. Phys. Ed.* 40(19), 2208–2218, 2002.
42. Bohnert, T., Stanhope, B., Gruszecki, K., *et al.*, *Polym. Compos.* 8(8), 557–562, 2000.
43. Pita, V.J.R.R. and Sampaio, E.E.M., Monteiro, E.E.C., *Polym. Test.* 21(5), 545–550, 2002.
44. Thomas, N.L., *J. Appl. Polym. Sci.* 94(5), 2022–2031, 2004.
45. Audic, J.L., Reyx, D., and Brose, J.C., *J. Appl. Polym. Sci.* 89(5), 1291–1299, 2003.
46. Nakamura, Y., Ikeda, H., Kanbe, M., *et al.*, *Polym. Compos.* 7(3), 187–193, 1999.
47. Corradini, E., Forti, A., and Curti, E., *Eur. Polym. J.* 33(10–12), 1651–1658, 1997.
48. Rubin, R.J. and Ness, P.M., *Transfusion* 29(4), 358, 1989.
49. Jiménez, A., Torre, L., Kenny, J.M., *Polym. Degrad. Stab.* 73(3), 447–453, 2001.
50. Ziska, J.J., Barlow, J.W., and Paul, D.R., *Polymer* 22(7), 918–923, 1981.
51. Barbiroli, G., Lorenzetti, C., Berti, C., *et al.*, *Eur. Polym. J.* 39(4), 655–661, 2003.
52. Ovchinnikov, Y.V., Tetel'Baum, B.Y., and Maklakov, A.J., *Vysokomol. Soedin. Ser. A* 13(11), 2422–2428, 1971.
53. Gontard, N., Guilbert, S., and Cuq, J.L., *J. Food Sci.* 58, 206–211, 1993.
54. Illmann, G., *SPE J.* 24, 71, 1967. added
55. Hartitz, J.E., *Polym. Eng. Sci.* 14, 392, 1974.
56. Marshall, B.I., *Brit. Plast.* 42, 70, 1969.
57. Jacobsen, U., *Brit. Plast.* 34, 328, 1961.

58. King, L.F. and Noël, F., *Polym. Eng Sci.* 12(2), 112, 1972.
59. Lower, E.S., in: *Pigment & Resin Technology*, pp. 7–9, MCB UP Ltd, 1991.
60. Keller, R., *Kunststoffe* 76, 586, 1986.
61. Holtzen, D.A., *Plast. Eng.* 33, 43, 1977.
62. US Patent 3926523, 1975.
63. US Patent 3006934, 1964.
64. Bigger, S.W., O'Connor, M.J., Scheirs, J., Janssens, J.L.G.M., Linssen J.P.H. and Legger-Huysman, A., in: *Polymer Durability*, R.L. Clough, N.C. Billingham, K.T. Gillen (Eds.), p. 249, American Chemical Society: Washington DC, 1996.
65. Birks, A.M., *Plast. Tech.* 23, 131, 1977.
66. Riedel, T., in: *Plastic Additives Handbook*, 3rd ed., R. Gachter, H. Muller (Eds.), p. 423, Hanser: Munich, 1990.
67. Mock, H.W. and Young, D.R., *Plast. Tech.* 20, 41, 1977.
68. Schumacher, P.A., *J. Plast. Film Sheeting* 3, 118–119, 1987.
69. Dunkelberger, D.L., *J. Vinyl Technol.* 9, 173, 1987.
70. Kharchenko, S., Migler, K.B., and Hatzikiriakos, S.G., in: *Polymer Processing Instabilities: Control and Understanding*, K.B. Migler, S.G. Hatzikiriakos (Eds.), pp. 237–260, Marcel Dekker: New York, 2005.
71. Horun, S., *Aditivi pentru prelucrarea polimerilor*, Bucureçti: Editurǎ Tehnica, 1978.
72. Ritchie, P.D., Critchley, S.W., and Hill, A. (Eds.) *Plasticizers, Stabilizers, and Fillers*, Iliffe Books Ltd.: London, 1972.
73. Krause, S., *J. Macromol. Sci. C* 7, 215–314, 1972.
74. Nielsen, L.E. and Landel, R.F., *Mechanical Properties of Polymers and Composites*, Marcel Dekker: New York, 1994.
75. Bucknall, C.B., *Toughened Polymers*, Applied Science Publishers: London, 1977.
76. Miles, I.S. and Rostami, S. (Eds.), *Multicomponent Polymer Systems*, Longman Singapore Publishers: Singapore, 1994.
77. Solomko, V.P., *Filled Crystalline Polymers*, p. 212, Naukova Dumka: Kyev, 1980.
78. Broutman, L.J. and Krock, R.H., in: *Composite Materials*, vol. 6, chap. 5, Academic Press: New York, 1974.
79. Demjén, Z., Pukánszky, B., Földes, E., and Nagy, J., *J. Colloid Interface Sci.* 190, 427–436, 1997.
80. Monte, S.J. and Sugerman, G., in: *Proceedings of the 110th Meeting of the Rubber Division*, p. 43, Am. Chem. Soc., 1976.
81. Nakatsuka, T., Kawasaki, H., and Itadani, K., *J. Appl. Polym. Sci.* 27, 259–269, 1982.
82. Nakatsuka, T., Kawasaki, H., and Itadani, K., *J. Colloid Interface Sci.* 82, 298–306, 1981.
83. Papirer, E., Schultz, J., and Turchi, C., *Eur. Polym. J.* 20, 1155–1158, 1984.
84. Gan, L.M., Zhang, L.H., Chang, H.S.O., and Chew, C.H., *Mater. Chem. Phys.* 40, 94, 1995.
85. Zhou, W., Qi, S., Li, H., and Shao, S., *Thermochim. Acta* 452, 36–42, 2007.

86. Zhou, W., Qi, S., An, Q., Zhao, H., and Liu, N., *Mater. Res. Bull.* 42, 1863–1873, 2007.
87. Rosenbaum, E.E., Randa, S.K., Hatzikiriakos, S.G., Stewart, C.W., Henry, D.I., and Buckmaster, M., *Polym. Eng. Sci.* 40, 179–190, 2000.
88. Veregin, R.P., Harbour, J.R., Kotake, Y., and Janzen, E.G., *Carbon* 25(4), 541–544, 1987.
89. Kim, Y.S. and Yang, Y.S., *Sens. Actuat. B: Chem.* 121(2), 507–514, 2007.
90. Lipatov, Y.S., *Physical Chemistry of Filled Polymers*, p. 64, Chimija: Moscow, 1977.
91. Katz, H.S. and Milewski, J.V. (Eds.), *Handbook of Fillers for Plastics*, VNR: New York, 1987.
92. Wang, Y. and Wang, J.J., *Polym. Eng. Sci.* 39, 190, 1999.
93. Košik, M., in: International *Conference on Burning of Organic Materials*, Tatranská Lomnica, p 1, Oct. 1975.
94. Fristrom, R.M., *J. Fire Flammability* 5, 289, 1974.
95. Liepins, R. and Pearce, E.M., *Environmental Health Perspectives*, vol. 17, pp. 55–63, 1976.
96. Hilado, C.J., *J. Cell. Plast.* 4, 339–341, 1968.
97. Matkó, Sz., Toldy, A., Keszei, S., Anna, P., Bertalan, Gy., and Marosi, Gy., *Polym. Degrad. Stab.* 88, 138–145, 2004.
98. Duquesne, S. and Bras, M.L., *J. Appl. Polym. Sci.* 82, 3262–3274, 2001.
99. Balabanovich, A.I., *J. Fire Sci.* 21, 285–298, 2003.
100. Costa, J.C., Oliveira, M., Machado, A.V., Lanceros-Méndez, S., and Botelho, G., *J. Appl. Polym. Sci.* 112, 1595–1600, 2009.
101. Finck, H.W., in: *Plastics Additives Handbook*, R. Gächter, H. Müller (Eds.), p. 571, Hanser Publishers: Berlin, 1990.
102. Williams, J.B., Geick, K.S., Falter, J.A., and Hall, L.K., *J. Vinyl Addit. Techn.* 1(4), 285, 1995.
103. Jenssen, H., Hamill, P., and Hancock, R.E.W., *Clin. Microbiol. Rev.* 19, 491, 2006.
104. Chan, D.I., Prenner, E.J., and Vogel, H.J., *Biochim. Biophys. Acta* 1758, 1184, 2006.
105. Hoffman, L.E. and Hendrix, J.L., Inhibition of *Bacillus ferrooxidans* by soluble silver. *Biotechnol. Bioengr.* 18, 1161–1165, 1976.
106. Inoue, Y., Hoshino, M., Takasashi, H., Noguchi, T., Murata, T., Kanzaki, Y., Hamashima, H., and Sasatsu, M., *J. Inorg. Biochem.* 92, 37–42, 2002.
107. Silvestry-Rodriguez, R., Sicairos-Ruelas, E.E., Gerba, P.G., and Nelly, R.B., *Rev. Environ. Contam. Toxicol.* 191, 23–45, 2007.
108. Grier, N., Silver and its compounds, in: *Disinfection, Sterilization and Preservation*, S. Block (Ed.), p. 380–428, Lea & Febiger: Philadelphia, 1983.
109. Silver, S., *Microbiol. Rev.* 27, 341–353, 2003.
110. Hidalgo, E., Bartolomé, R., Barrosso, C., Moreno, A., and Dominguez, C., *Skin Pharmacol. Appl. Skin Physiol.* 11, 140–151, 1998.
111. Romero, P.M., Jimenez, T.A., Greco, A., and Maffezzoli, A., *Eur. Polym. J.* 12, 57, 2005.

112. Han, S.P., Park, K.J., and Lee, K., *J. Appl. Polym. Sci.* 83, 1947, 2002.
113. Hoang, T. and Varshney, N., *J. Chem.* 41, 127, 2003.
114. Nass, L.I., *Encyclopedia of PVC*, vol. 1, B. Han, Y. Lu, translation [M], Chemical Industry Press: Beijing, 1987.
115. Gazit, S. and Bell, J.P., in: *Epoxy Resin Chemistry II*, R.S. Bauer (Ed.), p. 55, American Chemical Society: Washington, D.C., 1983.
116. Jones, R.G., Catterall, E., Bilson, R.T., and Booth, R.G., *J.C.S. Chem. Commun.* 1972, 22, 1972.
117. Sheng, J., Lu, X.L., and Yao, K., *J. Macromol. Sci. Chem. A* 27(2), 167, 1990.
118. Minoura, Y., Ueda, M., Mizunuma, S., and Oba, M., *J. Appl. Polym. Sci.* 13, 1625, 1969.
119. Coutinho, F. and Ferreira, M., *Eur. Polym. J.* 30(8), 911, 1994.
120. Mukundan, T., Annakutty, K.S., and Kishore, K., *Fuel* 72, 688, 1993.
121. Mukundan, T., Bhanu, V.A., and Kishore, K., *J. Chem. Soc. Chem. Commun.* 12, 780, 1989.
122. Zikmund, L., *Collect. Czech. Chem. Commun.* 37, 2911, 1972.
123. Razuvaev, G.A., Boguslavskaya, L.S., and Barabashina, R.A., *Zh. Org. Khim.* 8, 1601, 1972.
124. Murthy, K.S., Kishore, K., and Mohan, V.K., *Macromolecules* 27, 7109, 1994.
125. Matuana, L.M. and Mengeloqlu, F., *J. Vinyl Addit. Technol.* 8(4), 264–270, 2002.
126. Matuana, L.M., Woodhams, R.T., Balatinecz, J.J., and Park, C.B., *Polym. Compos.* 19(4), 446–455, 1998.
127. Sanchez, I.C., in: *Polymer Compatibility and Incompatibility: Principles and Practice*, K. Solc (Ed.), p. 59, Harwood Academic Publishers GmbH: New York, 1982.
128. Lyall, R., *Plast. Rubber Int.* 3, 92, 1983.
129. Heino, M., Kirjava, J., Hietaoja, P., and Seppälä, J., *J. Appl. Polym. Sci.* 65, 241, 1997.
130. Holsti-Miettinen, R., Seppälä, J., and Reima, I., *Polym. Eng. Sci.* 32, 868, 1992.
131. Rösch, J. and Mülhaupt, R., *Makromol. Chem. Rapid Commun.* 14, 503, 1993.
132. Lu, X., Zhang, M.Q., Rong, M.Z., Shi, G., and Yang, G.C., *Polym. Comp.* 23(4), 624–633, 2002.
133. Chabba, S. and Netravali, A.N., Green composites using modified soy protein concentrate and woven flax fabric, in: *CD Proceedings of 14th International Conference on Composite Materials (ICCM-14)*, San Diego, CA, July 14–18, 2003.
134. Keller, A., *Comp. Sci. Technol.* 63, 1307–1316, 2003.
135. Plackett, D., Andersen, T.L., Pedersen, W.B., and Nielsen, L., *Comp. Sci. Technol.* 63, 1287–1296, 2003.
136. Nishino, T., Hirao, K., Kotera, M., Nakamae, K., and Inagaki, H., *Comp. Sci. Technol.* 63, 1281–1286, 2003.
137. Bledzki, A.K. and Gassan, J., *Prog. Polym. Sci.* 24(2), 221–274, 1999.

138. Georgopoulos, S.T., Tarantili, P.A., Avgerinos, E., Andreopoulos, A.G., and Koukios, E., *Polym. Degrad. Stabil.* 90, 303–312, 2005.
139. Maldas, D. and Kokta, B.V., *Trends Polym. Sci.* 1(6), 174–178, 1993.
140. Nabi Saheb, D. and Jog, J.P., *Adv. Polym. Tech.* 18(4), 351–363, 1999.
141. Ellis, D.W. and O'Dell, J.L., *J. Appl. Polym. Sci.* 73(12), 2493–2505, 1999.
142. Habibi, Y., El-Zawawy, W.K., Ibrahim, M.M., and Dufresne, A., *Compos. Sci. Technol.* 68, 1877–1885, 2008.
143. Panaitescu, D.M., Donescu, D., Bercu, C., Vuluga, D.M., Iorga, M., and Ghiurea, M., *Polym. Eng. Sci.* 47, 1228–1234, 2007.
144. Riess, G. and Jolivet, Y., in: *Polyblends and Composites*, N.A.J. Platzer (Ed.), vol. 142, p. 243, ACS Advances in Chemistry Series, American Chemical Society: Washington, DC, 1975;.
145. Heikens, D., Hoen, N., Barentsen, W., Piet, P., and Landan, H., J. Polym. *Sci. Polm. Symp.* 62, 309, 1978.
146. Fayt, R., Jérôme, R., and Teyssié, Ph., *J. Polym. Sci., Polym. Lett. Ed.* 24, 25, 1986.
147. Fayt, R.; Jérôme, R.; Teyssié, Ph., *J. Polym. Sci., Polym. Phys. Ed.* 27, 775, 1989.
148. Teyssié, Ph., Fayt, R., and Jérôme, R., *Makromol. Chem., Macromol. Symp.* 16, 41, 1988.
149. Cohen, R.E. and Ramos, A.R., *Macromolecules* 12, 131, 1979.
150. Noolandi, J. and Hong, K.M., *Macromolecules* 15, 482, 1982.
151. Liebler, L., *Makromol. Chem., Macromol. Symp.* 16, 1, 1988.
152. van Gisbergen, J.G.M., Borgmans, C.P.J.H., van der Sanden, M.C.M., and Lemstra, P.J., *Polym. Commun.* 31, 16, 1990.
153. Konig, C., Van Duin, M., Pagnoulle, C. and Jérôme, R., *Prog. Polym. Sci.* 23, 707, 1998.
154. Di Lorenzo, M.L. and Frigione, M., *J. Polym. Eng.* 17, 429, 1997.
155. Horak, Z., Hlavata, D., Fort, V., Lednicky, F., and Vecerka, F., *Polymer* 37, 65, 1996.
156. Hlavata, D., Horak, Z., Lednicky, F., Hromadkova, J., Pleska, A., and Zanevskii, Y.V., *J. Polym. Sci., Polym. Phys. Ed.* 39, 931, 2001.
157. Creton, C., Kramer, E.J., Hui, C., and Brown, H.R., *Macromolecules* 25, 3075, 1992.
158. Utracki, L.A., *Polymer Alloys and Blends*, Hanser Publishers: New York, 1990.
159. Utracki, L.A. (Ed.), *Two-Phase Polymer Systems*, Hanser Publishers: New York, 1991.
160. Utracki, L.A., *Encyclopaedic Dictionary of Commercial Polymer Blends*, ChemTec Publishing: Toronto, 1994.
161. Datta, S. and Lohse, D., *Polymeric Compatibilizers*, Hanser Publishers: New York, 1996.
162. Bidaux, J., Smith, G. D., Bernet, N., Manson, J.E., and Hilborn, J., *Polymer* 37, 1129, 1996.
163. Macosko, C.W., Guegan, P., Khandpur, A.K., Nakayama, A., Marechal, P., and Inoue, T., *Macromolecules* 29, 5590, 1996.

164. Liu, N.C. and Baker, W.E., *Adv. Polym. Technol.* 11, 249–262, 1992.
165. Scott, C.E. and Lazo, N.D.B., in: *Reactive Polymer Blending*, W.E. Baker, C.E. Scott, G.-H. Hu (Eds.), pp 114–141, Hanser: Munich, 2001.
166. Martin, P., Carreau, P.J., Favis, B.D., and Jérôme, R., *J. Rheol.* 44, 569–583, 2000.
167. Lepers, J.-C. and Favis, B.D., *AIChE J.* 45, 887–895, 1999.
168. Scott, C.E. and Macosko, C.W., *Polymer* 36, 461–470, 1995.
169. Lee, M.S., Lodge, T.P., Macosko, C.W., *J. Polym. Sci., Polym. Phys. B* 35, 2835, 1997.
170. Sundaraj, U. and Macosko, C.W., *Macromolecules* 28, 2647, 1995.
171. Wallheinke, K., Potschke, P., and Stutz, H., *J. Appl. Polym. Sci.* 65, 2217, 1997.
172. Pu, H.T., Tang, X.Z., Xu, X.M., *Polym. Int.* 45, 169, 1998.
173. D'Orazio, L., Guarino, R., Mancarella, C., Martuscelli, E., and Cecchin, G., *J. Appl. Polym. Sci.* 65, 1539, 1997.
174. Zhang, X.M., Li, G., Wang, D.M., Yin, Z.H., Yin, J.H., and Li, J.S., *Polymer* 39, 15, 1998.
175. Chiang, C.R. and Chang, F.C., *Polymer* 38, 4807, 1997.
176. Brown, H.R., Char, K., Deline, V.R., and Green, P.F., Macromolecules 26, 4155, 1993.
177. Char, K., Brown, H.R., and Deline, V.R., *Macromolecules* 26, 4164, 1993.
178. Dai, C.A., Dair, B.J., Dai, K.H., Ober, C.K., Kramer, E.J., Hui, C.Y., and Jelinski, L.W., *Phys. Rev. Lett.* 73, 2472, 1994.
179. Wilett, J.L. and Wool, R.P., *Macromolecules* 26, 5336, 1993.
180. Cho, K., Kressler, J., and Inoue, T., *Polymer* 35, 1332, 1994.
181. Lee, Y. and Char, K., Macromolecules 27, 2603, 1994.
182. Shukla, S.R., Rao, G.V.G., and Athalye, A.R., *J. Appl. Polym. Sci.* 49, 1423–1430, 1993.
183. Liao, B., Huang, Y.H., and Cong, G.M., *J. Appl. Polym. Sci.* 66, 1561–1568, 1997.
184. Pickering, K.L., Abdalla, A., Ji, C., McDonald, A.G., and Franich, R.A., *Compos. Part A* 34, 915–926, 2003.
185. Raj, R.G. and Kokta, B.V., *Polym. Eng. Sci.* 31(18), 1358–1362, 1991.
186. Colom, X., Carrasco, F., Pagès, P., and Canavate, J., *Compos. Sci. Technol.* 63, 161–169, 2003.
187. Oksman, K. and Clemons, C., *J. Appl. Polym. Sci.* 67, 1503–1513, 1998.
188. Kazayawoko, M., Balatinecz, J.J., and Woodhams, R.T., *J. Appl. Polym. Sci.* 66, 1163–1173, 1997.
189. Rana, A.K., Mandal, A., and Bandyopadhyay, S., *Compos. Sci. Technol.* 63, 801–806, 2003.
190. Kokta, B.V., Maldas, D., Daneault, C., and Beland, R., *Polym. Compos.* 11(2), 84–89, 1990.
191. Mahlberg, R., Paajanen, L., Nurmi, A., Kivisto, A., Koskela, K., and Rowell, R.M., *Holz als Roh- und Werkstoff* 59, 319–326, 2001.

192. Zafeiropoulos, N.E., Williams, D.R., Baillie, C.A., and Matthews, F.L., *Compos. Part A* 33, 1083–1093, 2002.
193. Lyatskaya, Y., Gersappe, D., Gross, N.A., and Balazs, A.C., *J. Phys. Chem.* 100, 1449, 1996.
194. Eastwood, E.A. and Dadmun, M.D., *Macromolecules* 35, 5069–5077, 2002.
195. LeGrand, D.G. and Gaines, G.L. Jr., *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* 11, 442, 1970.
196. Owen, M.J. and Kendrick, T.C., *Macromolecules* 3, 458, 1970.
197. Rastogi, A.K. and St. Pierre, L.E., *J. Colloid Interface Sci.* 31, 168, 1969.
198. Brown, H.R., *Macromolecules* 22, 2859, 1989.
199. Cho, K. and Brown, H.R., *J. Polym. Sci., Polym. Phys. Ed.* 28, 1699, 1990.
200. Inoue, T., Shoen, T., Hashimoto, T., and Kawai, H., *Macromolecules* 3, 87, 1970.
201. Fayt, R., Jérôme, R., Teyssié, Ph., *J. Polym. Sci., Polym. Lett. Ed.* 19, 79, 1981.
202. Fayt, R., Hadjiandreou, P., Teyssié, Ph., *J. Polym. Sci., Polym. Chem. Ed.* 23, 337, 1985.
203. Wu, S., *Polym. Eng. Sci.* 27, 335, 1987.
204. Lifahitz, I.M. and Slyozov, V.V., *J. Phys. Chem. Solids* 19, 35, 1961.
205. Leibler, L., *Makromol. Chem., Macromol. Symp.* 16, 1, 1988.
206. Witten, T.A., Milner, S.T., and Wang, Z.G., in: *Multiphase Macromolecular Systems*, B.M. Culbertson (Ed.), Plenum: New York, 1989.
207. Shull, K.R., Winey, K.I., Thomas, E.L., and Kramer, E.J., *Macromolecules* 24, 2748, 1991.
208. Dai, K.H., Washiyama, J., and Kramer, E.J., *Macromolecules* 27, 4544, 1994.
209. Park, C., Yoon, J., and Thomas, E.L., *Polymer* 44, 6725–6760, 2003.
210. Park, M., Harrison, C., Chaikin, P.M., Register, R.A., and Adamson, D.H., *Science* 276, 1401–1404, 1997.
211. Thurn-Albrecht, T., Schotter, J., Kastle, A., Emley, N., Shibauchi, T., Elbaum, L.-K., Guarini, K., Black, C.T., Tuominen, M.T., and Russell, T.P., *Science* 290, 2126–2129, 2000.
212. Coakley, K.M. and McGehee, M.D., Appl. Phys. Lett. 83, 3380–3382, 2003.
213. Dadmun, M.D., *Macromolecules* 29, 3868, 1996.
214. Dadmun, M.D., *Mater. Res. Soc. Symp. Proc.* 461, 123, 1997.
215. Pellegrini, N.N., Sikka, M., Satija, S.K., and Winey, K.I., *Macromolecules* 30, 6640–6644, 1997.

Polymer Blends and Composites: Chemistry and Technology.
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5

Polymer Blends and Composites

Polymer blends and composites are of considerable scientific and commercial interest for altering polymer properties. The properties of a polymer system can be improved either by chemical modification or novel polymer architecture, but blends and composites are one of the effective and economical techniques with better technological properties [1]. In polymer blends and composites there is a specific interaction between polymer/polymer, polymer/filler or polymer/polymer/additives, resulting in properties which are different from those of basic polymers. Therefore, they have been the suggested method of providing materials with new properties [2].

Polymer blends and composites have become a prosperous commercial practice. Multiphase materials [3, 4] can be produced with excellent physical properties at low cost; however, they should have better morphological, viscoelastic and mechanical properties. Therefore, the use of polymer blends and composites in materials has advantages over the development of a completely new polymeric material.

The blending of polymers is an inexpensive route to the modification of various polymer properties. Due to its utility and simplicity, blending is currently a feasible method for improving polymer surface properties [5, 6]. Polymer-polymer phase behavior can be deceptively complex. Many molecular properties influence the physical characteristics of polymer, including molecular weight and its distribution, short- and long-chain branching, branch length and frequency distribution. Excellent control over the molecular weight and its distribution has contributed to a fundamental understanding of long-chain branch [7, 8]. Also, the properties of the polymers are dependent on the nature of the substituent.

The primary reason for the great interest in blends and composites lies in the major changes which can be achieved in the properties of polymers by introducing polymers or chemicals or modifiers. There are number of reasons to consider polymer blends and composites, namely:

- They offer the simplest route for combining outstanding properties of different existing polymers;
- They offer interesting engineering applications;
- They improve processing ability;
- They are a simple solution to the complex problem of disposal of polymer waste;
- The synthesis of new polymer is very costly;
- They are used as an alternative for tailoring degradability [9, 10];
- The source of raw materials for the manufacture of synthetic polymers appears to be limited;
- They are a cost-effective way for new materials and products to fill the economic and performance gap;
- They provide properties of importance which can be maximized;
- They produce materials and products with tailor-made properties;
- They are a convenient way of developing materials with novel or selectively enhanced properties which are possibly superior to those of the components [11].

Polymer blends and composites improve product performance by combining different polymers with specific properties in one material. Polymer is considered as matrix material in blends and composites. Polymer blends and composites are relatively simpler and cheaper to synthesize than polymer. The blending of conventional polymers has been extensively employed to develop new polymeric materials. Polymer blends have become a traditional method for producing new, high-performance polymeric materials.

5.1 Properties of Polymer Blends

Polymer blends are one of the most important materials in polymer sciences from both theoretical and practical points of view. Blends are made to avail technical advantages in order to obtain a specified portfolio of physical properties, without the need to synthesize specialized polymer systems [12–18]. Blending of polymers results in low-cost, excellent properties, and benefit may be obtained in blends possessing chemical or physical compatibility. Two kinds of polymer molecules may be combined in many ways to produce interesting materials, examples of which are polymer blends [19, 20], graft copolymers [21] and block copolymers [22].

Polymer blending has proved to be an economically viable and versatile way to control the performance of polymeric materials with readily available polymers. Polymer blends have a great influence on the thermal stability of individual polymers [23, 24]. However, the great challenge confronting the development of polymer blends is related to the thermodynamic immiscibility of most polymers. Due to its utility and simplicity, blending is a feasible method for improving polymer properties [25, 26].

Polymer blends exhibit:

- Maxima in several physical and mechanical properties as a function of the blend composition in the solid state [27];
- Mechanical, thermal, rheological, and other properties which strongly depend on their state of miscibility;
- Unique properties of the individual polymer that benefit the overall properties of a multicomponent system [28–33].

The interfacial layer plays an extremely important role in multiphase materials. It controls the adhesion between the different phases, the morphology of the dispersed phase and the properties of the blends.

Specific factors that generally affect the properties of polymer blends can be:

- Size and geometry of polymer chains, including molecular weight and chain branching;
- Chain repeating units and regularity of the chain determined by the mechanism of polymerization;
- Effect of arrangement of polymer molecules due to forces between polymer chains.

Depending on composition and temperature, semicrystalline-semicrystalline, semicrystalline-amorphous, and amorphous-amorphous states are possible. There is the presence of only one glass transition temperature (T_g) upon cooling, since the amorphous phase seems to remain a homogeneous mixture of both polymers. There are conflicting results not only in the compositional dependence of the glass transition but also in the depression of the equilibrium melting point ($T_m°$) of both components in compositions where crystallization is possible.

The properties of multiphase polymeric materials are determined by the properties of the component polymers and the microstructure in the blend. Therefore, controlling the microstructure becomes a key factor in determining the performance of polymer blends [34, 35]. The structure of conventional polymer blends is dependent on the physical properties of individual parameters [36].

Improvement of the mechanical, environmental, and rheological properties of blends is achieved by a micro-heterogeneous mixture of two or more polymers. Final blend morphology is based on:

- Material characteristics such as interfacial tension, melt viscosity, elasticity, and molecular weight;
- Processing conditions such as mixing time and temperature, screw speed, and mixer type;
- Blend composition.

5.1.1 Physicochemical Properties

The physicochemical properties of polymer blends depend on several factors based on the polymer matrix present [37]:

- Adhesion in polymer blends;
- Concentration and distribution;
- Relaxation characteristics;
- Composition of the blend;
- Temperature at which blending operation is conducted.

In two-phase polymer blends, colloidal properties [38], such as volume ratio of dispersed phase to polymer matrix, chemical nature of the additive and the polymer, size and shape of the dispersed particles, interfacial interactions between the matrix and the dispersed phase [39], should also be considered. Compatible polymers can include two polymers differing only in tacticity, molecular weight, or molecular weight distribution, or alternatively, a pair of polymers belonging to the same generic group. The physical properties (mechanical, transport, and optical) of blend materials crucially depend on this structure and the synergistic benefits from blend morphology. During its surface formation, isolated domain morphology is to be expected on wettability.

5.1.2 Morphological Properties

Polymer blend morphology depends on the arrangement of the phases based on whether they are continuous or discontinuous, and the degree of order in the crystalline or amorphous phases. The morphology of multiphase polymeric systems has a primary effect on its properties [40]. These systems:

1. Have polymer interactions in the amorphous phase only.
2. Lack both crystalline and amorphous interactions but still have good mechanical properties.

Morphology, composition, miscibility, interdiffusion, and interactions at interfaces are important qualities of polymer blends. For immiscible polymers, the morphology and properties of the blend are determined in large part by the interaction, interface, and adhesion between the polymers.

5.1.2.1 Blend Structure

The structure of the blends greatly depends on the structure of parent polymers. The microstructure affects the rheological properties of the mixture. Therefore, the properties of the final product are affected. The structure defines the important properties of chain stiffness, temperature sensitivity, and the segmental friction factor, but differences in the long-term properties of various species are usually masked by the order-of-magnitude effects determined by molecular weight distribution.

In polymer blends, it is necessary to know the structure morphology of the final product, since most of its properties, especially the mechanical properties, depend on the blend morphology. The crystals can be homogeneously dispersed or form various levels of superstructure. The structure of the blend will strongly affect its properties. Polymer blends of crystalline nature occupy only a small part due to the molecular incompatibility of the polymeric constituent with separate individual phases.

5.1.2.2 Phase Morphology

Chemistry deals with small molecules of less than 1000 atoms which cause no problem with the requirement of homogeneity in phases. The dividing line of 1000 atoms in going from small to large molecules or macromolecules was chosen by Staudinger [41, 42]. The interaction is between the polymer-polymer segments. This interaction has a large influence on property relationships. In polymer blends the various types of phase behaviour commonly encountered among polymer blend systems and the relationship to properties are the central factor. The modification of interfaces in heterophase polymer blend systems and its subsequent influence on the phase morphology are crucial toward obtaining novel materials with improved physical properties [43–47]. The major emphasis of polymer blends is on exhibiting strong intermolecular interactions. This has been the morphology of either single-phase materials or phase-separated blends, following an arbitrary and usually poorly thermal history.

Polymer phase separation is an important problem in the practical applications of polymeric materials composed of polymer blends, polymeric additives, etc. These materials show several types of phase separations, i.e., micro- and macrophase separations, and phase separations induced by chemical reactions and external fields. Depending on the strength of the interaction and the preferential adsorption of the two components, the phase diagram of the entire system may be altered.

The morphology of polymer blends [48] depends on the arrangement of the continuous or discontinuous phase, and the degree of order in the phases, namely, crystalline or amorphous. In blend systems forming separate phases, the important issues are phase morphology (size and shape) and the nature of the interface (wetting and adhesion) between phases. Immiscible blend properties will depend on the phase morphology and phase interaction as well as composition. Reducing the dispersed phase size is important for obtaining uniform blend properties while retaining the physical properties of both of the homopolymers [49–51]. Phase separation of polymer blends can lead to various morphologies, such as bicontinuous structure, islands, or holes, when altering the system characteristics such as the composition, molecular weight and architecture, film thickness, solvent, or changes in the exterior environment, including the substrate, pressure, temperature, and external fields.

A blend morphology that has dispersed particles with 0.1–5 μm diameter is usually required to attain most of the benefits. Structures significantly outside these limits show either only an average of component polymer properties or, more frequently, severe degradation in important properties.

Phase behavior of blends can be accounted for by the pair effects that configurational sequences and chemical have on an account of the interactions [52–55]. Phase separation occurs when the undiluted mixture is held above the glass transition temperature (T_g) of the system.

Phase behavior in a polymer mixture at a certain temperature is dominated by the directional specific nature of the interaction or by the compressible nature of the system. Phase behavior and the heating or mixing of an amorphous homopolymer blend also involve specific intermolecular interactions [56–58].

The phase structure of polymer blends and their properties lead to mechanical properties of technological significance. Polymer blends are usually two-component and heterogeneous systems [59–61]. For blend of two homopolymers, miscibility will generally result from specific intermolecular interactions. A stable one-phase system can be obtained only if the mixing is exothermic. Many intermediate situations can occur such as [62]:

- Separation increasing at the molecular level;
- Co-continuous morphology formation;
- Increasing phase size, phase separation in dispersed heterophase morphologies.

By controlling the morphology of the domains generated by the phase separations, it is possible for blends to design the physical properties of these polymeric materials such as permeability, electrical conductivity, and mechanical properties [12, 63].

The lack of compatibility between substances leads to phase separation. In blends, macroscale phase separation can lead to a material with very poor mechanical properties due to the presence of large domains which have poor interfacial bonding. In contrast, a compatible blend exhibits a high degree of mixing and mechanical properties which reflect an average between the constituent polymers. The properties of miscible blends will follow relationships that are functions of composition and to some extent the degree of interaction between the blend components.

The component with the high volume ratio in the blend tends to form the continuous phase. Likewise, the component with the lower viscosity ratio tends to be continuous. Consequently, there is a region in the middle of a viscosity ratio vs volume ratio space where both components and phases can exist continuously throughout the blend. This intermediate region of co-continuous phase formation would seem to be especially useful for preparing thermoplastic blends with improved properties.

5.1.2.3 Tacticity

The rheological and mechanical properties of polymer melts are crucial for processing as well as for final material performance in many applications of polymeric systems. Subtle variations in chain tacticity may lead to a significant impact on the related properties, such as crystallizability, thermal stability, and mechanical strength. Atactic polystyrene exhibits noncrystalline nature; however, both isotactic and syndiotactic polystyrene show crystallizable behavior. The crystallization rate is about one order faster for syndiotactic polystyrene than that for isotactic polystyrene at a given supercooling degree [64, 65]. For the vinyl polymers, such as polypropylene (PP) and poly(methyl methacrylate) (PMMA), the tacticity has an effect on chain conformations [66 –68] and molecular-dynamic simulation [69 –71].

5.1.2.4 Crystallization and Morphology

Pure crystallizable polymer has the problem of separating. Melt temperature (T_m) changes due to variations in the crystal thickness from that resulting from surface interactions [72]. Polymer blends may be divided into different categories as follows:

1. Crystalline polymer blends in which there are interactions between two polymers. Crystallizable components present in polymer blends offer rich morphology. In polymer blends, both polymers are crystallizable and can form mixed or separate crystals embedded in a compatible or incompatible amorphous phase. In blends, one of the components is crystallizable and the presence of other components may affect the crystallization process. Therefore, the crystallization kinetics and the final crystal morphology may be very different from that of the neat crystallizable component [73].
2. Crystalline/amorphous polymer blends in which crystallization must involve the segregation of amorphous diluent. Segregation of amorphous diluent is natural since the driving force of crystallization tends to separate the two components from being mixed. Various types of morphology may be created depending on the distance of segregation [74].

Polymer blends containing crystallizable components are of significant interest because of the rich morphology offered by these systems. In a melt-miscible crystalline/amorphous blend, crystallization must involve the segregation of amorphous diluent. Depending on the distance of segregation, various types of morphology may be created, which include:

1. Interlamellar segregation, where segregation of diluent occurs at lamellar level, so that the diluent is located in the interlamellar regions;

2. Interfibrillar segregation, where the diluent is segregated by a larger distance to the regions between the lamellar bundles in spherulites;
3. Interspherulitic segregation, where the diluent is segregated by the largest distance to the regions between spherulites [74]. A blend system does not necessarily display only one type of morphology. Different types of morphology may coexist, leading to multiple locations for the amorphous diluent [75–79].

The crystallization behavior and crystal morphology of miscible semicrystalline/semicrystalline polymer blends has significant influence on the crystallization kinetics and morphology due to differences in the melting points. The blends crystallize from the homogeneous melt, and the two components can crystallize simultaneously depending on blend composition and crystallization temperature when the melting point difference is small. The crystal morphology of the individual component can be manipulated by mixing components with different melting points and by changing the crystallization temperature or the composition of the blends.

5.1.2.5 Molecular Weight

Molecular weight of polymers, along with their nature, chemical structure, the form of polymer blends, identity of cross sizes of macromolecules, and segment mobility, influences polymer compatibility. Molecular weights of both crystalline and amorphous components are another important variable. The surface properties of the multicomponent polymer system are dramatically affected by the surface (interfacial) energy and, therefore, are different from the properties in bulk.

Consequently, the nature of the state and properties of macromolecular mixtures has become an important problem in polymer science. A binary polymer mixture at a given temperature and pressure can exhibit compatible (miscible) or, more often, essentially incompatible (immiscible) behavior. Clearly such divisions are highly arbitrary and will be functions of the thermal, solvent and mechanical history of the mixture as well as the fundamental interactions between the two macromolecules.

5.1.2.5.1 Molecular Weight Distribution (MWD)

Most commercial polymers have wide molecular weight distributions. The molecular weight distribution of a constituent is not the same in both phases and is not the same as the original distribution. The molecular weight distribution in each phase could change with blend composition. Phase composition depends on blend composition. Hence, blends of two commercial polymers are inherently multicomponent in nature. Polymer blend is a physical mixture of two or more polymers. Polymer blends are multiphase materials. Most polymers are mutually immiscible because of the large dimension of their molecules and weak mutual interaction.

Molecular weight distribution (MWD) is an important factor determining the dynamics of entangled polymers. Such blends control the lifetime of the entanglement network rather easily. Entanglements between the high-MW and low-MW components are significant, besides those due to the entanglements among themselves [80–88]. Binary blends of narrow MWD polymers include systems composed of linear chains trapped in network, thus having one component of high molecular weight which is virtually infinite.

5.1.2.6 *Particle Size and Particle Size Distribution*

The particle size and particle size distribution of polymer blends are important with respect to the impact strength. The dispersed particle size is smaller when the viscosity ratio is closer to unity and interfacial tension (γ) is lower [89–91].

The particle diameter (a_n) could be estimated as follows:

$$a_n = \frac{4\gamma}{G\eta_m}\left(\frac{\eta_d}{\eta_m}\right)^{\pm 0.84} \qquad \text{for } p > 1: 0.84, p < 1: -0.84 \tag{5.1}$$

where G is the effective shear rate; η_m and η_d are the viscosities of the matrix and dispersed phases, respectively; and p is the viscosity ratio (η_d/η_m) [89].

5.1.3 Surface Properties

In polymers with non-polarity, applications are restricted and polar functional groups are introduced directly onto the surface for general polymers. The surface composition of a multicomponent polymer system is usually different from the bulk [92–94] and the surface segregation of one component in the polymer blends can be expected. The surface composition and concentration of polymers influence many of their properties and applications such as wetting, coating, adhesion, dyeing, friction, and biocompatibility. Many chemical and physical methods have been used to modify the surface properties of polymer materials.

5.1.3.1 *Surface Composition and Concentration*

Chemistry at polymer surfaces and interfaces is central to the applications of many polymer materials [95]. Chemical modification of polymer surfaces of prepared substrates with controllable surface chemical structures can rationally address the control of macroscopic surface properties (adsorption, adhesion, wettability, and friction). The great challenge in the design of various bulk or surface properties is connected with the use of a non-changing polymeric backbone. This can be realized by the exchange of attached side chains to receive the desired characteristic features of such polymeric materials [96]. The ester moiety in PET clearly suggests more straightforward chemical strategies to modify a reactive polymer than the perfluoroalkane chains chemically resistant ones do in PTFE [97].

It is desirable for the properties at the surface of a polymer to be distinctly different from the bulk properties. Surfaces to promote adhesion, wettability, biocompatibility, chemical resistance, and hydrophobicity are all sought after for numerous applications, and the introduction of such properties is often achieved via a costly post-processing procedure [98].

The surface composition and concentration of polymers influence many of their properties and applications such as wetting, coating, adhesion, dyeing, friction, and biocompatibility. Due to the nonpolarity of polymers, their applications have been restricted and many chemical and physical methods have been used to modify the surface properties of polymer materials. Therefore, polar functional groups are introduced directly onto the surface. The surface composition of a multicomponent polymer system is usually different from the bulk [93, 99] and the surface segregation of one component in the polymer blends can be expected. This effect is believed to relate to the polymer surface region that is only several or several tens of angstroms thick.

PP/Ethylene-vinyl acetate blends could take the form of unique gradient dispersed phase structures in vertical sections by annealing. The particle size of the dispersed phase ethylene-vinyl acetate gradually increased along the direction of the sample surface from the center to the surface. It was also shown that the ethylene-vinyl acetate component in the blends increased along the vertical direction of the sample from the center to the surface with the formation of a gradient morphology. These results provide us with the possibility of modifying the surface properties of polymers and of obtaining the desired polymer blend performance through the control of the phase morphology.

Figure 5.1a schematically shows the initial dispersed phase ethylene-vinyl acetate with the uniform distribution in the PP matrix to form the

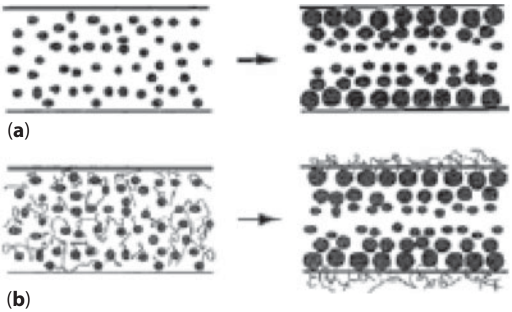

Figure 5.1 (a) Formation of the gradient phase morphology; (b) surface modification through formation of gradient phase morphology of polymer blends. (Reprinted with permission from [100]; Copyright © 1999 American Chemical Society. All rights reserved)

gradient phase morphology during annealing. The longer the annealing time, the more the particle size of the dispersed phase grew from the inside to the surface. The melt grafting with acrylamide on the ethylene-vinyl acetate should be brought to the sample surface (Figure 5.1b) with the ethylene-vinyl acetate. With ethylene-vinyl acetate as a carrier, the grafted polar groups were transported onto the surface of the material while forming an ethylene-vinyl acetate gradient dispersed phase [100].

5.1.3.2 Surface Tension

Polymer materials are extensively used as biomedical implants, biosensor materials, adhesives, lubricants, and corrosion resistant materials, because of their excellent surface properties. Polymer blends and copolymers provide ways to control the characteristics of a single polymer material by combining the properties of individual polymers. They are important polymer materials because their surface structures and properties may be different from those in the bulk, resulting in materials with both required surface and bulk properties [101–107]. Surface and interfacial tensions vary with both temperature and molecular weight.

Surface properties of polymer blends are often very different from that of the bulk material [105–107]. Surface composition of a polymer and/or copolymer blend is primarily controlled by the difference in surface free energy (S) of each component, molecular weight, end groups, architecture, and tacticity. The component with a lower γ often segregates to the free (air or vacuum) polymer surface to minimize the interfacial free energy [105]. A comprehensive understanding of the surface and interface of polymer blends is critical in controlling many important surface properties such as wettability, adhesion, friction, and biocompatibility.

There are many possible contributions of polymer chain ends to the molecular weight dependence of surface tension (γ). Polymer surface tension can be controlled to a certain extent through end-group modification. In order for polymer b to spread over the surface of polymer a, the necessary spreading coefficient is [108]:

$$S_{b/a} = \gamma_b - (\gamma_a + \gamma_{ab}) \tag{5.2}$$

where γ is the surface tensions; γ_{ab}, the interfacial tension between the polymers, should be positive.

If $|\gamma_a - \gamma_b| < \gamma_{ab}$, then neither polymer can spread onto the other. The modification of the surface tension (γ) of polymer mixtures or blends is important in many fundamental areas such as compatibilization, wetting, foaming, and lubrication.

5.1.3.3 Interfacial Modification

Interfaces in polymer blends are revealed by the interphase phenomena. In two-phase structure, the disperse phase is distributed in disperse medium in the shape of colloidal particles or may contain two continuous phase networks of dispersed polymer in polymer matrix. In a disperse system, the type of "network in network" is dependent on the ratio of components. Phase inversion occurs in polymer blends and transition of disperse phase into continuous matrix and interphase layer is also formed.

At polymer-polymer interfaces, chain end segregation is used for modifying interfacial properties, and the association of acid- and base functional end groups are used to reduce the interfacial tension between immiscible polymers [109]. Interfacial grafting of functionalized chain ends is also the basis of some reactive blending schemes designed to compatibilize and strengthen immiscible polymer blends during melt processing [110, 111]. The importance of the interphase is generally accepted [112, 113]. The effects of end groups on the bulk properties of the polymer are small, whereas their effect on the interfacial properties may be much greater. The interaction parameter increases as the molecular weight increases as a result of a reduction in the end group effects.

Interface between different phases should have a certain thickness. It is referred to as an interfacial layer or a transition layer. The structure of the interfacial layer of a polymer blend is expected to be temperature dependent. Multiphase without strong interfacial bonding will exhibit inferior mechanical properties. This is due to stresses which cannot be efficiently transferred between the phases [114–117]. The control of interfacial tension in immiscible polymer blends is important, due to its role in governing the blend morphology and associated mechanical properties. As interfacial tension is reduced, the dispersed phase particle size is also reduced [89]. The interfacial layer plays an extremely important role in polymer blends. It controls the adhesion between the different phases in blends, along with the morphology of the dispersed phase, and the mechanical properties.

Interaction energies can be determined by lowering the molecular weight of one or both polymer until the mixture becomes miscible. This method is only applicable when the interaction energy is relatively small and positive. Such pairs form immiscible blends when the molecular weights are high. However, as the molecular weight of one or both component is lowered, the combinatorial-entropy term becomes more and more important and eventually miscibility may occur.

The following equation is used for changes with mixing in pairwise interactions between randomly mixed chain units:

$$\chi = A/T + B \tag{5.3}$$

where χ is the interaction parameter; A and B specify the enthalpic and entropic parts of χ. Other forms of the temperature dependence [118] have in principle been independent of χ. The interfacial region might be as small as nanometers. This depends on the Flory-Huggins interaction parameter χ between the components.

In incompatible blends, proper control of overall blend morphology and good adhesion between the phases are required to achieve good mechanical properties [119]. It is crucial to still have good contact between the microscopic phases formed in the blend and to achieve a reasonable intermixing at the interface between the components. Immiscible polymer blends control the interfacial tension between two immiscible polymers. This is important because it governs the dispersed phase size and the adhesion between the two phases.

A variety of industrial processes involve the chemical reaction of polymers at an interface separating two immiscible polymer phases. Polymer blends frequently provide an attractive alternative to costly developments of new copolymer syntheses.

Figure 5.2 illustrates two polymer melt bulks separated by an interface. These bear functional end groups which can meet in the interface region only. Each reaction processes a diblock copolymer at the interface. The surface density of diblocks builds and eventually reduces the interfacial reaction rate. Poor interactions at the molecular level lead to high interfacial tension. Therefore, even melt mixing of the component becomes difficult which leads to unstable morphology and poor

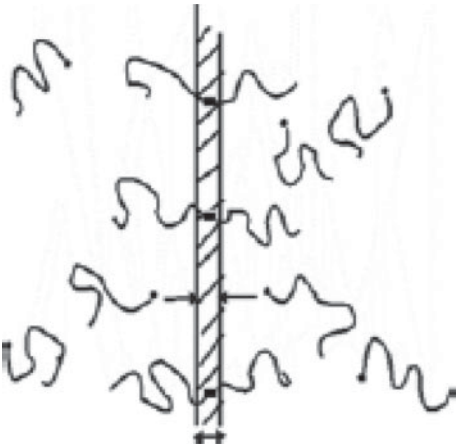

Figure 5.2 Two polymer melts separated by an interface diblock copolymer (Reprinted with permission from [118]; Copyright © 1996 American Chemical Society. All rights reserved)

interfacial adhesion. It further causes inferior mechanical properties of the blends. The interaction parameter depends on concentration, and the merging process may then occur sideways and pass through a complex pattern of metastable equilibria [120]. Polydispersity of the individual components involving nonrandomness of relatively strong specific interactions are introduced [121]. In polymer blends the interface between different phases should have a certain thickness and is referred to as an interfacial layer or a transition layer. The effect of compatbilizers is found to be temperature dependent.

5.1.3.4 Interfacial Adhesion

In later stages, immiscible polymer blends show phase separation and macrophase separated structure. This leads to a deterioration of mechanical properties due to immiscibility of the components and incompatibility of polymer blends. Due to the weak interfacial adhesion in the interfacial region, a larger amount of defects results in a low interfacial strength. A decrease in stress concentration at the interface is responsible for the increase of tensile strength [122]. Mechanical properties of polymer blends can be improved in the case of strong interfacial adhesion between the components and by adding small amounts of interfacial agents such as coupling agents, block and graft copolymers, etc. The higher interfacial adhesion between PC and PMMA causes the improved mechanical properties of this ternary blend.

5.1.5 Rheological Properties

The pure components show a constant shear viscosity and a very small first normal stress difference proportional to the square of the shear rate (second order behavior). Because of the limited elasticity of the pure components, all the elastic characteristics of the blend can be attributed to the interface. Polymer blends have addressed the problem of morphology development, with an emphasis on rheological considerations [123]. As a consequence, the rheology of the material will be strongly dependent on both the morphology and the interactions between the phases. The changes in the viscoelastic response caused by molecular weight distribution are most easily seen in terms of the elastic properties of the melt. The copolymer formation is known to be effective for morphology control.

The miscible blend will behave rheologically as if it were a pure material and its viscosity is expected to change monotonically with composition [124–127] and to exhibit composition average dependencies on shear rate and temperature. The rheological properties depend on a number of parameters, some of which may be controlled to achieve the desired results within the imposed constraints, such as choice of polymer (chemical species, molecular weight and its distribution, reactivity, degree of branching, components of mixtures, etc.), type and amount of additives (particulate solids, low molecular weight fluids, etc.), and environmental conditions (temperature, pressure, fluid surroundings, etc.). If the rheological properties vary with these parameters, it would be possible to do a better job of optimizing the selection or design of the material and the processes employed in handling it. Coupling agents can affect rheological properties of both filled and unfilled systems. Altering polymer rheology should also affect the melt.

Rheology on reactively compatibilized polymer blends is mainly focused on their linear viscoelastic behavior [128, 129]. The rheological behavior of polymer blends has been widely used due to its importance in processing. Multiple phases exist in this region but each phase contains some of each ingredient in the blend so that the rheological behavior may not be as severe as that cited below for immiscible mixtures. The most outstanding characteristic of different molten polymers is the similarity of their rheological response. This occurs due to the response of the polymeric system. It is more a function of its molecular weight and its distribution than of its particular chain structure.

Despite the many problems associated with the rheological behavior of immiscible blend systems, it is clear that these systems are providing useful new materials. One can safely project that continued work in this area will lead to commercially important new materials in the future. The rheological behavior of polymer blends has been used due to its importance in processing [12, 28, 121, 130–132].

The presence of multiple phases in the melt can lead to some unexpected blend viscosity behavior since the phases are comprised of essentially pure components and each phase, therefore, retains the rheological characteristics of the pure component. Both viscosity minima and viscosity maxima with the composition and the viscosities of immiscible mixtures are generally found to be functions of both shear stress and composition. This latter observation has been suggested to be an indicator of immiscibility [124].

5.1.6 Effect of Various Parameters

5.1.6.1 Effect of Pressure

Pressure effects on the miscibility of polymers [133–136] could be important in many situations where blends are used such as when mixing a blend in an extruder or forming articles from a blend by injection molding [137]. A rigorously incompressible system should be unaffected by pressure. However, the critical temperature (T_c) for polymer-polymer demixing is strongly affected by pressure (P), typically dTc/dP. It is clear that polymer blends show significant departures from this ideal limit [133, 138–142]. Most successful approaches in this area incorporate free volume effects, either into the free energy of the system or into an equation of state.

5.1.6.2 Effect of Compatibilizers

Compatibilizer can reduce the size of the dispersed phase, produce a uniform distribution of the dispersed phase, and stabilize the morphology of the blend [116, 117, 143–148]. From a practical applications perspective, diffusion processes in polymers that may take place during the production and processing of polymeric blends are highly desirable, as they may affect the stability and performance of these products.

The additions of small amounts of "compatibilizers," such as block or graft copolymers, which interact favorably with both major constituents, may alleviate the immiscibility problem. The compatibilizer is considered to be located mainly at the interface between the two immiscible polymers, where in many cases it induces local miscibility. It may provide an increased adhesion and an enlarged volume of the interdiffusion layer, or "interphase," between the phases [149, 150] and also reduce the interfacial energy between the phases and permit a more stable and finer dispersion [151–153]. In other cases, the properties of a polymeric product are optimized by blending it with other components. Two-phase materials containing graft or block copolymers are collectively known as "compatibilized"polymer blends. The blended polymers may be homopolymers or copolymers or a combination of both. Several blends of commercial importance are multicomponent in nature. The compatibilizing effect is then strongly dependent on the molecular masses of the individual blocks of the copolymers [154], which should be equal to or higher than those of the corresponding homopolymers in order to obtain the most efficient compatibilization [35, 155].

The introduction of functional groups which induce strong association between dissimilar chains is one of the most effective ways to enhance polymer miscibility. In this respect, hydrogen bonding between a proton donor and a proton acceptor of the polymers is particularly attractive.

- Immiscible polymers are brought together with the help of compatibilizers.
- Reactive polymers during blending utilize reactive compatibilizer with reactive group such as maleic anhydride, carboxylic acids and their derivatives, primary and secondary amines, hydroxyl and epoxide and ionic bonding reactive groups.

Addition of block or graft copolymers as compatibilizer during mixing reduces the interfacial tension and improves the adhesion between the phases by making entanglement or bridging the polymer chains near the interface of the blend [3, 156–159].

5.1.6.3 *Effect of Glass Transition Temperature (T_g)*

The glass transition temperature (T_g) is an important physical characteristic of polymers. Amorphous polymers, such as PS, PMMA, polybutadiene, etc., are hard and brittle at temperature below T_g. Upon heating to temperatures above T_g they become elastic like rubber or liquefy, depending on their molecular weight and/or degree of crosslinking. In the case of semicrystalline materials, such as PE, PP, PA, etc., T_g is well below the melting point and marks the temperature range in which, upon cooling, the brittleness increases markedly [161 –165].

Figure 5.3 shows a variety of miscible polymer blends with strong specific interactions along with an unusual compositional variation of their glass transition temperature (T_g) [165–168]. In contrast to fusion and crystallization phenomena, the T_g is not a phase transition as defined in thermodynamics. Rather, it is a kinetic effect. In the T_g approach, at high

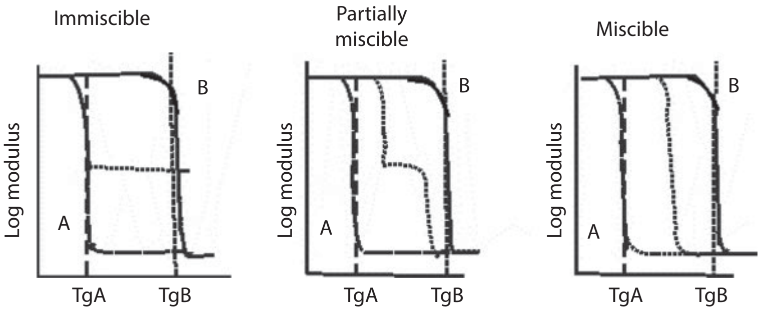

Figure 5.3 The Tgs of immiscible, partially miscible and miscible binary blends.

temperatures the molecules or segments of molecules increasingly impede one another's movement and the viscosity rises rapidly until the material finally solidifies.

The T_g reflects the molecular arrangement rate in supercooled liquid and thus is one of the most important factors among the many transitions and relaxations in polymers. For some miscible polymer blends interacting with strong specific intermolecular and intramolecular forces, the compositional dependence of T_g shows a maximum behavior, exhibiting a positive deviation from linearity with blend composition [169, 170].

There is a single T_g between two individual polymers for miscible blends, whereas immiscible blends have two T_gs. When T_g of miscible polymer blends shows the linear relationship against the polymer composition, the value of T_g is adequately expressed by the widely used Fox equation [171–177]:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

The equation is used to predict the T_g of copolymers, where W_1 and W_2 are the weight fraction of components 1 and 2 with T_{g1} and T_{g2} respectively.

The individual glass transition temperatures for phase-separated mixtures correspond closely to the pure component glass temperatures indicative of little or no intermixing. The miscibility of blends is to measure the glass transition temperature(s). Two T_gs indicate a two-phase system, and a single composition-dependent T_g is taken as evidence of the formation of a miscible blend and a miscible blend from the properties of the component polymers. When two amorphous polymer surfaces are brought into contact above the glass transition, inter-diffusion may occur. Incompatible polymer blends are characterized in terms of exhibiting more than one glass transition temperature. Normally, the joining temperature used is above the glass transition temperatures of all the relevant materials.

5.1.6.4 Effect of Critical Solution Temperature

Miscible polymers tend to phase separate at elevated temperatures. This lower critical solution temperature (LCST) behavior is typical for miscible polymer blends. The LCST behavior is interpreted in terms of equation of state or free-volume contribution. Some miscible polymers exhibit phase separation at low temperatures. Miscibility increases with increasing pressure in LCST blends. So far, high molar mass polymers have been shown to have only the LCST behavior [178, 179]. LCST behavior phase separates upon heating. Critical temperature with LCST increases with pressure.

Cooling an LCST mixture favors the mixed state by increasing the density, and increasing the pressure favors the single-phase state for the same reason. Increasing density decreases the intermolecular separation and so increases the interactions between the polymers, whether this favors or disfavors the mixed state. The precipitated phases are interconnected with each other as a result of the spinodal decomposition process. The major good features of miscible blends, lack of phase segregation in shear fields and good mechanical properties, may be retained even though the blend has been phase separated by exposure to temperatures above the LCST.

Low molecular weight binaries which show LCST behavior invariably have negative heats and volumes of mixing and positive excess heat capacities as a result of strong solute-solvent bonds. Dissimilar polymers are miscible if there is a net favorable interaction between them leading to a negative enthalpic contribution to the free energy of mixing. Phase separation of miscible blends at elevated temperatures, i.e., the lower critical solution temperature (LCST) behavior, is caused by a decrease in the magnitude of the favorable interaction to the point that it is overcome by the equation of state or free-volume contribution, as the latter is always positive and increases with increasing temperature [58, 180, 181]. The LCST behavior has been in numerous miscible blends.

In upper critical solution temperature (UCST), it is nearly always found that the critical temperature (Tc) increases with pressure effects to decrease the range of miscibility. This upper critical solution temperature (UCST) behavior is rather uncommon. It has been observed only when one component has low molar mass, i.e., when one component is an oligomer. UCST behavior phase separates upon cooling [182]. Polymer mixtures would be immiscible or would exhibit phase separation only upon lowering of temperature yielding a UCST. In a UCST, the mixed state is favored by heating, i.e., by lowering the density of the mixture. So when pressure is applied, the density is increased, which favors phase separation. At ambient pressure and a temperature just above the UCST, the mixed state is barely stable, and as the pressure is increased the density eventually rises enough to reverse the situation and produce phase separation.

The upper consolute point (UCST) is a much less common occurrence. A blend with a small positive exchange interaction parameter and a very small free volume term can exhibit both LCST and UCST behaviors. The two consolute points may merge to result in an hourglass-shaped phase diagram seen in polymer-solvent mixtures. The UCST behavior is rare [178–182].

Polymer blends have negligibly small mutual miscibility. Average chain lengths in two polymers will bring partial and eventually complete miscibility of either lower critical (LC) or upper critical (UC) miscibility. The LC and UC behavior is a slightly extended temperature dependence of the interaction function. Blend phase separates as temperature (T) is raised.

A schematic phase diagram for a symmetric binary mixture of linear homopolymers showing the TLCST and TUCST is given in Figure 5.4. Subsequently, it can be found of partially miscible blends of both UCST and LCST type, the latter becoming immiscible upon an increase in temperature, thus having a lower critical solution temperature (LCST) [183–187]. Therefore, increasing pressure reduces the miscibility range in UCST blends. The position of UCST and LCST is strongly dependent on the binary interaction parameter [186].

Blend has a negative interaction parameter that decreases algebraically when pressure becomes more negative, which indicates some specific

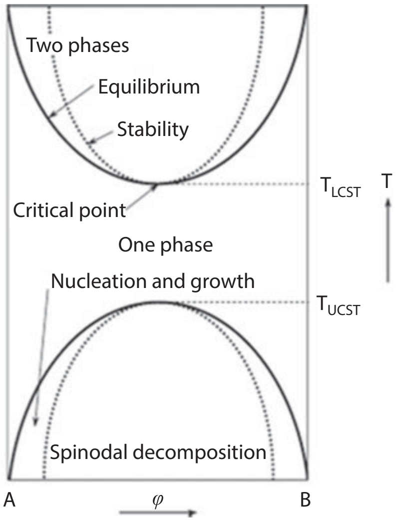

Figure 5.4 Schematic phase diagram for a symmetric binary mixture of linear homopolymers showing the T_{LCST} and T_{UCST} (Reprinted with permission from [178]; Copyright © 2011 Elsevier Ltd. All rights reserved)

interactions. A wide range of phase behavior at atmospheric pressure in blends is found [185, 187–191] and critical temperatures of polymer blends vary with pressure [192–194].

5.1.7 Properties of Polymer Blends

A great deal of interest as ones of the most polymer blends are being developed for a wide range of applications because of their thermoplastic, biodegradable, and biocompatible properties. Blending of two or more polymer components is a novel method for producing balanced properties for specific end uses. Blend properties are strongly influenced by the interface and the size scales of the minor phase developed by the processing conditions and then thereby their morphological development. Polymer blends possess properties such as high aspect ratio, mechanical strength, and other properties. This properties facilitate their use in variety of blends for commercial applications.

5.1.7.1 Mechanical Properties

The mechanical properties of a polymer blends are important to its practical use. In blends, the viscoelastic and mechanical properties of polymeric materials are strongly affected by structure, conformation, and molar mass of the chain. The polymer molar mass directly influences the topological properties of polymer melts which regulate the onset and the dynamics of the entangled regime, usually modeled by using the reputation concept [195]. The equilibrium and dynamic properties of polymers must ultimately be related to a number of characteristic molecular parameters. Particularly with composites, properties such as glass transition temperature (T_g), modulus, and toughness often depend on the extent of cure. Therefore, the optimization of polymer properties and the production of materials with consistent properties call for convenient and reliable methods for determining the extent of cure [196].

5.1.7.2 Tensile Properties

The Young's modulus can be influenced by the morphology. In the case of a bicontinuous structure, the network-like nature of the structure can improve the Young's modulus. Synergetic effects on tensile properties can be observed in miscible or partially miscible polymer blends [197]. For semicrystalline polymer blends, synergetic effects on tensile properties are attributed to the reduced average spherulite size, the increased overall crystallinity, and the formation of intercrystalline links [198]. In polymer blends, interconnected structures can show improved mechanical properties compared to those of blends with dispersed morphologies.

5.1.8 Viscoelastic Properties

Viscoelastic behavior of polymer blends, such as polymer melt, has revealed that the entanglement couplings between molecular chains constitute one of the most significant factors which determine the rheological properties. Theoretical treatments of the entanglement couplings in the concentrated systems cannot satisfactorily describe very strong interactions between molecular chains or segment. Rheological properties of various polymer blends, in the molten state generalize the effect of entanglement couplings. The rheological properties of polymer blends are strongly affected by the molecular weight and its distribution, especially in the terminal and rubbery zones. The bulk of the rubbery region of viscoelastic response is only slightly affected by the presence of the filler. The adsorption of polymer segments on the reinforced filler surface cannot cause a major loss in segmental mobility [199].

In branched polymers, the effects of branching are well characterized with respect to number, and length of branches as well as molecular weight distribution. The viscoelastic properties have an effect on molecular weight and its distribution on the rheological properties of amorphous polymers. It is highly important to measure not only the viscous but also the elastic properties in the rubbery and flow or terminal zones [200]. Typical viscoelastic materials and their behavior strongly depend upon time scale and temperature. The effect of branching on viscoelastic properties in polymer blends is also difficult to separate from that of molecular weight distribution [201].

5.1.9 Thermodynamic Properties

Polymer matrix undergoes a change in thermodynamic properties with transition temperature. Filler or fiber or crosslinking agent will have the thermodynamic properties continuation over the temperature range particularly with reinforcement agents. Adhesive strength and blend matrix interface directly related to mechanical reinforcement and crosslinking nature for crosslinked materials [202]. Both entropic and enthalpic factors are governed in terms of segment scale with local interactions. In polyolefins, the enthalpic driving force or demixing is quite weak and the nonideal contributions amplifies to the overall mixing free energy [203] with challenging set of materials.

5.1.10 Thermal Properties

Differences in thermal properties from low temperature through the glass transition temperature and into the liquid temperature regimes emphasize the effect of stereoregularity upon molecular motion in the glassy state, the change in specific heat at the glass transition temperature, and the entropy of the polymer blends [204]. Until recently, due to the advanced development of catalysts, polystyrene samples with different stereoregularities, that is, syndiotactic (s-PS), atactic (a-PS), and isotactic (i-PS), have become available for fair comparison to reveal the tacticity effects on thermal properties in blends.

5.1.11 Magnetic Properties

A few conjugated polymers have been to show magnetic properties under particular conditions. Examples of such materials are doped poly(aniline)s and poly(pyrrole)s, doped regio-irregular (and therefore poorly organized) poly(3-alkylthiophene)s, and doped and/or derivatized poly(acetylene)s [205].

A mutual magnetic interaction between these spins aligns them parallel or antiparallel, affording magnetic order. To achieve ferromagnetism in a (organic) molecule, unpaired electrons with the same spin orientation in the same molecule are required. Spins are deliberately introduced for the development of (conjugated) materials to introduce magnetism in organic (polymer) materials.

Usually only a diamagnetic contribution is expected in molecules with magnetic behavior. Magnetism in molecules arises from the intrinsic spin of unpaired electrons. The molecules are designed in such a way that they satisfy a conjugated but non-Kekule and non-disjoint connectivity among the nonbonding molecular orbitals of the unpaired electrons. In polymer blends, there are possibility of spins within one conjugated polymer chain couple ferromagnetically, which results in a high-spin (polymer) molecule [206–208].

5.1.12 Copolymerization and Blending

In reality, polymer blending is more complex. In blend systems, the effective property modification is dependent upon the miscibility or compatibility of polymers. Compatibility of polymers in a blend has optical clarity upon preparation. Compatibility blends must exhibit a single glass transition temperature [209, 210].

The copolymer formation is known to be effective for morphology control. Copolymerization and blending are commonly used to obtain polymers of desired properties. Therefore, copolymerization offers a convenient way of incorporating different monomers in the polymer chain. It is possible to tailor-make polymers having wide variations in their properties by incorporating more monomers into the polymer chain.

Also, there are two extreme situations at the molecular level in blending different polymers:

- Homogeneous blend – single phase, compatible;
- Heterogeneous blend – micro- or macro-phase separated.

Polymer blends of two commercial polymers are inherently multicomponent in nature. Blend properties, such as glass transition temperature (T_g), melting temperature (T_m), crystallinity, mechanical properties, etc., depend on the nature and physical state of the original polymers. Processing of blends depends on the interaction between polymers. The properties of a polymeric product are optimized by blending it with other polymers. The mixing ratio and processing steps derive the properties from blend systems. The properties also depend on the microstructure of the resulting blend.

Copolymerization and physical blending have been commonly adopted to improve the physical properties and extend the range of application of polymer blends. Copolymers have higher degradability rates than homopolymers, basically because of their reduced crystallinity.

5.2 Properties of Polymer Composites

Mixture of polymer with chemicals, such as fillers and additives, is called composite and depends on the composition present. Mixtures of structurally different species represent a logical step in microstructural complexity [211]. Polymer composites have been utilized to combine the best characteristics of polymer, and reinforcement materials such as filler, fiber, etc. They improve the performance of polymeric materials. It is necessary to fit the polymer composites relatively economically [212, 213].

5.2.1 Structure

Composite is a multiphase material. The phase distribution and geometry are controlled to optimize one or more properties. In composite, one phase is continuous and is called the matrix. The matrix phase typically is more compliant than the other phases, usually known as the reinforcement. It is tougher and supports and binds the reinforcement together. This phase provides protection from the environment for the reinforcement. It transmits load from one piece of reinforcement to the other usually by shear. It carries the shear stresses of the composite.

The other phase is often particulate or fibrous. It is distributed within the matrix. This phase is stiffer and stronger than matrix phase and provides stiffness and strength properties to the composites. It is often referred to as the reinforcement. The initial dispersed phase with the uniform distribution in the polymer matrix to form the gradient phase morphology during annealing [100]. The longer the annealing time, the more the particle size of the dispersed phase grew from the inside to the surface.

Polymer chain orientation plays a major role in the determination of the mechanical properties of polymers. Uniaxial oriented polymers generally possess higher Young's modulus and tensile strength in the direction of stretch but are embrittled in the transverse direction. In polymer composite systems, care needs to be taken at a molecular level when characterizing the molecular orientation in the individual phases.

The elastic properties of oriented polymer (Figure 5.5a) composites are known to depend on such factors as [214]:

1. Molecular orientation of matrix polymer;
2. Volume-fraction and size of filler;
3. Fraction of void introduced by the drawing in the preparation of oriented composites.

Figure 5.5b schematically shows unoriented composites have practically no voids and are caused by the drawing of unoriented composites. Oriented composites filled with extremely small particles exhibit a prominent positive reinforcement effect, whereas those with relatively larger particles exhibit a negative one. The modulus of oriented polymer composites is considered to be related to the changes of molecular orientation and void fraction accompanied by drawing of unoriented composites.

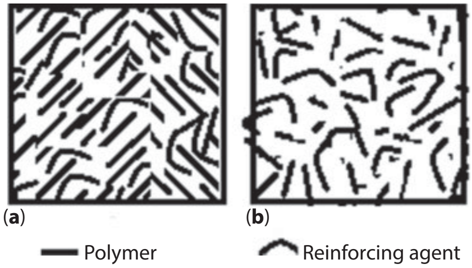

Figure 5.5 Oriented (a) and unoriented (b) in polymer composites.

5.2.2 Crosslinking

Prediction of miscibility is a nontrivial task even when the problem is confined to that of compressible mixture. Interfacial polymer reactions are of fundamental importance as a probe of polymer statics and dynamics at surfaces [215–218]. Crosslinking probably provides the most effective means of preventing such aging because the addition of free chains in a network tends to expel other constituents. Mechanical strength is developed through the formation of an entanglement network across the interface. Interpenetrating polymer network (IPN) components are capable of forming a three-dimensional system of stable physical bonds for preparing composite materials with diverse properties which can be processed in any step [219]. IPNs are crosslinked networks which are prepared with improved physical properties.

5.2.3 Reinforcement

Polymer composite is a structural system composed of a matrix of polymer reinforced with a fibrous form of another material. The resultant material has vastly improved properties over the properties of the individual constituent. The drive for improved structural performance has led to the development of lighter, stronger materials to achieve higher performance. Properties such as strength, stiffness, environmental resistance, fatigue resistance, damage tolerance, and creep resistance are all tailored in a composite.

An enhanced reinforcing efficiency is obtained both due to micromechanical reasons (the high aspect ratio due to the reduction to a molecular size of the fiber diameter) and as a consequence of the increased fraction of tie molecules, which results in the case of having, instead of a macroscopic fiber, the same amount of reinforcing agent in the form of finely dispersed microfibrils. Reinforcement should be at a maximum in the case of a homogeneous dispersion of the microfibrils in the matrix.

5.2.4 Crystalline Behavior

The crystallization behavior of polymer is a basic problem in polymer physics. The filler in a polymer will especially affect the crystallization behaviour of the polymer-based composites very much [220, 221] because the filler may adsorb the polymer molecules and act as crystal nuclei. The polymer crystallization process is limited to idealized conditions such as isothermal crystallization with constant external conditions.

An increase in crystallinity on the surface may result in high scratch hardness. It can also embrittle the material. A higher crystallinity in the skin may contribute to the higher amount of debonding, cracking, and scratch whitening. There is no difference in crystallinity between polymers with or without filler [222].

5.2.5 Mechanical Properties

Polymers can have either amorphous or semicrystalline structure. The degree of crystallinity and the size and distribution of the crystallites in a semicrystalline polymer have a large effect on the mechanical properties of these materials. If the polymer has amorphous structure, inelastic behaviour depends on the molecular chain flexibility, entanglement and on differences in the structure of the molecular chains. The mechanical behaviour of polymeric materials depends on both time and temperature. Material behavior of polymers can change from brittle to viscoplastic depending upon loading conditions and temperature. Mechanical behavior of polymer is viscoelastic–viscoplastic and highly nonlinear [223 –225].

Mechanical properties of composites tend to deviate only to a relatively small extent from those anticipated on the basis of a linearly additive scheme.

Thermoplastic polymer composites:

- Are often tougher;
- Do not have any advantage in static properties or fatigue;
- May also have inferior compression strength.

Thermoset polymer composites:

- Have superior abrasion and dimensional characteristics;
- Have better flexural and impact properties;
- Are crosslinked and derive their stiffness and strength from the inherent properties of the monomer units;
- Have very high molecular weight which ensures high levels of molecular entanglement.

5.2.6 Tribological Properties

Scratches/marring is a complicated problem in the mechanical processing of composites [226, 227]. Scratch performance of polymers is determined both by the scratch stress field associated with the indenter geometry and by material properties. The geometry of the indenter has significant effects on the scratch resistance of polymer [228]. Sharp indenters create deeper and more brittle failure modes. Low modulus polymers, an increase in modulus and a decrease in friction coefficient can reduce the scratch depth and size of the plastic zone on the scratch surface [229, 230]. Three methods are used to improve the tribological properties of a given polymer material, namely:

1. Modifying the polymer's molecular structure, e.g., crystallinity;
2. Using composite with scratch-resistant polymers;
3. Producing polymer composites with various fillers and additives.

Lubricant and interface modifier are known to be able to decrease the coefficient of friction and enhance the rigid filler effectiveness.

5.2.7 Conductive Properties

Conductive properties of polymer composites correlate to the conductivity of the mix ratio of polymer matrix and conducting filler. Depending on the detail of the composite microstructure in conducting polymer composites, as an excessive amount of filler may often distort other properties of the matrix material. Anisotropy also has a strong influence on the conductivity; specifically, the conductivity is increased along the direction of the extrusion axis, thereby reducing the volume fraction of the conductive filler necessary to achieve a desired conductivity. The electrical conductivity of polymer composites can be increased by dispersing a conductive filler throughout the polymer matrix or by blending soluble conducting polymers in solution with insulating polymers.

5.2.8 Electrical Properties

The electrical properties of the composites are affected by the microstructure formed during processing. Changes in the processing conditions can lead to significant variations in morphology and changes in the electrical performance [231]. The common structural feature of nearly all of these polymers is conjugation in the polymer backbone, permitting extensive oxidation or reduction and hence a high concentration of charge carriers. Three transport mechanisms are possible for conducting polymers: transport along a polymer chain (intramolecular), transport between chains (intermolecular), and transport between polymer particles (macroscopic) [232].

Dielectric properties are influenced by the number of polar groups present and their relative mobility within the matrix material. As the curing proceeds, both the dielectric constant and the dielectric loss factor decrease. This decrease would be a consequence of the reaction and subsequent decrease in number of functional polar end groups as well as a decrease in molecular mobility resulting from the formation of a cross-linked network [233].

5.2.9 Barrier Properties

Barrier properties that diffuse through a heterogeneous, two-phase medium can be expected to be dependent on the properties of the individual phases, and the amount, shape, size, size distribution, and orientation of the dispersed phase, and on diffusion through arrays of spheres, cylinders, and ellipsoids [234, 235]. Diffusion takes place through two types of heterogeneous media: (i) laminates, where layers of different properties are sandwiched together, and (ii) particulate composites, where discrete particles of one phase are dispersed in a continuum of another. The optimum configuration to minimize the diffusivity is by maximizing the resistance in the polymer matrix. The extent of diffusivity reduction can be with variables such as the filler loading level and filler geometry.

5.3 Summary

- Polymer blends and composites enhance the product development and characterization of required product needs. Polymer blends and composites provide a viable route and are a highly promising approach for performance end products.
- Proper balance of properties is achieved by the control of phase morphology. Polymer blends are greatly influenced by properties and result from specific required properties.
- Polymer blends are a popular form of new thermoplastic engineering materials and constitute a rapidly changing field. Polymer blends are a cheaper way to produce new polymers compared to synthesis of new monomers and/or new methods of polymerization.
- Polymer blend is a mixture of two or more different kinds of polymer chains which are not covalently bonded together. Blending of chemically different polymers is an important

tool in industrial production for tailoring products with optimized material properties [3].

- Phase behavior of multicomponent polymeric materials is a crucial factor in determining their physical properties and subsequently their utility. Phase separation on a macroscopic scale is a basic phenomenon.
- The transition from compatibility to incompatibility occurs at definite ratio of components for each polymer-polymer system.
- In polymer composites, polymer can be filled with other fillers or fibers by careful combination. Composite formation involves the permanent adhesive bonding together of two or more materials to give a product which has a combination of desirable properties of each component.
- Phase geometry and morphology are characteristic physical parameters rather than individual constituents. These parameters play an important role in determining properties of blends and composites [36].

References

1. Elias, H.G., *Macromolecules*, chap. 34, pp. 50–51, Plenum Press: New York, 1984.
2. Utracki, L.A., *Polym. Eng. Sci.* 35, 2, 1995.
3. Utracki, L.A., *Polymer Alloys and Blends*, Hanser Publishers: Munich, 1989.
4. Utracki, L.A., *Two-Phase Polymer Systems*, Hanser Publishers: Munich, 1991.
5. Xie, X.-M., Xiao, T.-J., Zhang, Z.-M., and Tanioka, A., *J. Colloid Interface Sci.* 206, 189, 1998.
6. Schroeder, K., Klee, D., Hocker, H., Leute, A., Benninghoven, A., Mittermayer, C., *J. Appl. Polym. Sci.* 58, 699, 1995.
7. Carella, J.M., Gotro, J.T., and Graessley, W.W., *Macromolecules* 19, 659, 1986.
8. Lohse, D.J., Milner, S.T., Fetters, L.J., Xenidou, M., Hadjichristidis, N., Mendelson, R.A., Garcia-Franco, C.A., and Lyon, M.K., *Macromolecules* 35, 3066, 2002.
9. Cha, Y. and Pitt, C.G., *Biomaterials* 11, 108–112, 1990.
10. Tsuji, H., Mizuno, A., and Ikada, Y., *J. Appl. Polym. Sci.* 70, 2259–2268, 1998.
11. Malkin, A., Asadsky, A., Chalykh, A., and Kovriga, V., *Experimental Mathematic Polymer Physics*, A.Ya Malkin (Ed.), Mir Publishers, 1983.
12. Paul, D.R. and Newman, S. (Eds.), *Polymer Blends*, Academic Press: New York, 1978.
13. Folkes, M.J. and Hope, P.S., *Polymers Blends and Alloys*, Blackie Academic Press: New York, 1992.

14. Kang, T.K., Kim, Y., Kim, Y., Cho, J., and Ha, C.S., *Polym. Eng. Sci.* 37, 603, 1997.
15. Ha, C.S., Kim, Y., and Cho, W.J., *J. Appl. Polym. Sci.* 51, 1381, 1994.
16. Ryou, J.H., Ha, C.S., and Cho, W.J., *J. Polym. Sci. A, Polym. Chem.* 31, 325, 1993.
17. Ha, C.S., Ryou, J.H., Cho, W.J., and Roe, R.J., *Polymer* 31, 325, 1993.
18. Kim, K.H., Cho, W.J., and Ha, C.S., *J. Appl. Polym. Sci.* 59, 407, 1996.
19. Work, J.E., *Polym. Eng. Sci.* 13, 46, 1973.
20. Callan, J.E., Hess, W.M., and Scott C.E., *Rubber Chem. Technol.* 44, 814, 1971.
21. Sperling, L.H. (Ed.), *Recent Advances in Polymer Blends, Grafts and Blocks*, Plenum: New York, 1974.
22. Bi, L.K. and Felters, L.J., *Macromolecules* 8, 90, 1975.
23. Rincon, A. and McNeill, I.C., *Polym. Degrad. Stab.* 40, 125, 1993.
24. Kovacic, T., Klaric, I., Nardelli, A., and Baric, B., *Polym. Degrad. Stab.* 40, 91, 1993.
25. Xie, X.-M., Xiao, T.-J., Zhang, Z.-M., and Tanioka, A., *J. Colloid Interface Sci.* 206, 189-194, 1998.
26. Schroeder, K., Klee, D., Hocker, H., Leute, A., Benninghoven, A., and Mittermayer, C., *J. Appl. Polym. Sci.* 58, 699, 1995.
27. Cizek, E.P., in: *Polymer Blends*, S. Newman, D.R. Paul (Eds.), vol. 1, Academic Press: New York, 1978.
28. Manson, J.A. and Sperling, L.H., *Polymer Blends and Composites*, Plenum: New York, 1976.
29. Kreuse, S., in: *Polymer Blends*, D.R. Paul, S. Newman (Eds.), chap. 2, Academic Press: New York, 1978.
30. Coran, A.Y., Das, B., and Patel, R.P., US Patent 4130535, 1978.
31. Sen, A.K., Mukherjee, B., Battacharyya, A.S., De, P.P., and Bhowmick, A.K., *Polym. Degrad. Stab.* 281, 36, 1992.
32. Michaeli, W., Cremer, M., and Bluhm, R., *German Plastics* 83, 992, 1993.
33. Wenig, W. and Asresahegn, M., *Polym. Eng. Sci.* 3, 877, 1993.
34. Creton, C., Kremer, E.J., Hui, C.Y., and Brown, H.R., *Macromolecules* 25, 3075, 1992.
35. Boucher, E., Folkers, J.P., Hervet, H., Leger, L., and Creton, C., *Macromolecules* 29, 774, 1996.
36. Dickie, R.A., Cheung, M.-F., and Newman, S., *J. Appl. Polym. Sci.* 17, 65–78, 1973.
37. Bucknall, C.B., *Toughened Plastics*, Applied Science Publishers Ltd.: London,1977.
38. Kulenev, V.N., *Polymer Blends* [in Russian], Khimiia: Moscow, 1980.
39. Karger-Kocsis, J., Kallo, A., and Kuleznev, V.N., *Acta Polym.* 32(9), 578–581, 1981.
40. Nielsen, L.E., *Mechanical Properties of Polymers and Composites*, Vol 1 & 2, Marcel Dekker: New York, 1974.
41. Staudinger, H., *Organische Kolloidchemie*, 3rd ed., Vieweg Verlag: Braunschweig, 1950.

42. Staudinger, H. and Fritschi, J., *Helv. Chim. Acta* 5, 788, 1922.
43. Utracki, L.A., *Polymer Blends Handbook*, 1st ed., Kluwer Academic Publishers: Dordrecht, 2002.
44. Hadjichristidis, N., Pispas, S., Pitsikalis, M., Iatrou, H., and Lohse, D.J., in: *Encyclopedia of Polymer Science and Technology*, 3rd ed.; H.F. Mark (Ed.), vol. 6, pp. 349–385, John Wiley & Sons: New York, 2002.
45. Creton, C., Kramer, E.J., and Hadziioannou, G., *Macromolecules* 24, 1846–1853, 1991.
46. Peiffer, D.G. and Rabeony, M., *J. Appl. Polym. Sci.* 51, 1283–1289, 1994.
47. Polizu, S., Favis, B.D., and Vu-Khanh, T., *Macromolecules* 32, 3448–3456, 1999.
48. Bever, M.B. and Shen, M., *Mater. Sci. Eng.* 15, 145, 1974.
49. Patterson, H.T., Hu, K.H., and Grindstaff, T.H., *J. Polym. Sci.* 34, 31, 1971.
50. Gaillard, P., Ossenbach-Sutter, M., and Reiss, G., *Makromol. Chem., Rapid Commun.* 1, 771, 1980.
51. Anastasiadis, S.H., Gancarz, I., and Koberstein, J.T., *Macromolecules* 22, 1449, 1989.
52. Balazs, A.C., Sanchez, I.C., Epstein, I.R., Karasz, F.E., and MacKnight W.J., *Macromolecules* 18, 2188, 1985.
53. Balazs, A.C., Karasz, F.E., MacKnight, W.J., Ueda, H., and Sanchez, I.C., *Macromolecules* 18, 2784, 1985.
54. Cantow, H.-J. and Schulz, O., *Polym. Bull.* 15, 449, 1986.
55. Chai, Z., Sun, R. and Karasz, F.E., *Macromolecules* 25, 6113, 1992.
56. Hamada, F., Shiomi, T., Fujisawa, K., and Nakajima, A., *Macromolecules* 13, 729, 1980.
57. ten Brinke, G. and Karasz, F.E., *Macromolecules* 17, 815, 1984.
58. Flory, P.J., *J. Am. Chem. Soc.* 87, 1833, 1965.
59. Takayanagi, M., Harima, H., and Iwata, Y., *J. Soc. Mat. Sci. (Japan)* 12, 389, 1963.
60. Fujino, K., Ogawa, Y., and Kawai, H., *J. Appl. Polym. Sci.* 3, 2147, 1964.
61. Okamoto, T. and Takayanagi, M., *J. Polym. Sci. C* 23, 597, 1968.
62. Teyssie, Ph., *Makromol. Chem., Macrom. Symp.* 22, 83–87, 1988.
63. Utracki, L.A., Polymer Alloys and Blends, Carl Hanser: New York, 1990.
64. Cimmino, S., Pace, E.D., Martuscelli, E., and Silvestre, C., *Polymer* 32, 1080, 1991.
65. Wang, C., Lin, C. C., and Tseng, L.C., *Polymer* 47, 390, 2006.
66. Fuchs, K., Friedrich, C., and Weese, J., *Macromolecules* 29, 589, 1996.
67. Jones, T.D., Chaffin, K.A., Bates, F.S., Annis, B.K., Hagaman, E.W., Kim, M.H., Wignall, G.D., Fan, W., and Waymouth, R., *Macromolecules* 35, 5061, 2002.
68. Liu, C., Yu, J., He, J., Liu, W., Sun, C., and Jing, Z., *Macromolecules* 37, 9279, 2004.
69. Antoniadis, S.J., Samara, C.T., and Theodorou, D.N., *Macromolecules* 32, 8635, 1999.
70. Madkour, T.M. and Soldera, A., *Eur. Polym. J.* 37, 1105, 2001.

71. Arrighi, V., Batt-Coutrot, D., Zhang, C., Telling, M.T.F., and Triolo, A., *J. Chem. Phys.* 119, 1271, 2003.
72. Khambatta, F.B., Warner, F., Russell, T., and Stein, R.S., *J. Polym. Sci., Polym. Phys. Ed.* 14, 1391, 1976.
73. Martuscelli, E., *Polym. Eng. Sci.* 24, 563, 1984.
74. Stein, R.S., Khambatta, F.B., Warner, F.P., Russell, T., Escala, A., and Balizer, E., *J. Polym. Sci., Polym. Symp.* 63, 313, 1978.
75. Defieuw, G., Groeninckx, G., and Reynaers, H., *Polym. Commun.* 30, 267, 1989.
76. Defieuw, G., Groeninckx, G., and Reynaers, H., *Polymer* 30, 595, 1989.
77. Hudson, S.D., Davis, D.D., and Lovinger, A.J., *Macromolecules* 25, 1759, 1992.
78. Huo, P.P., Cebe, P., and Capel, M., *Macromolecules* 26, 4275, 1993.
79. Sauer, B.B. and Hsiao, B.S., *J. Polym. Sci., Polym. Phys. Ed.* 31, 901, 1993.
80. Watanabe, H. and Kotaka, T., *Macromolecules* 17, 2316, 1984.
81. Poh, B.T., Adachi, K., and Kotaka, T., *Macromolecules* 20, 2568;2574, 1985.
82. Watanabe, H., Sakamoto, T., and Kotaka, T., *Macromolecules* 18, 1008;1436, 1985.
83. Adachi, K., Nakamoto, T., and Kotaka, T., *Macromolecules* 22, 3111, 1989.
84. Montfort, J.-P., Marin, G., and Monge, P., *Macromolecules* 19, 1979, 1986.
85. Struglinski, M.J., Graessley, W.W., and Fetters, L.J., *Macromolecules* 21, 783, 1988.
86. Berglund, C.A., Carriere, C.J., and Ferry, J.D., *J. Rheol.* 25, 251, 1981.
87. Roovers, J., *Macromolecules* 20, 148, 1987.
88. Osaki, K., Takatori, E., and Kurata, M., *Macromolecules* 20, 1681, 1987.
89. Wu, S., *Polym. Eng. Sci.* 27, 335, 1987.
90. Wu, S., *J. Appl. Polym. Sci.* 35, 549, 1988.
91. Liu, Z.H., Zhang, X.D., Zhu, X.G., Qi, Z.N., and Wang, F.S., *Polymer* 38, 5267, 1997.
92. Takahara, A., Tashita, J., Kajiyama, T., Takayanagi, M., and Macknight, W.J., *Polymer* 26, 978, 1985.
93. Cowie, J., Devlin, B., and McEwen, I., *Polymer* 34, 501, 1993.
94. Xie, X.-M., Matsuoka, M., and Takemura, K., *Polymer* 33, 1996, 1992.
95. Feast, W.J., Munro, H.S., and Richards, R.W., *Polymer Surfaces and Interfaces*,John Wiley and Sons: New York, 1993.
96. Appelhans, D., Wang, Z.-G., Zschoche, S., Zhuang, R.-C., Haussler, L., Friedel, P., Simon, F., Jehnichen, D., Grundke, K., Eichhorn, K.-J., Komber, H., and Voit, B., *Macromolecules* 38, 1655–1664, 2005.
97. Chen, W. and McCarthy, T.J., *Macromolecules* 31, 3648–3655, 1998.
98. Narrainen, A.P., Hutchings, L.R., Ansari, I., Thompson, R.L., and Clarke, N., *Macromolecules* 40, 1969–1980, 2007.
99. Thomas, H. and O'Malley, J.J., *Macromolecules* 14, 1316, 1981.
100. Xie, X.-M., Chen, Y., Zhang, Z.-M., Tanioka, A., Matsuoka, M., and Takemura, K., *Macromolecules* 32, 4424–4429, 1999.

101. Ratner, B.D. and Castner, D.G., *Surface Modification of Polymeric Biomaterials*, Plenum Press: New York, 1996
102. Feast, W.J. and Munre, H.S., *Polymer Surfaces and Interfaces I*, John Wiley and Sons: New York 1987.
103. Feast, W.J., Munre, H.S., and Richards, R.W., *Polymer Surfaces and Interfaces II*, John Wiley and Sons: New York, 1992.
104. Park, J.B. and Lakes, R.S., *Biomaterials: An Introduction*, Plenum Press: New York, 1992.
105. Richards, R.W. and Peace, S.K., *Polymer Surfaces and Interfaces III*, John Wiley and Sons: Chichester, UK, 1999.
106. Garbassi, F., Morra, M., and Occhiello, E., *Polymer Surfaces: From Physics to Technology*, John Wiley and Sons: Chichester, UK, 1998.
107. Andrade, J.D., *Polymer Surface Dynamics*, Plenum Press: New York, 1988.
108. Harkins, W.D., *The Physical Chemistry of Surface Films*, p. 175, Reinhold: New York, 1952.
109. Fleischer, C.A., Morales, A.R., and Koberstein, J.T., *Macromolecules* 27, 379, 1994.
110. Scott, C.E. and Macosko, C.W., *Polymer* 35, 5422, 1994.
111. Scott, C. and Macosko, C., *J. Polym. Sci. B: Polym. Phys.* 32, 205, 1994.
112. Nielson, L.E., *Mechanical properties of Polymers and Composites*, Vol 2, Marcel Dekker: New York, 1974.
113. Bohn, L., *Rub. Chem Technol.* 41, 495, 1968.
114. Datta, S. and Lohse, D., *Polymeric Compatibilizers*, Hanser Publishers: Munich, 1996.
115. Lyatskaya, Y., Gersappe, D., Gross, N.A., Balazs, A.C., *J. Phys. Chem.* 100, 1449, 1996.
116. Lee, M.S., Lodge, T.P., and Macosko, C.W., *J. Polym. Sci., Polym. Phys. B* 35, 2835, 1997.
117. Sundaraj, U. and Macosko, C.W., *Macromolecules* 28, 2647, 1995.
118. Koningsvald, R., *Adv. Colloid Interface Sci.* 2, 151, 1968.
119. Lestriez, B., Chapel, J.P., and Gerard, J.F., *Macromolecules* 34, 1204, 2001.
120. Solc, K. and Koningsveld, R., *J. Phys. Chem.* 96, 4056, 1992.
121. Olabki, O., Robeson, L.M., and Shaw, M.J., *Polymer-Polymer Miscibility*, Academic Press: New York, 1979.
122. Weidisch, R., Stamm, M., Michler, G.H., Fischer, H., and Jerome, R., *Macromolecules* 32, 742–750, 1999.
123. Utracki, L.A., *Polymer Blends and Alloys: Thermodynamics and Rheology,* Hanser: Munich, Germany, 1989.
124. Kongarov, G.S. and Bartenev, G.M., *Rubber Chem. Technol.* 47, 1188, 1974.
125. Slonimskii, G.L. and Komskaya, N.F., *Rubber Chem. Technol.* 31, 244, 1958.
126. Priest, E.M. Jr. and Porter, R.S., *Polymer J.* 4, 154, 1973.
127. Schmidt, L.R., *J. Appl. Polym. Sci.* 23, 2463, 1979.
128. Bayram, G., Yilmazer, U., and Xanthos, M., Polym. Eng. Sci. 41, 262–274, 2001.

129. Shi, D., Ke, Z., Yang, J.H., Gao, Y., Wu, J., and Yin, J.H., *Macromolecules* 35, 8005–8012, 2002.
130. Plochocki, A.P., *J. Appl. Polym. Sci.* 16, 987, 1972.
131. Plochocki, A.P., *Trans. Soc. Rheol.* 10, 287, 1976.
132. Utracki, L.A. and Kamal, M.R., *Polym. Eng. Sci.* 22, 96, 1982.
133. Janssen, S., Schwahn, D., Mortensen, K., and Springer, T., *Macromolecules* 26, 5587, 1993.
134. Hammouda, B. and Bauer, B.J., *Macromolecules* 28, 4505, 1995.
135. Hammouda, B., Balsara, N.P., Lefebvre, A.A., *Macromolecules* 30, 5572, 1997.
136. An, L., Horst, R., and Wolf, B.A., *J. Chem. Phys.* 107, 2597, 1997.
137. Migler, K.B. and Han, C.C., *Macromolecules* 31, 360, 1998.
138. Fytas, G. and Kumar, S., *Phys. Rev. Lett.* 81 594, 1998.
139. Wallheinke, K., Potschke, P., and Stutz, H., *J Appl. Polym. Sci.* 65, 2217, 1997.
140. Pu, H.T., Tang, X.Z., and Xu, X.M., *Polym. Int.* 45, 169, 1998.
141. D’Orazio, L., Guarino, R., Mancarella, C., Martuscelli, E., and Cecchin, G., *J. Appl. Polym. Sci.* 65, 1539, 1997.
142. Zhang, X.M., Li, G., Wang, D.M., Yin, Z.H., Yin, J.H., and Li, J.S., *Polymer* 39, 15, 1998.
143. Chiang, C.R. and Chang, F.C., *Polymer* 38, 4807, 1997.
144. Heino, M., Kirjava, J., Hietaoja, P., and Seppala, J., *J. Appl. Polym. Sci.* 65, 241, 1997.
145. Brown, H.R., Char, K., Deline, V.R., and Green, P.F., *Macromolecules* 26, 4155, 1993.
146. Brown, H.R., Char, K., and Deline, V.R., *Macromolecules* 26, 4164, 1993.
147. Chen, C.C. and White, J.L., *Polym. Eng. Sci.* 33, 923, 1993.
148. Gleinser, W., Friedrich, C., and Cantow, H.-J., *Polymer* 35, 128, 1994.
149. Tang, T. and Huang, B., *Polymer* 35, 281, 1994.
150. Fayt, R., Jerome, R., and Teyssie, P., *J. Polym. Sci., Polym. Lett. Ed.* 19, 79, 1981.
151. Riess, G. and Jolivet, Y., *Copolymers, Polyblends and Composites*, N.A.J. Platzer (Ed.), pp. 243–256, American Chemical Society: Washington, DC, 1979.
152. Tucker, P.S., Barlow, J.W., and Paul, D.R., *Macromolecules* 21, 2794, 1988.
153. Folkes, M.J. and Hope, P.S., *Polymer Blends and Alloys*, Blackie Academic and Professional, an Imprint of Chapman & Hall: UK, 1993.
154. Creton, C., Kremer, E.J., Hui, C.-Y., and Brown, H.R., *Macromolecules* 25, 3075, 1992.
155. Kim, S.-J., Shin, B.-S., Hong, J.-L., Cho, W.-J., and Ha, C.-S., *Polymer* 42, 4073, 2001.
156. Richardson, M.J., in: *Comprehensive Polymer Science*, C. Booth, C. Price (Eds.), vol 1, p. 867, Pergamon Press: Oxford, 1989.
157. Winderlich, B., *Thermal Analysis*, Academic Press: Boston, 1990.
158. Sperling, L.H., *Introduction to Physical Polymer Science*, Wiley: New York, 1992.

159. Angell, C.A., *Science* 267, 1939, 1995.
160. Wetton, R.E., in: *Polymer Characterisation*, B.J. Hunt, M.I. James (Eds.), p. 178, Blackie: London, 1993.
161. Coleman, M.M., Graf, J.F., and Painter, P.C., *Specific Interactions and the Miscibility of Polymer Blends*, Technomic, Publishing Co. Inc.: Lancaster, PA, 1991.
162. Coleman, M.M., Yang, X., and Painter, P.C., *Macromolecules* 25, 4414, 1992.
163. Espi, E., Alberdi, M., Fernandez-Berridi, M.J., and Iruin, J.J., *Polymer* 35, 3712, 1994.
164. Serman, C.J., Xu, Y., Painter, P.C. and Coleman, M.M., *Polymer* 32, 516, 1991.
165. Kuo, S.-W. and Chang, F.-C., *Macromolecules* 34, 5224, 2001.
166. Takeda, K., Murata, K., and Yamashita, S., *J. Phys. Chem. B* 103, 3457, 1999.
167. Fox, T.G. and Loshaek, S., *J. Polym. Sci.* 15, 371, 1955.
168. Fox, T.G. and Flory, P.J., *J. Polym. Sci.* 14, 315, 1954.
169. Cowie, J.M.G., Harris, S., Ribells, J.L.G., Meseguer, J.M., Romero, F., and Torregrosa, C., *Macromolecules* 32, 4430, 1999.
170. Shi, Y. and Jabarin, S.A., *J. Appl. Polym. Sci.* 81, 11, 2001.
171. Ishida, H. and Lee, Y.H., *J. Appl. Polym. Sci.* 81, 1021, 2001.
172. Park, M.S., Kim, J.K., *J. Polym. Sci., Polym. Phys.* 40, 1673, 2002.
173. Balsamo, V., Calzadilla, N., Mora, G., and Muller, A.J., *J. Polym. Sci., Polym. Phys.* 39, 771, 2001.
174. Roe, R.J. and Zin, W.C., *Macromolecules* 13, 1221, 1980.
175. Zachaius, S.L., ten Brinke, G., MacKnight, W.J., and Karasz, F.E., *Macromolecules* 16, 381, 1983.
176. Flory, P.J., *Principles of Polymer Chemistry*, Cornell University Press: Ithaca, NY, 1953.
177. Patterson, D. and Robard, A., *Macromolecules* 11, 690, 1978.
178. Xue, L., Zhang, J., and Han, Y., *Prog. Polym. Sci.* 37, 564–594, 2012.
179. Schmitt, B.J., *Angew. Chem.* 91, 286, 1979.
180. Inoue, T., *Macromolecules* 18, 2089, 1985.
181. Ueda, H. and Karasz, F.E., *Macromolecules* 18, 2719, 1985.
182. Cong, G., Huang, Y., MacKnight, W.J., and Karasz, F.E., *Macromolecules* 19, 2765, 1986.
183. White, R.P., Lipson, J.E.G., and Higgins, J.S., *Macromolecules* 43, 4287, 2010.
184. Lohse, D.J., Fetters, J.L., Doyle, M.J., Wang, H.-C., and Kow, C., *Macromolecules* 26, 3444, 1993.
185. Graessley, W.W., Krishnamoorti, R., Reichart, G.C., Balsara, N.P., Fetters, L.J., and Lohse, D.J., *Macromolecules* 28, 1260, 1995.
186. McMaster, L.P., *Macromolecules* 6, 760, 1973.
187. Balsara, N.P., Fetters, L.J., Hadjichristidis, N., Lohse, D.J., Han, C.C., Graessley, W.W., and Krishnamoorti, R., *Macromolecules* 25, 6137, 1992.
188. Krishnamoorti, R., Graessley, W.W., Balsara, N.P., and Lohse, D.J., *Macromolecules* 27, 3073, 1994.

189. Krishnamoorti, R., Graessley, W.W., Fetters, L.J., Garner, R.T., and Lohse, D.J., *Macromolecules* 28, 1252, 1995.
190. Krishnamoorti, R., Graessley, W.W., Dee, G.T., Walsh, D.J., Fetters, L.J., and Lohse, D.J., *Macromolecules* 29, 367, 1996.
191. Reichart, G.C., Graessley, W.W., Register, R.A., Krishnamoorti, R., and Lohse, D.J., *Macromolecules* 30, 3036, 1997.
192. Walsh, D.J. and Rostami, S., *Macromolecules* 18, 216, 1985.
193. Rostami, S. and Walsh, D.J., *Macromolecules* 18, 1228, 1985.
194. Wolf, B.A. and Blaum, J., *J. Polym. Sci.: Polym. Symp.* 61, 251, 1977.
195. Doi, M. and Edwards, S.F., *The Theory of Polymer Dynamics*, Oxford University Press: Oxford, 1986.
196. Phelan, J.C. and Sung, C.S.P., *Macromolecules* 30, 6845–6851, 1997.
197. Cangelosi, F. and Shaw, M.T., in: *Polymer Compatibility and Incompatibility Principles and Practices*, Solc, K. (Ed.), MMI Press: New York, 1982.
198. Lee, M.S. and Chen, S.A., *Polym. Eng. Sci.* 33, 686, 1993.
199. Kraus, G., Rollmann, K.W., and Gruver, J.T., *Macromolecules* 3(1), 92, 1970.
200. Onogi, S., Masuda, T., and Kitagawa, K., *Macromolecules* 3(2), 109, 1970.
201. Fujimoto, T., Narukawa, H., and Nagasawa, M., *Macromolecules* 3, 57, 1970.
202. Droste, D.H. and Dibenedetto, A.T., *J. Appl. Polym. Sci.* 13, 2149, 1969.
203. Maheshwari, S., Tsapatsis, M., and Bates, F.S., *Macromolecules* 40, 6638–6646, 2007.
204. O'Reilly, J.M., Bair, H.E., and Karasd, F.E., *Macromolecules* 15, 1083–1088, 1982.
205. Nechtschein, M., Devreux, F., Genoud, F., Gugliemi, M., and Holczer, K., *Phys. Rev. B* 27, 61–78, 1983.
206. Lahti, P.M. (Ed.), *Magnetic Properties of Organic Materials*, Marcel Dekker: New York, 1999.
207. Wasserman, E., Murray, R.W., Yager, W.A., Trozzolo, A.M., and Smolynsky, G., *J. Am. Chem. Soc.* 89, 5067, 1967.
208. Teki, Y., Takui, T., Itoh, K., Iwamura, H., and Kobayashi, K., *J. Am. Chem. Soc.* 108, 2147, 1986.
209. Sheldon, R.P., in: *Composite Polymeric Materials*, p. 145, Elsevier Science Publishing Co. Inc: New York, 1982.
210. Krause, S., in: *Polymer Blends*, D.R. Paul, S. Newman (Eds.), pp. 15–113, Academic Press Inc.: London, 1978.
211. Bates, F.S., *J. Appl. Crystallogr.* 21, 681, 1988.
212. Utracky, L.A., *Commercial Polymer Blends*, p. 117, Chapman & Hall: London, 1998.
213. Vinckier, I., Moldenaers, P., and Mewis, J., *J. Rheol.* 40, 613, 1996.
214. Sumita, M., Shizuma, T., Miyasaka, K., and Ishikawa, K., *Polym. Prepr., Jpn.* 29(9), 1839, 1980.
215. de Gennes, P.G., *Scaling Concepts in Polymer Physics*, Cornell University Press: Ithaca, NY, 1985.
216. de Gennes, P.G., *J. Colloid Interface Sci.* 27, 189, 1987.

217. Zheng, X., Sauer, B.B., Van Alsten, J.G., Schwarz, S.A., Rafailovich, M.H., Sokolov, J., and Rubinstein, M., *Phys. Rev. Lett.* 74, 407, 1995.
218. Halperin, A., Tirrel, M., and Lodge, T.P., *Adv. Polym. Sci.* 100, 31, 1992.
219. Sperling, L.H., *Interpenetrating Polymer Networks and Related Materials*, New York: Plenum, 1982.
220. Xu, W.B., Ge, M.L., and He, P.S., *J. Polym. Sci. B: Polym. Phys. Ed.* 40, 408, 2002.
221. Xu, W.B., Ge, M.L., and He, P.S., *J. Appl. Polym. Sci.* 82, 2281, 2001.
222. Zheng, Q.A., Peng, M., and Yi, X.S., *Mater. Lett.* 40, 91, 1999.
223. Chu, J., Xiang, C., Sue, H.J., and Hollis, R.D., *Polym. Eng. Sci.* 40(4), 944–955, 2000.
224. Colak, O.U., *Int. J. Plast.* 21, 145–160, 2005.
225. Colak, O.U. and Dusunceli, N., *J. Eng. Mater. Tech.* 128, 572–578, 2006.
226. Williams, J.A., *Trib. Int.* 29, 675, 1996.
227. Briscoe, B.J., Pelillo, E., and Sinha, S., *Polym. Eng. Sci.* 36, 2996, 1996.
228. Briscoe, B.J., Evans, P.D., Pelillo, E., and Sinha, S.K., *Wear* 200, 137–147, 1996.
229. Xiang, C., Sue, H.-J., and Chu, J., *ANTEC* 99, 3463, 1999.
230. Chu, J., Xiang, C., Sue, H.J., and Hollis, R.D., *Polym. Eng. Sci.* 41, 23–31, 2001.
231. Marr, D.W.M., Wartenberg, M., Schwartz, K.B., Agamalian, M.M., and Wignall, G.D., *Macromolecules* 30, 2120–2124, 1997.
232. McKean, D.R. and Stille, J.K., *Macromolecules* 20, 1787–1792, 1987.
233. Marand, E., Baker, K.R., and Graybeal, J.D., *Macromolecules* 25, 2243–2252, 1992.
234. Crank, J., *Mathematics of Diffusion*, 2nd ed., pp. 266–285, Clarendon Press: Oxford, UK, 1975.
235. Barrer, R.M., in: *Diffusion in Polymers*, J. Crank, G.S. Park (Eds.), chap. 6, Academic Press: New York, 1968.

Polymer Blends and Composites: Chemistry and Technology.
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6

Polymer Blends: Thermodynamics

Laws of thermodynamics underlie the mechanism of formation of polymer blends. The polymer blends initially produce a more or less finely dispersed two-phase system in which the two phases initially consist of the two unmixed polydisperse constituents. Because of favorable thermodynamics, miscible mixtures are easily formed by simple melt blending. In the structure of polymer blend, a role is played by interphase phenomena. It is characteristic of polymer blend structure to be dependent on the number of components [1–5].

6.1 Thermodynamics and Blend Properties

Polymer blends are based on the control of chemical and physical interactions between blend components. Molecular weights (MW) of both crystalline and amorphous components may influence both the kinetic and thermodynamic parameters governing the segregation distance. The long-chain nature of polymers leads to two competing thermodynamic and kinetic factors. They affect the formation and stability of these micron-sized structures.

Acid-base or ion-dipole hydrogen bonding and transition metal complexation have been used to enhance interaction and thermodynamic miscibility of suitably functionalized components, resulting in improved compatibility [6, 7]. Therefore, there is thermodynamic interaction between the blend components, and this interaction is a function of their physical and chemical structures. Blends with less extreme immiscibility may be staged by another thermodynamic mechanism even if they are strictly binary. Simple physical mixture of two different polymers may be homogeneous or heterogeneous multiphase. The intermediate stage of phase separation is a process displaying behavior with a modified thermodynamic driving force based on a changing local composition.

Most of the fundamental studies on polymer blend thermodynamics are restricted to binary systems. For a mixture of high molecular weight materials, the combinatorial entropy term is negligible and a negative exchange interaction is required for a miscible system. The synergistic benefits of blending derive from blend morphology [8]. Coarse phase morphology arises from the incompatibility and the subsequent sharp interfaces between homopolymer phases. Therefore, two-phase material has poor properties compared to the counterpart of the polymers. Primarily this is due to the lack of stress transfer across the sharp interface [9].

The practical problem exhibited with exothermic mixing is its difficulty due to lack of ability to predict quantitatively the mixing thermodynamics of strongly interacting systems. In laboratories, polymer-solvent interactions often predominate with misleading results. The heat of mixing is a function independent of molecular weight. Polymers whose analogues show negative heats of mixing could be expected to be miscible. Moreover, key thermodynamic quantities, such as the changes in enthalpy and volume as a result of mixing, are very difficult to obtain experimentally for polymeric systems.

6.2 Entropy of Mixing

The combination of two factors means that most polymer blends have the morphology of phase-separated domains. The long-chain nature of polymers leads to these important factors, which when combined make the micron-scale structure of blends. They are:

1. The entropy of mixing for macromolecules is very small, so that most pairs of polymers are immiscible or insoluble

in each other. Even a relatively small change in entropy is reflected upon mixing macromolecular species. Therefore, low entropy of mixing leads to most polymer pairs forming immiscible polymer blends. This results in thermodynamic incompatibility and heterogeneous blends are much more common. Because of the small entropy of mixing associated with long-chain macromolecules, most homopolymer mixtures are immiscible [10].

2. The physical properties of blends, such as mechanical, transport, optical, etc., crucially depend on the polymers' chain structure. It makes the dynamics of these mixtures very slow and completes phase separation of a blend which takes a very long time.

Most polymer blends made by mixing either bulk polymers or solutions of polymers have the morphology of phase-separated domains [11]. Mixing of cyclic/linear polymer blends can be thermodynamically favored due to the entropy gain involved when going from pure cycles to cyclic/linear blends [12, 13]. It is thermodynamically unfavorable for most polymers to form homogeneous mixtures. Although in the limit of high molar mass polymers, the entropic contribution is usually regarded to have a negligible impact upon the free energy balance. However, some polymer blends in which at least one of the components consists of a random copolymer have been found to be miscible for a certain copolymer composition range, even though none of the binary combinations of the corresponding homopolymers is miscible [14].

Most polymers are mutually immiscible from the thermodynamic standpoint since the entropic contribution to the free energy of mixing is negligible. For high molecular weight polymers with large molar volumes, the combinatorial entropy terms are small. High molecular weight polymers during blending are intrinsically immiscible, and therefore phase separate under appropriate conditions because of the vanishing entropy of mixing. The combinatory entropy term in the Flory-Huggins theory accounts for the theory of random copolymer blends and has provided for the effect of chemical composition on miscibility [15–17].

6.3 Enthalpy of Mixing

Dissimilar polymers are only miscible if there are favorable specific interactions between them leading to a negative contribution to the Gibbs free energy of mixing. Most pairs of high molar mass polymers are immiscible.

This is due to the fact that the combinatorial entropy of mixing of two polymers is less than that for two low molar mass compounds. The positive mixing enthalpy together with negligible entropy contribute to the free energy of mixing. High interfacial tension leads to low interfacial area, low domain adhesion and finally poor mechanical properties [18]. The enthalpy of mixing is primarily dependent on the energy change associated with changes during mixing [19]. It is much less dependent on chain lengths. In the enthalpy of polymers mixing ΔH < 0, the interaction energy between heterogeneous molecules is higher than between homogeneous ones. Enthalpy contributions often dominate the free energy of mixing in polymeric systems.

The introduction of interacting groups by chemical modification of a polymer or by copolymerization leads to negative contributions to the enthalpy of mixing. This has been shown to lead to improved miscibility of an otherwise incompatible polymer pair [18]. Most polymer pairs are immiscible due to their unfavorable enthalpy changes. Therefore, there is phase-separated morphology in the blends.

6.4 Specific Enthalpy

During the processing of polymers, the melting of solid particulates, such as pellets, beads, flakes and granules, is the most important elementary step [20, 21]. In the processing equipment, polymers are compressed by heating from room or feed temperature to processing temperature. The amount of thermal energy required is based on their specific enthalpy. In Figure 6.1,

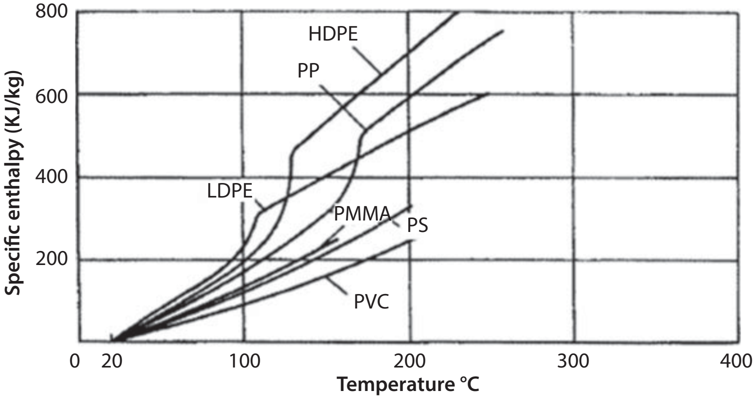

Figure 6.1 Specific enthalpy as a function of temperature for different polymers. (Reprinted with permission from [22]; Copyright ©1998 All rights reserved)

the specific enthalpies of three polycrystalline (HDPE, LDPE and PP) and three amorphous (PS, PMMA and PVC) polymers are shown [22]. The area under the curve from room to processing temperature is the thermal energy needed per unit mass for a specific polymer. Crystalline materials require higher thermal energy because of the crystalline portion of the structure.

6.5 Free Energy of Mixing

The miscibility of thermodynamic solubility with free energy of mixing (ΔG) between them is negative. In thermodynamics of polymer-polymer blends, the primary requirement in order for two polymers to be miscible is the necessity of having negative Gibbs free energy of mixing (ΔG). The free energy of mixing associated with blending randomly selected high molecular weight polymers would be positive. It is indicative of immiscibility or multiple amorphous phase formation.

6.5.1 Gibbs Free Energy

The main thermodynamic condition of polymer compatibility is the negative value of Gibbs free energy:

$$\Delta G = \Delta H - T\Delta S \tag{6.1}$$

where ΔG is Gibbs free energy; ΔH is the free enthalpy; and ΔS is the entropy.

At $\Delta G < 0$ the spontaneous mixing occurs and at $\Delta G > 0$ the system is incompatible.

The competition between values of change of enthalpy and entropy of mixing determines ΔG.

For $\Delta G < 0$, $|\Delta H| > |T\Delta S|$, the main thermodynamic requirement of compatibility conditions is $\Delta S < 0$. Macromolecules in blends are more ordered than among macromolecules analogous to them. They are formed with combined and ordered polymer structures.

The delicate balance between the entropic ΔS and enthalpic ΔH is the contribution to ΔG, which has a negligible impact upon the free energy balance. By setting aside the free volume or equation of state contribution to ΔG, the focus of attention shifts to the enthalpy term [23]. The dominant factor in the promotion of polymer-polymer miscibility is a favorable or exothermic interaction between segments, or portions of segments, of different polymer species.

6.5.2 Thermodynamics of Mixing

Equilibrium thermodynamics govern the direction in which non-equilibrium phase separation will tend in a blend.

1. Phase structure depends on compatibility of mixed components in polymer blends. The concept of miscibility and the possibility of liquid-liquid phase separation for binary polymer blends will be in terms of classical equilibrium thermodynamics. The specific interactions between polymer pairs with their interacting groups can provide thermodynamic driving forces for miscibility between polymers.
2. Most of the polymers are thermodynamically incompatible. Most of the systems that do mix still show phase separation (partial miscibility) when conditions are changed, e.g., upon a change in temperature, pressure, molecular weight, or composition. Characterizing, and potentially predicting, this behavior is of central practical interest.
3. Pressure effects are of interest from a fundamental standpoint since the thermodynamics of typical polymer blends are understood in the framework of the incompressible random phase approximation [24–28].

In a practical blend the domain sizes and final morphology will be governed by phase- separation thermodynamics coupled with the transport and interfacial properties of the blend components. The thermodynamic immiscibility of polymer blends is as predicted by thermodynamic excess functions on the actual state of aggregation of a blend. The blend morphogies could be controlled by both dissolution/diffusion of polymer in the polymerizable monomer and thermodynamic combined with reaction kinetics [29].

To have miscibility, i.e., a homogeneous phase, it is necessary for the free energy of mixing to be negative; however, for this phase to be stable against phase segregation an additional requirement must be met. The importance of specific interactions in yielding a negative heat of mixing ΔH_m is due to the negligible contribution of the entropy of mixing ΔS_m for higher molecular weight polymers in the following expression:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \tag{6.2}$$

The free energy of mixing has both enthalphic (ΔH_{mix}) and entropic (ΔS_{mix}) contributions. These contributions are generally functions of composition, temperature and in the case of ΔS_{mix}, molecular weight. The entropic contribution is quite small at the molecular weights normally encountered in commercial polymers. The requirement that $\Delta G_{\text{mix}} < 0$ is equivalent to requiring the heat of mixing to be exothermic or negative. When free energy of mixing (ΔG_m) of the system is positive, blend leads to phase separation with reduction of blend properties.

6.5.3 Flory-Huggins Theory

The Flory-Huggins theory [30, 31] is used to describe binary systems. In this theory, a single parameter is used to characterize the interactions between component pairs. In principle, blend should depend only on the chemical identity of monomer pairs. It should be independent of blend composition and component molecular weight. Binary blends may be used to predict the properties of multicomponent blends. The theory has been generalized to multicomponent systems [32].

The interactions that involve blending appear to be more complicated than accounted for by simple dispersive forces. Regarding thermodynamics of mixing in the melt state, a natural starting point of two-component blends is the Flory-Huggins equation. In the thermodynamics of mixing, the most widely used expression for the free energy of mixing is that first proposed by Huggins [30], Flory [19], and Staverman [33]:

$$\frac{\Delta G_m}{VRT} = \frac{\phi_1}{v_1 N_1}\ln\phi_1 + \frac{\phi_2}{v_2 N_2}\ln\phi_2 + \phi_1\phi_2\frac{\chi}{v} \tag{6.3}$$

where V is the total volume of the sample; R is the gas constant; T is the absolute temperature; N_i is the degree of component I (= 1 or 2); ϕ_i is the volume fraction of component; v_i is the molar volume; v is the reference volume; and χ is the interaction parameter reflecting the interactions between the repeat units of the two polymers.

In this theory, a single parameter, ϕ, is used to characterize the interactions between component pairs. In principle, χ should depend only on the chemical identity of monomer pairs and should be independent of blend composition and component molecular weight. Thus the results of binary experiments may be used to predict the properties of multicomponent blends.

The Flory-Huggins theory would be adequate for polymeric mixtures. The observation that measured ϕ parameters in binary systems show a composition dependence [34, 35] is a manifestation of this inadequacy. Additional parameters required for characterizing polymer blends will become evident when we understand the origins of such observations.

A simple thermodynamic model for polymer-polymer blends based on the theories of Flory and Huggins leads to the important conclusion that to have miscibility in the limit of high molecular weights requires a negative interaction parameter. Polymer blending is a simple, effective approach to develop new material exhibiting combinations of properties that cannot be obtained by individual polymers [36, 37]. Miscibility is governed by the thermodynamics represented by the Gibbs free energy mixing:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \tag{6.4}$$

The mixtures are miscible when the value of ΔG_{mix} is negative. In the case of free energy of mixing ΔG_m of the system being positive, blend leads to phase separation with reduction of blend properties.

A polymer mixture is miscible only if the value of ΔG_{mix} is negative and the second derivative of ΔG_{mix} with respect to composition is positive. Since the combinatorial entropy terms are very small for high molecular weight polymers, the enthalpic contribution plays a dominant role in the sign of ΔG_{mix}. In other words, a mixture should be miscible if ΔH_{mix} approaches zero or is negative. Weak dispersive forces or van der Waals interactions between repeat units of two polymers usually lead to zero or positive value of heat of mixing. If specific interactions such as hydrogen bonds or dipole-dipole interactions are established, a negative enthalpy of mixing (or heat of mixing) can be obtained. Therefore, the evaluation of heat of mixing is of prime relevance to judge polymer-polymer miscibility.

With binary blends, the Flory-Huggins equation is [30, 31, 26–29, 38–41]:

$$\frac{\Delta G_m}{k_B T} = \frac{\phi_1 \ln \phi_1}{\upsilon_1 N_1} + \frac{\phi_2 \ln \phi_2}{\upsilon_2 N_2} + \chi \frac{\phi_1 \phi_2}{\upsilon} \tag{6.5}$$

where ΔG_m is the free energy of mixing per unit volume; k_S is Boltzmann's constant; T is the absolute temperature; and ϕ_i, υ_i and N_i are volume fractions, volumes per monomeric unit, and polymerization indices of the components. Many of the polymer blends are immiscible due to the unfavorable thermodynamics of mixing. The phase behavior of multicomponent polymeric materials is a crucial factor in determining their physical properties and subsequently their utility.

Although lacking completeness, the Flory-Huggins approach [18, 42] is often relied upon to provide a convenient and readily acceptable insight into the thermodynamics of polymer blends.

Immiscibility is a rule in polymer blends due to both ΔH_{mix} and ΔS_{mix} being unfavorable. The ΔS_{mix} is unfavorable due to the large molecular weight per unit volume of a few molecules. The ΔH_{mix} is also unfavorable because the van der Waals dispersion force is of the form of – AB/r^6, where A and B are Hamaker constants [42],

$$\Delta H_{\text{mix}} = -2\frac{AB}{r^6} + \frac{AA}{r^6} + \frac{BB}{r^6} = \frac{(A-B)^2}{r^6} \tag{6.6}$$

which are always positive. The miscibility between two polymer mixtures can be achieved when the specific interactions such as hydrogen bonding, dipole-dipole interaction, or ionic interactions are established.

Compatibility improves with reactive compatibilization, in which graft or block copolymers are formed *in situ* during melt processing in terms of appropriate reactive functionalities. It has emerged as an effective way of solving the problem associated with incompatible polymer mixtures [43]. The utility of theory for designing novel advanced materials depends, to a large extent, on its ability to describe the essential molecular factors determining the system's thermodynamics and consequently its phase behavior.

Most products made of polymers are a mixture of more than one component and, in many instances, of more than one polymer. Mixing polymers and additives is essential to enable processing and to obtain good product properties. Three-component systems are calculated by the phase behavior of multicomponent systems. The classical Flory-Huggins equation is used for the free energy of mixing [19], which for three components can be expressed as,

$$\begin{aligned}\frac{\Delta g_{\text{mix}}}{kT} &= \frac{\phi_A}{N_A v_A}\ln\phi_A + + \frac{\phi_B}{N_B v_B}\ln\phi_B + \frac{\phi_C}{N_C v_C}\ln\phi_C \\ &\quad + \frac{\phi_A\phi_B}{v_{AB}}\chi_{AB}^{FH} + \frac{\phi_A\phi_C}{v_{AC}}\chi_{AC}^{FH} + \frac{\phi_B\phi_C}{v_{BC}}\chi_{BC}^{FH}\end{aligned} \tag{6.7}$$

where ΔG_{mix} is the free energy of mixing per unit volume; ϕ_i is the volume fraction of component I; N_i is the number of segments per molecule; V_i is the segmental volume; and v_{ij} and χ_{ij}^{FH} are the average segmental volume and interaction parameter between i and j respectively.

The χ parameter in binary and multicomponent blends is independent of blend composition, component molecular weight, and molecular architecture over the accessible temperature range. However, interdiffusion will occur as the system strives for the thermodynamic equilibrium state in which mutual solubility reigns to some degree. The diffusion process may be slow, but it cannot be stopped unless special measures are taken.

The solubility parameter and Flory-Huggins interaction parameter of the thermodynamic interaction between a polymer and a polymer stationary phase reveals information about the interaction. The specific interaction volume of probes, V_g^0, is related to the Flory-Huggins interactions parameter between the polymer and polymeric stationary phase, χ, by the following equation [41, 44–51]:

$$\chi = \ln\left(\frac{273.16R\upsilon_2}{V_g^0 P_1^\circ V_1}\right) - 1 + \frac{V_1}{M_2\upsilon_2} - \frac{P_1^\circ}{RT}\left(B_{11} - V_1\right) \tag{6.8}$$

where R is the gas constant; T is the temperature; V_2 is the specific volume; M_2 is the molecular weight of the stationary phase; and P_1°, V_1, and B_{11} are the vapor pressure, molar volume and the second viral coefficient of the polymer respectively.

The Flory-Huggins interaction parameter can be related to the solubility parameters of two components by the following equation [51, 52]:

$$\chi = \left(V_1/RT\right)\left(\delta_1 - \delta_2\right)^2 \tag{6.9}$$

where δ_1 and δ_2 are the solubility parameters of the polymer and polymer stationary phase respectively; and V_1 is the volume of the probe. The above equation implies that χ is always positive. A negetive value of χ, can occur in systems with a specific interaction. A specific interaction exists between polymer and polymer stationary phase in which the interaction parameter can have a negative value.

6.6 Thermodynamics of Miscible Polymers

Miscibility is a function of the microstructure of the polymers, such as polydispersity, molecular weight, tacticity, presence of comonomer, and thermodynamic variables such as temperature, pressure and blend composition. A small difference in conformation affects the blending process [53].

Compatibility depends on the temperature and regimes of mixing. Thermodynamic compatibility is improved under heating or under the action of external mechanical fields. Diffusion phenomena of blends are realized with temperature rise under the influence of heat motion. Thermodynamic compatibility of polymers may be improved by formation of combined structures or by increase of energetic interaction between macromolecules. Incompatible systems may become partially compatible or compatible under the change of chemical structure of macromolecules of components by introduction of functional groups leading to strong chemical interaction under modification of one of the mixing polymers by change of monomer units by copolymerization or oxidation.

Thermodynamic state of aggregation for polymer blends is in the early stages of development. The specific interactions between polymer pairs with their interacting groups can provide thermodynamic driving forces for miscibility between polymers. Thermodynamically miscible blends have physical properties that uniquely vary with blend composition in a smooth and continuous fashion between the property values of the pure components. Polymer blends form a single amorphous phase with physical blends. This is due to the high consistency of polymer blend components. The specific interactions between polymer pairs with their interacting groups can provide thermodynamic driving forces for miscibility between polymers.

Increased interaction between the two different polymers leads to the improved miscibility of the blends [54]. Many of the polymer blends known so far are found to be incompatible. But some polymer blends show compatible behavior due to various reasons such as specific interactions between the blend components. The compatibility is, however, characterized by the occurrence of a change in the negative free energy during mixing, which is very rare in the case of high molecular weight polymers. However, this is more or less exhibited by binary blends having specific interactions between the blend components such as dipole-dipole interaction, hydrogen bonding, ion-dipole interaction, ion-ion complex formation, and repulsive interaction [55, 56]. Thermodynamically miscible polymers can significantly influence the viscosity value [57–59]. Nucleation and crystalline growth are dependent on the concentration and segment mobility.

To form a miscible blend, the free energy of mixing $\Delta G_m \leq 0$ and the second derivative with respect to composition $\delta^2 \Delta G_m / \delta\phi^2 > 0$, where $\Delta G_m = \Delta H_m - T \Delta S_m$ and ΔH_m and ΔS_m are the enthalpy and entropy of mixing, respectively. The Gibbs free energy of mixing ΔG_m contains three contributions: a combinatorial entropy of mixing, an exchange interaction, and a free-volume effect. For high molecular weight polymers ΔS_m is negligible and the sign of ΔG_m is dominated by ΔH_m. In general, ΔH_m is negative only if there are specific associative interactions between two polymers [60]. Therefore, the formation of miscible polymer blends depends on the occurrence of exothermic interactions such as hydrogen bonding [61], dipole-dipole interactions [62], acid-base interactions [63], or transition metal complexation [64].

Blends with polymer segment level of scale are homogeneous, then formation of miscible blends require that the free energy of mixing, ΔG_{mix} be negative [18, 19, 41, 65–67]. The formation of a totally miscible system is required to ensure stability against phase separation:

$$\left(\partial^2 \Delta G_{\text{mix}} \middle/ \partial \phi_i^2\right)_{T,P} > 0 \tag{6.10}$$

where ϕ_i is the volume fraction of component *i*; *T* is the absolute temperature; and *P* is the pressure.

When only dispersive or van der Waals forces are present, the enthalpy of mixing will almost always be positive or zero, ultimately leading to contributions to ΔG_m, which are unfavorable to mixing. In general, to exhibit miscibility, there needs to be some degree of interaction between the polymers, resulting in a favorable heat of mixing being exothermic.

6.7 Lower Critical Solution Temperature

This ideal behavior can be complicated in some miscible blend systems by phase separation upon heating the melt above the lower critical solution temperature (LCST). Basic thermodynamic theory leads one to expect LCST behavior is negative [68].

The LCST is the transition that occurs when mixtures of low molecular weight polymers show exothermic heats of mixing during sufficient heating from single-phase, miscible behavior of multiphase behavior [69]. This transition is often seen in miscible polymer blends. The LCST transition occurs with the stability (equation) criterion or its equivalent:

$$\left(\frac{\partial^2 G}{\partial \phi}\right)_V + \left(\frac{\partial V}{\partial P}\right)_{T,\phi} \left(\frac{\partial^2 G}{\partial \phi_i \partial V}\right)^2 > 0 \tag{6.11}$$

where *G* is the free energy of a binary system (cal); ΔG_{mix} is the free energy of mixing (cal); ΔU_{mix} is the potential energy of mixing of pure components; *V* is the system volume (cm3); ν is the specific volume (cm^3/g); ΔS_{mix} is the entropy of mixing (cal/K); Δh_{mix} is the enthalpy of mixing pure components (cal); $\Delta H_{\text{mix}}'$ is the enthalpy of mixing per unit volume (cal/cm^3); and ϕ_i is the volume fraction of component *i*.

Lower critical solution temperature (LCST) behavior is a thermodynamic and therefore reversible phenomenon. The rate at which phase splitting and recombination occur can determine the resultant phase morphology.

6.8 Thermodynamics of Immiscible Polymers

Incompatible blends are one of the areas providing the greatest scientific and technological challenge. The challenge is the concerted effort in three areas, i.e., thermodynamics, processing and new compatibilizers [70].

Phase separation on a macroscopic scale is a basic phenomenon. It is a thermodynamic decrease in the size of the phases to micrometer dimensions, which leads to microphase-separated, colloidal systems that are strongly influenced by surface properties.

- To understand the properties of materials, their phase structure must be established.
- The characteristics of the basic phases change with the types of molecules that make up the phase (small molecules, flexible or rigid macromolecules). Changes in the properties of the phase also occur with their sizes (macro-, micro-, or nanophase).
- For flexible macromolecules (polymers) the most notable mesophase is the condis phase. Condis phase is more or less a known mesophase in polymers, and is referred to as a solid ordered (positional and orientational) phase, but conformationally disordered internally. Metastable nanophase separation is common with semicrystalline polymers.

Blending of dissimilar polymers to produce high performance materials is attracting great attention. Immiscible polymers are mostly dealt with by reactive blending. The reactive blending involves *in-situ* reaction of functionalized components to form a block or graft copolymer at the interface between phases [71–77]. Polymer blends has been related to the thermodynamically immiscibility of most polymers.

6.9 Summary

- The thermodynamic interactions in binary blends represent the first level of complication beyond the simple thermodynamic interactions present.
- The free energy of mixing must be negative for miscibility, which requires enthalpy of mixing to be zero or negative.
- The combination of entropy of mixing of two polymers is drastically smaller than that of low molecular weight

compounds and the enthalpy of mixing is a positive quantity or near zero.

- The enthalpy of mixing is often a positive quantity.
- In thermodynamic immiscibility, the polymer-containing binary blends usually exhibited poor phase dispersion and interfacial adhesion, which in turn resulted in unsatisfactory mechanical properties.
- The adverse entropy effects lead to many polymers being generally not miscible.

References

1. Coleman, M.M., Painter, P.C., and Graf, J.F., *Specific Interactions and the Miscibility of Polymer Blends*, Technomic Publishing Co.: Lancaster, PA, 1991.
2. Zhu, S., Rafailovich, M.H., Sokolov, J., Gersappe, D., Winesett, D.A., and Ade, H., *Nature* 400, 49, 1999.
3. Pernot, H., Baumert, M., Court, F., and Leibler, L., *Nat. Mater.* 1, 54, 2002.
4. Alice, N.C.W., Lindway, M.J., and MacKnight, W.J., *Macromolecules* 27, 3027, 1994.
5. Pham, H.H. and Winnik, M.A., *Macromolecules* 39, 142, 2006.
6. Datta, S. and Lohse, D., *Polymeric Compatibilizers*, Munich: Hanser, 1996.
7. Araki, T., Tran-Cong, Q., and Shibayama, M., *Structure and Properties of Multiphase Polymeric Materials*, New York: Marcel Dekker, 1998.
8. Lohse, D.J., Datta, S., and Kresge, E.N., *Macromolecules* 24, 561–566, 1991.
9. Di Lorenzo, M.L. and Frigione, M.J., *Polym. Eng.* 17, 429, 1997.
10. de Gennes, P.G., *Scaling Concepts in Polymer Physics*, Cornell University: Ithaca, NY, 1979.
11. Datta, S. and Lohse, D.J., *Macromolecules* 26, 2064–2076, 1993.
12. Nachlis, W.L., Bendler, J.T., Kambour, R.P., and MacKnight, W.J., *Macromolecules* 28, 7869–7878, 1995.
13. Khokhlov, A.R. and Nechaev, S.K., *J. Phys. (Paris)* 6, 1547–1555, 1996.
14. Huh, W. and Karasz, F.E., *Macromolecules* 25, 1057–1061, 1992.
15. Kambour, R.P., Bendler J.T., and Bopp. R.C., *Macromolecules* 16, 753, 1983.
16. ten Brinke, G., Karasz, F.E., and MacKnight, W.J., Macromolecules 16, 1827, 1983.
17. Paul, D.R. and Barlow, J.W., *Polymer* 25, 497, 1984.
18. Paul, D.R. and Newman, S. (Eds.), *Polymer Blends*, vols. 1, 2, Academic Press: New York, 1978.
19. Flory, P.J., *Principles of Polymer Chemistry*, chap. 12, Cornell University Press: New York, 1962.
20. Tadmor, Z. and Gogos, C.G., *Principles of Polymer Processing*, John Wiley & Sons: New York, 1979.

21. Tadmor, Z. and Gogos, C.G., *Principles of Polymer Processing*, chap. 9, John Wiley & Sons: New York, 1979.
22. Gogos, C.C., Tadmor, Z., and Kim, M.H., *Adv. Polym. Technol.* 17(4), 285–305, 1998.
23. Barlow, J.W. and Paul, D.R., *Polym. Eng. Sci.* 27, 1482, 1987.
24. Wolf, B.A. and Blaum, J., *J. Polym. Sci. B* 61, 251, 1977.
25. Hajduk, D., Gruner, S.M., and Fetters, L.J., *Macromolecules* 29, 1473, 1996.
26. Lefebvre, A.A., Lee, J.H., Balsara, N.P., Hammouda, B., Krishnamorti, R., and Kumar, S., *Macromolecules* 32, 5460, 1999.
27. Beiner, M., Meier, G., Fytas, G., and Kumar, S., *Phys. Rev. Lett.* 81 594, 1998.
28. Rabeony, M., Lohse, D.J., Garner, R.T., Han, S.J., Graessley, W.W., and Migler, K.B., *Macromolecules* 31, 6511, 1998.
29. Lestriez, B., Chapel, J.P., and Gerard, J.F., *Macromolecules* 34, 1204, 2001.
30. Huggins, M.L., *J. Chem. Phys.* 9, 440, 1941.
31. Flory, P.J., *J. Chem. Phys.* 9, 660, 1941.
32. Scott, R.L., *J. Polym. Sci.* 9, 423, 1952.
33. Staverman, A.J. and Van Santen, J.H., *Recl. Trav. Chim. Pays-Bas* 60 76, 1941.
34. Han, C.C., Bauer, B.J., Clark, J.C., Muroga, Y., Matsushita, Y., Okada, M., Tran-cong, Q., Chang, T., and Sanchez, I.C., *Polymer* 29, 2002, 1988.
35. Bates, F.S., Muthukumar, M., Wignall, G.D., and Fetters, L.J., *J. Chem. Phys.* 89, 535, 1988.
36. Ruzette, A.-V.G. and Mayes, A.M., *Macromolecules* 34, 1894, 2001.
37. Gonzalez-Leon, J.A. and Mayes, A.M., *Macromolecules* 36, 2508, 2003.
38. Huggins, M.L., *J. Phys. Chem.* 46, 151, 1942.
39. Flory, P.J., *J. Chem. Phys.* 10, 51, 1942.
40. Scott, R.L. and Magat, M., *J. Chem. Phys.* 13, 172, 1945.
41. Olabisi, O., Robeson, L.M., and Shaw, M.J., *Polymer-Polymer Miscibility*, Academic Press: New York, 1979.
42. Hamaker, H.C., *Physica* 4, 1058, 1937.
43. Ide, F. and Hasegawa, A., *J. Appl. Polym. Sci.* 18, 963, 1974.
44. Utracki, L.A., *Polymer Alloys and Blends: Thermodynamics and Rheology*, Academic Press: New York 1989.
45. Deshpande, D.D., Patterson, D., Schreiber, H.P., and Su, C.S., *Macromolecules* 7, 530, 1974.
46. Mandal, B.M., Bhattacharya, C., and Bhattacharyya, S.N., *J. Macromol. Sci. Chem. A* 26, 175, 1989.
47. Conder, J.R. and Young, C.L., *Physicochemical Measurement by Gas Chromatography*, Wiley: New York, 1979.
48. Vilcu, R. and Lecu, M., *Polymer Thermodynamics by Gas Chromatography*, Vasilescu, V., trans., Elsevier: Amsterdam, 1990.
49. Langer, S.J., Sheehan, R.J., and Huang, J.C., *J. Phys. Chem.* 1982, 86, 4605.
50. Su, C.S., Patterson, D., and Schreiber, H.P., *J. Appl. Polym. Sci.* 20, 1025, 1976.
51. Flory, P.J., *Principles of Polymer Chemistry*, Cornell University Press: Ithaca, New York, 1953.

52. Hildebrand, J.H., Prausnitz, J.M., and Scott, R.L., *Regulated and Related Solutions*, Van Nostrand Reinhold Co: New York, 1970.
53. Yoshida, H., Zang, G.Z., Kitamura, T., and Kawai, T., *J. Therm. Anal. Cal.* 64, 577–583, 2001.
54. Ratnam, C.T. and Zaman, K., *Die Angew. Makromol. Chem.* 269, 42–48, 1999.
55. Ryou, J.H., Ha, C.S., Cho, W.J., *J. Polym. Sci. A: Polym, Chem.* 31, 325, 1993.
56. Ha, C.S., Ryou, J.H., Cho, W.J., and Roe, R.J., *Polymer* 31, 325, 1993.
57. Boutahar, K., Carrot, C., and Guillet, J., *Macromolecules* 31, 1921, 1998.
58. Zhao, R. and Macosko, C.W., *J. Rheol.* 46, 145, 2002.
59. Narayanan, B., Pryamitsyn, V.A., and Ganesan, V., *Macromolecules* 37, 10180, 2004.
60. Lu, X. and Weiss, R.A., *Macromolecules* 25, 3242–3246, 1992.
61. Ting, S.P., Bulkin, B.J., Pearce, E.M., and Kwei, T.K., *J. Polym. Sci. A: Polym. Chem.* 19, 1451, 1981.
62. Woo, E.M., Barlow, J.W., and Paul, D.R., *J. Appl. Polym. Sci.* 28, 1347, 1983.
63. Zhow, Z.L. and Eisenberg, A., *J. Polym. Sci. C: Polym. Lett.* 21, 233, 1983.
64. Sen, A. and Weisa, R.A., *Polym. Prepr.* 28, 220, 1987.
65. Paul, D.R. and Barlow, J.W., *J. Macromol. Sci.: Rev. Macromol. Chem.* 18, 109, 1980.
66. Barlow, J.W. and Paul, D.R., *Annu. Rev. Mater. Sci.* 11, 299, 1981.
67. Walsh, D.J., Higgins, J.S., and Maconnachie, A. (Eds.), *Polymer Blends and Mixtures*, NATO series E 89, Martinua Nijhoff Publishers: Dordrecht, The Netherlands, 1985.
68. Prigogine, I. and Defay, R., *Chemical Thermodynamics*, Longmans, Green, & Co.: London, 1952.
69. Rowlinson, J.S., *Liquids and Liquid Mixtures*, Academic Press: New York, 1967.
70. Capaccio, G., Gardner, A., Hope, P., and Wilkinson, K., *Makromol. Chem. Macromol. Symp.* 38, 267, 1990.
71. Baker, W.E., and Saleen, M., Polym. Eng. Sci. 27, 1634, 1987.
72. Angola, J.C., Fujita, Y., Sakai, T., and Inoue, T., *J. Polym. Sci. B: Polym. Phys.* 26, 807, 1988.
73. Oshinski, A.J., Keskkula, H., and Paul, D.R., *Polymer* 33, 268, 1992.
74. Okamoto, M. and Inoue, T., *Polym. Eng. Sci.* 33, 175, 1993.
75. Gonzalez, M.A., Keskkula, H., and Paul, D.R., *J. Polym. Sci. B: Polym. Phys.* 33, 1751, 1995.
76. Scott, E.C. and Macosko, C.W., *Polymer* 36, 461, 1995.
77. Li, H., Chiba, T., Higashida, N., Yang, Y., and Inoue, T., *Polymer* 38, 3921, 1997.

Polymer Blends and Composites: Chemistry and Technology.
Muralisrinivasan Natamai Subramanian.

7

Polymer Blends

Polymer blends are designed to generate materials with optimized chemical, structural, mechanical, morphological and biological properties. Improvement of the performance of polymeric materials for many important industrial applications is achieved with complementary properties. Polymer blend yields average properties of its individual components. For the two-polymer system there is a possibility of mutual influence of the filler on the matrix and vice versa [1].

The technological and service properties of polymer blends are determined by mutual distribution of the components, and the type, size distribution, and shape of structures formed by one polymer in the other [2]. Polymer blends:

- Fill the economical and performance gaps;
- Improve processing ability;
- Have interesting engineering applications;
- Have importance in the preparation of materials with new desirable properties;
- Are an economically viable and versatile way for tailoring new specific materials [3, 4];

- Are the most efficient way to satisfy new requirements for material properties that demand advanced materials from a scientific as well as commercial point of view;
- Are a relatively simple solution to the complex problem of providing desired properties which are more economical than traditionally developed new polymers;
- Enable properties of importance to be maximized based on engineering into one material with certain combinations of desired properties exhibited individually by the component polymers.

From the development of polymer materials, polymer blends have reached the status of being considered an important technology. Increased industrial application of polymer blend to commercial utility has grown significantly. Due to its utility and simplicity, blending is used for improving polymer properties [5, 6].

7.1 Type of Blends

Polymers blends with thermoplastics are attractive not only for their low cost, but also their technical performance. Processing, transformation and simplicity in recycling has been directed towards polymer-polymer blending to develop the desired final properties

Mixture of polymer with chemicals or other polymer(s) is called blend. The basis of polymer blends is to exploit certain unique properties of individual polymers for multicomponent systems for the benefit of the overall properties. Polymer blends are gaining greater importance due to their unique properties different from the basic polymers. Blending of one polymer with another polymer is a very common practice [7–12].

Polymer blends range from completely compatible mixtures to phase-separated systems.

- Lower molecular weight fractions of one of the polymers are more miscible with the other constituent than the higher molecular weight fractions.
- In polymer exhibiting partial miscibility, both equilibrium phases consist of high molecular weight fractions of the major constituent and lower molecular weight fractions of the minor constituent.

7.2 Blend Properties

Polymer blends are physical mixtures of structurally different polymers which adhere together through secondary bond forces and have no covalent bond between them [7]. Functional group interactions (hydrogen bonding or dipolar interaction) between the monomer units in the constituent polymers help in part to overcome entropic effects in the polymer blends [13–15].

7.2.1 Interaction Parameters

Polymer blends are generally multiphase systems characterized by high interfacial tension and weak phase adhesion, leading to coarsely phase-separated structures and inferior ultimate mechanical properties [16]. Interaction parameter changes other than temperature are chemically achieved by using a copolymer as one of the components of the interface. The role played by the interaction parameter provides the weld strength of incompatible polymer interfaces [17].

There are three types of interaction forces, namely dispersive, polar, and hydrogen bonding.

- Dispersion forces are the result of a fluctuating atomic dipole formed from a positive nucleus and a negative electron cloud. They occur in all molecules and usually contribute a dominating portion of intermolecular interaction.
- Polar forces can be divided into two types, permanent and induced dipoles. Two molecules, each containing permanent dipoles, can form Keesom interactions. These interactions are the result of symmetrical dipole-dipole orientation. Two molecules, one of which contains a permanent dipole, can form an induced interaction by polarization of the nondipole molecule.
- Hydrogen bonding forces are reactive molecular interactions. They are explained in many ways: electron pair acceptor-electron pair donor, proton donor-proton acceptor, and Lewis acid-Lewis base. The interaction between hydrogen bonding forces is also unsymmetrical, that is, donor-type and acceptor-type molecules are required to initiate hydrogen bonding.

7.2.2 Colloidal Properties

In two-phase polymer blends, colloidal properties should be considered [18]. Blends can be considered to be a special kind of heterogeneous colloidal system. The blends differ from the classical colloidal systems in transient layer between its components. The volume ratio of dispersed phase to polymer matrix, chemical nature of the additive and the polymer, size and shape of the dispersed particles, interfacial interactions between the matrix and the dispersed phase is necessary in order to blend [19].

7.2.3 Morphology

The great majority of useful blends are immiscible, and their outstanding performance stems from their multiphase morphologies. Hence, the control and the prediction of morphologies are of great importance for the optimization of desired properties. There needs to be proper interfacial tension leading to a phase size small enough to allow the material to be considered as macroscopically homogeneous; and an interfacial adhesion strong enough to assimilate stresses and strains without disruption of the established morphology. Blends of heterogeneous phase retain their own properties which are summed up in a final product.

The morphology depends on whether the arrangement of the phases is continuous or discontinuous and if it is based on crystalline or amorphous phase. Morphology of multiphase polymeric systems has a primary effect on blend properties [20–22]. Blending behavior of commercial polymer blends and their effects on subsequent processing behavior are concerned with changes in the morphology of the polymer blend. The morphology and blend properties also depend on parameters such as composition, viscosity ratio, and processing conditions during mixing [23].

Polymer blend morphology depends on whether the arrangement of the phases is continuous or discontinuous and the degree of order in the crystalline or amorphous phases. Single glass transition temperature (T_g) blends have interphase connections but are still not compatible.

Polymer blends may be divided into three categories as follows:

1. With crystalline interactions between two polymers
2. With polymer interaction in the amorphous phase only.
3. Lack both crystalline and amorphous interactions but still have good mechanical properties.

7.2.4 Phase Separation

Phase separation is due primarily to differences in molecular geometry, molecular weight, and functional group incompatibility. It results upon blending in significant proportions. Therefore, direct blending delivers formation and coalescence of sizable dispersed phase domains, low adhesion between phases, and poor final properties [24–27]. The improved adhesion between the phases of the blend that occur at the boundary has been utilized [28–32].

To overcome the drawback of phase separation in blends, generally the following are considered:

- Interactive polymers [33–35];
- Preparation using opportune additives [36, 37];
- Graft or block copolymers acting as compatibilizers;
- Reactive mixing (the compatibilizer is formed *in situ*) [38, 39].

One of the important factors controlling the phase separation process and the morphologies generated is the location of the composition of the initial blend with respect to the critical composition.

7.2.5 Crystallinity

The degree of crystallinity is one of the major factors determining the final properties of the blend by the size and distribution of segregated phases within the mixture. The main controlling factors include chemical composition, crystal structure and morphology, molecular weight (MW), and processing. Semicrystalline polymer blends are particularly difficult, the components may form structures consisting of alternating regions of crystalline and amorphous materials in addition to phase separating into domains [40, 41].

Polymer blends in which both polymers are crystallizable can form mixed or separate crystals embedded in a compatible or incompatible amorphous phase. The crystals can be homogeneously dispersed or form various levels of superstructure. The structure of the blend will strongly affect its properties. Polymer blends of crystalline nature occupy only a small part due to the molecular incompatibility of the polymeric constituent with separate individual phases. Co-crystallization and co-crosslinking result in more stable morphologies that resist coalescence [42].

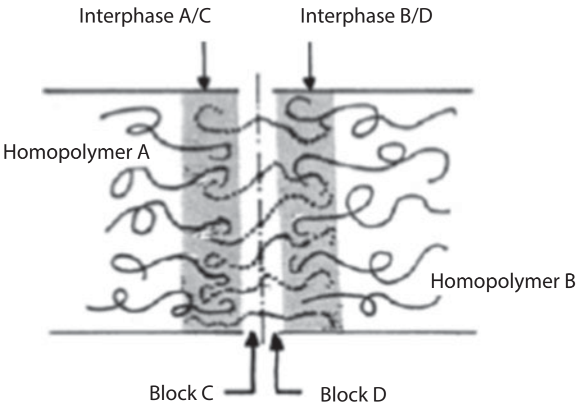

Figure 7.1 Schematic diagram of the formation of an interphase between two immiscible homopolymers, A and B, in the presence of block copolymer, C-block-D. (Reprinted with permission from [43]; Copyright © 2000 American Chemical Society. All rights reserved)

7.2.6 Dispersion

It is challenging to obtain good dispersibility in polymer blends which dissolve within each other with difficulty if they are only mechanically blended. However, it may be possible to obtain good solubility in the blend of these undissolved polymers by introducing a certain suitable interpolymer that has good solubility with each polymer to be blended. Two polymers can be brought into a state of fine mutual dispersion, stable only because of kinetic barriers to phase separation. In immiscible polymer-polymer dispersions, controlling the morphology (phase structure) and the interfacial adhesion between the phases is required in order to obtain an optimized product. Interfacial tension, the shear rate of mixing, and the viscosity ratio of the blend components are key parameters governing the degree of dispersion. The schematic in Figure 7.1 shows the formation and dispersion of interphase between two immiscible homopolymers, A and B, in the presence of block copolymer, C-block-D.

7.2.7 Physicochemical Properties

Physicochemical properties [44] of polymer blends depend on several factors based on the polymer matrix present:

- Adhesion in polymer;
- Concentration and distribution;
- Relaxation characteristics;

- Composition of the blend and composite;
- Temperature at which blending or composite operation is conducted.

7.3 Compatibilization

Immiscible polymers exhibit inferior mechanical properties [45]. The mechanical properties or thermal stability of immiscible polymers can be improved by physical or chemical compatibilization to create materials with better performance [46]. Mechanical compatibilization of polymer blends is an attractive route with unique property combinations and polymer compatibilizer can be used for recycling mixed polymer scrap. Blends of polyethylene terephthalate (PET) and any polyolefin (PO) would be grossly incompatible and a very effective compatibilizer would be needed to give the blend adequate mechanical properties for any subsequent application [47].

7.3.1 Reactive Compatibilizers

Reactive compatibilizers appear to be more stable than the addition of a previously synthesized copolymer [48, 49]. In reactive compatibilization, the copolymers that are formed lie at the interface and contribute to reduce the interfacial tension to fix the morphology [50]. Important applications and processes require economical reactive compatibilization of polymers.

7.4 Classification

Polymer blends are mixed systems of two or more finished polymers which can be modified through mixing two or more macromolecular compounds. Polymer blends are classified as:

- Miscible blends;
- Immiscible blends.

7.4.1 Miscible Blends

A variety of miscible polymer blends with strong specific interactions show an unusual compositional variation of their T_g [51–54].

- Symmetric interfaces form miscible blends;
- Polymers interpenetrate into each other;

- Produce blends with good mechanical properties and good cohesion between phases.

Degree of miscibility of polymer blends depends on interpenetration and is generally neither easy to determine experimentally nor easy to predict theoretically. Polymer miscibility results in a mixture with two different chains/segments that are in proximity within a domain small enough. It may be several or tens of repeat units regardless of the types of interactions. A proton-donating polymer is likely to be miscible with a proton-accepting polymer [55].

7.4.2 Immiscible Blends

Most of the polymer blends are immiscible with poor physical properties in comparison with their individual polymers. This is due to the lack of favorable interaction between phase blends. It leads to large interfacial tension in the melt blend which makes it difficult to deform the dispersed phase during mixing. In immiscible blends a decrease in stress concentration at the interface is responsible for the increase of tensile strength [56].

Immiscible polymer blends exhibit different types of morphologies which depend on composition, viscosity ratio and elasticity ratio between the components, interfacial tension, process conditions, etc. [57–60]. Immiscible blends offer attractive developing materials with a useful combination of properties.

Asymmetric interfaces form immiscible blends. Blend systems can be strongly limited by the incompatibility between the polymers. Blends have a multiple glass transition temperature with immiscibility. Generally there is immiscibility among the high molecular weight polymer pairs as well as mechanical incompatibility [16].

The types of immiscible polymer blends are:

- Blend having dispersed domain structure in matrix phase;
- Blend having co-continuous structure.

Asymmetric blend compositions with the minor component form the dispersed phase in the continuous phase of the major component [61–64].

The control of microstructure is very important for determining the physical properties of multicomponent blends in immiscible polymer blends [36, 65]. Polymers are normally not miscible because of the large size of their molecules. Polymer-polymer interfaces are sufficiently narrow. There is little entanglement between the different polymers [66].

Mechanical properties of immiscible blends should be very sensitive to the phase morphology generated during processing and should also be widely varied in chemical type. The chemical type of immiscible blends could be significantly improved by addition of certain block copolymers. Most polymer blends of high molecular weight polymers are intrinsically immiscible, and therefore phase separate under appropriate conditions. Heterogeneous structures would result in the blend. In ternary blends containing block copolymers, formation of interlocking or interpenetrating network phases is the ideal morphology for an immiscible blend. It allows for equal sharing of imposed stresses by the component [67].

7.4.3 Immiscible and Miscible Blends

Immiscible and miscible blends require either the addition of an extra component or the synthesis by chemical modification of one or more of its constituent polymers. Blend miscibility is improved by:

- Simply replacing one of the linear components with a cyclic version of the same polymer;
- Addition of copolymer additives [68];
- *In-situ* generation of interfacially active polymers by (a) using reactive components with complementary functional groups [69] or (b) solid-state shear pulverization [70].

Copolymers, such as block, graft, etc., bear segments that are compatible with each component. These copolymers are extensively used to promote blend compatibility. Copolymers may be added separately or formed *in situ* by blending functionalized polymers.

7.4.4 Binary Blends

In binary polymer blends, phase separation between components may intervene in the morphology formation when the constituent polymer crystallizes, and a complicated morphology will be formed by a cooperative effect of phase separation and crystallization [71–77]. In binary blend, an effect of entanglements between different components is to amplify and should keep the content of the component dilute enough to entangle only with other components; such blend is called dilute blend.

The composition of the blend C_o is described by the molecular concentration of the minor phase. The equilibrium solubility is denoted C_e, and in general for the blends considered here C_o, C_e.

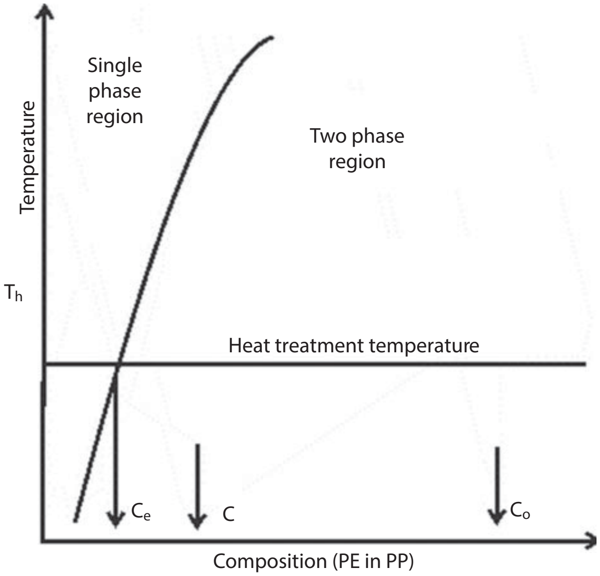

Figure 7.2 Portion of an equilibrium phase diagram for a binary blend in liquid state.

The composition of the blend is C_o. Particle coarsening takes place at an experimental heat treatment temperature (T_h). C_e is the equilibrium solubility of PE and PP at any given temperature and C is the supersaturated composition due to the presence of small particles. Figure 7.2 illustrates an equilibrium diagram of binary blend in liquid state.

It is experimentally established and commonly recognized that in binary immiscible blends the size and distribution of the dispersed particles are the result of a competitive process between breakup and coalescence [78, 79]. Interfacial tension, the shear rate of mixing, and the viscosity ratio of the blend components are key parameters governing the degree of dispersion.

In binary blends, the crystallization kinetics and degree of crystallinity varies dramatically depending on the composition of crystallizable polymer in the crystallizable/noncrystallizable blends.

7.4.5 Ternary Blends

In ternary immiscible blends where two minor phases are dispersed in a continuous matrix, not only the dispersed particle sizes but also the formation of the two dispersed phases in the matrix are important factors affecting their performance. Due to increased industrial interest, the application of polymer blend to commercial utility has grown significantly. Symmetric interfaces are formed between polymers having the same chemical composition such as polystyrene/polystyrene. Any chain segment in a homopolymer molecule comprises the same monomer unit. Chain segment in a copolymer molecule may consist of some number of two different monomers in random combination that is covalently bonded.

Besides the binary systems, ternary blends are also gaining importance [80, 81]. In ternary blends containing block copolymers, formation of interlocking or interpenetrating network phases is the ideal morphology for an immiscible blend. It allows for equal sharing of imposed stresses by the component [67].

In ternary immiscible blends where two minor phases are dispersed in a continuous matrix, not only the dispersed particle sizes but also the formation of the two dispersed phases in the matrix are important factors affecting their performance. For a ternary blend system consisting of polymers 1, 2, and 3, where polymer 3 is the continuous matrix, three phase formations are expected, as shown schematically in Figure 7.3: “capsule formation” of 2 encapsulated by 1, (b) “stack formation” of 1 and 2 stuck together, and (c) “isolated formation” of 1 and 2 dispersed separately. It is known that the morphology development of nonreactive ternary immiscible blends is mostly governed by the balance of interfacial tensions between each component [82].

Polymeric ternary blends have specific characteristics that lead to improved physical properties, ease of processing, or lower cost. They have applications such as coatings, adhesives, or drug delivery

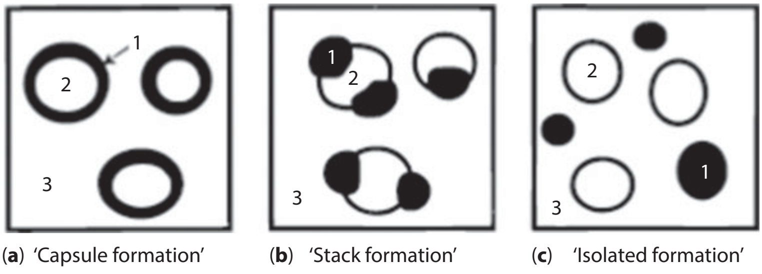

Figure 7.3 Schematic description of phase formations that appear in ternary immiscible polymer blends composed of polymer 1, 2 and 3. (a) Capsule formation of 2 capsulated by 1. (b) Stack formation of 1 and 2 stuck together. (c) Isolated formation of 1 and 2 dispersed separately. (Reprinted with permission from [83]; Copyright © 1997 American Chemical Society. All rights reserved)

systems [36, 84–86]. The ternary blends can vary in composition and individual components.

7.4.6 Homopolymer and Copolymer Blends

Homopolymer and block copolymer blends are certain ways to control the morphologies. Homopolymer effectively changes the volume occupied by each block chain and hence modifies the interface which leads to the morphology change. In case of high molecular weight homopolymer, the polymer tends to locate in the middle of the block copolymer. Therefore, block copolymer is hardly affected by homopolymers and the local structure of the domains is kept with the generation of vesicle structures [87, 88].

7.4.7 Thermoset-Thermoplastic Blends

Thermoset-thermoplastic blends are materials resulting from the mixing of thermoplastic with thermoset precursor such as diepoxy-diamine system. Due to the molar mass increase of the thermoplastic precursor there is a subsequent reaction with the initial mixture of homogeneity, and a liquid-liquid phase separation occurs at a given conversion [89].

Polyetherimide (PEI) and polystyrene (PS) are two non-functionalized thermoplastics. They are composed of a thermoset precursor diglycidyl ether of bisphenol A (DGEBA) and an aromatic diamine as curing agent, 4,4′-methylenebis(3-chloro-2,6-diethylaniline) (MCDEA). Before any reaction, both blends exhibit an upper critical solution temperature (UCST). PS is less soluble than PEI in the thermoset precursor. At curing temperature both types of thermoplastic are soluble. The liquid-liquid phase separation will arrive for PS than for PEI during isothermal cure [90].

7.4.8 Reactive Copolymer Blends

The reactive copolymer styrene-maleic anhydride (SMA) is miscible with PS, PPO, PMMA, and SAN at certain concentrations of MA functionality. The immiscible binary blends of all these polymers with PA6 can be compatibilized through addition of SMA as a third component. In all these ternary blends (PA6/X/SMA), the amino end groups of PA6 will react with the anhydride groups of SMA during melt mixing, giving rise to the formation of a graft copolymer and resulting in a compatibilizing effect. The addition of SMA to polyamide leads to an increase in the melt viscosity [91].

7.4.9 Commercial Blends

Many commercial blends are true blends having a combination of two or more similar polymers, e.g., linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE). Formulations containing a number of incompatible polymers, e.g., rubber-toughened materials such as high-impact polystyrene; or even a material that contains a polymeric plasticizer, e.g., poly(ethylene-co-vinyl acetate) in poly(vinyl chloride) [92], are two of the concepts used for blending two or more polymers together as a means of modifying macroscopic properties. Other widely adopted concepts are given below.

7.4.9.1 Polyolefin Blends

Polyolefin (PO) is an important class of polymers due to its low cost, light weight, low coefficient of friction, high barrier properties to moisture, good optical properties, and ease of processing. High-density polyethylene is an ideal polymer for film and container applications. However, its high permeability to solvents and vapors, such as hydrocarbons, limits its potential. The functionalization of polyolefin has become a commercially viable approach for producing materials with improved properties. Polyolefin blends are of critical importance to the success of the material.

Properties of various polyolefin blends such as low- and high-density polyethylene (LPPE, HDPE) and polypropylene are structurally very similar; they do not form a microscopically homogeneous blend. These polymers form a multiphase system in which interphase adhesion should suffice to provide good blend properties. At certain composition ranges some properties, such as elongation and impact strength, are very poor; other properties, such as tensile modulus and yield strength, are good and there are even compositions which exhibit positive synergism in their ultimate tensile strength [93].

Polyolefin blends improve the properties and processability of the homopolymers involved [7, 36, 94, 95]. The lack of reactive groups has limited many of the polyolefin end uses, particularly when the interaction with other material is important. The use of block and graft copolymers as compatibilizers improves the interfacial interaction between polymers and other materials [96–98]. Blends of polyolefin (PO) and polyamide (PA) polymers combining properties of both components are combined with the thermal and mechanical properties of PA with insensitivity to moisture characteristics. However, PO/PA blends are immiscible. This is mainly due to differences in viscoelastic properties, structure, and morphology between these materials [99].

Different blending methods have been used to prepare PO/PA blends without the addition of a third component. The ethylene component is modified chemically or prepared in the form of a copolymer. A third component, homopolymer, or copolymer is added to the mixture to act as a compatibilizing agent [100].

Functionalized polyolefin compatibilizers are added to aid both adhesion and mixing in the PO/PA systems by grafting reactive groups, such as maleic anhydride (MAH) [101, 102] and acrylic acid [103, 104], onto the polyolefin backbone through reactive processing. An amidation reaction occurs between the amine (NH2) terminal groups of PA and the acid groups (COOH) of the copolymer, in addition to possible hydrogen bonding between the two phases, at least when the copolymer is in acid form [105].

The blending of polyamides and polyolefins combines the high mechanical resistance but poor impact properties of the former and the easy processability, low cost, and high impact resistance of the latter; in ideal cases a useful property balance for many applications may be obtained [106–108]. To overcome the immiscibility of these heterogeneous systems a small number of polar groups are introduced into the backbone of the polyolefins using diverse means [109, 110].

Polyolefin-elastomer blend improves the impact strength of automotive parts and other mechanical applications. It is an alternative to poly(vinyl chloride) flooring [111, 112]. Ethylene propylene diene rubber (EPDM) as immiscibly blends with polypropylene as impact modifier. It is the most common and commercially utilized blend of polyolefins. HDPE can be added with this blend to achieve maximum toughness [113–115]. In polyolefin, poly(butene-1) forms miscible blends with polypropylene [116, 117].

Nonpolar polymers, such as polyolefins, are immiscible with polyamides and polyesters. Grafting polyolefins with functional monomers yields reactive polymer. Nonpolar ethylene propylene rubber and styrene ethylene/butylenes styrene copolymer also forms immiscible blends. These reactive polymers are suitable as compatibilizers for polyolefin-based blends. Polyolefins have good moisture stability, processability, and low cost. They are nonpolar in nature. The addition of polypropylene to polybutene-1 increases the crystallization rate of polybutene-1 and would have utility as a nucleation additive.

In-situ compatibilization of blends of polyolefins with polar polymers, such as polyesters and polyamides, can be efficiently performed by suitable modification of polyolefin chains with reactive groups (i.e., carboxyl derivatives, epoxies, etc.) which are able to give rise, during melt blending, to chemical reactions with the functional groups of the polar component [121]. The formation of a graft copolymer between the polymer components causes a reduction of interfacial tension with an improvement of phase dispersion and promotes adhesion through interpenetration and entanglements at the polymer-polymer interface.

Maleic anhydride (MAH) has been widely used as a grafting monomer to functionalize polyolefins because of the higher reactivity of the anhydride group [122–124]. Functionalization of polyolefins is generally carried out for modification of some of the properties like adhesion and dyeability. They are commonly used as *in-situ* compatibilizers of polymer alloys or multilayer structures involving incompatible polymers such as polyolefins/polyamides, polyesters, and so forth [125–127].

7.4.9.2 Polyethylene Blends

Polyethylene (PE) consists of a variety of branched and linear molecules. Polyethylene does not include any polar group in its backbone. Chemical modification of polyethylene has been used successfully to overcome problems associated with poor dispersion and interfacial adhesion in a polyethylene blend system with other polymer or filler. Blends of PE and PP are binary systems that have attracted attention due to their being immiscible in the unfavorable thermodynamics of mixing.

Chemical modification of polyethylene has been used successfully to overcome problems associated with poor dispersion and interfacial adhesion in a polyethylene blend system. The hydrophilicity of polyethylene increases with the grafting level of MA in polyethylene. Polyethylene should have a certain grafting level of MA in matrix to obtain good dispersion in matrix.

The use of PE-PP blends is related to their practical importance (i.e., their use as an insulating material in the cable industry, as components of industrial products, as film materials, etc.). An important feature of PE-PP blends is that they can be used as raw materials for polymer recycling. The aim of PP-PE blends is improvement of the impact resistance of PP, reduction of its brittleness temperature, etc.

7.4.9.2.1 High-Density Polyethylene Blends

High-density polyethylene (HDPE) materials have low cost, low moisture absorption, and improved processability, as well as good impact resistance and flexural modulus [108]. In order to achieve maximum toughness, HDPE can be added to blend [108, 113–115]. HDPE immiscibly blends with butyl rubber [128], providing improved chemical resistance,

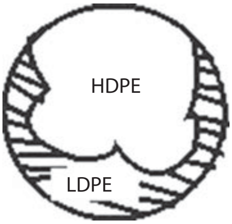

Figure 7.4 Schematic representation of encapsulation in side-by-side two phase flow.

compression set and high temperature mechanical properties compared to the unvulcanized blends. Both LDPE and HDPE blend immiscibly with ethylene copolymers to improve environmental stress crack resistance, toughness, filler acceptance, film tear resistance, flexibility, etc. The HDPE and LDPE in blends crystallize independently, as shown in Figure 7.4, with only minimal interaction. Amorphous phase is more ambiguous in HDPE than LDPE due to the more complex physical picture required for highly crystalline polymers.

However, in LDPE only ethylene sequences of the chain crystallize. Consequently, the crystallizable parts of LDPE are structurally identical to HDPE, and the reason that these two do not cocrystallize in blends is apparently due to morphology or unfavorable surface effects. Aside from crystallizability, copolymer content is grounds for immiscibility. Styrene-acrylonitrile copolymers are compatible [129] provided the comonomer contents of two polymers do not differ.

In the solid state, the branch points of LDPE are concentrated in the amorphous phase. It is hard to make amorphous phase miscibility in the LDPE-HDPE system. However, it does appear rather certain that there will be very strong interactions which can provide mechanisms for good blend properties.

7.4.9.2.2 Low-Density Polyethylene Blends

Low-density polyethylene (LDPE)/polypropylene (PP) blends are hindered by the low compatibility of this polymer pair. The compatibility might be improved by addition of a compatibilizing agent and electron beam irradiation. When two polymers are mixed together, the most frequent result is a system that exhibits almost total phase separation due to the entropy of mixing [130]. Addition of trimethylol propane trimethacrylate (TMPTMA) during sample processing is used to improve miscibility. The polyfunctional monomer (TMPTMA) may reduce the interfacial tension and increase the adhesion force between the polymer phases, allowing a finer dispersion and more stable morphology [131]. Degradation of

PP can be avoided by addition of antioxidants such as phenols, quinines and polyfunctional monomer [132–134].

7.4.9.2.3 Linear Low-Density Polyethylene Blends

Time-temperature results conclude that linear low-density polyethylene blends (LLDPE) and low-density polyethylene (LDPE) are miscible in the molten state in all blend compositions. Molten blends of LLDPE with LDPE are miscible in the LLDPE branching range 10–30 branches/100 °C. Viscosity results and time-temperature superposition results reveal that all the considered m-LLDPE/LDPE blends, except 47.5% m-LLDPE/52.5% LDPE blend, are miscible in the molten state [135].

The density of LLDPE and LDPE is similar to blends with LDPE and HDPE. Although the rheological and mechanical characteristics of blends generally vary smoothly and proportionately between the parent materials, the melt flow properties present a more complex picture [95, 136, 137]. The rheology of LLDPE/LDPE blends shows that the molecular weight of the LLDPE plays an important role. Commercial samples of LLDPE differ both in molecular weight and in the comonomer used during the polymerization.

7.4.9.3 Polypropylene Blends

Incompatible binary blend of polypropylene (PP) and polycarbonate (PC) occurs after melt blending near the phase inversion region, as well as at lower PC concentration by selectively imposing phase inversion and controlling the time of mixing.

The structure-property relationships in crystalline/crystalline polyblends of two homolog crystalline polyolefins, polypropylene and polybutene-1, are highly compatible in all proportions under normal operating conditions [138]. In polypropylene (PP) and polybutylene (PB), the PP is the higher melt material and PB crystallizes from the melt. The rate of conversion depends on such factors as temperature [139], pressure [140], orientation [141] and the presence of low and high molecular weight additives [139]. Polybutylene exhibits an extended strain hardening region [142]. The creep resistance of PB compared to that of PP is outstanding [143]. Mainly PP and PB are blended to reduce the brittle temperature and stiffness of PP. Polypropylene increases its impact resitance at temperatures between −120 °C and 20 °C when blended with EPDM and SBR. Polypropylene/SEBS blends show better impact and mechanical properties at −190 °C and −30 °C.

A novel oxazoline-functionalized polypropylene is effective as a compatibilizer for PP/PBT and PP/PA6 blends. This polypropylene-based compatibilizer mixes well with the polypropylene and is capable of reacting with the carboxylic and amine end groups of PBT and PA6. Significant improvements in blend toughness were achieved without reduction in strength and stiffness. These effects were related to a stabilized morphology of finely dispersed minor phase well attached to the matrix. The enhanced interfacial interactions between the two phases, in particular at high PBT content, were evidenced by increased melt viscosity.

7.4.9.4 Poly(ethylene oxide) Blends

Poly(ethylene oxide) (PEO) and poly(vinyl acetate) (PVAc) blends should be compatible, which is due to the fact that the solubility parameters of the two components are quite close. PEO can act as a proton acceptor and form miscible blends with many proton-donating polymers, since there is a partial negative charge on the oxygen atom. There is a partial positive charge on the carbonyl carbon atom of PVAc. Therefore, PVAc may interact favorably with PEO, and they form a miscible couple.

The miscibility of PEO/PVAc blends [144–150] has been studied from various aspects, including morphology, dynamic mechanical properties, rheological properties, thermal behavior, crystallization, and viscosity in dilute solution. The glass transition temperature of PEO/PVAc blends indicates that the amorphous phases of two components are miscible.

7.4.9.5 Polystyrene Blends

Polystyrene (PS) is a clear and amorphous polymer, with good thermal- and radiation-resistant properties. PS is available in a wide range of formulations; for general purpose PS crystal is used for foam molding, and impact grades (styrene-butadiene block copolymers) for injection molding and extrusion. The use of PS is limited because of its susceptibility to degradation from UV radiation, and chemical attack from aromatic and chlorinated hydrocarbons also may cause problems in application areas.

Polymer blends, such as PS/poly(vinylmethylether) [151], Polycaprolactone/poly(styrene-co-acrylonitrile) [152], and PMMA/poly (styrene-co-acrylonitrile) [153], exhibit lower critical solution temperature (LCST). With high-impact polystyrene, appropriate amounts of polybutadiene and polystyrene-polybutadiene graft copolymer are added to the polystyrene matrix.

Because PS is incompatible with PE [154] their blends normally form either dispersed or continuous phase structures, depending on the chemical composition of two-component polymers. Typically, these blends exhibit weak adhesion (i.e., poor stress transfer) between the PS and PE phases, which manifest as inferior mechanical properties in the final blends [155]. Compatibilization promotes the formation of an interlocking structure in PS/PE blends, which allows more equal sharing of imposed stresses and might therefore improve the mechanical properties of the blends [156–169].

Polystyrene (PS) and poly(oxyethylene) (POE) are not miscible over wide ranges of temperature, composition, and molecular weight [170–172]. Miscibility can be enhanced by using styrene copolymers containing functional groups that hydrogen bond to the POE. The use of functionalized comonomers such as hydroxystyrenes [173], acrylic acid [174], or methacrylic acid [175] reduces the enthalpy of mixing for compatibilization of immiscible polymer blends.

Polystyrene (PS) has low heat distortion temperature and poly(2,6-dimethyl phenylene oxide) (PPO) has low processability. Blending PS with PPO improves heat distortion temperature with economical processing characteristics [176–178]. Applications include appliance housings, automotive dashboards, pump components, and television components.

The immiscible blends formed by PS and PMMA exhibit a pearlescent appearance used for decorative applications [94]. Asymmetric interfaces are formed by two polymers of unlike composition, polystyrene/poly(methyl methacrylate). Interfacial fracture toughness is improved between PS and epoxy through segregation of carboxylic acid chain ends grafted to the epoxy surface. Polystyrene is known to be immiscible with PVC. Copolymers of α-methylstyrene and methacrylonitrile, and copolymers of styrene and acrylonitrile (SAN), are used as compatibilizing agents [179].

7.4.9.5.1 High-Impact Polystyrene Blends

High-impact polystyrene (HIPS) with appropriate amounts of polybutadiene and polystyrene- polybutadiene graft copolymer is added to the polystyrene matrix. Two-phase materials containing graft or block copolymers are collectively known as “compatibilized” polymer blends.

Impact modified polystyrene in which a dispersed rubber phase is incorporated to improve ductility and impact resistance through craze formation is commonplace, and several commercially significant thermoplastic blends are known, notably poly(pheny1ene oxide)/polystyrene, acrylonitrile-butadiene-styrene (ABS)/polycarbonate, and poly(viny1 chloride) (PVC)/poly(methyl methacrylate) (PMMA).

7.4.9.6 Polyvinylchloride Blends

Polyvinylchloride (PVC) is one of the most important polymers and is very often blended with other polymers, which results in heterogeneous blends [180–183]. PVC is a weak proton donor and improved miscibility is expected with acceptor type polymers. It is thermally unstable and is quite frequently blended and compounded with other materials acting as stabilizers or plasticizers which make polymer blending a natural extension. When large amounts of rubbery polymers are added, they can act as macromolecular plasticizers.

Blends affect the thermal stability of PVC. However, PVC blends are made for two reasons:

- PVC is produced in large quantity and has many applications;
- PVC is a homopolymer.

Polymer blend with PVC offers three advantages:

- Improves impact strength of PVC;
- Improves processing ability;
- Has higher heat distortion temperature than a system using liquid plasticizer.

For industrial purposes, the discoloration of PVC is very often used to determine the thermal stability. Polymers such as polybutadiene (PB) and polyacrylonitrile (PAN) show a discoloration under the conditions of degradation. Degradation of pure PVC is compared with its behavior in blends with PS, SAN, HIPS, and ABS. These components can show the effect of a nitrile group or a C–C double bond on the thermal stability of PVC.

Plasticized blends of poly(vinyl chloride)/nitrile rubber combine the low-temperature flexibility and ease of processing of nitrile rubber and the high-temperature permanence and flame-retardent properties of poly(vinyl chloride). Another example is blends of poly(phenylene oxide) with styrene copolymers. These blends have the excellent dimensional stability at high temperatures and good electrical properties of poly(pheny1ene oxide) combined with the lower melt viscosity, shear sensitivity, and cost of polystyrene [184, 185]. Terpolymers of methyl methacrylate, butadiene, and styrene (MBS) are similar to ABS, having a rubber domain and a polymer matrix [186].

Due to the structure and solubility parameters of polybutadiene (PB), incompatible PVC-PB blends are greatly different from those of PVC. Mechano-chemical interactions between PVC and PB molecular chains lead to the formation of a few graft and block copolymers that enhanced adhesion and mixing at the interphase. Alteration of processing temperature or composition ratios destroys the network structure of PB, leading to phase inversion. When PB forms a network structure enveloping the primary PVC particles, the PVC-PB blend has the optimum impact strength [187, 188]. Some partially miscible systems that show large glass transition temperature ($T_{g)}$ changes, which are indicative of high interactions and as a consequence high solubility, show mechanical properties below the additivity rule (PVC-PS system) [189].

PVC has relatively low heat distortion temperature. Several α-methylstyrene/acrylonitrile co- and terpolymers improve heat distortion temperature in compounding with PVC [179, 187, 188, 190].

7.4.9.7 Polyesters

Many polyesters have been found to be miscible with chlorinated polymers. Polycaprolactone is the most widely studied polyester and has been found to be miscible with PVC, poly(epichlorohydrin), chlorinated polyester, chlorinated polyethylene (CPE), poly(chlorostyrene), and chlorinated polypropylene (PP). The formation of these miscible blends has been attributed to the specific interaction between polymer molecules via hydrogen bonding or dipole-dipole C=O * * C-Cl interaction.

The pure copolyester is shown to retain its crystallizability at these conditions, and the addition of additional titanium butoxide polymerization catalyst to that already in the copolyester has little effect. However, mixtures of the copolyester with polycarbonate show a rapid deterioration in copolyester crystallizability, and addition of polymerization catalyst increases the rate of deterioration. As a result of these reactions, not only is the crystallization of the copolyester reduced, but the bright yellow coloration characteristic of titanium phenate compounds is formed. Melt compounding the copolyester prior to melt mixing of the copolyester with the polycarbonate alleviates this problem. Water white, transparent blends are produced in which the copolyester retains its full ability to crystallize.

Titanium catalyst has the ability to promote transesterification reactions between these materials. Transesterification reactions, particularly, can be controlled and eliminated by appropriate use of additives. PET as modifier blends with PBT with miscible phase behavior. It is commercially available for ready use. This blend exhibits improved surface gloss over PBT alone. PET/PBT films have been suggested as pressure-resistive adhesive tape support [191–194].

Mixtures of polyesters can undergo relatively rapid interchange reactions upon exposure to melt processing conditions in the presence of suitable catalysts. Poly(butylene terephthalate) will crosslink with the polyhydroxyether of bisphenol-A at temperatures above 230 °C but no reactions between these miscible components occur at lower temperatures. There is no evidence of chemical reactions between components in their blends of polycarbonate with various polyesters and thus comparable properties are cited for both melt-processed and solution-processed mixtures.

Poly(ε–caprolactone) blends immiscibly with unsaturated polyesters. It is used as low profile additive for unsaturated polyester [195]. It improves surface and imparts better toughness. Styrene butadiene rubber (SBR) is incompatible with polyethylene terephalate (PET). These polymers possess low mechanical properties. High miscibility is required to have better mechanical and impact properties among different phases. Grafting of rubber with maleic anhydride (MAH) builds chemical links between rubber and polyester. With the addition of benzoyl peroxide (BPO) as initiator, a free radical reaction leads to the occurrence of a grafting process between anhydride and rubbers [196].

7.4.9.8 Polyamide Blends

Polyamide (PA) is an engineering polymer and finds its application in electrical, mechanical and automotive parts due to its very high strength, wear and heat resistance, ease of fabrication and processing, and excellent barrier properties to oils. The applicability of PA is limited by its relatively high price, poor impact strength, and poor dimensional stability, as well as poor barrier properties to moisture [197]. Polyamides are rubber toughened to improve tough nylon products.

The most common reactive pair for commercial blends is polyamide/anhydride, which is generally used for the reactive blending of polyamide/polyphenylene ether/styrene-butadiene copolymer, polyamide/ethylene-propylene rubber, and polyamide 6/acrylonitrile-butadiene-styrene copolymer blends [198].

Polyamide–maleic-anhydride-functionalized polyolefin (PA–PO-g-MAH) blends compatibility strategy consists in a maleation of the polyolefin phase followed by a reactive processing favoring copolymer formation by imidization between anhydride and amine chain ends. The polyolefin is most often ethylene-propylene copolymer rubber, polypropylene or polyethylene, and the polyamide is commonly PA6 or PA6,6 [97, 199–208].

Reactive compatibilization of PA-based blends generally makes use of the high reactivity of the polyamide amine end groups with anhydride functionality that can be incorporated in the second phase [83, 209–212]. It is motivated in compatibilized blends of polyamides with ABS materials [213–215]. The mechanical properties and morphology of PA/ABS blends are compatibilized with imidized acrylic polymers (IA) which are miscible with the styrene-acrylonitrile copolymer (SAN) matrix of ABS and have glutaric anhydride and methacrylic acid functionalities which can react with the amine end groups of polyamides [216].

In polyamide (PA)/polyethylene (PE) copolymer system (Figure 7.5), an interfacial reaction between subinclusions and the dispersed phase resulted in a complete stabilization and high retention of the subinclusions, even for a relatively low dispersed phase viscosity and at long mixing times.

The reactive process of polyamide/PP blends offers better dimensional stability and lower permeability than pure polyamide with economical benefit [49].

Modification of polyamide 6 as blend components covers various polymers, among which are styrenic copolymers, such as SAN, acrylonitrile-butadiene-styrene (ABS), and hydrogenated styrene-butadiene-styrene (SEBS), due to significant interest, especially ABS and SAN [217–221].

Specific interactions have yielded miscibility in blends of nylon 6/ethylene-acrylic acid copolymers [222], poly(vinylchloride)/ethylene-ethyl acrylate carbon monoxide terpolymers [223], PVC/poly-ε-caprolactone [224] and PVC/ethylene-vinylacetate-SO_2 terpolymers [186].

The morphological and rheological properties of blends of PA 6 and styrene-acrylonitrile copolymer (SAN) are reactively compatibilized by a styrene-acrylonitrile-maleic anhydride terpolymer (SANMA).

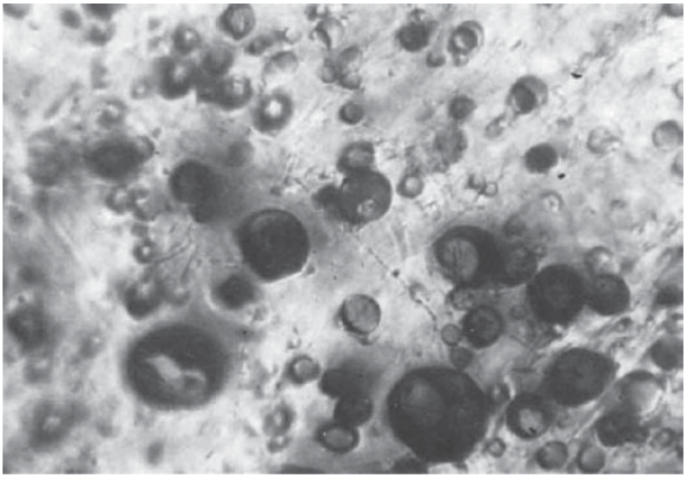

Figure 7.5 Dispersibility of mechanically blended polymer of Nylon 6 and PP. (Reprinted with permission from [199]; Copyright © 1974 John Wiley & Sons, Inc. All rights reserved)

The types of morphology with a PA 6 and a SAN blend [225, 226] have different rheological and morphological behavior giving asymmetric interfacial properties which stem from the comb-like architecture of the *in-situ* generated compatibilizing agent. The compatibilization of PA/SAN blends with a series of imidized acrylic polymers has varied functionality for reaction and miscibility with SAN. Styrene-acrylonitrile-maleic anhydride terpolymers (SANMA) may also be miscible with SAN, and the maleic anhydride portion reacts with amine end group of polyamide [227–229].

The effects of reactive reinforced interface on the morphology and tensile properties of amorphous polyamide (α-PA) and SAN blend have been investigated using SANMA copolymer as a reactive compatibilizer. In addition, *in-situ* polymerization was another effective way to control morphologies of polymer blends in order to improve the dispersion. The main focus has been on rubber- or thermoplastic-modified thermoset polymers, e.g., epoxy resin/thermoplastic systems [230–233].

The microstructures of nylon 6,6/PP blends containing SEBS-*g*-MA are rather complex. An in-depth understanding of the optimized morphologies for maximum toughness is much desired when formulating novel blends with a good balance of tensile strength and fracture toughness. The formula to toughen nylon 6 using SEBS-*g*-MA could not be directly translated into that to toughen nylon 6,6 [234] due, for example, to fundamental differences in the chemical nature between the two polyamides. In PP-*g*-MA, the MA grafting occurs onto PP chain ends after β scission. Anhydride-grafted structure can be either single succinic type anhydride or low molecular mass poly-MA [235]. Anhydride functions lie at chain ends and the number average MW decreases when the grafted anhydride concentration increases.

7.4.9.9 Acrylics Blends

Poly(methylmethacrylate) PMMA/PVC blends have heat resistance and chemical and flammability resistance in material for injection molding and extrusion applications. The major applications of these blends are interior paneling, trim, and seat backs in mass transit vehicles. Commercially available PMMA is miscible with PVC [236, 237]. However, the phase behavior is considered to be only partially miscible [20]. CPE blends with PVC have been used as impact modifiers and as secondary plasticizers [238]. Chlorine content with 42% weight and 30% chlorine has miscibility and immiscibility respectively. Impact modification will generally require phase separation and plasticization will require miscibility.

Low molecular weight acrylics, styrene/acrylics and poly(α–methylstyrene) blend easily with PVC and improve processing, thermoformability, gloss and ductility [239]. Commercial PMMA systems are miscible with PVC [240]. Miscibility allows improved processability by breaking the structures of PVC particles. However, the phase behavior is considered to be only partially miscible. Systems with lower T_g, and consequently lower solubility, show changes in tensile strength with composition almost corresponding to additivity such as for PMMA/PS blends [241].

Poly(methyl methacrylate) PMMA and poly(vinylidene fluoride) (PVF_2) form miscible blends in which PMMA acts as polymeric plasticizer added in low amounts. PMMA improves processing and both PMMA and PVF_2 are resistant to UV degradation. Application includes weatherable film [242–246].

The miscibility is also strongly influenced by the tacticity of PMMA. The compatibility of this blend is more "physical" than "chemical." The interactions between the blend constituents are of the van der Waals type [247–251], and no strong specific interactions are present. PMMA is miscible with neither polystyrene nor with polyacrylonitrile [36]. Miscible blends have random copolymers of styrene and acrylonitrile (SAN) and poly(methyl methacrylate) (PMMA). Mixtures of SAN and PMMA can be miscible. The phase behavior of SAN/PMMA blends is a function of the microstructural details of each polymer: the acrylonitrile (AN) content of the SAN [36, 252–256] and the tacticity of the PMMA. The intermolecular charge-transfer interaction between SAN and PMMA is responsible for miscibility. SAN and PMMA may have different segmental dynamics close to T_g. PEO and PMMA form a single-phase blend in the melt [257, 258].

As PEO is a semicrystalline polymer, the blends with PEO concentrations higher than 20–30% show amorphous (PEO/PMMA) and crystalline (pure PEO) phases. In mixtures of PMMA with SAN or of polystyrene (PS) with poly(vinyl methyl ether) (PVME), the temperature above which phase separation will occur is within the normal process temperature range.

Upon blending, PEO, originally helical, takes a planar zigzag structure. The morphology of the blends is influenced by the molecular mass of PEO and blend composition. In general, both crystallization rate and degree of crystallinity decrease with the increase of PMMA content [259]. The addition of PEO greatly increases the conductivity contribution. It is known that both PMMA and PEO absorb water. The results of an investigation of the average free volume of different PEO/PMMA blends, covering a large range of compositions, indicated a large dilation of free volume on blending, suggesting that the free volumes are largely influenced by segmental conformation and packing rather than specific interactions [260].

The most common criterion for miscibility is the detection of a single T_g at a temperature intermediate to that of pure polymers. There has been a tremendous surge in miscible polymer blends in industrial applications because they offer an inexpensive route to new polymeric materials. The scope of practical applications of an amorphous polymer can be increased by blending it with a polymer of higher T_g. However, there is no reliable method for predicting the viscosity of miscible blends. Empirical relations [261] for the composition dependence of viscosity are kept too general to have any predictive capabilities.

7.4.10 Acrylonitrile-Butadiene-Styrene (ABS) Blends

Acrolonitrile-butadiene-styrene (ABS) consists of two incompatible phases, the polybutadiene rubber phase and the SAN rigid phase. The rubber phase is finely dispersed and embedded in the rigid SAN phase as matrix. When PVC and ABS were mixed, the PVC interacted more easily with the SAN phase than with the rubber phase because of the polarity of the phases. Whether PVC and SAN were compatible in a blend or not depended primarily upon the level of acrylonitrile (AN) content in the SAN. The PVC-ABS blends could be considered a two-phase system composed of a soft polybutadiene (rubber) phase and a rigid PVC/SAN copolymer phase of mutually miscible components.

Acrolonitrile-butadiene-styrene (ABS) blends are miscible [262] with PVC and improve the flame resistance, toughness and processability of ABS in injection molding, extrusion and thermoforming applications while compounding. In specific applications of the commercial blends, the acrylonitrile content of ABS is probably critical relative to miscibility and the phase behavior [263]. The blends of PVC with copolymers of acrylonitrile (AN) and 1,3-butadiene are among the few early examples of miscible polymer blends. It has been pointed out that acrylonitrile-butadiene rubber (NBR) will be miscible with PVC.

The blend has significant commercial applications because a minor portion of PVC improves the ozone resistance of NBR and a minor portion of NBR in PVC decreases the need for volatile plasticizer and improves the flexural properties. PVC-NBR blends bridge the gap between PVC compounds employing phthalate-type plasticizers and polymeric-type plasticizers [264].

The high heat resistance of ABS is based on the blending of α-methylstyrene (α-mS)/acrylonitrile (AN) and styrene (S)/acrylonitrile (AN) copolymers, both at their azeotropic compositions of 69:31 and 76:24 of (α-mS):AN and S:AN respectively [256, 265]. These blends improve the

10–20 °C higher heat distortion temperatures required for ABS. Blends of elastomers and ABS-type blends are devoted to melt flow of blends of crystalline polymers. Application of these blends includes short-term boiling water exposure, parts requiring high temperature due to finishing operations, and appliances.

7.4.11 Polycarbonate Blends

Polycarbonate offers toughness and heat resistance. ABS offers environmental stress crack resistance and lower cost. ABS and polycarbonate blends exhibit poor weld strength due to binary phase. Applications include automotive interior trim, business machines, electrical housings, and recreational vehicle and mass transit uses. ABS and polysulfone blends provide improved thermal and toughness properties for electroplated parts requiring high temperature.

The choice of the materials is dictated by their technological, mechanical and thermal characteristics, as well as by the geometry of the items. However, the ABS-based materials are highly incompatible with the polypropylene matrix, so that the recycling is not possible without a preliminary mechanical separation of the components, which makes the entire process not economically feasible.

Bisphenol A polycarbonate/acrylonitrile-butadiene-styrene (PC/ABS) is an engineering polymer blend which is also used in electronical engineering, transportation and construction. PC/ABS alloy is a well-known commercial polymer which is is easily blended. It is widely used in engineering thermoplastics due to an appropriate combination of two components.

Polycarbonate immiscibly blends with polyethylene. The benefit of this blend has been its key property of high energy absorption at low temperatures [266]. Polycarbonate (PC) has been blended with various polymers such as PS [267–269], PE [267, 270], PP [267, 271], PMMA [272], poly(styrene-co-acrylonitrile) [272], poly(ABS) [273], and some polyesters [274–276]. PC and PMMA are partially miscible [277] with two glass transition regions.

Because of their good ductility even after aging, PC-ABS blends are important industrial materials. One of the strongest effects of the toughening of polymers is the change in brittle-ductile transition [278]. Poly-ε-caprolactone is miscible with PC [279] since it is one of many possible aliphatic polyesters. Miscibility in polymer-polymer blends is the result of the exothermic heat of mixing caused by some specific interaction between polar groups within the two polymer [280].

Polycarbonate is partially miscible with PET [281] and completely miscible with PBT [282]; and is completely miscible with poly(1,4-cyclohexanedimethylene terephthalate) (PCDT) and with its copolyester containing isophthalic acid [279]. It is also completely miscible with poly(ε-caprolactone) (PCL) [283]. The polyester-polycarbonate blend system is miscible.

Polycarbonate/poly(ε-caprolactone) (PC/PCL) blends have been extensively studied due to different aspects of their behavior like miscibility, crystallization kinetics, antiplasticization, and mechanical properties [283–288]. This blend system is a homogeneous mixing of the components in the melt and in the amorphous phase.

Because thermoplastics including PC/ABS blends are easily combustible, flame-retardant formulations are desirable to reduce the probability of burning in the initial phase of a fire. Contrary to additive-type flame retardants (FRs), which are present as fillers, reactive-type FRs are introduced into the resin system via a chemical reaction [289–292]. However, the addition of large amounts of FRs could produce undesirable products and result in difficulties with processability.

Reactive-type FRs have functional groups that bond with the matrix polymer. It can also be noted that reactive compatibilizers have been found to increase the mechanical strength of polymer blends [293–295]. The mechanical, thermal, and rheological properties of PC/ABS blend systems with brominated epoxy resin (BER) used as a reactive-type FR were investigated. Compounding was performed by a twin-screw extruder.

To improve its mechanical properties, ABS needs to be blended with other high-performance engineering polymers, such as PC [274]. The PC/ABS blends are known to possess high impact strength and many other desirable properties. Furthermore, since they can be easily processed, PC/ABS blends have been widely utilized as an engineering thermopolymer [296, 297]. Because polymer blends allow the production of a synergistic balance of properties between the constituents, hybridization of the best properties can be easily accomplished [298].

7.4.12 Chlorinated Polyethylene Blends

Blends of poly(viny1 chloride) (PVC) and chlorinated polyethylene (CPE) form a high impact polymer multiphase system. The initial separation of secondary PVC particles is into primary PVC particles by the soft

CPE phase. Due to the stability of the primary PVC particles an interpenetrating network of the two phases is formed which is dependent on the temperature and shear conditions of the melt. Above a specific temperature, PVC primary particles melt and the interpenetrating network is transformed into a system of fine dispersed CPE particles in a PVC matrix.

Chlorinated polyethylene (CPE) is structurally similar to PVC with the only difference being the C1 content. The compatibility of these modifiers is dependent upon the chlorine content and the distribution of the chlorine atoms on the polyethylene backbone. Chlorinated polyethylene blends with PVC have been used as impact modifiers and as secondary plasticizers [238]. Impact modification will generally require phase separation and plasticization will require miscibility.

7.4.13 Biopolymer Blends

7.4.13.1 Poly(lactic acid) Blends

Synthetic polymers hardly decompose due to their higly chemical stability, causing a serious environmental pollution problem. The development of novel polymers has only focused on their high performance and the damage caused by polymer waste to the environment has been ignored. The problems of waste management can be solved by replacing bioresistant synthetic polymers with biodegradable polymers, which are friendly to the ecosystem and are easily degraded to carbon dioxide and water by enzymes or microorganisms [299].

The most important property of biodegradable polymers is their biodegradability, which is substantially affected by their morphology, crystal structure, and degree of crystallinity. Degree of crystallintiy not only influences the physical properties of the polymers but also their final biodegradability.

A combination of PLA with polystyrene (PS) is a potential bioblend with proposed applications in material packaging and tissue engineering [300]. PS-PLA block copolymers have been found to exhibit a rich variety of nanopatterns [301–303] and cocontinuous structures [304] which form during phase segregation of PS and PLA and arise from the immiscibility of the two polymers [305]. Selective removal of either component gives rise to ordered nanochannels suitable as catalytic supports or scaffolds in tissue engineering. Improving the physical properties of these materials depends on control of the interface between the two polymers which controls its microstructure [313]. Thus, characterization of the morphology of PS-b-PLA block copolymers, as well as PS-PLA blends, remains key in the development of novel, high-performance, PS-PLA-based materials.

7.4.14 Poly(ε-caprolactone) Blends

Then low glass transition of poly(ε-caprolactone) (PCL) enables the PC to crystallize at a rate that is much higher than PC crystallization in the presence of low molecular weight plasticizers, indicating that PCL acts as a very effective macromolecular plasticizer [283, 285, 288, 306].

7.4.15 Cyclic Polymer Blends

Cyclic polystyrene (PS) exhibits a slightly higher LCST (lower critical solution temperature) and is less mobile than linear PS in blends with linear poly(vinyl methyl ether) (PVME) [307]. Cyclic poly(dimethylsiloxane) with linear poly(methylphenylsiloxane) [308] and cyclic polycarbonate with a number of linear amorphous polymers are evidenced by reduced calorimetric T_gs [309, 310]. Increased miscibility for cyclic/linear polymer blends as compared to linear/linear polymer blends can be due to topological effects. Excluded volume due to topology leads to significantly reduced entropy for pure cyclic polymers. There is no unavailable configurational space for linear/linear and cyclic/linear blends since they can interpenetrate freely.

Thus, miscibility differences between cyclic/linear blends and linear/linear blends could be attributed to loss of the end groups. Blends of PVME with cyclic PS end-group effects are not expected to play a major role [307]. The loss of end groups might be expected to influence blend miscibility in cyclic bisphenol A carbonate oligomers [310].

7.4.16 Polyethylene Oxide Blends

The miscibility of poly(ethylene oxide) (PEO) and poly(vinyl acetate) (PVAc) blends [144–150] should be compatible from various aspects, including morphology, dynamic mechanical properties, rheological properties, thermal behavior, crystallization, and viscosity in dilute solution. This is due to the fact that the difference between the solubility parameters of two components is quite close.

7.4.17 Other Polymer Blends

Poly(ethylene oxide) (PEO) can act as a proton acceptor and form miscible blends with many proton-donating polymers. This is due to a partial negative charge on the oxygen atom. There is also a partial positive charge on the carbonyl carbon atom of PVAc. Therefore, PVAc may interact favorably with PEO, and they form a miscible couple.

The glass transition temperature of PEO/PVAc blends indicated that the amorphous phases of two components are miscible. The miscibility and miscible extent decrease with increasing molecular weight of PVAc, and the critical points shift to high PEO concentration with an increase of the molecular weight of PVAc.

Poly(ethylene oxide) (PEO) is a low-T_g semicrystalline polymer and poly(tetramethyl bisphenol A polycarbonate) (TMPC) is a high-T_g non-crystalline polymer. The relevant temperatures are: T_m for PEO (~65 °C), T_g for PEO (~−60 °C) and T_g for TMPC (~190 °C). The wide separation between the glass transition temperatures in this system enables us to study the role of the mobilities of the different blend components in the development of adhesion between these blends.

Copolymerization of maleic anhydride with styrene (SMA) has better miscibility with PVC than PS alone. The interaction between the α-hydrogen of PVC and the carbonyl functional group promoted the miscibility [311]. Because both styrene and butadiene are nonpolar and immiscible with PVC, the copolymer of both (styrene-butadiene rubber, SBR) is predicted to be immiscible. However, SBR works as a good impact modifier for PVC [312].

Polymers of thermoplastic (TP) and thermoset (TS) blends have been widely for two main applications: (i) toughness improvement of TS networks with high performance ductile thermoplastics [89] and (ii) new processing routes for intractable high-temperature-resistant TP polymers such as poly(phenylene ether) (PPE) [313].

Polyvinyl alcohol (PVA)-starch blend plastics are one of the most popular biodegradable plastics and are widely used in packaging and agricultural mulch films [314]. Many combinations of water-soluble polymers that exhibit acidic or basic characteristics yield miscible blends such as poly(acrylic acid)-poly(ethylene oxide) and poly(methyl methacrylic acid)-poly(vinylpyrroldone) [315].

Blend miscibility involves copolymers of styrene and acrylonitrile (SAN) with PMMA [316] and poly(ε-caprolactone) (PCL) [317]. SAN forms miscible blends with poly(phenyl acrylate) [318]. Miscible binary constituents involve at least copolymer. Miscibility occurs in a range of copolymer compositions.

7.5 Advantage of Polymer Blends

There are advantages to using polymer blends to replace engineering polymers in the automotive industry [24, 319, 320]. The advantages of polymer blends and composites can be used to:

- Achieve an economic or property advantage;
- Exploit the unique properties of individual polymers for multicomponent systems;
- Improve the impact strength, resistance to environmental stress cracking, optical properties, crystallization rate, low temperature impact strength, rheological properties and overall mechanical behavior [95].

7.6 Summary

- Polymer blends can replace the synthesis of new polymers.
- Polymer blends are a comparatively cheap method.
- An efficient way to achieve a set of target properties is through mixing two polymer species to form a blend.
- Establishing an optimum blend would give a consistent and satisfactory product with minimal variations.
- Polymer blends have good processing ability.
- Polymer blends enhance design of application-specific materials.
- Polymer blends offer a wide range of easily controlled physical properties, and thus better fine tuning of the final product.
- The effects of viscosity ratio, processing condition and composition on morphology and physical properties are important in polymer blends.
- The structure of polymer-polymer interfaces is important in areas of polymer blends.
- Major problems in the blend approach are the macrophase separation (large domain sizes) and non-mixing of the polymers.

- As entanglement is a prerequisite for strength in polymer systems, interfaces between two immiscible polymers are normally weak.
- Simple blends often lead to poor mechanical properties with unstable morphologies. In such cases compatibilization of blends is necessary.
- Blends of waste or recycled plastics are very comparable to the synthesis of polymer because different properties of waste plastics are blended to create a new polymer.

References

1. Ulkem, I., Bataille, P., and Schreiber, H.P., *J. Macromol. Sci. Pure Appl. Chem.* 31(3), 291–303, 1994.
2. Paul, D.R. and Bucknall, C.B., *Polymer Blends*, Wiley: New York, 2000.
3. Misra, A., Sawhney, G., and Kumar, R.A., *J. Appl. Polym. Sci.* 50, 1179, 1993.
4. Rosch, J., *Polym. Eng. Sci.* 35, 1917, 1995.
5. Xie, X.-M., Xiao, T.-J., Zhang, Z.-M., and Tanioka, A., *J. Colloid Interface Sci.* 206, 189, 1998.
6. Schroeder, K., Klee, D., Hocker, H., Leute, A., Benninghoven, A., and Mittermayer, C., *J. Appl. Polym. Sci.* 58, 699, 1995.
7. Manson, J.A. and Sperling, L.H., *Polymer Blends and Composites*, Plenum Press: New York, NY, USA, 1976.
8. Kreuse, S., in: *Polymer Blends*, D.R. Paul, S. Newman (Eds.), chap. 2, Academic Press: New York, 1978.
9. Coran, A.Y., Das, B., and Patel, R.P., US Patent 4130535, 1978.
10. Sen, A.K., Mukherjee, B., Battacharyya, A.S., De, P.P., and Bhowmick, A.K., *Polym. Degrad. Stab.* 281, 36, 1992.
11. Michaeli, W., Cremer, M., and Bluhm, R., *German Plastics* 83, 992, 1993.
12. Wenig, W. and Asresahegn, M., *Polym. Eng. Sci.* 3, 877, 1993.
13. Painter, P.C., Park, P., and Coleman, M.M., *Macromolecules* 21, 66, 1988.
14. Lai, C.H., Paul, D.R., and Barlow, J.W., *Macromolecules* 21, 2492, 1988.
15. Lai, C.H., Paul, C.R., and Barlow, J.W., *Macromolecules* 22, 374, 1989.
16. Vocke, C., Atila, U., and Seppala, J., *J. Appl. Polym. Sci.* 72, 1443, 1999.
17. Norton, L.J., Smigolova, V., Pralle, M.U., Hubenko, A., Dai, K.H., Kramer, E.J., Hahn, S., Berglund, C., and DeKoven, B., *Macromolecules* 28, 1999, 1995.
18. Kulenev, V.N., *Polymer Blends* [in Russian], Khimiia: Moscow, 1980.
19. Karger-Kocsis, J., Kalló, A., and Kuleznev, V.N., *Acta Polym.* 32(9), 578–581, 1981.
20. Krause, S., *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* 7, 251, 1972.
21. Bever, M.B. and Shen, M., *Mater. Sci. Eng.* 15, 145, 1974.

22. Nielsen, L.E., in: *Mechanical Properties of Polymers and Composites*, Marcel Dekker: New York, NY, USA, 1974.
23. Brydson, J.A., *Plastics Materials*, Butterworth Scientific: London, 1982.
24. Utracki, L.A., *Commercial Polymer Blends*, Chapman & Hall: London, 1998.
25. Utracki, L.A., *Polymer Alloys and Blends*, chap.1 and chap. 7, Hanser: Munich, 1989.
26. Bisio, A.T. and Xantos, M., *How to Manage Plastics Waste: Technology and Market Opportunities*, Hanser: Munich, 1995.
27. Wu, S., *Polymer Interfaces and Adhesion*, Marcel Dekker: New York, 1982.
28. Bly, J.H., *Electron Beam Processing*, vol. 6, p. 55–730, International Information Associates: Yardley PA, 1988.
29. Bennet, E.W. Jr., *Radiat. Phys. Chem.* 14, 947–951, 1979.
30. Bly, J.H., Brandt, E.S., and Burgess, R.G., *Radiat. Phys. Chem.* 14, 931–935, 1979.
31. Carstens, T.J. Jr., PVC the versatile plastic, in: *Proceedings of the 1998 Regional Technical Meeting for Society of Plastics Engineers*, Detroit, MI, USA, SPE, 1998.
32. Hirschler, M.M., in: *Developments in Polymer Stabilization*, G. Scott (Ed.), vol. 5, pp. 107–153, Applied Science Publisher: London, 1982.
33. Eisenberg, A., Smith, P., and Zhou, Z.-L., *Polym. Eng. Sci.* 22, 1117, 1982.
34. Zhou, Z.-L. and Eisenberg, A., *J. Polym. Sci.: Polym. Phys. Ed.* 21, 595, 1983.
35. Rutkowska, M. and Eisenberg, A., *Macromolecules* 17, 821, 1984.
36. Paul, D.R. and Newman, S. (Eds.), *Polymer Blends*, Academic Press: New York, 1978.
37. Barlow, J.W. and Paul, D.R., *Polym. Eng. Sci.* 24, 525, 1984.
38. Eguiazabal, J.I., Calamorra, M.E., Cortazar, M.M., and Iruin, J.J., *Polym. Eng. Sci.* 24, 608, 1990.
39. Robeson, L.M., *J. Appl. Polym. Sci.* 30, 4081, 1985.
40. Kirste, R.G., Kruse, W.A., and Schelten, J., *Makromol. Chem.* 162, 299, 1972.
41. Higgins, J.S. and Stein, R.S.J., *J. Appl. Crystallogr.* 11, 346, 1978.
42. Datta, S. and Lohse, D., *Polymeric Compatibilizers*, Hanser: Munich, 1996**.**
43. Chun, S.B. and Han, C.D., *Macromolecules* 33, 3409–3424, 2000.
44. Bucknall, C.B., *Toughened Plastics*, Applied Science Publishers Ltd.: London, 1977.
45. Koning, C., van Duin, M., Pagnoulle, C., and Jerome, R., *Prog. Polym. Sci.* 23, 707–757, 1998.
46. Joseph, S., Lauprötre, F., Negrell, C., and Thomas, S., *Polymer*, 46, 9385, 2005.
47. Rudin, A., Loucks, D.A., and Goldwasser, J.M., *Polymer Engineering & Science*, 20, 741, 1980.
48. Araki, T., Tran-Cong, Q., and Shibayama, M., *Structure and Properties of Multiphase Polymeric Materials*, Marcel Dekker: New York, 1998.
49. Majumdar, B. and Paul, D.R., in: *Reactive Compatibilization. Polymer Blends*, D.R. Paul, C.B. Bucknall (Eds.), vol. 1, pp. 539–579, Wiley: New York, 2000.

50. Fayt, R., Jérôme, R., and Teyssié, Ph., *J. Polym. Sci., Polym. Phys.* 20, 2209–2217, 1982.
51. Coleman, M.M., Graf, J.F., and Painter, P.C., *Specific Interactions and the Miscibility of Polymer Blends: Practical Guides for Prediction and Designing Miscible Polymer Mixtures*, Technomic Publishing Co. Inc.: Lancaster, PA, 1991.
52. Coleman, M.M., Yang, X., and Painter, P.C., *Macromolecules* 25, 4414, 1992.
53. Espi, E., Alberdi, M., Fernandez-Berridi, M.J., and Iruin, J.J., *Polymer* 35, 3712, 1994.
54. Serman, C.J., Xu, Y., Painter, P.C., and Coleman, M.M., *Polymer* 32, 516, 1991.
55. Jiang, M., Li, M., Xiang, M., and Zhou, H., *Adv. Polym. Sci.* 146, 121, 1999.
56. Feast, W.J., Munro, H.S., and Richards, R.W. *Polymer Surfaces and Interfaces*, John Wiley and Sons: New York, 1993.
57. White, J.L. and Min, K., *Macromol. Chem. Macromol. Symp.* 16, 19, 1988.
58. White, J.L. and Min, K., in: *Polymer Blends and Mixtures*, D.J. Walsh, J.S. Higgins, A. Maconnachie (Eds.), p. 413, Martinus Nijhoff: Dordrecht, The Netherlands, 1984.
59. Han, C.D., *Rheology of Polymer Processing*, Academic Press: New York, 1976.
60. Han, C.D., *Multiphase Flow in Polymer Processing*, Academic Press: New York, 1981.
61. Wei, Z., Xuequan, Z., Baotong, H., and Zhiliu, F., *J. Appl. Polym. Sci.* 58, 515–521, 1995.
62. Eberhard, B., Agnesa, F., Lyda, R., Milan, L., Manfred, R., and Gottfried, H., *J. Appl. Polym. Sci.* 37, 467–478, 1989.
63. Hsu, C.C. and Geil, P.H., *Polym. Eng. Sci.* 27, 1542–1556, 1987.
64. Takashi, O., Toshiaki, S., and Shiro, N., *Polymer* 38, 1073–1079, 1997.
65. Paul, D.R. and Bucknall, C.B., *Polymer Blends*, John Wiley & Sons: New York, 2008.
66. Flory, P.J., *Principles of Polymer Chemistry*, Cornell University Press: New York, 1953.
67. Paul, D.R., in: *Polymer Blends*, D.R. Paul, S. Newman (Eds.), vol. 2, chap. 1, Academic Press: New York, 1978.
68. Anastasiadis, S.H., Gancarz, I., and Koberstein, J.T., *Macromolecules* 22, 1449–1453, 1989.
69. Orr, C.A., Cernohaus, J.J., Guegan, P., Hirao, A., Jeon, H.K., and Macosko, C.W., *Polymer* 42, 8171, 2001.
70. Lebovitz, A.H., Khait, K., and Torkelson, J.M., *Polymer* 44, 199–206, 2003.
71. Endres, B., Garbella, R.W., and Wendorff, J.H., *Colloid Polym. Sci.* 263, 361, 1985.
72. Briber, R.M. and Khoury, F., *Polymer* 28, 38, 1987.
73. Burghardt, W.R., *Macromolecules* 22, 24482, 1989.
74. Nojima, S., Terashima, Y., and Ashida, T., *Polymer* 27, 1007, 1986.
75. Nojima, S., Satoh, K., and Ashida, T., *Macromolecules* 24, 942, 1991.
76. Tanaka, H. and Nishi, T., *Phys. Rev. Lett.* 55, 1102, 1985.

77. Tanaka, H. and Nishi, T., *Phys. Rev. A* 39, 783, 1989.
78. Macosko, C.W., Guegan, P., Khandpur, A.K., Nakayama, A.N., Marechal, P., and Inoue, T., *Macromolecules* 29, 5590, 1996.
79. Sundararaj, U. and Macosko, C.W., *Macromolecules* 28, 2647, 1995.
80. Hsu, W.P., *J. Appl. Polym. Sci.* 92, 2797–2802, 2004.
81. Fortelny, I., Krulis, Z., Michalkova, D., and Harak, Z., *Angew. Makromol. Chem.* 270, 28–32, 1999.
82. Hobbs, S.Y., Dekkers, M.E., and Watkins, V.H., *Polymer* 29, 1598, 1988.
83. Horiuchi, S., Matchariyakul, N., Yase, K., and Kitano, T., *Macromolecules* 30, 3664, 1997.
84. Brannock, G.R. and Paul, D.R., *Macromolecules* 23, 5240, 1990.
85. Comyn, J., Brady, F., Dust, R.A., Graham, M., and Haward, A., *Int. J. Adhes. Adhes.* 18, 51, 1998.
86. Lee, D.W., Hwang, S.J., Park, J.B., and Park, H.J., *J. Microencapsul.* 20, 179, 2003.
87. Kotzumi, S., Hasegawa, H., and Hashimoto, T., *Makromol. Chem., Macromol. Symp.* 62, 75, 1992.
88. Hasegawa, H. and Hashimoto, T., in: *Comprehensive Polymer Science*, S.D. Aggarwal, S. Russo (Eds.), suppl. 2, chap. 14, p. 497, Elsevier Science Ltd.: Oxford, 1996.
89. Williams, R.J.J., Rozenberg, B.A., and Pascault, J.P., *Adv. Polym. Sci.* 128, 95, 1996.
90. Bonnett, A., Pascault, J.P., Sautereau, H., Taha, M., and Camberlin, Y., *Macromolecules* 32, 8517–8523, 1999.
91. Vankan, R., Degée, P., Jeŕôme, R., and Teyssié, Ph., *Polym. Bull.* 33, 221, 1994.
92. Paul, D.R. and Newman, S., *Polymer Blends*, vols. 1 and 2, Academic Press: New York, 1978.
93. Deanin, R.D. and Sansone, M.F., *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, 19(1), 211, 1978.
94. Olabisi, O., Robeson, L.M., and Shaw, T.H., *Polymer-Polymer Miscibility*, Academic Press: New York, 1979.
95. Bhateja, S.K. and Andrews, E.H., *Polym. Eng. Sci.* 23, 888, 1983.
96. Riess, G., Periard, J., and Bonderet, A., *Colloidal and Morphological Behavior of Block and Graft Copolymers*, Plenum Press: New York, 1971.
97. Epstein, B., US Patent 4174358, 1979.
98. Lohse, D., Datta, S., and Kresge, E., *Macromolecules* 24, 561, 1991.
99. Kamal, M.R., Jinnah, I.A., and Utracki, L.A., *Polym. Eng. Sci.* 24, 1337, 1984.
100. Hudec, I., Sain, M.M., and Sunova, V., *J. Appl. Polym. Sci.* 49, 425, 1993.
101. Lu, M., Keskula, H., and Paul, D.R., *Polym. Eng. Sci.* 34, 33, 1994.
102. Abacha, N. and Fellahi, S., *Macromol. Symp.* 178, 131, 2002.
103. Dagli, S.S., Kamdar, K.M., and Xanthos, M., *SPE ANTEC Preprints* 18, 1993.
104. Rahma, F. and Fellahi, S., *Polym. Int.* 49, 519, 2000.
105. Macknight, W.J., Lenz, R.W., Musto, P.V., and Somani, R.J., *Polym. Eng. Sci.* 25, 1124, 1985.

106. Kyu, B., Yun, S., and Jin, S., *Eur. Polym. J.* 27, 349, 1991.
107. Raval, H., Devi, S., Singh, Y., and Mehta, M., *Polymer* 32, 1703, 1992.
108. Fairley, G. and Prud'homme, R., *Polym. Eng. Sci.* 27, 1495, 1987.
109. Jois, Y. and Harrison, J., *Rev. Macromol. Chem. Phys. C* 36, 433, 1996.
110. Kazimnaqvi, M. and Choudhary, M., *Rev. Macromol. Chem. Phys. C* 36, 601, 1996.
111. Abstracts of papers, Advanced Polymers via Macromolecular Engineering (APME) Conference, Montreal, Canada, June 21–26, 2003.
112. Pazzagli, F. and Pracella, M., *Macrom. Symp.* 149, 225–230, 2000.
113. D'Orazio, L., Greco, R., Mancarella, C., Martuscelli, E., Ragosta, G., and Silvestre, C., *Polym. Eng. Sci.* 22, 536, 1982.
114. Morris, H.L., *J. Elast. Plast.* 6, 1, 1974.
115. Fischer, W.K., *Mod. Plast.* 51, 116, 1974.
116. Piloz, A., Decroix, J.Y., and May, J.F., *Angew. Makromol. Chem.* 54, 77, 1976.
117. Siegmann, A., *J. Appl. Polym. Sci.* 27, 1053, 1982.
118. Heino, M., Kirjava, J., Hietaoja, P., and Seppälä, J., *J. Appl. Polym. Sci.* 65, 241, 1997.
119. Holsti-Miettinen, R., Seppälä, J., and Reima, I., *Polym. Eng. Sci.* 32, 868, 1992.
120. Rösch, J. and Mülhaupt, R., *Makromol. Chem., Rapid Commun.* 14, 503, 1993.
121. Brown, S.B., in: *Reactive Extrusion, Principles and Practice*, M. Xanthos (Ed.), chap. 4, Hanser Publishers: Munich, 1994.
122. Gaylord, N.G. and Mehta, M., *J. Polym. Sci. Polym. Lett. Ed.* 20, 481, 1982.
123. Gaylord, N.G., Mehta, M., and Mehta, R., *J. Appl. Polym. Sci.* 33, 2549, 1987.
124. Minuoura, Y., Ueda, M., Mizunuma, S., and Oba, M., *J. Appl. Polym. Sci.* 13, 1625, 1969.
125. Ma, C.T. and Chang, F.C., *J. Appl. Polym. Sci.* 49, 913, 1993.
126. Chang, F.C. and Hwu, Y.C., *Polym. Eng. Sci.* 31, 1509, 1991.
127. Liu, W.B. and Chang, F.C., *Polym. Prepr.* 34, 803, 1993.
128. Coran, A.Y. and Patel, R., *Rubber Chem. Technol.* 53, 141, 1982.
129. Molau, G.E., *J. Polym. Sci. B* 3, 1007, 1965.
130. Bertin, S. and Robin, J.J., *Eur. Polym. J.* 38 2255–2264, 2002.
131. Pospisil, J., Horak, Z., Krulis, Z., Nespurek, S., and Kuroda, S.I., *Polym. Degrad. Stab.* 65, 405–414, 1999.
132. Camacho, W. and Karisson, S., *Polym. Degrad. Stab.* 78, 385–391, 2002.
133. Waldman, W.R. and De Paoli, M.A.D., *Polym. Degrad. Stab.* 60, 301–308, 1998.
134. Kotzev, G., Touleshkov, N., and Christova, D., *Macromol. Symp.* 181, 507–511, 2002.
135. Pérez, R., Rojo, E., Fernándeza, M., Leal, V., Lafuente, P., and Santamaría, A., *Polymer* 46, 8045–8053, 2005.
136. Acierno, D., Curto, D., LaMantia, F.P., and Valenza, A., *Polym. Eng. Sci.* 26, 28, 1986.
137. Utracki, L.A. and Schiund, B., *Polym. Eng. Sci.* 27, 1512, 1987.
138. Foglia, A.J., *Appl. Polym. Symp.* 11, 1, 1969.

139. Rudin, I.D., *Poly(1-Butene): Its Preparation and Properties*, MacDonald Tech & Sci.: London, 1969.
140. Powers, J. and Quinn, F.A. Jr., *Bull. Am. Phys. Soc.* 9, 285, 1964.
141. Imada, K., Yamamoto, T., Shigematsu, K., and Takayanagi, M., *J. Mater. Sci.* 6, 537, 1971.
142. Rohn, C.L. and Tinger, H.G., *Mod. Plast*. March 1971, 12.
143. Plenikowski, J. and Umminger, O., *Kunstst.* 55, 822, 1965.
144. Kalfoglou, N.K., *J. Polym. Sci., Polym. Phys. Ed*. 20, 1295, 1982.
145. Kalfoglou, N.K., Sotiropoulou, D.D., and Margaritis, A.G., *Eur. Polym. J*. 4, 389, 1988.
146. Munoz, E., Calahorra, M., and Santamaria, A., *Polym. Bull.* 7, 295, 1982.
147. Martuscelli, E., Silvestre, C., and Gismondi, C., *Makromol. Chem*. 186, 2161, 1985.
148. Silvestre, C., Karasz, F.E., MacKnight, W.J., and Martuscelli, E., *Eur. Polym. J.* 23, 745, 1987.
149. Addonizio, M.L., Martuscelli, E., and Silvestre, C.J., *Polym. Mater*. 7, 63, 1990.
150. Chen, X., Hu, H., Yin, J., and Zheng, C., *J. Appl. Polym. Sci*. 56, 247, 1995.
151. Bank, M., Leffing, J., and Thies, C., *J. Polym. Sci. (A-2)* 10, 1097, 1972.
152. McMaster, L.P., *Macromolecules* 6, 760, 1973.
153. McMaster, L.P., *Adv. Chem. Ser.* 142, 43, 1975.
154. Simenson, J. and Rials, T.G., *J. Thermoplast. Compos. Mater.* 9, 292, 1996.
155. Yang, L.Y., Smith, T.G., and Bigio, D.J., *J. Appl. Polym. Sci.* 58, 117, 1995.
156. Fortelný, I., Hlavatá, D., Mikeisová, J., Michálková, D., Potroková, L., and Sloufová, I., *J. Polym. Sci. B, Polym. Phys.* 41, 609, 2003.
157. Taha, M. and Frerejean, V. *J. Appl. Polym. Sci.* 61, 969, 1996.
158. Fayt, R., Jérôme, R., and Teyssié, P., *J. Polym. Sci. B, Polym. Phys.* 33, 801, 1995.
159. Yang, L.Y., Bigio, D., and Smith, T.G., *J. Appl. Polym. Sci.* 58, 129, 1995.
160. Li, T., Topolkaraev, V.A., Baer, E., Ji, X.Z., and Quirk, R.P., *J. Polym. Sci. Polym. Phys.* 33, 667, 1995.
161. Li, T., Carfagna, C. Jr., Topolkaraev, V.A., Hiltner, A., Ji, X.Z., Quirk, R.P., and Baer, E., *Adv. Chem. Ser.* 252, 335, 1996.
162. Tjong, S.C. and Xu, S.A., *J. Appl. Polym. Sci.* 68, 1099, 1998.
163. Tjong, S.C. and Xu, S.A., *Polymer* 32, 208, 2000.
164. Xu, B., Simensen, J., and Roceefort, W.E., *J. Appl. Polym. Sci.* 76, 1100, 2000.
165. Fortelný, I., Mikeisová, J., Hrinádková, J., Haisová, V., and Horák, Z., *J. Appl. Polym. Sci.* 90, 2303, 2003.
166. Fortelný, I., Slouf, M., Ĩsikora, A., Hlavatá, D., Haisová, V., Mikeîsová, J., and Jacob, C., *J. Appl. Polym. Sci.* 100, 2803, 2006.
167. Diehl, C.F., Guest, M.J., Chaudhary, B.I., Cheung, Y.W., Van Volkenburgh, W.R., and Walther, B.W., in: *ANTEC '99 SPE Conference Proceedings*, vol. 57, p. 2149, SPE: Brookfield, CT, 1999.
168. Karjala, T.P., Hoenig, S.M., Guest, M.J., Cheung, Y.W., Finlayson, M.P., Walther, B.W., and Montanye, J.R., in: *ANTEC 2000 SPE Conference Proceedings*, vol. 58, p. 1833, SPE: Brookfield CT, 2000.

169. Tjong, S.C. and Xu, S.A., *Plast. Rubber Compos. Process. Appl.* 26, 184, 1997.
170. Yilmaz, E., Yilmaz, O., and Caner, H., *Eur. Polym. J.* 32(8), 927–933, 1996.
171. Abdel-Azim, A.-A., Atta, A.M., Farahat, M.S., and Boutros, W.Y., *J. Appl. Polym. Sci.* 69, 1471–1482, 1998.
172. Ting, S.P., Bulkin, B.J., and Pearce, E.M., *J. Polym. Sci., Polym. Chem.* 19(6), 1451–1473, 1981.
173. Jin, X., Zhang, S., and Runt, J., *Macromolecules* 36(21), 8033–8039, 2003.
174. Pilar, J., Sikora, A., Labsky, J., and Schlick, S., *Macromolecules* 26(1), 137–143, 1993.
175. Akiba, I., Ohba, Y., and Akiyama, S., *Macromolecules* 32(4), 1175–1179, 1999.
176. Macknight, W.J., Stoelting, J., and Karasz, F.E., *Adv. Chem. Ser.* 99, 29, 1971.
177. Shultz, A.R. and Gendron, B.M., *J. Appl. Polym. Sci.* 16, 461, 1972.
178. Shultz, A.R. and Beach, B.M., *Macromolecules* 7, 902, 1974.
179. Lee, Y.C. and Trementozzi, G.A., US Patent 3644577, assigned to Monsanto Co., 1972.
180. Kemper, B., in: *Kunststoff-Handbuch*, K.H. Felger (Ed.), vol. 2/1, PVC, p. 503, Hanser Verlag: München, Wien, 1986.
181. Gächter, R. and Müller, H. (Ed.), *Taschenbuch der Kunststoff-Additive*, 2nd ed., Hanser Verlag: München, Wien 1983.
182. Chin, W.K. and Hwang, I.L., *Annu. Tech. Conf., Soc. Plast. Eng.* 33, 1379, 1987.
183. Braun, D. and Bezdadea, E., Theory of degradation and stabilization mechanisms, in: *Encyclopedia of PVC*, L.I. Nass (Ed.), 2nd ed., p. 397, Dekker: New York 1986.
184. Billmeyer, F.W. Jr., *Textbook of Polymer Science*, 2nd ed., Wiley: New York, 1962.
185. Jalbert, R.L., in: *Modern Plastics Encyclopedia*, J. Agranoff (Ed.), McGraw-Hill: New York, 1975.
186. Hickman, J.J. and Ikeda, R.M., *J. Polym. Sci. B* 11, 1713, 1973.
187. Gong, K. and Liu, B., *SPE ANTEC*, 1225, 1986.
188. Krause, S., *J. Macromol. Sci. Rev. C* 7, 251, 1972.
189. Liu, X.D. and Bertilsson, H., *J. Appl. Polym. Sci.* 74, 510–515, 1999.
190. Sugimoto, K., Tanaka, S., and Fujita, H., US Patent 3520953, assigned to Japanese Geon Co. Ltd., 1970.
191. Wood, A.S., *Mod. Plast.* 56, 44, 1979.
192. Li, H.M. and Wong, A.H., *Polymer Combatibility and Incompatibility: Principles and Practices*, K. Solc (Ed.), Harwood Academic Publishers: New York, 1982.
193. Escala, A., Balizer, E., and Stein, R.S., *Polym. Prepr. Am. Chem. Soc. Div., Polym. Chem.* 19, 152, 1978.
194. Gall, J.S., US Patent 4008199, assigned to Celanese Corp., 1977.
195. Atkins, K.E., *Polymer Blends*, D.R. Paul, S. Newman (Eds.), chap. 23, Academic Press: New York, 1978.
196. Sheng, J., Lu, X.L., and Yao, K., *J. Macromol. Sci. Chem. A* 27(2), 167, 1990.
197. Favis, B.D. and Chalifoux, J.P., *Polym. Eng. Sci.* 27, 1591, 1987.

198. Macosko, C.W., Jeon, H.K., and Hoye, T.R., *Prog. Polym. Sci.* 30, 939–947, 2005.
199. Ide, F. and Hasegawa, A., *J. Appl. Polym. Sci.* 18, 963, 1974.
200. Takeda, Y., Heskkula, H., and Paul, D.R., *Polymer* 33, 3173, 1992.
201. Brown, D. and Elsenlohr, U., *Kunststoffe.* 65, 139, 1975.
202. Rosch, J. and Mulhaupt, R., *Makromol. Chem. Rapid Commun.* 14, 503, 1993.
203. Liang, Z. and Williams, H.L., *J. Appl. Polym. Sci.* 44, 699, 1992.
204. Chuang, H.K. and Han, C.D., *J. Appl. Polym. Sci.* 30, 165, 1985.
205. Hobbs, S.Y., Bopp, R.C., and Watkins, V.H., *Polym. Eng. Sci.* 23, 380, 1983.
206. Serpe, G., Jarrin, J., and Dawans, F., *Polym. Int.* 30(9), 553, 1990.
207. Schlag, S., Rŏsch, J., and Friedrich, Chr., *Polym. Bull.* 30, 603, 1993.
208. Utracki, L.A. and Sammut, P., *Polym. Networks Blends* 2, 23, 1992.
209. Triacca, V.J., Ziaee, S., Barlow, J.W., Keskkula, H., and Paul, D.R., *Polymer* 32, 1401, 1991.
210. Vermeesch, I. and Groeninckx, G., *J. Appl. Polym. Sci.* 53, 136, 1994.
211. Zhang, X., Yin, Z., and Yin, J., *J. Appl. Polym. Sci.* 62, 893, 1996.
212. Horiuchi, S., Matchariyakul, N., Yase, K., Kitano, T., Choi, H.K., and Lee, Y.M., *Polymer* 37, 3065, 1996.
213. Lavengood, R.E., Patel, R., and Padwa, A.R., US Patent 4777211, assigned to Monsanto, 1988.
214. Aoki, Y. and Watanabe, M., US Patent 4987185, assigned to Monsanto Kasei Co., 1991.
215. Tomono, H., Yamamoto, I., and Aoki, Y., US Patent 4981906, assigned to Monsanto Kasei Co., 1991.
216. Majumdar, B., Keskkula, H., and Paul, D.R., *Polymer* 35, 5453, 1994.
217. Wilkinson, N., Laugel, L., Clemens, M.L., Harding, V.M., and Marin, M., *Polymer* 40, 4971, 1999.
218. Majumdar, B., Paul, D.R., and Oshinski, A.J., *Polymer* 38, 1787, 1997.
219. Liu, X.D., Mantia, F.L., and Scaffaro, R., *J. Appl. Polym. Sci.* 86, 449, 2002.
220. Ohishi, H. and Nishi, T., *J. Appl. Polym. Sci.* 83, 2300, 2002.
221. Cho, K., Seo, K.H., and Ahn, T.O., *J. Appl. Polym. Sci.* 68, 1925, 1998.
222. Matzner, M., Schober, D.I., Johnson, R.N., Robeson, L.M., and McGrath, J.E., in: *Permeatbility of Plastic Films and Coatings to Gases, Vapors and Liquids*, H.B. Hopfenburg (Ed.), Plenum Press: New York, 1975.
223. Robeson, L.M. and McGrath, J.E., Paper presented at the 82nd National Meeting of AIChE, Atlantic City, New Jersey, August 31, 1976.
224. Olabisi, O., *Macromolecules* 8, 316, 1975.
225. Sailer, C. and Handge, U.A., *Macromolecules* 40, 2019–2028, 2007.
226. Sailer, C. and Handge, U.A., *Macromol. Symp.* 254, 217–225, 2007.
227. Majumdar, B., Keskkula, H., Paul, D.R., and Harvey, N.G., *Polymer* 35, 4263, 1994.
228. Lavengood, R.E., Padwa, A.R., and Harris, A.F., US Patent 4713415, assigned to Monsanto, 1987.
229. Kudva, R.A., Keskkula, H., and Paul, D.R., *Polymer* 41, 239, 2000.

230. Ishii, Y. and Ryan, A.J., *Macromolecules* 33, 158, 2000.
231. Cui, J., Yu, Y.F., Chen, W.J., and Li, S.J., *Macromol. Chem. Phys.* 199, 1645, 1998.
232. Oyanguren, P.A., Riccardi, C.C., Williams, R.J.J., and Mondragon, I., *J. Polym. Sci. Phys.* 36, 1349, 1998.
233. Alig, I. and Jenninger, W., *J. Polym. Sci. Phys.* 36, 2461, 1998.
234. Oshinski, A.J., Keskkula, H., and Paul, D.R., *Polymer* 33, 268, 1992.
235. De Roover, B., Sclavons, M., Carlier, V., Devaux, J., Legras, R., and Momtaz, A., *J. Polym. Sci. A: Polym. Chem. Ed.*, 33, 829, 1995.
236. Forger, G.R., *Mater. Eng.* 85, 44, 1977.
237. Walsh, D.J. and McKeown, J.G., *Polymer* 21, 1330, 1980.
238. Hammer, C.F., *Polymer Blends*, D.R. Paul, S. Newman (Eds.), vol. 2, p. 219, Academic Press: New York, 1978.
239. Lutz, J.T. Jr., *Plastics Compounding*, p. 34, Jan/Feb 1981.
240. Zelinger, J., Volfova, E., Zahradnikova, H., and Pelzbauer, Z., *Int. J. Polym. Mater.* 5, 99, 1976.
241. Scarso, L., Cerri, E., and Pezzin G., US Patent 3772409, assigned to Montecatini Edison S.p.A., 1973.
242. Nishi, T. and Wang, T.T., *Macromolecules* 5, 909, 1975.
243. Paul, D.R. and Altamirano, J.O., *Adv. Chem. Ser.* 142, 354, 1975.
244. Noland, J.S., Hsu, N.N.C., Saxon, R., and Schmitt, J.M., *Adv. Chem. Ser.* 99, 15, 1971.
245. Miller, C.H. Jr., US Patent 3458391, American Cyanamid Co., 1969.
246. Koblitz, F.F., Petrella, R.G., Dubert, A.A., and Christofas, A., US Patent 3253060, assigned to Pennwalt Chemicals Corp., 1966.
247. Colby, R.H., *Polymer* 30, 1275, 1989.
248. Silvestre, C., Cimmino, S., Martuscelli, E., Karasz, F.E., and MacKnight, W.J., *Polymer* 28, 1190, 1987.
249. Ramana Rao, G., Castiglioni, C., Gussoni, M., Zerbi, G., and Martuscelli, E., *Polymer* 26, 811, 1985.
250. Cimmino, S., Martuscelli, E., and Silvestre, C., *Polymer* 30, 393, 1989.
251. Lu, X. and Weiss, R.A., *Macromolecules* 25, 3242, 1992.
252. Stein, D.J., Jung, R.H., Ilers, K.H., and Sendus, H., *Angew. Makromol. Chem.* 36, 89–100, 1974.
253. Naito, K., Johnson, G.E., Allara, D.L., and Kwei, T.K., *Macromolecules* 11, 1260–1265, 1978.
254. McBrierty, V.J., Douglass, D.C., and Kwei, T.K., *Macromolecules* 11, 1265–1267, 1978.
255. Kressler, J., Kammer, H.W., and Klostermann, K., *Polym. Bull.* 15, 113–119, 1986.
256. Suess, M., Kressler, J., and Kammer, H.W., *Polymer* 28, 957–960, 1987.
257. Subramanian, R., Huang, Y.S., Roach, J.F., and Wiff, D.R., *Mater. Res. Soc. Symp. Proc.* 171, 217–224, 1990.
258. Martuscelli, E., Denne, G., Rossi, E., and Segre, A.L., *Polymer* 24, 266, 1983.

259. Li, X. and Hsu, S.L., *J. Polym. Sci., Polym. Phys. Ed.* 22, 1331, 1984.
260. Martuscelli, E., Pracella, M., and Yue, W.P., *Polymer* 25, 1097, 1984.
261. Wu, S.J., *Polym. Sci. B: Polym. Phys.* 25, 2511, 1987.
262. Slocombe, R.J., *J. Polym. Sci.* 26, 9, 1957.
263. Shur, Y.J. and Ranby, B.G., *J. Appl. Polym. Sci.* 20, 3121, 1976.
264. Shaw, M.T., *Polym. Eng. Sci.* 22, 115, 1982.
265. Irvin, H.H., US Patent 3010936, assigned to Borg-Warner Corp., 1961.
266. Paul, D.R. and Barlow, J.W., *J. Macromol. Sci., Rev. Macromol. Chem. C* 18(1), 109, 1980.
267. Zabrzewski, G.A., *Polymer* 14, 348, 1973.
268. Konori, T. and Geil, P.H., *J. Macromol. Sci. Phys. B* 18(1), 93, 1980.
269. Rudin, A. and Brathwaite, N.E., *Polym. Eng. Sci.* 24, 1312, 1984.
270. Bye, D.J. and Miles, I.S., *Eur. Polym. J.* 22, 185, 1986.
271. Varnell, D.F. and Runt, J.P., *Macromolecules* 14, 1350, 1981.
272. Gardlund, Z.G., in: *Polymer Blends and Composites in Multiphase Systems*, C.D. Han (Ed.), Advances in Chemistry Series No. 206, p. 129, American Chemical Society: Washington DC, 1984.
273. Keitz, J.D., Barlow, J.W., and Paul, D.R., *J. Appl. Polym. Sci.* 29, 3131, 1984.
274. Suarez, H., Barlow, J.W., and Paul D.R., *J. Appl. Polym. Sci.* 29, 3253, 1984.
275. Cruz, C.A., Barlow, J.W., and Paul, D.R., *Macromolecules* 12, 726, 1979.
276. Preston, W.E., Barlow, J.W., and Paul, D.R., *J. Appl. Polym. Sci.* 29, 2251, 1984.
277. Avakian, R.W. and Allen, R.B., *Polym. Eng. Sci.* 25, 462, 1985.
278. Inberg, J.P.F. and Gaymans, R.J., *Polymer* 43, 3767–3777, 2002.
279. Cruz, C.A., Paul, D.R., and Barlow, J.W., *J. Appl. Polym. Sci.* 23, 589, 1979.
280. Paul, D.R., Barlow, J.W., Bernstein, R.E., and Wahrmund, D.C., *Polym. Eng. Sci.* 18, 1225, 1978.
281. Wahrmund, D.C., Paul, D.R., and Barlow, J.W., *J. Appl. Polym. Sci.* 22, 2155, 1978.
282. Mohn, R.N., Paul, D.R., Barlow, J.W., and Cruz, C.A., *J. Appl. Polym. Sci.* 23, 575, 1979.
283. Jonza, J.M. and Porter, R.S., *Macromolecules* 19, 1946, 1986.
284. Cheung, Y.W., Stein, R.S., Wignall, G.D., and Yang, H.E., *Macromolecules* 26, 5365, 1993.
285. Cheung, Y.W. and Stein, R.S., *Macromolecules* 27, 2512, 1994.
286. Cheung, Y.W., Stein, R.S., Lin, J.S., and Wignall, G.D., *Macromolecules* 27, 2520, 1994.
287. Cheung, Y.W. and Stein, R.S., *Macromolecules* 27, 3589, 1994.
288. Balsamo, V., Calzadilla, N., Mora, G., Müller, A.J., *J. Polym. Sci. B: Polym. Phys.* 39, 771, 2001.
289. Jang, J., Chung, H., Kim, M., Sung, H., *Polym. Testing* 19, 269, 2000.
290. Kuo, P.L., Wang, J.S., Chen, P.C., and Chen, L.W., *Macromol. Chem. Phys.* 202, 2175, 2001.
291. Don, T.M. and Bell, J.P., *J. Appl. Polym. Sci.*, 69, 2395, 1998.
292. Ton, T.M., Yeh, C.H., and Bell, J.P., *J. Appl. Polym. Sci.* 74, 2510, 1999.

293. Tjong, S.C. and Meng, Y.Z., *Eur. Polym. J.* 36, 123, 2000.
294. Cho, C.G., Park, T.H., and Kim, Y.S., *Polymer* 38, 4687, 1997.
295. Jang, L.W., Lee, K.H., Lee, D.C., Yoon, J.S., Chin, I.J., Choi, H.J., and Lee, K.H., *J. Appl. Polym. Sci.* 78, 1998, 2000.
296. Karauchi, T. and Ohta, T., *J. Mater. Sci.* 19, 1699, 1984.
297. Maurar, F.H.J., Palmar, J.H.M., and Booij, H.C., *Rheol. Acta* 24, 243, 1985.
298. Choi, H.J., Park, S.H., Yoon, J.S., Lee, H.S., and Choi, S.J., *Polym. Eng. Sci.* 35, 1636, 1995.
299. Johnson, D.A., Maclean, W.D., and Jacobson, R., *Proceedings of the 3rd Biomass Conference of the Americas*, Montreal, Quebec, Canada, August 24–29, 1997, pp. 925–932, 1997.
300. Mohamed, A., Gordon, S.H., and Biresaw, G.J., *Appl. Polym. Sci.* 106, 1689–1696, 2007.
301. Olayo-Valles, R., Lund, M.S., Leighton, C., and Hillmyer, M.A., *J. Mater. Chem.* 14, 2729–2731, 2004.
302. Zalusky, A.S., Olayo-Valles, R., Wolf, J.H., and Hillmyer, M.A., *J. Am. Chem. Soc.* 124, 12761–12773, 2002.
303. Ho, R.M., Tseng, W.H., Fan, H.W., Chiang, Y.W., Lin, C.C., Ko, B.T., and Huang, B.H., *Polymer* 46, 9362–9377, 2005.
304. Sarazin, P. and Favis, B.D., *Biomacromolecules* 4, 1669–1679, 2003.
305. Bates, F.S. and Fredrickson, G.H., *Annu. Rev. Phys. Chem.* 41, 525–557, 1990.
306. Hatzius, K., Li, Y., Werner, M., and Jungnickel, B.J., *Angew. Makromol. Chem.* 243, 177, 1996.
307. Santore, M.M., Han, C.C., and McKenna, G.B., *Macromolecules* 25(13), 3416–3423, 1992.
308. Kuo, C.M., Clarson, S.J., and Semlyen, J.A., *Polymer* 35(21), 4623–4626, 1994.
309. Kambour, R.P., Nachlis, W.L., and Carbeck, J.D., *Polymer* 35(1), 209–211, 1994.
310. Nachlis, W.L., Bendler, J.T., Kambour, R.P., MacKnight, W.J., *Macromolecules* 28(23), 7869–7878, 1995.
311. Bourland, L.G. and Braunstein, D.M., *J. Appl. Polym. Sci.* 32, 6131, 1986.
312. Zhou, P., Zhou, T., and Sun, Z., *Polymer* 27, 1899, 1986.
313. Venderbosch, R.W., Meijer, H.E.E., and Lemstra, P.J., *Polymer* 36, 2903, 1995.
314. Bastioli, C., Bellotti, V., Giudice, L.D., and Gilli, G., *J. Environ. Polym. Degrad.* 1, 181–191, 1993.
315. Bimendina, L.A., Roganov, V.V., and Bekturov, Y.A., *Vysokomol. Soedin. A* 16, 2180, 1974.
316. Nishimoto, M., Keshkula, H., and Paul, D.R., *Macromolecules* 23, 3633, 1990.
317. Wang, Z. and Jiang, B., *Macromolecules* 30, 6223, 1997.
318. Rana, D., Mandal, B.M., and Bhattacharyya, S.N., *Polymer* 34, 1454, 1993.
319. Hudson, R., *Commodity Plastics – An Engineering Materials?*, Rapra Technology Ltd: Shawbury, 1994.
320. Utracki, L.A., *Polymer Alloys and Blends*, chap. 1, Hanser: Munich, 1989.

Polymer Blends and Composites: Chemistry and Technology.
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8

Polymer Composites

Polymer composites are widely used in science and industry due to their broad range of properties which are different from basic polymers. Polymer composites artfully use reinforcing materials with differing properties to obtain a synergistic effect. They are developed with specific properties of polymers and are useful in total industrial design applications to reduce part weight and increase fuel value. Great emphasis is placed on the technological application of existing polymers.

Polymer composites are materials manufactured by combining two or more components with often very different products. Materials work together to give the composite unique properties. The use of polymer composites is of practical importance because they are developed to have specific properties of polymers. Therefore, composites permit the combination of attractive features.

The important advantages of using polymeric composites as compared to conventional metals are ease of processing, manufacturing versatility, and low overhead production cost. Composites are used in a variety of applications ranging from household appliances to aeronautics. Polymer composites can be used in a large variety of applications, including wall boards, furniture, insulation boards, ceiling boards, and roof tiles [1, 2].

8.1 Polymeric Phase

Polymers are commonly admixed with a variety of natural and synthetic compounds to improve their performance. Polymer composites come in all shapes and sizes. They come with an enormous variety of useful materials. Continuous and distributed phases can be metallic, polymeric, ceramic or organic. Polymeric phase is usually called matrix phase. Polymeric phase typically:

- Provides environmental protection;
- Supports and binds reinforcing agents together;
- Is tougher than reinforcing phase;
- Is more compliant;
- Carries shear stresses of the composite;
- Transmits load from one piece of reinforcement to the other usually by shear.

8.2 Reinforcing Phase

Polymer composites are controlled by the reinforcing material content present in them. Reinforcing phase is distributed within the matrix. It is often fibrous or particulate and provides the composite with its high stiffness and strength properties. The spectrum of properties is larger than that of pure polymers. At the heart of their performance, it is the fillers in the polymers that modify the resin properties. Precipitated silica, alumina, and mica are known to bring improvements in mechanical properties to polymeric composites [3–5]. Reinforcement phase typically:

- Is stiffer and stronger than polymer;
- Provides the composite with its high stiffness and strength properties;
- Can reduce environmental pollution by addition of filler or fibers due to the relative amount of polymeric materials being reduced; and smoke from burning will also be reduced [6].

8.3 Classification

Industrial and economic activities result in a continuous demand for new, low-cost materials able to meet increasingly stringent conditions. Industrially important composites are multicomponent systems. Polymer

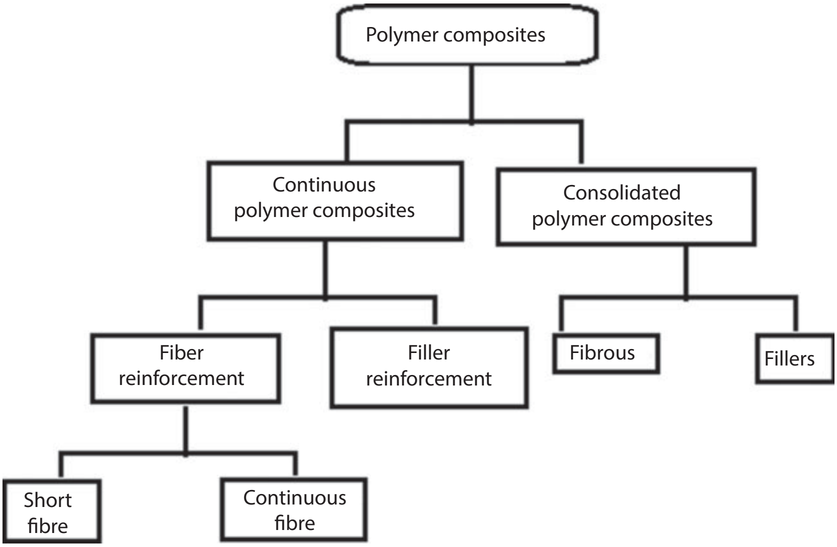

Figure 8.1 Classification of polymer composites.

composites cover a wide range of structures and morphologies. In Figure 8.1, a broad classification of polymer composites is given based on their structural configuration. Composite may also have more than one continuous phase, which may interpenetrate to produce the composite. The multiple continuous phases and possibly reinforcement material differ in formation or distribution. They can also be laminated together to make a composite.

Polymer composites are structural systems consisting of a polymer matrix reinforced with fibrous forms or particulates, which are modified to have specific characteristic properties with low usage of polymer. They are simply a multiphase material that has vastly improved properties over the properties of the individual constituents.

8.4 Characteristics

Polymer consolidated composites generally offer an attractive combination of density, strength, and stiffness at low cost. The unique aspect of designing parts with polymer composites is that the mechanical properties of the materials can be tailored to fit a certain application. Composites exhibit properties that are isotropic or anisotropic depending on the desired end result. The cost economy may be associated with the processing method. In the case of low production level parts to high production parts, the process becomes highly cost prohibitive [7].

Structural performance improves with development of lighter, stronger materials to achieve high performance. Composites are able to be tailored for properties such as strength, stiffness, environmental resistance, fatigue resistance, damage tolerance, and creep resistance by prudent selection of the form, orientation and quantity of the multiphase.

8.4.1 Physical Properties

Polymer composites are multiphase materials in which phase distribution and geometry have been controlled to optimize one or more properties. High quality materials are developed due to their complex structure. The most important factors of the materials are physical, mechanical and thermal properties.

The density of the composites varies mainly due to:

- Changes in composition, i.e., polymer content;
- Changes in the morphology of the composite; the morphology of the composite may vary due to different packing structures of the particles induced by processing conditions or the shape and size of the filler.

One of the characteristics of polymer composites is creep, which is the deformation over time of a material under stress. It has resulted in poor performance in certain applications. Creep and creep rupture are essential to composites in long-term loading applications. They occur due to a combination of elastic deformation and viscous flow known as viscoelastic deformation [8]. The filler or fiber type and polymer matrix ductility and void content of the composites are the main structural parameters affecting the impact behavior of composites in applications [9]. Impact resistance is the ability of a material and its structure to survive impact-induced damages.

The toughness of composites can be improved in several ways:

- By increasing matrix toughness;
- By optimizing the interface (or interphase) between the filler and the matrix through the use of coupling agents, compatibilizer, and sizes;
- By optimizing the filler-related properties such as filler content, particle size, and dispersion;
- Aspect ratio and orientation distributions also play a role in toughness of composites containing more fibrous materials [10].

In polymer composites the interfacial properties and other properties are influenced by the polymer matrix and fiber modification [11–14].

8.5 Reinforcing Agents

Many of the characteristic properties of polymer composites are achieved by the incorporation of filler either in particulate or fiber form. These materials are often used to enhance mechanical properties such as tensile strength, rigidity, etc. They also improve thermal properties such as deflection temperature. Reinforcing agents are essential components of many polymeric products. One of the functions of reinforcing agents is to make polymer composites heavier. The other function is to increase mechanical properties. The use of reinforcing agents can vary over a wide range. Two kinds of interactions exist in filled polymeric materials. The polymer adheres to the surface of the particles forming an interphase with properties differing from those of the polymer materials [15–19] and the particles also may interact with each other creating aggregates [20–22]. Composites, including high-modulus, high-strength fibers such as graphite, boron, high tensile glass, ceramic and aramid, are used in conjunction with polymers. Glass, carbon/graphite and mica are most often used as reinforcement materials.

8.5.1 Advantages

Reinforcing agents are used to modify the physical properties such as flexural modulus and heat distortion temperature, or to impart some special function in polymer composites.

8.5.2 Shortcomings

High reinforcing agent loadings may adversely affect processability, ductility and strength of the compound.

8.6 Fillers

Fillers are small particles (<100 μm) used as reinforcing agents, which are valuable and complex with higher loadings. Fillers might initially be as cheap bulking materials. Fillers improve functional effects which include processing and modification of properties of the final compound. The prominent physical effect of fillers is the increase in stiffness. Therefore, composites are stiff but brittle. Optimum composition of the composite will depend to a significant extent on the choice of filler, intended end use, characteristics or properties, such as mechanical properties, and the rate and degree of biodegradability desired in the product.

The general classification of filler particles is normally based on two primary properties: particle size and surface area. The physiochemical parameters of the filler, such as specific surface area, dispersion characteristics, wettability with polar and nonpolar reagents, surface adsorption, and surface structure, determine the relationship of surface energy and the mechanical properties of the composite. The chemical composition and interfacial bonding of the filler is essential in deciding its use.

Important factors affecting the behavior of fillers are:

- Shape and size: Most fillers are ground rock or ores, processed to obtain the material in particulate form. They do not fracture uniformly and the particles tend to be of irregular size and shape. The particles of fabricated fillers, such as silicates and calcium carbonates, are more uniform.
- Chemical nature: Fillers are rigid with no elongation to fracture. They determine the degree of reactivity with the matrix material, which is important for good adhesion between different phases.

Filling with different organic or inorganic substances enables the production of composites with improved properties of polymer. Filler changes the kinetics and thermodynamics of polymer crystallization. The fillers can improve the toughness, processibility, and heat distortion temperature of polymer composites; and conductive fillers can even make the insulative polymer composite become electrically conductive. Surface modification of the filler may be used to address some of its shortcomings.

The inorganic reinforcing particulate fillers usually display high surface energy because of the hydrophilic ionic nature of the inorganic filler. However, the hydrophobic polymer does not wet or interact interfacially with the filler due to the difference in surface energies. Therefore, it is essential to modify the filler surface to improve surface wetting and adhesion between the filler and matrix [23–25]. This may be improved by chemically incorporating specific interaction sites onto the filler surface or coating it with reactive surfactants or coupling agents.

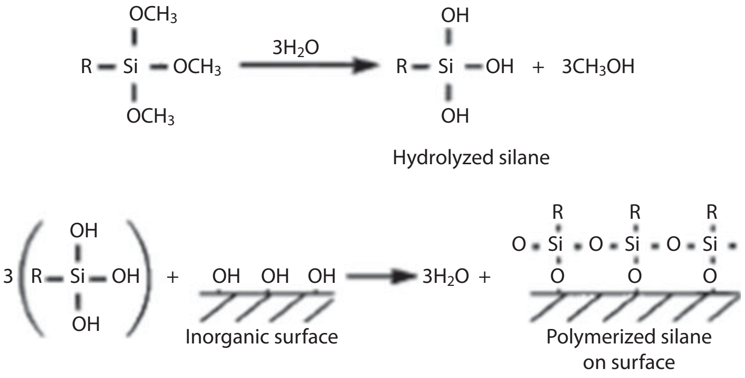

Figure 8.2 Hydrolysis of silane followed by reaction with an inorganic surface.

8.6.1 Surface Modification

Silanes are the most common surface modifiers [26] but are costly and do not give optimal performance for fillers with basic surfaces devoid of hydroxyl functional groups (Figure 8.2). Carboxylic acid or acid anhydride functional modifiers have proven to be effective for fillers.

Titanates are capable of acting as coupling agents in polymer composites [27, 28]. The titanates allow high filler loadings in thermoplastics without adversely affecting the melt flow behavior.

8.6.2 Boron Trinitride

Boron trinitride (BN) is a low atomic numbered nonmetallic compound; its melting temperature (~3000 °C) is very high so as to be used as thermal insulation. BN/polymer composites can decrease thermal expansion and increase thermal conductivity while enhancing the electrical insulation properties [29, 30]. Also, the addition of a small amount of BN in polymers might enhance extrusion property by increasing their flowablity [31].

8.6.3 Carbon Black

Carbon black is a very important filler, especially in the rubber industry. Its fine particle size, high particle porosity, and compatibility with organic materials make it an obvious candidate for use as fillers [32]. The strong interaction between polymer and carbon black particles improves the mechanical properties of the composites [33, 34]. The conductivity of a polymer-CB composite depends upon factors such as carbon black content, the physical and chemical properties of the carbon black chosen, and the chemical structure and crystallinity of the polymer and process conditions [35, 36].

8.6.4 Mineral Fillers

Minerals are added to polymers to modify selected physical properties and reduce cost. This blend technology has been mainly developed in the elastomers field where high levels of fillers (especially carbon black) can provide increased tensile strength, modulus, and hardness. Adding high levels of minerals or fillers to plastics, especially crystalline plastics, has been less successful [37] because of poor mineral-polymer adhesion. Based on the decrease in surface free energy, polyethylene should wet a clean mineral surface and have good adhesion.

The mineral increases the modulus but elongation and impact strength are drastically reduced. Some minerals do not give active catalysts and cannot be used directly for composite synthesis. These minerals are either basic, such as calcium carbonate, or have absorbed alkali metal ions such as feldspar or mica. This problem can be solved by surface coating the mineral with alumina or silica or other non-volatile acidic substances [38].

Minerals serve as a cost-reducing technology by increased mineral addition, which leads to a decreased polymer requirement. The exploitation of mineral and polymer processing and chemistry has led to minerals being used as functional additives, bringing specific properties to the final composite [39]. The main problem faced with the usage of mineral fillers as reinforcing agents is their tendency to agglomerate [40]. To aid this problem, surface treatment is used on the mineral filler. Surface energy of the filler plays a major role in dispersion aspects of the composite. A frequent problem in the polymer field is that large concentrations of minerals bring about dramatic and commercially unacceptable decreases in elongation and impact strength, leading to brittle parts. This brittleness is usually attributed to stress concentrations because of inhomogeneous mineral dispersion.

8.6.4.1 Calcium Carbonate ($CaCO_3$)

Calcium carbonate ($CaCO_3$) is one of the strongest inorganic fillers in the polymer industry. Conventional ground calcium carbonate (GCC) is used as a cost-reducing filler in polymer systems. It replaces part of the higher cost polymer in a composite with a lower-cost mineral. Likely additional benefits in terms of environmental impact can also be made by replacingf an oil-based polymer with a mineral, potentially reducing the carbon footprint. However, this is likely to be very dependent on the mineral loading as any additional processing steps required to incorporate the mineral must be considered. The use of low aspect ratio calcium carbonate particles offers little in terms of reinforcement to the composite [41] except at very fine particle sizes [42] of <1 μm.

Increasingly, with the development of specialized or engineered calcium carbonate grades additional advantages to the composite can be realized, both in terms of mechanical properties and also in terms of processing improvements and energy savings [43] through the enhanced thermal conductivity of the composite. Such engineered grades will tend to be optimized in terms of the particle size, particle size distribution and surface chemistry for a specific composite property and application.

8.6.4.2 Mica

Mica has some potential in the plastics industry as a reinforcing filler material. Mica is a thermally stable and tough material possessing high specific properties. It is also a low-cost material and readily available, which are important factors for the plastics industry when considering a filler material for thermoplastics.

In polymer composites, use of mica suitably delaminates and orients within a polymer matrix [44–46]. Mica is capable of imparting a high degree of reinforcement [47]. Its mechanical properties, such as Young's modulus, is twice that of glass fibers. Mica may be used at high loadings. It is economical and available in abundance.

8.7 Fibers

Composites have the ability to impregnate high volume percentages of fiber with polymer. Their success comes from both polymer and fibers being bound together. Benefits in the form of improved properties are to be expected from the presence of long fibers. Polymer composites with short-fiber reinforcement require high fiber/matrix interface for efficient load transfer.

The primary reason for using a polymer is to provide a continuous matrix to house the high strength fibers. In this case, it is the fiber properties that are important and not so much those of the polymer. The role of the polymer becomes that of a binder, consolidating a solid material, such as short fibers, into products.

Thermoplastics have sought to improve mechanical properties by increasing fiber length, such as in fiber reinforced thermoplastic sheets requiring simply heat and pressure to mold, thereby obtaining improved impact resistance. Thermosetting resin is moving towards gains in productivity by partially cured systems and reduction in fiber length, with consequent loss of properties.

8.7.1 Fiber Length

Fiber length in the composite is important, not so much to ensure adequate load transfer into the fiber, since with interface chemistry this can be achieved with quite modest aspect ratio, but to maximize the impact energy required to damage the composite. This probably occurs by increasing the fracture path length and reducing the stress raising effect of fiber ends. Since the properties of such composites are critically dependent on fiber properties the control of fiber alignment is also of major significance, and for highly critical structures placement within a few degrees is important. The dependence on fiber properties demands the use of the highest level of fibers possible, commensurate with good impregnation and coupling between fibers. Maximum fiber levels are achieved with controlled fiber-to-fiber orientation allowing maximum packing density, where volume packing of 65 percent can be achieved.

8.7.2 Synthetic Fibers

Carbon, graphite, glass, and aramid fabrics are the most commonly used fabrics for fiber reinforced polymer composites. Synthetic fibers have constant diameters, smooth surfaces, and considerable rigidity. Synthetic fibers of polyethylene and polypropylene are suitable for composites and have the advantage of recyclability due to the fact that thermoplastic fibers can be reprocessed, unlike cellulosic or glass fibers [48]. They have potential application as thermoformable panels in the automotive industry, and as building materials, furnishings and structural packaging materials. The composites can provide a strong thermoformable structural core that can be covered by decorative laminates, fabrics, or carpet.

8.7.2.1 Carbon Fiber

Carbon fiber (CF) not only offers the maximum extent of strength and wear resistance enhancement but also boosts the thermal conductivity that is crucial from a tribo-point of view. The rapid dissipation of frictional heat produced at the asperity contacts protects the matrix from degradation and fibers from delamination and helps in the retention of all performance properties. Moreover, in general, carbon fibers help in imparting additional lubricity because of the layer-lattice structure of graphite. A notable advance in the polymer industries has been the use of fiber and particulate fillers as reinforcement in polymer matrix [49]. Carbon fibers have been successfully used as reinforcement in polymer matrix composites for their excellent properties. Since carbon fibers possess high strength, high modulus, and low density, the addition of carbon fibers to polymer is one possible way to enhance the mechanical properties.

High loading of carbon fiber in polymer has some practical problems such as the extensive breakage of fiber which occurs during mixing due to the brittle nature of the fibers. Processing of CF with polymers results in extensive breakage of fibers, which is controlled by the melt viscosity and other processing parameters involved in making these composites. Breaking of such fibers affects the mechanical properties of the polymer composites. Carbon fibers are advanced fibers which are lighter and stronger than fiberglass but more expensive to produce. They are used in aircraft structures and expensive sports equipment such as golf clubs.

8.7.2.2 Fiberglass

Fiberglass is the first modern composite material with wide use in boat hulls, sports equipment, building panels, and many car bodies. The matrix is a polymer and the reinforcement that has been made into fine threads and often woven into a sort of cloth. On its own fiberglass is very strong but is brittle when bent sharply. The polymer matrix holds the fiberglass together and protects it from damage by sharing the forces acting on it.

Glass fibers are not electrically conductive and therefore not suitable for applications that require the ability to discharge electrostatic potentials. Sufficient conductivity is not provided by glass fibers for electrostatic painting, or even to shield from radio frequency or lightning strikes. They are not excellent thermal conducting material. Glass fibers account for around 90% of the reinforcement used in structural reinforcement polymer applications [50].

The most widely used glass fiber is "E-glass fiber," which contains SiO_2 as the main component with the remainder being oxides of other metals such as Al, Mg, Ca, etc. The fiber surfaces have distinct properties from the bulk. After contact with water, the surface oxides are hydrated and form metal hydroxide groups which are considered to be adsorption sites of coupling agent molecules. The compositions of metal oxides near the surface are much different from that of hulk water [51, 52]. Often an organosilane compound, known as a coupling agent, is used at the interphase between glass fiber and resin matrix to increase the compatibility of the two foreign materials of fiberglass reinforced composites. E-glass fibers are commonly used reinforcing material. By introducing them into mass transit applications, composites help to increase fuel efficiency and decrease maintenance costs due to their low weight.

Characteristics of glass fiber materials are:

- Weldability;
- Interface compatibility;
- Resistance to chemical attack;
- Rapid bonding in production;
- Less corrosion and fatigue problems;
- Long life.

8.7.2.3 Aromatic Polyamide Fibers

Aromatic polyamide fibers are used as light woven fabric pre-impregnated with epoxy polymers and fabricated into solid laminates or skin for sandwich panels containing a honeycomb core. They offer a good balance of tensile strength and modulus which provides the major incentive for their use as composite reinforcement fiber. Laminates with a unidirectional reinforcement have a specific compressive strength similar to that of aluminum. Laminates have resistance to repeated impacts and to dynamic flexural fatigue, vibration damping, thermal behavior, and transparency to electronic signals.

8.8 Composites Classification

Composites can be classified by shape, aspect ratio(s), geometric arrangement and concentration. Figure 8.3 illustrates the polymer reinforcement geometry.

Polymer composites with ultrafine phase dispersion are endowed with unique properties not shared by conventional materials. They are particle- or fiber-filled composites. However, getting a proper intimate composite of reinforcing agents into a polymer matrix presents a very difficult challenge [53, 54]. The macroscopic properties are determined by molecular factors such as degree of phase separation, morphology, domain sizes, interfaces, and the composition of different phases.

The variety of phase compositions produce structures with differing critical sizes (see Figure 8.4). Composites can be classifed as:

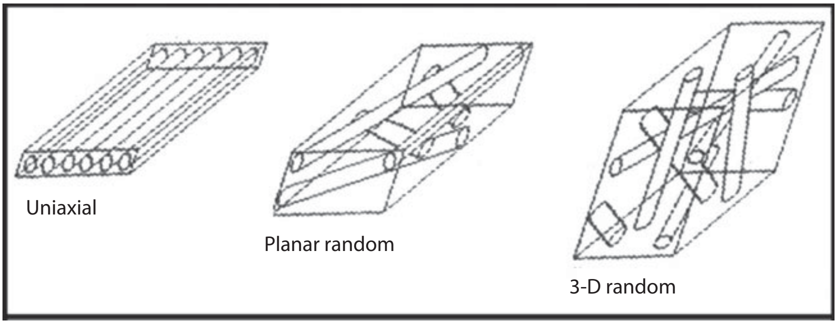

Figure 8.3 Polymer reinforcement geometry.

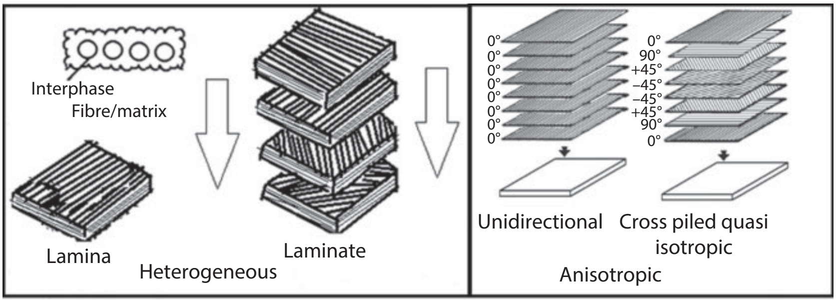

Figure 8.4 Schematic showing the heterogeneous and anisotropic structures of reinforced polymer matrix.

- Reinforcement/fibers;
- Lamina;
- Laminates;
- Components.

Heterogeneous structures are often considered homogeneous and anisotropic structures are considered isotropic structures of reinforced polymer matrix.

8.8.1 Mechanical Properties

The mechanical properties of composites can be improved in several ways:

1. Increase the matrix toughness;
2. Optimize the interface (or interphase) between the reinforcing agents and the matrix toughness using coupling agents, compatibilizer, and sizes;

3. Optimize the filler-related properties such as filler content, particle size, and dispersion;
4. Aspect ratio and orientation distributions also play a role in toughness of composites containing more fiberous materials.

The mechanical strength, modulus and wear resistance of polymers largely determine the suitability of these materials for applications like gears, bearings, cams, etc. [55].

8.8.2 Thermoplastic Composites

Thermoplastic composites are involved only in melt to freeze operations. In general, the mechanical properties of particulate-filled polymer composites strongly depend on the size, shape, distribution of filler particles in the matrix polymer and good adhesion at the interface surface [56, 57].

8.8.3 Filler Reinforced Polymeric Composites

Filler reinforced polymeric composite systems with well-dispersed particles and well-oriented crystal structures typically exhibit significant improvements in physical and mechanical properties compared to their non-filled counterparts. The reinforcement effect of a polymer composite strongly depends not only on the filler's structural parameters, dispersion and orientation, but also on the polymer's crystallization and orientation [58–64]. Inorganic material-filled polymer composites have the advantages of the polymeric properties together with the characteristics of the inorganic particles. The homogeneous dispersion of the filler particles in the polymeric matrix may improve the material characteristics [65, 66].

8.8.4 Conducting Polymer Composites

Conducting polymer composites have been used for various applications such as fuel cells [67], anticorrosion coatings [68], EMI shielding devices [69], etc. To improve the conductivity of insulating polymers, conducting fillers like metal particles [70], carbon black, graphite particles [71], etc., are added to the polymer. The conductivity of the composite depends on particle size, aspect ratio, and orientation of fillers along with processing techniques. It is desirable to have low filler loading retaining high conductivity which eases processing. Because the particle sizes of carbon black, graphite-filled polymer composites are in micron range, high conductivity is obtained at higher loading.

8.8.5 Fiber Reinforced Composites

Fiber reinforced composites are now an important class of engineering materials. They offer outstanding mechanical properties, unique flexibility in design capabilities and ease of fabrication. However, their superior strength and stiffness properties can be used to full advantage only when the behavior of these materials is properly understood under different loading and environmental conditions. Environmental factors influence the fibers, matrix, and interface simultaneously.

Fiber polymer composites have achieved applications in decking, furniture components, door moldings, packing pellets and interior panels of automobiles [72–74]. Volume fraction and orientation of reinforcing material decides the properties such as stiffness, strength, thermal conductivity, and other properties of composites. Silane coupling agents are most effectively used to improve the mechanical strength of fiberglass reinforced plastics (FRP); in aggressive environments, such as humid atmospheres, the mechanism of hydrolytic degradation is of major concern [75].

Apart from the choice of maximum fiber performance, the attainment of high specific properties in structural, fiber reinforced composites requires polymer systems with high stiffness and yield strength to control fiber buckling in the compressive mode and interfacial adhesion between fibers, together with good shear strength to promote load transfer.

8.8.6 Continuous Fiber Composites

Continuous fiber reinforced (CMC) composites are suitable for high performance requirements such as high temperature resistance and hardness; they also have toughness and damage tolerance. They are also of use where the use of a composite is indicated but the environment and wear conditions preclude polymer matrices [76].

Continuous fiber is:

- Traditional;
- Initially semi-finished item is prepared;
- Prepreg is produced, released, laid-up in a polymer bag;
- Finally molded into an item or a sheet.

The alignment of continuous fiber reinforcements may be:

- Uniaxial;
- Biaxial/multiaxial planar/random planar;
- Three dimensional.

Thermoplastic composites reinforced with continuous fibers have attracted attention due to their wide range of advantages over thermosets, including practically unlimited shelf life, short process cycle times, reformability, increased moisture and impact resistance, and, above all, increased toughness. The widespread application of thermoplastic matrix-based composites is hampered by high material and processing costs. Isotactic polypropylene (PP) offers economic benefits, and its mechanical property profile is closely matched to that of the engineering thermoplastics.

8.8.7 Discontinuous Fiber Reinforced Polymers

The discontinuous fiber reinforced polymers have superior productivity and formability. Their strength is remarkably low due to fiber length and/or matrix properties. This varies from continuous fiber reinforced polymers. Low fiber volume fraction causes strength degradation in discontinuous glass fiber length [77]. The low yield stress of thermoplastic polymers is frequently used for the matrix. The final failure mode is changed from breaking mode to matrix cracking mode.

The alignment of discontinuous reinforcements may be:

- Unidirectional;
- Bidirectional;
- Planar random;
- Three-dimensional random.

8.8.8 Carbon Fiber Reinforced Composites

Carbon fiber reinforced composites do not suffer from the fatigue and corrosion problems that affect metals. However, they have other drawbacks such as poor impact tolerance and deterioration from the effects of heat and moisture.

8.9 Thermoset Composites

Thermoset resin composite materials are extensively employed for primary and secondary load-carrying components. Thermoset composites often involve complex chemical reaction(s). Recycling of thermoset polymer composites is not easy. The three-dimensional network of the thermoset polymer system must be broken down either through the cleavage of cross-links, or through the carbon-carbon linkage of the chain backbone. This is a much more severe process and the fragmented products obtained by such cleavage are entirely different from the starting thermoset or even its precursor thermoplastic material. The technology for recycling thermoset polymers including rubbers is complex, costly and less viable commercially [78].

Thermosetting composites reinforced with fibers are replacing light metals in weight-sensitive industrial applications, particularly transportation. There is an increased acceptance of composites as branch due to its expanding technical and physical properties over a long period of time. Thermoset composites become permanently hard when heated above a critical temperature. They will not soften again upon reheating.

Thermosetting polymer composites are prepared from resins of low molecular weight. They are polymerized by the addition of a curing agent. Curing takes place during the shaping step. Due to their low viscosity during shaping, thermosets have favorable processing properties. The generally good performance of composites has resulted in a large variety of applications. Numerous ways of processing thermosetting matrices meet a lot of different chemical, thermal, mechanical, electrical, and economic needs. Advanced structural thermoset composites are based on aligned carbon fibers and epoxy resins or polyimides for aerospace and aircraft industries. The phenolics, urea and melamine-formaldehyde resins are used in polymer composites due to their low costs. Other applications are reinforced epoxy resins in high voltage insulation and for furniture; and glass fiber reinforced unsaturated resins for boats, etc.

High temperature thermoset composites are an amorphous, liquid or liquefiable resin based on reactive building blocks. This can be converted into a solid upon gelation followed by vitrification, i.e., conversion of material into glassy state by thermal or catalytic methods. These composites are irreversibly changed from fusible, soluble products into highly intractable crosslinked material. They cannot be molded by flow and must be fabricated during a crosslinking process.

8.9.1 Advantages

Important advantages of thermoset composites are:

- Radiation resistance;
- Corrosion resistance;
- High specific mechanical properties;
- The possibility of forming large area [79].

Thermoset composites are relatively vulnerable to compression. The deformation and failure in compressive and bending loads may stem from the coordinated buckling and slippage along the fibers [79]. This has led to concerns about their structural integrity during and after exposure to compressive and bending loads.

8.10 Thermoplastic vs Thermoset Composites

Thermoplastic composite materials have the following advantages over traditional construction materials based on thermosetting resins:

- Processing of thermoplastic composites generally requires relatively high temperatures and pressure, and therefore demands the use of special equipment and procedures [80–82];
- Thermoplastic polymer composites are recyclable. Recycling simply involves a reversible physical change by heating the resin above its processing temperature for shaping it and then cooling it to room temperature to obtain the desired recycled product.
- Materials technologies to enable production of safe and cost-effective lightweight vehicles have been identified as critical to reducing fuel consumption in automobiles, light trucks, and mass transit vehicles. Reducing weight can improve the price-to-performance ratio of transportation systems. Novel innovative lightweight materials provide avenues to produce increased fuel efficiency and reduced emission of harmful pollutants, without compromising on performance and size.
- Thermoplastic composites are tougher. They do not appear to have any advantage in static properties or fatigue over

thermosets. The compression strength of thermoplastics may often be inferior.
- Thermoset composites have superior abrasion and dimensional characteristics.
- Thermoplastic composites have better flexural and impact properties. Thermoset composites are crosslinked whereas composites of thermoplastic are not crosslinked and the inherent properties, such as stiffness and strength, come from monomer units. Molecular chain length with very high molecular weight ensures high levels of molecular entanglement, which acts as crosslinks in thermoset composites.
- Thermoplastic composites have better resistance to moisture and a variety of industrial solvents.
- Thermoplastic matrix composites are preferred to thermosetting composites when high toughness and high productivity are required.

8.11 Summary

- Polymer composites are light as well as strong and are resistant to corrosion and fatigue damage.
- New material can be made that exactly meets the requirements of a particular application with reduced machining.
- Tapered sections and composed contours are easily accomplished.
- By choosing an appropriate combination of matrix and reinforcement material it is possible to avoid wastage and tailor material for strength to stiffness requirements.
- Polymer composites provide design flexibility because many of them can be molded into complex shapes with a reduced number of parts in complex assemblies.
- Polymer composites have low thermal expansion and absorb radar microwaves
- A downside of polymer composites is often their cost with expensive raw materials. Even though the resulting product is more efficient, the raw materials are often expensive.
- Polymer composites lack established design allowance and it is difficult to locate defects in linear elastic to failure.

References

1. Kulkarni, S.M. and Kishore, *J. Appl. Polym. Sci.* 84(13), 2404–2410, 2002.
2. Verbeek, C.J.R., *Mater. Lett.* 52(6), 453–457, 2001.
3. Trakulsujaritchok, T. and Hourston, D.J., *Euro. Polym. J.* 42, 2968, 2006.
4. Gatos, K.G., Martínez Alcázar, J.G., Psarras, G.C., Thomann, R., and Karger-Kocsis, J., *Compos. Sci. Technol.* 67, 157–167, 2007.
5. Inubushi, S., Ikeda, T., Tazuke, S., Satoh, T., Terada, Y., and Kumagai, Y., *J. Mater. Sci.* 23, 1182–1188, 1988.
6. Cha, S.W., Yoon, J.D., Uto, N., *Cell. Polym.* 23, 229–241, 2004.
7. Zampaloni, M., Pourboghrat, F., Yankovich, S.A., Rodgers, B.N., Moore, J., Drzal, L.T., Mohanty, A.K., and Misra, M., *Compos. Part A* 38, 1569–1580, 2007.
8. Park, B.D. and Balatinez, J.J., *Polym. Compos.* 19, 377–382, 1998.
9. Bledzki, A.K., Gassan, J., and Zhang, W., *J. Cell. Plast.* 19, 550–562, 1999.
10. Utracki, L.A. and Vu Khanh, T., in: *Multicomponent Polymer Systems*, I.S. Miles, S. Rostami (Eds.), Polymer Science and Technology Series, Longman Scientific & Technical: Harlow, 1992.
11. Peltonen, P., Pääkkönen, E.J., Järvelä, P.K., and Törmälä, P., *Plast. Rubb. Comp. Proc. Appl.* 23, 111–126, 1995.
12. Cameron, R. and Constable, R.C., *Polym. Polym. Comp.* 1, 45–52, 1993.
13. Constable, R.C., Evaluation of chemically modified polypropylene with various glass fiber types, for performance enhancement in glass filled polypropylene, in: *Proceedings of ANTEC '94*, pp. 1549–1552, 1994.
14. Cantwell, W.J., Tato, W., and Kausch, H.H., *J. Thermoplast. Comp.* 4, 304–317, 1992.
15. Yue, C.Y. and Cheung, W.L., *J. Mater. Sci.* 26, 870, 1991.
16. Vollenberg, P.H.T. and Heikens, D., *Polymer* 30, 1656, 1989.
17. Stamhuis, J.E. and Loppé, J.P.A., *Rheol. Acta* 21, 103, 1982.
18. Sumita, M., Tsukini, H., Miyasaka, K., and Ishikawa, K., *J. Appl. Polym. Sci.* 29, 1523, 1984.
19. Zorll, U., *Gummi, Asbest, Kunstst.* 30, 436, 1977.
20. Pukánszky, B., in: *Polypropylene: Structure, Blends and Composites*, J. Karger-Kocsis (Ed.), vol. 3, p. 1, Chapman and Hall: London, 1995.
21. Rothon, R., *Particulate Filled Polymer Composites*, Longman Scientific & Technical: Harlow, 1995.
22. Ess, J.W. and Hornsbv, P.R., *Plast. Rubber Process. Appl.* 8, 147, 1987.
23. Boluk, M.Y. and Schreiber, H.P., *Polym. Comp.* 7, 295, 1986.
24. Mascia, L., *Thermoplastic Materials Engineering*, Applied Science Publishers Ltd.: London, 1982.
25. Liang, J.Z. and Li, R.K.Y., *Polym. Int.* 49, 170–174, 2000.
26. Plueddemann, E.P., in: *Silane Coupling Agents*, 2nd ed., p. 1, Plenum Press: New York, 1991.

27. Monte, S.J. and Sugerman, G., in: *Proceedings of 31st Annual Technical Conference of Reinforced Plastics/Composites*, Section 6-E, SPI, 1976.
28. Monte, S.J. and Sugerman, G., in: *Proceedings of 33rd Annual Technical Conference of Reinforced Plastics/Composites*, Section 2-B, SPI, 1978.
29. Zhou, W., Qi, S., Li, H., and Shao, S., *Thermochim. Acta* 452, 36–42, 2007.
30. Zhou, W., Qi, S., An, Q., Zhao, H., and Liu, N., *Mater. Res. Bull.* 42, 1863–1873, 2007.
31. Rosenbaum, E.E., Randa, S.K., Hatzikiriakos, S.G., Stewart, C.W., Henry, D.L., and Buckmaster, M., *Polym. Eng. Sci.* 40, 179–190, 2000.
32. Rothon, R.N., Particulate fillers for polymers. *Rapra Rev. Reports* 12(9), 13–14, 2002.
33. Chung, D.D.L., *Carbon Fiber Composites*, p. 113, Butterworth-Heinemann, 1994.
34. Pramanik, P.K., Khastgir, D., and Saha, T.N., *Composites* 23(3), 183–191, 1992.
35. Xanthos, M., *Functional Fillers for Plastics*, p. 324, Wiley-VCH Verlag, 2005.
36. Yui, H., Wu, G., Sano, H., Sumita, M., and Kino, K., *Polymer* 47(10), 3599–3608, 2006.
37. Nieisen, L.E., *Mechanical Properties of Polymers*, pp. 126–135, Reinhold Publishing Corp.: New York, I962.
38. Howard, E.G. Jr., US Patent 4187210, assigned to E. I. Du Pont De Nemours And Company, 1980
39. Lapcik, L., Jindrova, P., Lapcikova, B., Tamblyn, R., Greenwood, R., and Rowson, N., *J. Appl. Polym. Sci.* 110(5), 2742–2747, 2008.
40. Mareri, P., Bastide, S., Binda, N., and Crespy, A., *Compos. Sci. Technol.* 58, 747–752, 1998.
41. Rothon, R.N., *Particulate-Filled Polymer Composites*, 2nd ed., Rapra Technology: Shrewsbury UK, 2003.
42. Pukansky, B., *Composites* **21**, 3, 1990.
43. Ansari, D.M. and Higgs, R.P., Presented at the 1997 TAPPI *Polymers, Laminations and Coatings Conference*, August 24–28, Toronto, Ont. Canada, 1997.
44. Xanthos, M., Hawley, G.C., and Antonacci, J., in: *Proceedings of the 33rd Annual Technical Conference of Reinforced Plastics/Composites*, Section 2-D, SPI, 1978.
45. Newman, S. and Meyer, F.J., *Polym. Compos.* 1, 37, 1980.
46. Katz, H.S. and Milewski, J.V., *Handbook of Fillers and Reinforcements of Plastics*, chap. 20, Reinhold: Toronto, 1978.
47. Lusis, J., Woodhams, R.T., and Xanthos, M., *Polym. Eng. Sci.* 13, 139, 1973.
48. Houshyar, S. and Shanks, R.A., *Macromol. Mater. Eng.* 288, 599, 2003.
49. Chand, N. and Gautam, K.K.S., J. Mater. Sci. Lett. 13, 230–233, 1994.
50. Errajhi, O.A.Z., Richardson, M.O.W., and Zhang, Z.Y., Impact resistance and damage characteristics of aluminised E-glass fibre reinforced unsaturated polyester composite. The Polymetric Composite Institute of South Africa (PCISA), pp. 453–460, 2004.

51. Wong, R., *Adhesion* 4, 171, 1972.
52. Rastogi, A.K., Rynd, J.P., and Stassen, W.N., in: *Proceedings of the 31st Annual Technical Conference of Reinforced Plastics/Composite Institute*, Section 6-B, SPI, 1976.
53. Rodriguez, N.M., *J. Mater. Res.* 8, 3233, 1993.
54. Rodriguez, N.M., Chambers, A., and Baker, R.T.K., *Langmuir* 11, 3862, 1995.
55. Throp, J.M., *Tribol. Int.* 15, 69–74, 1982.
56. Jancar, J. and Kucera, J., *Polym. Eng. Sci.* 30, 707–720, 1990.
57. Ruckenstein, E. and Park, J.S., *Polymer* 33, 405, 1992.
58. Jouault, N., Vallat, P., Dalmas, F., Said, S., Jestin, J., and Boue, F., *Macromolecules* 42, 2031, 2009.
59. Chen, W.C., Lai, S.M., and Chen, C.M., *Polym. Int.* 57, 515, 2008.
60. Termonia, Y., *Polymer* 48, 6948, 2007.
61. Mccarron, A.P., Raj, S., Hyers, R., and Kim, M.K., *J. Nanosci. Nanotechnol.* 9, 7368, 2009.
62. de Silva, A., Rocha, M., Moraes, M., Valente, C., and Coutinho, F., *Polymer Test.* 21, 57, 2002.
63. Jeevananda, T., Kim, N.H., Lee, J.H., Basavarajalah, S., Urs, M.V.D., and Ranganathaiah, C., *Polym. Int.* 58, 775, 2009.
64. Fu, X. and Qutubuddin, S., *Polymer* 42, 807, 2001.
65. Postole, G., Caldararu, M., Ionescu, N.I., Bonnetor, B., Auroux, A., and Guimon, C., *Thermochim. Acta* 434, 150–157, 2005.
66. Jiang, T., Jin, Z., Yang, J., and Qiao, G., *J. Mater. Process. Technol.* 209, 561–571, 2009.
67. Cooper, J.S., *J. Power Sources* 129, 152, 2004.
68. Radhakrishnan, S., Siju, C.R., Mahanta, D., Patil, S., and Madras, G., *Electrochem. Acta* 54(4), 1249, 2009.
69. Pande, S., Singh, B.P., Mathur, R.B., Dhami, T.L., Saini, P., and Dhawan, S.K., *Nanoscale Res. Lett.* 4, 329–334, 2009.
70. Maaroufi, A., Haboubi, K., El Amarti, A., and Carmona, F., *Mater. Sci.* 39(1), 265–270, 2004.
71. Zhang, Q., Xiong, H., Yan, W., Chen, D., and Zhu, M., *Polym. Eng. Sci.* 48(11), 2090–2097, 2008.
72. Selke, S.F. and Wiehman, I., *Compos Part A* 35, 321–326, 2004.
73. Clemons, C., *Forest Prod. J.* 52(6), 10–18, 2002.
74. Nabi Saheb, D. and Jog, J.P., *Adv. Polym. Technol.* 18(4), 351–363, 1999.
75. Ishida, H. and Koenig, J.L., *J. Polym. Sci.: Polym. Phys. Ed.* 18, 233–237, 1980.
76. Anon., Developments in composites, *Aircr. Eng. Aerosp. Tec.* 65, 14–15, 1993.
77. Okabe, T., Motani, T., Nishikawa, M., and Hashimoto, M., *Nippon Fukugo Zairyo Gakkaishi* 35(6), 256–265, 2009.
78. Throne, J.L., *Adv. Polym. Technol.* 7(4), 347, 1987.
79. Peng, Y.P., *Materials Review* 14(1), 13–17, 2000.

80. Karger-Kocsis, J. (Ed.), *Polypropylene: Structure, Blends and Composites*, Chapman & Hall: London, 1995.
81. Cogwell, F.N., *Thermoplastic Aromatic Polymer Composites: A Study of the Structure, Processing and Properties of Carbon Fiber Reinforced Polyetheretherketone and Related Materials*, Butterworth-Heinemann Ltd.: Oxford, 1992.
82. Newaz, G.M. (Ed.), *Advances in Thermoplastic Matrix Composite Materials*, American Society for Testing and Materials: Philadelphia, 1989.

Polymer Blends and Composites: Chemistry and Technology.
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9

Biocomposites

Biocomposites can be of great importance to the materials world, not only as a solution to growing environmental threats but also for alleviating the uncertainty of the petroleum supply [1, 2]. Eco-friendly biocomposites from plant-derived fiber (natural/biofiber) and crop-derived polymers (biopolymer) are novel materials for both now and in the future.

Biocomposites consist of a polymer matrix and a reinforcement of natural fibers. They can be used as a replacement for synthetic fiber reinforced polymer. These biocomposites are used in applications ranging from automobiles to building materials due to their comparable strength and stiffness.

9.1 Natural Fillers

Natural fillers like wood, cotton, and cellulose are less expensive than polymer. Therefore, natural fillers are proposed for use in composites. The use of a filler in addition imparts improvements to polymer properties such as mechanical reinforcement and greater thermal resistance of degradable materials. However, they are degradable during compounding.

9.1.1 Wood Flour

Wood flour is used as inexpensive filler in polymers of thermoplastics and thermosets. The cost, availability, renewability and recyclability or wood offer the potential to expand into large-volume, low-cost, high-performance structural composites. Automobiles and durable goods are presented as emerging technologies that can provide biomass-derived low-cost, high-performance materials that can compete with the totally synthetic materials.

9.2 Natural Fibers

Natural fibers have many advantages such as low density, low equipment abrasiveness, high stiffness and strength, relatively low cost, and good biodegradability [3]. Natural fibers can be flexible, have variable diameters along the length of each fiber and have rough surfaces. They are also sensitive to temperature and moisture and usually have irregular cross sections. However, the inherent high moisture absorption of natural fiber brings about dimensional changes in the lignocellulose-based fibers [4].

Natural fibers are renewable raw materials and they are recyclable. Natural fibers can serve as raw materials for polymer composites in place of synthetic polymer composites which result in environmental pollution and vast waste generation. The mechanical and physical properties of natural fibers vary considerably with natural polymer composite products. These properties are determined by the chemical and structural composition, which depend on the fiber type and its growth circumstances. Cellulose, the main component of all natural fibers, varies from fiber to fiber.

The use of natural fibers as reinforcement competes with technical fibers such as glass or carbon fibers. However, natural fibers are moisture sensible with rising moisture content, which lowers the mechanical properties. Because natural fibers are easily influenced by the environment, the effects of aging and degradation are often desirable with natural fiber composite materials. Use of natural fibers has dramatically increased in biocomposites. Advances in natural fiber development and composite science offer significant opportunities for improved materials from renewable resources with enhanced support for global sustainability [5, 6]. Natural fibers are subject to degradation in acids and in alkaline solutions, as well as under

UV rays. Use of natural fiber reinforced composites depends on the different environmental conditions, which are likely to influence the effects of age-related degradation.

The most important natural fibers are jute, flax and coir. Various applications of natural fibers as reinforcement in polymers have proved encouraging. Ramie, jute and kopak fibers are more resistant than other plant fibers against bacteria and fungi influences [7]. The low resistance of natural fibers against environmental factors decisively affects the mechanical properties of the composites [8]. Jute and sugar cane fibers are used in low-cost housing and rice husk-based composites have been developed for planking [9–12]. Biodegradable polymer matrices are the basis for environmentally friendly polymer composites.

Natural fibers possess excellent sound-absorbing efficiency, and they are more shatter resistant and have better energy management characteristics than synthetic fiber-based composites. Natural fibers are effective in improving the mechanical strength and impact properties of the products. The composite depends on the fabrication method, interfacial adhesion, fiber type, and reinforcement from the characteristics of the fiber, including diameter and average length/diameter ratio (L/D) of the specific fiber.

Natural fibers offer many advantages:

- Low density;
- High specific strength and modulus;
- Renewable nature;
- Less breakage of the fiber during mixing compared to inorganic reinforced fibers [13–15].

Fibers are discontinuous and not available in aligned form. Therefore, they presumably will not be oriented in preforms or prepreg tapes to conveniently provide a high level of mechanical strength and stiffness in one or two dimensions.

9.2.1 Treatments of Natural Fibers

9.2.1.1 Silanes

After hydrolysis, silanes undergo condensation and the bond formation stage. Silanols can form polysiloxane structures by reaction with the hydroxyl group present in the natural fibers. The effect of silane treatment on the mechanical properties of biocomposites improves the properties after chemical modification [16–18].

9.2.1.2 *Benzoylation and Acrylation*

Benzoylation and acrylation treatments of natural fibers [19] lead to improvement in the interfacial adhesion between fiber and polyolefin matrix. Benzoylation makes the fibers more reactive due to their attachment to the benzoyl ($C_6H_5C{=}O$), thus forming chemical links with the active sites on the matrix; and acrylation reaction is initiated by free radicals of the cellulose molecule [20].

9.2.1.3 *Coupling Agents*

Coupling agents comprise bonding agents and surfactants (surface acting agents), including compatibilizers and dispersing agents. Coupling agents have been used to improve the dispersion, adhesion, and compatibility of a system containing hydrophilic cellulose and a hydrophobic matrix. These agents can modify the interface by interacting with both the fiber and the matrix, thus forming a link between the components [21].

Maleated polyolefins are the most commonly used coupling agents. Other coupling agents, such as isocyanates and silanes, are also used for limited applications. Maleic anhydride (MAH), which is grafted onto the polypropylene (PP) backbone by reactive extrusion [22], is the most common chemical modifier to increase the reactivity and polarity of PP. There is a significant increase of both fiber and polymer adhesion [23] and properties with addition of MAH-grafted PP [22, 24]; the level of improvement depends on the concentration of grafted PP with MAH and on the type of fiber used on its chemical reactivity [22, 25, 26]. Polypropylene backbone is grafted with maleic anhydride by reactive extrusion.

9.2.1.4 *Dispersing Agents*

Dispersing agents are a cheaper route to improve properties and make more practical sense for high-volume, low-cost composite systems [27]. These agents act as bridges that link wood fibers and thermoplastic polymers by one or more of the following mechanisms: covalent bonding, polymer chain entanglement, and strong secondary interactions as in the case of hydrogen bonding [28, 29].

9.2.2 Wood Fibers

Wood fibers are an important raw material source due to their widespread occurrence, stability, hardness, lightness, elasticity and renewability. Wood fibers are related to their anatomical structure, physical and mechanical properties, and chemical composition. They are a porous material in which 70% of the volume is made up of air-filled cells. The remaining percentage of wood fibers is substance or cell walls (constituents of wood fibers). Wood fibers material is not durable in its natural form against vegetal (some fungi that cause rotting) and animal destructors (insects, termites, limnoria and chelura).

Cellulose and lignin are chief constituents of wood fibers. The softwood fibers are fairly homogeneous as they basically consist of only two cell types, whereas hardwood fibers are composed of mixtures of four or five cell forms and are thus relatively heterogeneous in structure [30–34]. However, wood-polymer composites are used to preserve against:

- Biological degradation;
- Dimensional instability;
- Mechanical effects;
- Burning;
- Effects of radiation on wood and wood/(co)polymer composites.

9.2.3 Cellulosic Fibers

Cellulosic fibers have a high Young's modulus as compared to commodity thermoplastics. They contribute to the higher stiffness of the composites [35, 36].

The primary advantages of lignocellulosic fibers as fillers/reinforcements in plastics are:

- Low densities;
- Non-abrasiveness;
- High filling levels possible resulting in high stiffness properties;
- High specific properties;
- Easy recyclability;
- Will not fracture when processing over sharp curvatures (unlike brittle fibers);
- Biodegradable;
- Availability of a wide variety of fibers throughout the world;
- Would generate rural jobs;
- Increases non-food agricultural/farm-based economy;
- Low energy consumption;
- Economical.

9.2.4 Other Natural Fibers

The use of natural fibers, such as oil palm empty fruit bunch fiber, jute fiber, or bamboo fiber, as filler material can reduce the material cost significantly and at the same time yield high strength-to-weight ratios [37–39]. Such material has significant potential for use in load-bearing applications such as display shelves, material handling pallets, crates, heavy-duty pipes, etc.

Rice husks and straw have limited results due to their high abrasive character, low nutritional value and high resistance to degradation, low density and high ash residue. The ash from rice husk achieved through a special burning process is a moderate reinforcing filler for polymer composites.

9.2.5 Shortcomings

- The use of natural fibers in industrial practice is limited by difficulties associated with surface interactions.
- Poor interfacial adhesion leads to composites with poor mechanical properties [40, 41].

9.3 Thermoplastic Materials

Thermoplastic materials that currently dominate as matrices for natural fibers are polypropylene (PP), polyethylene (PE), and poly(vinyl chloride) (PVC); while thermosets, such as phenolics and polyesters, are common matrices. Commonly used polymer materials such as PE, PP, PVC or polyamide are good electrical and thermal insulators.

9.4 Natural Polymer Composites

Thermoplastic wood-polymer composites as a continuous phase can result in better water resistance and dimensional stability with low polymer content. They can be used to replace impregnated wood in many outdoor applications. These wood composites use conventional processing techniques, such as injection molding, extrusion, etc., however, mixing the polar and hydrophilic fibers with nonpolar and hydrophobic polymer matrix can result in difficulties in dispersing the fibers in the matrix. The efficiency of the composite also depends on the amount of stress transferred from the matrix to the fibers. This can be maximized by improving the interaction and adhesion between the two phases and also by maximizing the length of the fibers retained in final composites [35]. Natural fiber composites have the potential ecological and economic advantages of lignocellulosic fibers. Efforts to understand their structure relationship and explore new methodologies for producing new materials are of commercial importance.

9.5 Wood-Polymer Composites

Natural fibers have been used as reinforcement in low-melting-point thermoplastic polymers [42]. These organic filler particles are low-cost renewable reinforcements that enhance material properties such as stiffness and strength. Their advantages are that they are environmentally friendly and have low density in comparison with conventional inorganic fillers. The thermoplastics that are commonly used as matrix are Polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), and acrylonitrile butadiene styrene (ABS). This is because their processing temperatures are below the temperature at which wood degrades or burns (about 220 °C). The demand for PVC-wood composites has increased drastically due to their use in window and door profiles, decking, railing and siding. Typically PVC can be mixed with wood filler at 40–80%. Counter-rotating intermeshing twin-screw extruders are used in manufacturing PVC composites.

Wood flour is preferred over wood fiber in WPCs in applications such as decking and flooring. The WPC products typically contain much less wood [43]. The wood flour content in WPCs mainly depends on the product applications and the processing methods [44–48].

Wood-polymer composites have wood fiber as reinforcement agent with low cost, high relative strength and stiffness. They give low density to the product because they are a natural resource. Addition of wood fibers increases stiffness which can replace polymers in many applications. Proper additives are used to improve the adhesion between polymer and wood fiber. In polymer-wood composites, the polymerization of various monomers substantially reduces the maximum rate of degradation for phosphonate-treated wood flour [49].

Commercial composite formulations typically employ high wood loading, high molecular weight matrix resin, and various additives such as lubricants and coupling agents.

Coupling agents improve the toughness of wood-polymer composites. The properties of a wood-composite are significantly improved by the addition of an isocyanate compound to the vinyl or acrylic monomer treating mixture. Hexamethylene diisocyanate (HMDIC) is a difunctional reagent which has two reactive functional groups. HMDIC modification of wood relies on modifying the predominant wood cell wall polymer by reacting wood hydroxyl groups with a diisocyanate group to form a wood-urethane derivative [50]. Some researchers have concluded that the isocyanates also react with accessible -OH groups.

The anhydride groups present in the maleated polyethylene (MAPE) can covalently bond to the hydroxyl groups of the fiber surface. Any MA that has been converted to the acid form can interact with the fiber surface through acid-base interactions. The improved interaction and adhesion between the fibers and the matrix leads to better matrix to fiber stress transfer [51].

The reaction of a polyolefin in the melt with maleic anhydride (MAH) in the presence of a free radical precursor, results in the appendage of individual MAH units onto the polyolefin backbone, accompanied by crosslinking and/or chain scission. Crosslinking is the predominant side reaction in the case of low-density polyethylene (LDPE) [52, 53], while the presence of propylene units, as in polypropylene, results in extensive degradation [54]. The reaction of ethylene-propylene copolymer rubber with MAH yields a maleated product, accompanied by both crosslinking and scission [55].

Increased moisture content of the composites reduces their mechanical properties and dimensional stability [44]. However, it is found that the incorporation of coupling agents, such as functionalized polyolefin, can improve the overall properties through enhanced compatibility between the hydrophilic wood filler and the hydrophobic polymer matrix [56–58].

9.5.1 Properties

Wood-polymer composites have dimensional stability and their compressive strength and hardness are higher [30, 59]. The elasticity of wood fiber is approximately 40 times greater than that of polyethylene and overall strength is about 20 times higher. The addition of wood fiber to the polymer matrix decreases creep response during loading but it is still a problem. Crosslinking the polymer matrix with silane improves the toughness and reduces creep during long-term loading of wood polymer composites due to improvement in the adhesion at the interface.

9.5.2 Advantages

The advantages of wood-polymer composites are [43, 60, 61]:

- Low density;
- Low equipment abrasiveness;
- Economical cost;

- Good biodegradability;
- Hydrophobicity;
- Decay resistance;
- Ability to add different wood species and colored pigments [62];
- Ease of processability;
- High productivity;
- Versatility.

9.5.3 Disadvantages

The disadvantages of wood-polymer composites are [63]:

- Mechanical properties, such as strength and toughness, are inadequate in some specific applications;
- Limitation of the thermal stability of wood filler;
- Difficulty in obtaining good dispersion of wood filler;
- Requires additional additive to create strong interfacial addition [64–70].

9.5.4 Applications

The applications of wood polymer composites:

- Flooring in the construction sector is the main application;
- Have better specific properties and find applications in diverse fields ranging from appliances to spacecraft.

9.6 Biocomposites

Biocomposites are made from natural fibers and biobased polymers. They are designed to be compatible with the environment. They have structural properties.

9.6.1 Glucose-Based Biocomposites

Glucose-based polymers are considered biobased polymers with potential application for use in biocomposites. The curing characteristics and water absorption behavior of the glucose-based polymers and epoxy resins are used as a matrix in biocomposites. The effects of water absorption on the hydrophilic polymer matrices with natural polymer as function of curing temperature causes changes in the mechanical properties of the polymers cured at different temperatures depending on the crosslinking of the matrix. The matrix cured at higher temperature has a comparatively tightly crosslinked network structure which exhibits microcracking as a degradation mechanism due to the trapping of the absorbed water within the natural polymer.

9.6.2 Polylactide Composites

Polylactide (PLA) composites with natural fibers have cost effectiveness and light weight. Natural fibers generally result in an increase in the modulus of PLA composites. Short natural fibers, such as chopped hemp [71] and abaca fibers [72], are shown to increase not only the tensile and flexural strengths of PLA composites but also the impact properties.

Short natural fiber reinforced PLA composites are prepared by melt compounding (i.e., extrusion) and injection molding. Conversely, the low-cost flour-type fibers, such as wood flour [73] and ground bamboo fiber [74], showed little or even detrimental effect on the tensile strength of PLA composites and decreased the impact strength [75]. The different effects of short and flour-type natural fibers were most likely related to the large difference in their L/D ratios.

It is well known that stress transfer can only be developed effectively at a certain level of L/D ratio for short fiber/polymer composites [76]. Nevertheless, use of flour-type natural fibers has the advantage of better mixing and easier processing besides being more economical. Therefore, there is still great interest in utilizing those low-cost cellulosic fillers for polymer composites. Strength of the PLA composites with both short natural fibers and flour-type natural fibers can be greatly increased by improving interfacial adhesion through fiber surface modification [7, 8] or by using isocyanate-type coupling agents [74].

9.7 Future Trends

- Natural/biofiber composites (biocomposites) are emerging as a viable alternative to synthetic fiber reinforced composites, especially in automotive applications [77].
- Biocomposites and innovative technologies can reduce the widespread dependence on fossil fuel. They can deliver performance and strength with lower weight and can be

stronger for the same weight of synthetic fiber reinforced composites [78].

- Exterior applications are more critical. The components must be able to withstand extreme conditions, such as wet weather, and not splinter due to mechanical impacts (chipping).
- Like any other engineering components, proper design of structures made from this material is necessary to ensure successful application.

9.8 Summary

- Natural fiber polymer composites with UV resistance and dimensional stabilities are much better than those of solid wood.
- Natural fillers have traditionally had a smaller percentage of the filler market for thermoplastics than mineral or glass-fiber reinforcements.
- Density of wood-polymer composites is almost twice that of solid lumber.
- Wood polymers are of vital socioeconomic and industrial importance. The preservation of wood present in polymers is a key issue in the building and furniture industries.
- Optimization of processing operations of wood-filled plastics is needed to reduce costs and compete with solid wood and conventional wood composite products.
- Maleic anhydride (MA) can be used as a coupling agent providing bonds both to a filler containing hydroxyl groups (esterification) and to the polymer matrix (through peroxide addition). This method can be applied both to cellulosic and mineral fillers.

References

1. Mohanty, A.K., Misra, M., and Drzal, L.T., *J. Polym. Environ.* 10(1), 19–26, 2002.
2. Mohanty, A.K., Misra, M., and Drzal, L.T., *Compos. Interfaces* 8, 313, 2001.
3. Bledzki, A.K., Reihmane, S., and Gassan, J., *Polym.-Plast. Technol. Eng.* 37, 451–468, 1998.
4. Rout, J., Misra, M., Tripathy, S.S., Nayak, S.K., and Mohanty, A.K., *Compos. Sci. Technol.* 61, 1303–1310, 2001.

5. Wool, R.P., *Chemtech* 29, 44, 1999.
6. Mohanty, A.K., Misra, M., and Hinrichsen, G., *Macromol. Mater. Eng.* 276/277, 1, 2000.
7. Höck, P., Verstärkung von Polypropylen mit Flachsfasern-Einsatz von Haftvermittlern zur Verbesserung der Faser-Matrix-Haftung, 17, IKV-Kolloqium, Aachen, 1994.
8. Selzer, R., SAMPE, The Materials and Processes Society. Kaiserslautern, 28 March 1995.
9. Nickel, J. and Riedel, U., *Materials Today* 44–48, 2003.
10. George, M., *Materials Today* 36–43, 2003.
11. Mohanty, A.K., Misra, M., and Drzal, L.T., *J. Polym. Environ.* 10(1–2), 19–26, 2002.
12. Baillie, C., *Compos. Sci. Technol.* 63, 1223, 2003.
13. Lightsey, G.R., *Polym. Sci. Technol.* 17, 193, 1981.
14. Theberge, J.E. and Hohn, E., *Polym. Plast. Technol. Eng.* 16, 41, 1981.
15. Raj, R.G., Kokta, B.V., and Oaneault, C., *Int. J. Polym. Mater.* 14, 223, 1990.
16. Hill, C.A.S. and Abdul Khalil, H.P.S., J. Appl. Polym. Sci. 78(9), 1685–1697, 2000.
17. John, M.J., Francis, B., Varughese, K.T., and Thomas, S., *Compos. Part A* 39(2), 352–363, 2008.
18. Mathew, L., Joseph, K.U., and Joseph, R., *Prog. Rubber Plast. Recycl. Technol.* 20(2), 337–349, 2004.
19. Li, X., Panigrahi, S., Tabil, L.G., and Crerar, W.J., Flax fiber reinforced composites and the effect of chemical treatments on their properties, in: *Proceedings of CSAE/ ASAE Annual Intersectional Meeting*, Winnipeg, Canada, 24–25 September, 2004.
20. Li, X., Tabil, L.G., and Panigrahi, S., *J. Polym. Environ.* 15(1), 25–33, 2007.
21. Gaylord, N.G., in: *Copolymers, Polyblends and Composites*, N. Platzer (Ed.), p. 76, Academic Press: New York, 1975.
22. Constable, R.C. and Amur, A.M., Chemical Coupling of Glass-Filled Polypropylene Using Acid or AnhydrideModified Polypropylenes, in: *Proceedings of ANTEC '1991*, pp. 1892–1896, 1991.
23. Mäder, E., Jacobasch, H.-J., Grundke, K., and Gietzelt, T., *Compos. Part A: Appl. S.* 27A, 907–912, 1996.
24. Peltonen, P., Pääkkönen, E.J., Järvelä, P.K., and Törmälä, P., *Plast. Rubb. Comp. Proc. Appl.* 23, 111–126, 1995.
25. Constable, R.C., Evaluation of chemically modified polypropylene with various glass fiber types, for performance enhancement in glass filled polypropylene, in: *Proceedings of ANTEC '94*, pp. 1549–1552, 1994.
26. Hojabr, S. and Boocock, J.R.B., Enhancement of filled polyolefin's properties by addition of polymeric coupling agents, in: *Proceedings of ANTEC '1995*, pp. 3620–3627, 1995.
27. Hull, D., *An Introduction to Composite Materials*, Cambridge University Press: Cambridge, 1981.

28. Raj, R.G. and Kokta, B.V., Improving the mechanical properties of HDPE wood fiber composite with additives/coupling agents, in: *Proceedings of the 49th Annual Technical Conference*, Montreal, Canada, pp. 1883–1885, Society of Plastic Engineers, 1991.
29. Maldas, D. and Kokta, B.V., *J. Adhes. Sci. Technol.* 3, 529–539, 1989.
30. International Atomic Energy Agency, Impregnated fibrous materials, Report of a Study Group, Bangkok, 20–24 November, 1967, Vienna, Austria, IAEA, 1968.
31. Hug, R.E., *Forest Prod. J.* 17, 16, 1967.
32. Meylan, B.A. and Butterfield, B.G., *Three-Dimensional Structure of Wood*, 2nd ed., Chapman and Hall Ltd.: London, New York, 1990.
33. Meyer, R.W. and Leney, L., *Forest Prod. J.* 18, 51, 1968.
34. Core, H.A., Cote, W.A., and Day, A.C., *Wood Structure and Identification*, 2nd ed., Syracuse University Press: New York, 1979.
35. Bigg, D.M., Hiscock, D.F., Peterson, J.R., and Bradbury, E.J., *J. Thermoplast. Compos.* 1, 146–160, 1998.
36. Rowell, R.M., Sandi, A.R., Caulfield, D.F., and Jacobson, R.E., The utilization of natural fibers in plastic composites: Problem and opportunities, in: *Lignocellulosic Plastic Composites*, A.L. Leao, F.X. Carvalho, E. Frollini (Eds.), USP and UNESP: Brazil, 1997.
37. Bledzki, A.K. and Gassan, J.C., *Compos. Sci. Technol.* 24, 221–274, 1999.
38. Bledzki, A.K., Zhang, W., and Chate, A., *Compos. Sci. Technol.* 61, 2405–2411, 2001.
39. Munikenche Gowda, T., Naidu, A.C.B., Chhaya, R., *Compos. Part A* 30, 277–284, 1999.
40. Najafi, S.K., Hamidinia, E., and Tajvidi, M., *J. Appl. Polym. Sci.* 100, 3641–3645, 2006.
41. Mansour, S.H., Asaad, J.N., Iskander, B.A., and Tawfik, S.Y., *J. Appl. Polym. Sci.* 109, 2243–2249, 2008.
42. Schut, H.J., *Plastics Technology*, March, pp. 46–52, 1999.
43. Clemons, C., *Forest Prod. J.* 52, 1018, 2002.
44. Lin, X.Z. and Qunfang, G.D., *J. Appl. Polym. Sci.* 85, 2824–2832, 2002.
45. George, J., Bhagawan, S.S., and Thomas, S., *Compos. Sci. Technol.* 58, 1471, 1998.
46. Mishra, S. and Naik, J.B., *J. Appl. Polym. Sci.* 68(4), 681–686, 1998.
47. Wang, W. and Morrell, J.J., *Forest Prod. J.* 54(12), 209–212, 2004.
48. Yang, H.S., Park, H.J., Lee, B.J., and Hwang, T.S., *Compos. Struct.* 72, 429–437, 2006.
49. Yap, M.G.S., Que, Y.T., Chia, L.H.L., and Chan, H.S.O., *J. Appl. Polym. Sci.* 43, 2057, 1991.
50. Tadokoro, H., Kobayashi, M., Yoshidome, H., Tai, K., and Makino, D.J., *Chem. Phys.* 49, 3359, 1968.
51. Sanadi, R.A., Caulfield, D.F., and Jacobson, R.E., *Agro-Fiber–Thermoplastic Composites*, CRC Press: New York, 1997.

52. Gaylord, N.G. and Mehta, M., *J. Polym. Sci., Polym. Lett. Ed.* 20, 481, 1982.
53. Gaylord, N.G., Mehta, M., and Kumar, V., in: *Modification of Polymers*, C.E. Carraher, Jr., J.A. Moore (Eds.), p. 171, Plenum Press: New York, 1983.
54. Gaylord, N.G. and Mishra, M.K., *J. Polym. Sci. Polym. Lett. Ed.* 21, 23, 1983.
55. Gaylord, N.G., Mehta, M., and Mehta, R., *J. Appl. Polym. Sci.* 33, 2549, 1987.
56. Li, Q. and Matuana, L.M., *J. Appl. Polym. Sci.* 88, 278–286, 2003.
57. Keener, T.J., Stuart, R.K., and Brown, T.K., *Compos. Part A, Appl. Sci. Manufact.* 35, 357–362, 2004.
58. Wang, Y., Yeh, F.C., Lai, S.M., and Chan, H.C., *Polym. Eng. Sci.* 43(4), 933–945, 2003.
59. Hug, R.E., *Forest Prod. J.* 17, 16, 1967.
60. Meyer, J.A., *Wood Sci. Technol.* 14, 49, 1981.
61. Meyer, J.A., *Forest Prod. J.* 32, 24, 1982.
62. Bldezki, A.K., Reihmane, S., and Gassan, *J., Polym. Plast. Technol. Eng.* 37, 451, 1998.
63. Saheb, D.N. and Jog, J., *Adv. Polym. Technol.* 18(4), 351–363, 1999.
64. Matuana, L.M., Balatineez, J.J., and Park, C.B., *Polym. Eng. Sci.* 38, 765, 1998.
65. Maidas, D. and Kokta, B.V., *J. Vinyl Technol.* 15, 38, 1993.
66. Matuana, L.M., Park, C.B., and Balatineez, J.J., *Polym. Eng. Sci.* 38, 1862, 1998.
67. Matuana, L.M., Park, C.B., and Balatineez, J.J., *Polym. Eng. Sci.* 80, 1943, 2001.
68. Matuana, L.M. and Mengeloglu, F., *J. Vinyl Addit. Technol.* 7, 67, 2001.
69. Lu, J.Z., Wu, Q., and Negulescu, I.I., *Wood Fiber Sci.* 34, 434, 2002.
70. Jiang, H., Kamdem, D.P., Bezubic, B., and Ruede, P., *J. Vinyl Addit. Technol.* 9, 138, 2003.
71. Garcia, M., Garmendia, I., and Garcia, J., *Appl. Polym. Sci. 107*, 2994, 2008.
72. Shibata, M., Ozawa, K., Teramoto, N., Yosomiya, R., and Takeishi, H., *Macromol. Mater. Eng. 288*, 35, 2003.
73. Pilla, S., Gong, S., O'Neill, E., Rowell, R.M., and Krzysik, A.M., *Polym. Eng. Sci. 48*, 578, 2008.
74. Lee, S.H. and Wang, S., *Compos. Part A: Appl. Sci. Manuf. 37*, 80, 2006.
75. Huda, M.S., Drzal, L.T., Misra, M., and Mohanty, A.K., *J. Appl. Polym. Sci. 102*, 4856, 2006.
76. Sheldon, R.P., *Composite Polymeric Materials,* p. 88, Applied Science Publisher: London, 1982.
77. Mapleston, P., Automakers see strong promise in natural fiber reinforcements. *Mod. Plast.* April, 73, 1999.
78. Misra, M., Mohanty, A.K., and Drzal, L.T., Natural/bio-fiber reinforced polyolefin composites: Bio-based opportunities and challenges in the materials world, in: *Proceedings of 8th Annual Global Plastics Environmental Conference (GPEC 2002) – Plastics Impact on the Environment*, February 13 & 14, 2002, Detroit, MI, pp. 383–392, SPE Environ. Div.: Troy, MI, 2002.

Polymer Blends and Composites: Chemistry and Technology.
Muralisrinivasan Natamai Subramanian.

10

Processing Technology

Polymer blends and composites can be converted into shaped components having thermal and oxidative stabilities with mechanical properties. Processing involves physical change from solid to shapes either by melting in the case of thermoplastic polymers or chemical reactions with respect to thermoset polymers. Polymer blends and composites improve mechanical properties to have adequate strength and toughness.

Processing and shaping is a process of deformation, flow and solidification of materials. Therefore, processing of blends and composites may be defined as converting polymer with reinforcing agents at a specified rate of production into a shaped product of good quality. Polymeric materials are in molten state during processing. Various mechanical responses will be produced during processing [1].

10.1 Processing Technology

The majority of processing steps rely on molten states which ensure polymer flow through numerous geometrical constraints. Therefore, the nature of flow has very complicated process control parameters such as temperature and pressure. The rate of heat transfer in molten and solid polymers is to a large part controlled by the thermal conductivity of the polymer. Thermal conductivity of a polymer in the solid state has to be a function of temperature, molecular weight and molecular orientation.

10.2 Processing Requirements

Processing mostly involves physical change from solid or liquids either by melting in the case of thermoplastics or chemical reactions with respect to thermosets [2].

Polymer blends and composites are converted for the following reasons:

- Financial incentives;
- Scientific interests;
- Specific processing and performance requirements;
- Recycling post-consumer wastes to upgrade their properties.

Polymer blends and composites are processed in numerous ways based on time and capital. Factors in selecting polymers are:

- Choice of processing;
- Method of assembly;
- Finishing and decoration;
- Quality control and inspection;
- Economics.

Polymer processing characteristics are crucial in predicting the behavior in manufacturing techniques such as injection molding, extrusion, etc. Specific heat of a polymer is necessary for evaluating the heat and shear energy needed during the plasticating operation and also the heat to be removed for subsequent extrudate or part cooling.

Processing technology is to be considered as shaping method through a melt. The shaping methods are:

- Injection molding through an additional processing stage;
- Injection and compression molding in the case of different shapes and sizes;
- Extrusion processes such as sheet, profiles, etc.;
- Calendaring uses a series of heavy rolls to convert polymer melt into sheet form;

- Various other processes such thermoforming, rotational molding, etc.

10.3 Processing Polymer Blends

Devolatilization and mixing are the most important operations in the manufacturing of polymer blends and composites. Mixing yields compositional uniformity, which is required to obtain good properties in the final product. Certain characteristics of the final product are to be achieved by process control parameters.

10.3.1 Devolatilization

In many polymer processing operations it is necessary to remove the volatile components from polymer melts or solutions in order to improve product quality, reduce product cost, and eliminate health hazards. The volatile species can be residual monomers, reaction by-products, or solvents. Devolatilization involves the application of a reduced pressure or vacuum to extract volatile vapors and often the injection of a stripping agent to enhance the devolatilization performance. As a result, the devolatilization process often generates bubbles of the volatile component and the stripping agent. Water and nitrogen are two commonly used stripping agents [3].

10.3.2 Mixing

Mixing during polymer blending and reactive extrusion is critical because the final properties of a polymer product depend on the quality of mixing. A physically homogeneous mixture can occur due to intermolecular association that provides a favorable energetic contribution to the mixing process. The properties of polymers also depend on the type of equipment used for blending and on mixing conditions. Mixing can be accompanied by the formation of a transition layer owing to strong shear deformations.

Mixing of incompatible polymers is a simple and efficient method of design of new materials with improved properties. The technological and service properties of polymer blends are determined by mutual distribution of the components, and the type, size distribution, and shape of structures formed by one polymer in the other. In this case, varying the intensity of mechanical action makes it possible to change the degree of heterogeneity of polymer blends at various structural levels and obtain materials with properties other than those of the initial blend components [4, 5].

The polymer blending operation is likely to be straightforward and without incident, and the resulting single-phase miscible blend will have a transparent melt and a single composition-dependent glass transition temperature [6–17]. Polymer blend processing is characterized by high temperature, heating rates and short reaction times. The blend constituents are capable of specific interactions with sufficient strength to promote miscibility, and individually possess comparable stabilities and melt viscosities at the processing conditions. Processing of polymer blends are widely used to convert polymeric materials into finished products.

- Melt blend of polymers use batch mixer or continuous extruder;
- End products use fabrication equipment such as injection molding machine, extruder, etc.

10.4 Selection of Polymers

Before processing polymeric materials to be blended the following points have to be considered:

- Mechanical: Type and magnitude of normal service stresses; loading pattern and time under load; fatigue resistance; deflections under overloads allowable and abuse; impact resistance.
- Temperature: Normal range of operating temperatures; maximum and minimum service temperatures.
- Environmental: Solvent and vapor attack; reactions with acids, alkalis, water, etc.; water absorption effects; UV light exposure and weathering; Oxidation, erosion by sand, rain etc.; attack by fungi, bacteria or insects.
- Electrical: Resistivity; dielectric loss; antistatic properties, flammability; toxicity of additives or degradation products.
- Appearance: Transparency, surface finish, color matching and retention.
- General parameters: Tolerances and dimensional stability; environmental acceptability; leaching of additives; permeability to vapors and gases; wear resistance.
- Materials costs: Cost of capital plant; molds and processing machines;

- Speed of production: Number of moldings/units required; operating costs of components include maintenance and fuel consumption.

10.4.1 Immiscible Polymer Blends

Blending of immiscible polymers is an important route to high performance materials, often with synergistic improvements in properties. During processing, immiscible blends resist phase coalescence, which leads to poor interfacial adhesion in the solid state and causes premature mechanical failure depending upon the nature of the applied stress and the failure mechanism. This is in turn is affected by the flow conditions during blending and subsequent processing.

Compatibilizer, a reactive agent by chemical reaction at the interface during melt mixing, is a cost-effective technique. Compatibilizer is miscible with one blend component and is capable of reacting with complementary groups of the other component when added to the components before blending. During melt mixing the reaction occurs at the interface and generates block or graft copolymers, which leads to compatibilization of the two phases [18].

10.5 Machine Selection

A machine for producing good polymer blends and composites:

- Must be able to perform the processes of wetting, separation and distribution, which are essential for good dispersion;
- Must achieve excellent longitudinal and transverse mixing in order to ensure homogeneous wetting and distribution of the polymers;
- Must generate sufficiently high shearing forces in the material to make separation of the agglomerates possible. The shearing force r can be increased both by increasing the shear rate γ and by increasing the viscosity η in accordant with $r = \eta : \gamma$;
- Must allow for intensive heat exchange in order to cool the product and thus avoid that the energy introduced into the material by shearing leads to overheating of the product and simultaneously to reduction of its viscosity;

- Must have facilities for melt venting/devolatilizing so that the volatiles which hinder wetting of the polymers can be removed;
- Must be easy to clean, resulting in short downtimes;
- Must ensure constant and reproducible material quality;
- Must be capable of single installation for processing a wide range of blend formulations;
- Must effect energy input sparingly and at a uniform rate so that the polymers which are sensitive to temperature and pressure are incorporated without damage and without over-stressing the product.

10.6 Processing Polymer Composites

10.6.1 Melt Mixing

Melt mixing is a method of composite preparation. This process involves the mixing of different components with a polymer at a temperature beyond the melting point of the polymer. It is used mainly for thermoplastics, especially in the preparation of conductive or antistatic composites.

Melt mixing offers the advantage of introducing no foreign components (e.g., solvents) into the blend. For this reason and because of the simplicity and speed of melt mixing, it has economic advantages which make it the primary commercial blending method. By using proper equipment it is possible to obtain excellent dispersion and equilibration of the components. Temperature, time and environment for the mixing can usually be carefully controlled.

The primary disadvantage of melt mixing is that both the components must be in the molten state, which can mean that temperatures may be high enough to cause degradation. Removal of oxygen, while helpful, is not a guarantee against degradation; shear stresses during melt mixing are high enough to cause chain scission, for example. While most mixing with commercially available equipment proceeds satisfactorily, one occasionally runs across pairs of polymers which are difficult to mix. In many cases, a large difference in the melt viscosity of the components explains the difficulty. Another disadvantage of melt mixing is the cost of the equipment involved. Also, even laboratory-size mixing equipment generally works well only with large amounts of material. A final disadvantage is the low mechanical strength and high viscosity of the prepared compounds that contain high levels of additives [19, 20].

10.7 Thermoset Polymers

There are various methods for manufacturing polymer composite parts. The choice of process is based upon the final product used and geometry as well as the number of parts. In addition, it requires:

- Processing flexibility;
- Problem-free processing over a wide range of applications;
- Quality constancy;
- Consistent material quality;
- Economy;
- Price;
- Low reject rate;
- Final cost calculation.

10.8 Processing Technology for Polymer Blends and Composites

10.8.1 Injection Molding

Injection molding is one of the most important processing methods for producing polymer blend parts [21, 22]. It concerns the softening of granules of plastic in a heated cylinder, within which a screw turns to mix the plastic. By thrusting the screw forward in the cylinder, a known quantity of polymer is rapidly injected into a closed, relatively cool mold. The majority of injection molding machines will run fully automatically. Molds, which may be of virtually any realistic size, may also be complex and require retractable mold parts, or cores, to form features which are not in the opening direction of the mold. Injection molding can be used for thermosets and is becoming increasingly popular due to the high degree of automation possible.

Figure 10.1 is a graphical representation of processing window:

- Temperature: Barrel zones, tool, die zone;
- Pressures: Injection max, hold;
- Time: Injection, hold, tool opening;
- Shot size: Screw travel.

Three main steps, namely filling, packing/holding, and cooling, are present during processing. In the filling stage, a hot polymer melt rapidly fills a

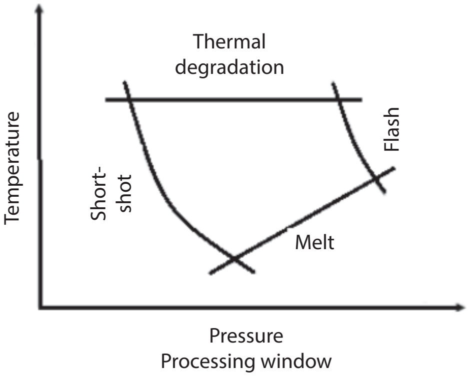

Figure 10.1 Graphical representation of processing window.

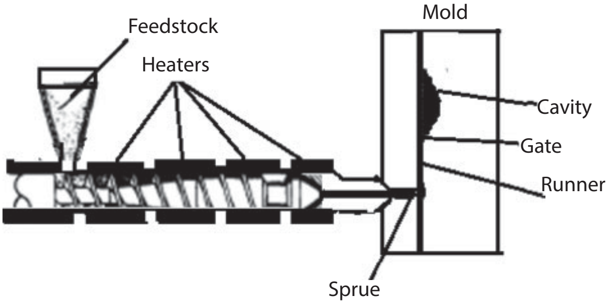

Figure 10.2 Schematic representation of the multigated injection molding operation using a reciprocating-type screw injection molding machine.

cold mold, reproducing a cavity of the desired product shape. In the packing/holding stage, the pressure is raised and extra material is forced into the mold to compensate for the determining effects that both temperature decrease and crystallinity development have on density during solidification. The cooling stage starts at the solidification of a thin section at the cavity entrance, namely gate; starting from that instant, no more material can enter or exit from the mold impression and holding pressure can be released. The solid layer on the mold surface reaches a thickness sufficient to assume required rigidity and the product is ejected from the mold.

In injection molding (Figure 10.2) of short fiber reinforced polymer composite artifacts, in a conventional machine, the fibers are aligned along the flow diection only in the subskin area. Using lower injection speed to improve the fiber orientation, the surface finish becomes poor and the orientation is also not uniform from the beginning of mold filling to the end of the cavity [23].

The multigated injection molding operation offers considerable control over fiber orientation. This technique introduces post-mold filling reciprocating flow during solidification and has been used to orient fibers in polymer matrices [24] and semicrystalline polymers [25].

The cooling phase of the injection molding process accounts for the majority of the overall cycle time. A reduction in cooling time will in turn reduce the overall cycle time and thereby increases the throughput rate. In continuous cooling, the cooling fluid is run through the channels of the mold continuously throughout the cycle, even during component ejection. The temperature is close to the running temperature of the tool. The tool running temperature is the temperature required at the surface of the cavity during injection.

Thermosetting composites can be accomplished by using either a reciprocating screw injection or a plunger-type molding machine. In a reciprocating screw injection molding machine:

- Operational principles involved with molding thermosetting materials are similar to those with thermoplastic polymers;
- Both thermoset and thermoplastic polymers can be fabricated in molding machine and are identical except for the injection unit;
- The process is readily automated and thus economically feasible.

Granules of a thermosetting material or its composite are carefully heated in the barrel at a temperature that softens the material and yet is not high enough to crosslink them prior to their entering the mold cavity. The mold is heated to the desired curing temperature; cure can proceed rapidly once the mold is filled, yielding an optimal cycle time and the best balance of physical properties of the molded parts.

The major advantage of the plunger-type injection molding machine over the screw injection molding machine is that fiber reinforcing thermosetting composites can be fabricated without destroying the fiber integrity. However, frictional heat, poor mixing, and back flow are the major problems limiting the use of the process. Improvements in the injection molding machine may alleviate these problems.

Crosslinking in thermoset occurs in a mold [26–28]. In injection molding:

- The material can thermally expand after it has been forced into an environment where the temperature must be high enough to promote the chemical reactions and the expansion

will continue until the heat evolution and consequent temperature rise is completed.
- The material shrinks as soon as the reactions occur, and shrinkage will continue until the reaction is almost completed and the mold is subsequently cooled down to the ejection temperature.

Mechanical properties of the injection-molded parts are strongly dependent on the direction of injection. The nature of anisotropic shrinkage found in thermosetting material strongly depends on the reinforcing nature and orientation of the fillers used. Natural fiber-filled compound exhibits significantly greater shrinkage in the flow direction than in the transverse direction whereas a compound filled with non-reinforcing filler, such as wood flour, exhibits no difference in shrinkage between the two directions [29–32].

10.8.2 Extrusion Technology

Extrusion technology is a high temperature short time process. It combines mixing, kneading, shearing, melting, shaping and forming. Extruded polymeric material is an important and expanding aspect of extrusion technology. Polymer blends, polymers and reinforcing agents participate in the extrusion process,and involve many phase changes during processing.

10.8.2.1 Single Screw Extrusion

Extrusion process involves a helically flighted screw which supplies a balanced flow of molten polymer through a die. The die shapes molten polymer which is cooled and solidified into different dimensions with the help of cooling fixtures and haul-off to pull the extruded products. Therefore, the product obtained during extrusion tends to be a simple and constant cross-section.

Extrusion industries are being pushed hard by resin costs and the demand for high product performance and consistent quality. The production of film, sheet, profile, tubing and pipe depends on the inconsistency in the products. Therefore, the operational parameters in the extrusion process, such as pressure, temperature, screw rotation rate, etc. (Figure 10.3), should be controlled in order to have the end product meet specifications. However, the product may still show inconsistencies.

Screw pumps can be viewed as melt pumps. Throughput is the combination of screw rotation and pressure gradient in the screw channel. Throughput is constant along the channel, while pressure development

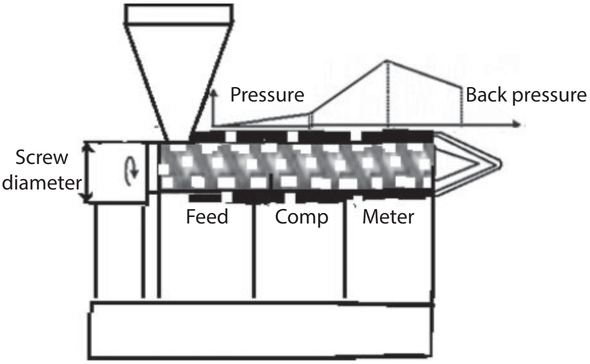

Figure 10.3 Single screw extruder.

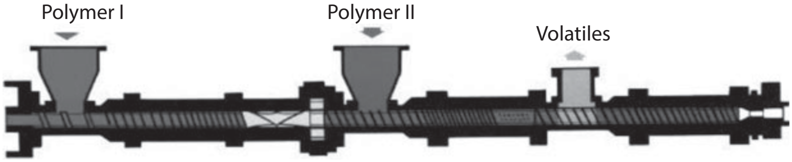

Figure 10.4 Schematic representation of a single screw extruder with polymer mixing at different points with removal of volatiles.

begins at atmospheric pressure and ends at back pressure at the die exit in the case of extrusion. Melt pool and solid bed coexist in the channel and the pressure gradient existing at the channel is due to the melt flow. The pumping rate can change as the various forces in the screw channel fluctuate. It can substantially decrease as the back pressure increases.

A standard single screw extruder is divided into three zones, namely, feed, compression and metering, according to their depth. The screw rotates at a constant rate in an extruder. In an injection molding machine, the screw operates differently from an extruder screw. The screw has to slide backward while rotating during the melt preparation. The screw then pushes the melt forward through the nozzle and remains idle in between these steps. The processing of polymer materials along a screw is usually divided into four steps, namely, solid conveying, delay, melting, and pumping [21]. Screw extruders may be used for pumping, blending, heating, solvent removal, and chemical reaction of doughs, jellies, catalysts, clays, and the like.

In the two-step process, all components in the first step are premixed in batches or, as shown in Figure 10.4, polymers with additives are mixed at two different stages in the subsequent continuous extrusion step, and a homogeneous concentrate is produced in the making phase and finally pelletized in the single-step process wherein the developed components are metered into the compounder as separate feed stream.

Sometimes the material fed with adequate properties may be degraded due to the presence of contaminants or exposure of excessive temperature, pressures and residence time inside the machine. However, extrusion is a process and does not improve the quality of the blend fed into the machine. The product quality can be controlled by precisely maintaining the blending and melting process to improve the quality and process stability. Therefore, the melt material is improved before it is delivered to the die.

10.8.2.2 Twin Screw Extrusion

Lately the use of co-rotating and counter-rotating twin screw extruders in industries that process, modify, and even produce polymers has gained importance because of their versatility and advantages as processing and reaction machines. The complexity of the flow in twin screw extruders, as well as the large number of parameters and interrelated variables that affect the flow, make this process difficult to understand, control, and optimize.

The heat of reaction strongly determines the temperature of the reaction mixture, which, in turn, has a strong influence on the viscosity. The viscosity of the reaction mixture is dependent largely on the rotational speed of the screw and other processing/operational variables such as polymer concentration and temperature.

The feed temperature and the barrel temperature influence the number-average and weight-average molecular weights along the extruder length. The feed temperature is an important variable in the early stages, and the barrel temperature is also important in the latter stages. Generally, the increase in the screw speed decreases the residence time but increases the product temperature because of higher viscous dissipation. Despite the reduction in residence time by increasing the rotational speed, the viscosity is lower at higher speeds. This reflects the loss of molecular weight because the temperature is higher at higher screw speeds [33].

Twin screw extruder can be used in two ways; extrusion (flush) or cycle blends. The immiscible blend is manually premixed by rolling the given blend ratio in a bag before being fed into the extruder. A nitrogen blanket is used to minimize polymer degradation (Figure 10.5).

Dispersive and distributive mixing are required to produce a useful polymer product. The former results in the breakup of cohesive agglomerates (filler particles or the minor phase of an immiscible polymer blend), while the latter increases the homogeneity of the mixture through the generation of interfacial area. The dispersive mixing process is quantitatively

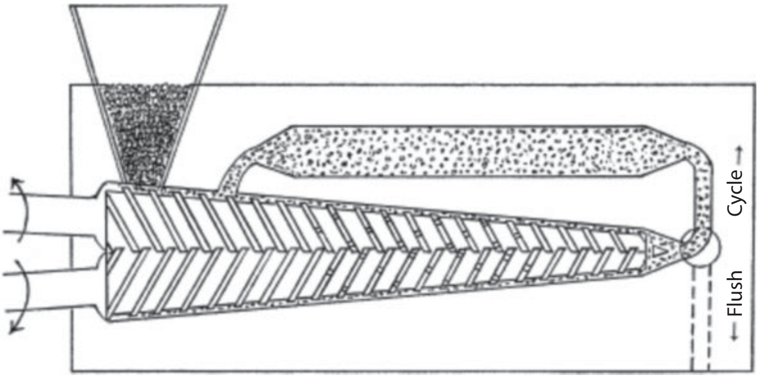

Figure 10.5 Schematic diagram of a conical twin screw extruder, in which immiscible polymers are extruded with preset temperature along the extruder axis. (Reprinted with permission from [34]; Copyright © 2002 Elsevier Sciences Ltd. All rights reserved)

investigated by following the size reduction of the agglomerates. Conversely, the generation of interfacial area is very difficult to quantitatively measure; therefore, there is a lack of experimental data on distributive mixing in extruders during polymer blending.

10.8.2.2.1 Co-rotating Twin Screw Extruders

Co-rotating twin screw extruders are the most used polymer processing machinery for melting, homogenizing, blending and dispersing of polymers and additives. Dissipative melting [21] occurs in intermeshing co-rotating twin screw extruders. Polymeric feedstock is fed into co-rotating twin screw extruders mainly in the form of pellets, powders, beads, flakes, and granules. Energy raises the temperature of polymer solids from room temperature to their melt processing temperatures. The melt processing temperatures of polymer are normally higher than their transition temperature.

Conductive melting without melt removal is not practiced except in powder processing, such as rotational molding, compression molding, and ram extrusion, because the rate of melting decreases with the time of contact. With melt removal, the melting operative is in the melting zone of single screw extruders and injection molding machines, where the solid and molten regions are segregated. The solid phase is simply compressed and the molten phase is heated by conduction [21, 35, 36].

In dissipative mix melting the dominant source of energy for melting is the mechanical energy introduced through the shafts and converted into thermal energy by a number of heat generating phenomena (Figure 10.6). The irreversible deformation of the polymer solids, interparticle friction,

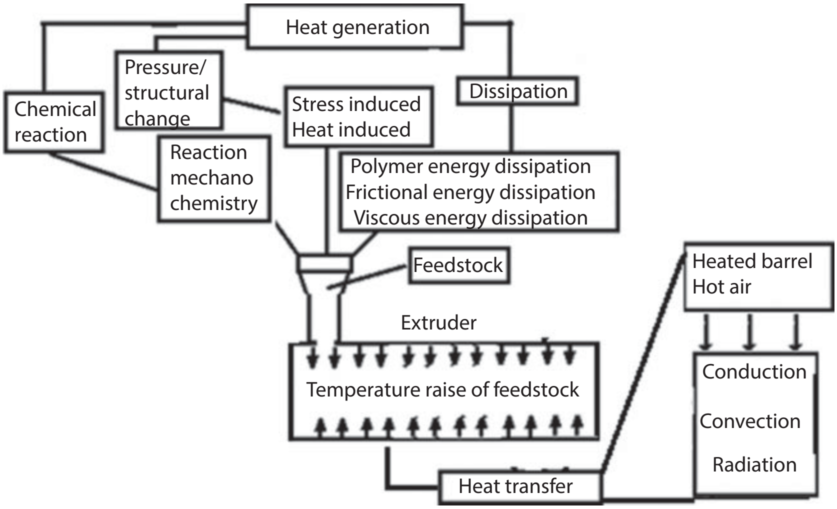

Figure 10.6 Flowchart of the possible heating/melting mechanisms in co-rotating twin screw extruders.

and viscous energy dissipation of the portion of the polymer solids compacted solid bed which has melted [37].

The dominant presence of polymeric solids, which deform individually and undergo frictional heating at their boundaries, renders the deforming beds to be other than a continum in compacted kneading elements of co-rotating twin screw extruders. Melting of reinforcement agents is normally consumed in the melting section in most polymer melt processing equipment. Phase size reduction in blending happens in the melting process.

10.8.3 Thermoforming

Thermoforming defines a set of techniques which allow the production of thin wall polymer shapes starting from flat sheets or films. In this process, the polymeric sheet is clamped and heated above its glass transition temperature or melting temperature where the material is softened. The polymeric material has a marked viscoelastic behavior and can be easily formed. The sheet is then placed on a metal mold and forced to assume the desired shape with the help of vacuum or air pressure. After cooling, the part is refined. Good understanding of the process rheology leads to a better control of thickness distribution and to the process optimization.

One of the advantages of thermoforming is that it does not cause any pollution. Thermal post-forming of the sheets to form three-dimensional moldings can be an efficient way to produce the final product. Twin sheet thermoforming had been considered, but the supply base could not provide parts this large.

Thermoforming is a secondary process which involves the shaping of sheet or foil, usually be vacuum or compressed air. Tooling costs can be extremely low. Thermoforming is one of the manufacturing processes in which polymeric sheet stock is re-shaped into a new geometry with the use of heat to soften the sheet not to melt and forcing it into or onto a mold where it is cooled and frozen into the new geometry. The hot material uses force that may be in the form of mechanical pressure, compressed air pressure, drawing a vacuum between the sheet and the mold or any combination of these forces as shown in Figure 10.7.

The effects of applied force to the stretching of the hot sheet material towards the amount of deformation possible are based on tool design. Regardless of the force applied to the sheet, a decision must be made regarding the use of either a positive (plug) or negative (cavity) mold

Thermoforming is a rapid processing technique for producing large thermoplastic composites with the aid of pressure, vacuum, and heat. In this process, thermoplastic composite sheets are heated to the forming temperature of the polymer. Pressure is applied to form the sheet to the shape of the tooling. The tool is generally made of aluminum, wood, epoxy and/or structural foam. Once the part is cooled, it is demolded and trimmed to the final shape [38, 39].

Twin sheet thermoforming is a process used for three reasons: 1) The parts must maintain some structural rigidity. They cannot "sag" into the grain tank in the closed position, and must support the edge. 2) The parts must also fit within a narrow design envelope. 3) Twin-sheet provides a higher stiffness/weight ratio than steel doors.

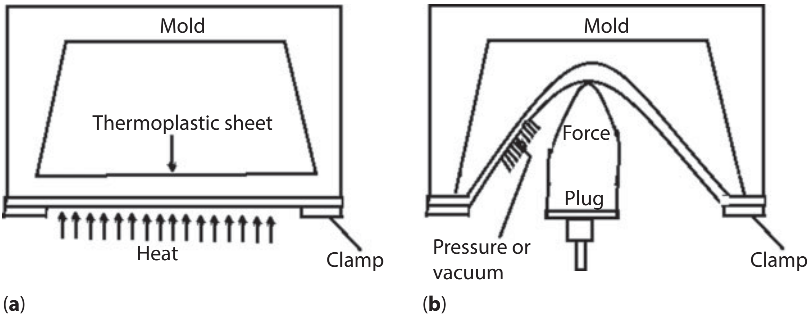

Figure 10.7 Thermoforming process: (a) Thermoplastic sheet is clamped onto mold and heated; (b) Heated sheet is forced into mold by plug or pressure/vacuum.

Thermoforming is used to fabricate the flat geometry which is an obvious match to flat stock thermoform materials. The geometry of relatively large flat parts naturally points to thermoformed plastic parts to replace metal.

10.8.4 Reactive Blending

Reactive blending is usually carried out with polymers that are immiscible but which contain reactive groups able to react at the interface during melt processing. Thus, it is possible that *in-situ* block copolymers, graft copolymers or networks are formed directly at the interface, reinforcing the usually weak interface and simultaneously enabling a smaller particle size to be achieved [40, 41]. Because of the direct formation of the compatibilizer at the interface, this method has a number of advantages compared to the application of preformed compatibilizers, which also might be dispersed in the bulk phases and not located at the interface. The limitation of reactive blending is the smaller number of suitable polymers having reactive groups. The most popular reaction to overcome this problem is the grafting of maleic anhydride.

Reactive blending is the compatibilization of immiscible polymer pairs by chemical reactions which take place during the process of melt mixing. Reactive extrusion blending may enhance compatibility and thus modify the mechanical properties of the reactive polymer blend [42], in comparison with the physical blend of the homopolymers.

Reactive extrusion is a processing method in which an extruder is used as a chemical reactor for the continuous synthesis and modification of polymers at elevated processing temperatures. This cost-effective method provides good mixing and heat transfer at high viscosities [43, 44].

Reactive extrusion is implemented through the following means:

- Several types of chemical processes for controlled degradation of high molecular weight polymers [45–47];
- Grafting or functionalization by introduction of functional groups or monomers into a polymer backbone [48–50];
- Crosslinking reactions [51–54];
- Polymerization of monomers to form high molecular weight polymers [55–57].

Reactive blending and reactive polymerization processes are rarely performed together. The reactive polymerization process includes the following steps:

- A monomer/peroxide solution is absorbed in solid suspension-type porous PVC particles;
- The particles are extruded at a high temperature to polymerize the absorbed monomer. The compatibility of the polymer formed with PVC depends on the specific monomer used and on its concentration.

10.8.4.1 Reactive Extrusion

Reaction extrusion is one of the most interesting processes that can enhance the desired properties by grafting or compatibilization using an appropriate processing technique [58]. Using a reaction extrusion technique, mechanical properties of a multiphase polymer blend can be significantly improved by the size and shape of the phase generated during its preparation [59–61].

Randomly oriented fibers provide good formability. However, they do not have the advantages of the highly directional properties often desired in composite parts. The sheets with aligned, discontinuous fibers appear to have been used with more success than continuous fibers during forming [62].

One of the shortcomings experienced with fiber reinforced composite is that the formation of straight, continuous fiber or woven fiber composite sheets typically results in wrinkling of the fibers and distortions.

In reactive compatibilization, graft or block copolymers are formed *in situ* during melt processing in terms of appropriate reactive functionalities. It has emerged as an effective way of solving the problem associated with incompatible polymer mixtures [63]. Two-phase materials containing graft or block copolymers are collectively known as compatibilized polymer blends.

In reactive extrusion process, the polymer blend takes place simultaneously with its processing and shaping at elevated temperatures into a finished polymer product. It is an inexpensive method that provides good mixing and heat transfer at high viscosities [43, 44], and may lead to improved compatibility. Reactive blends prepared through *in-situ* compatibilization have similar dispersed particles compared to the corresponding physical blends [64]. Reactive extrusion is for functionalization by introduction of functional groups or monomer into a polymer backbone [48–50, 57, 65, 66], crosslinking reactions [51–54].

In reactive blending, the compatibilization of immiscible polymer pairs is achieved by chemical reactions taking place during the process of melt mixing. Reactive extrusion blending may enhance compatibility and thus modify the mechanical properties of the reactive polymer blend [42], in comparison with the physical blend of the homopolymers.

10.8.4.2 Prepolymer

Polymers or oligomers have molecules that are capable of entering, through reactive groups, into further polymerization, thereby contributing more than one structural unit to at least one type of chain of the final polymer.

10.8.5 Curing

Chemical reactions that take place during the curing reaction of a thermoset determine the polymer morphology, which is a key factor in determining the properties of the cured thermoset. Curing agents or hardeners for an application depend upon the viscosity of the mixture, the mass of the system and the temperature. They are chemically active compounds used to convert hard, infusible thermoset polymer material.

Curing agents convert epoxy resins into hard, infusible thermosets. They promote the crosslinking reaction either by polyadditon or by homopolymerization. The curing reaction occurs without the formation of any by-product.

Curing is a chemical process which converts a prepolymer or a polymer into a polymer of higher molar mass and connectivity and finally into a network. Curing is typically accomplished by chemical reactions induced by heating, photoirradiation, or electron beam irradiation, or by mixing with chemical curing agent.

The curing of thermoset polymer composites involves the formation of a three-dimensional network. This is done through reactions among polyfunctional groups. The curing process starts from the formation and linear growth of a chain. The chain starts to branch and then to crosslink. As the curing proceeds, the molecular weight increases rapidly, the molecular size expands and several chains are linked together into a network of infinite molecular weight. A gelation is a typical characteristic of thermoset polymers and a phenomenon that takes place during thermosetting polymer cure reactions [67, 68].

10.8.5.1 Autoclave Curing

Autoclave curing is a process to produce fiber reinforced polymeric parts in a final shape. Optimization in processing has been in industry as a means to understand and improve product quality. It requires a processing cycle to consolidate the laminate uniformly to the required thickness, to ensure minimal porosity, and to cure the resin to a specified condition. For efficient production, the optimization must be accomplished in the shortest possible time. However, it has limitations such as the thermal inertial of a large autoclave, together with its charge of molds and laminates. The polymeric materials may be heated and cooled, so processing cycles typically last at least five hours or often much longer.

10.8.6 Lay-Up and Spray-Up Techniques

Thermosetting polymer composites are prepared using manual lay-up and spray-up techniques. Manual lay-up involves setting a fibrous fabric on a one-sided and open mold, then spreading the polymer material over the mold with a manual roller across the fabric. Polymer and chopped fibers are spread with an air-assisted gun on a one-sided mold because an open mold is used in both processes. The final net shape cannot be readily controlled.

Prepolymeric material or liquid polymer is injected into a closed mold containing fibrous preform. The main drawback is the release of volatile organic compounds during the curing process. Liquid composite molding processes are used for safer working conditions and for better dimensional accuracy. Heating of the mold results in the polymer either being cured or polymerized into a crosslinked network with entrapment of fibers. Pre-impregnation of fabrics with prepolymer material may also be carried out. For high-performance industrial applications, such as civil infrastructure and transportation, the composites utilize fillers such as glass, carbon, aramid or natural fibers in continuous or chopped form.

10.8.7 Pultrusion

Pultrusion is a continuous manufacturing technique for thermoset composite products. It may be used to manufacture constant cross-sectional shapes. The process consists of impregnating fiber as a reinforcing material into a polymer bath and passing the impregnated fiber towards a shaping die in which the polymer is subsequently cured. Curing or polymerization is generally activated by heat in an autoclave after compressing the mixture into a closed mold. Filament winding is another way to continuously manufacture hollow composite parts. Fibers are continuously conveyed to a rotating mandrel after impregnation with polymer bath.

10.8.8 Sheet Molding Compound

A single sheet molding compound (SMC) part is used in production to ensure that the SMC exhibits equivalent rigidity to steel panels and to determine placement of molded-in ribs. The selection criteria are:

- SMC stiffness/weight exceeds reaction injection molding (RIM);
- Dimension stability of SMC exceeds RIM;
- Optimized design intent—less crown on part—to reduce tooling expenditure.

Polymer composite manufacturing processes are utilitized in producing components. Styling appearance and shielding parts are made from SMC, RIM, resin transfer molding (RTM), injection molding, and rotational molding. Wear-resistant and functional parts are made with injection molding, extrusion and compression, cold forming, blow molding, casting and overmolding.

The wetting of fibers and their distribution in the matrix is an important step during composite manufacturing. This is because mechanically weak regions, such as matrix-rich areas or fiber contacts, are founded on incomplete or imperfect impregnation. Impregnation of fiber bundles with matrix indicates the penetration of matrix between the individual fibers.

The high viscosity of polymer in a thermoplastic melt increases with thermoset polymer. The difficulty of impregnation is due to the reduced matrix flow [69, 70].

Hot compaction, as shown in Figure 10.8 [70–72], is melting of the reinforcement during composite preparation, causing a reduction of the mechanical properties of the composite. In hot compaction technique, single polymer composites are produced by using a matrix in the form of fibers. Initial studies have shown that the reinforcement is completely wetted by the matrix without melting fibers by using a suitable combination of temperature and pressure.

The production of single thermoplastic polymer composite materials is achieved through routes such as film stacking followed by melting, hot compaction, powder and solution impregnation [73, 74].

The wetting of fibers and their distribution in polymer matrix is an important step during composite manufacturing. Mechanically weak regions are found in matrix-rich areas or fiber contacts due to incomplete

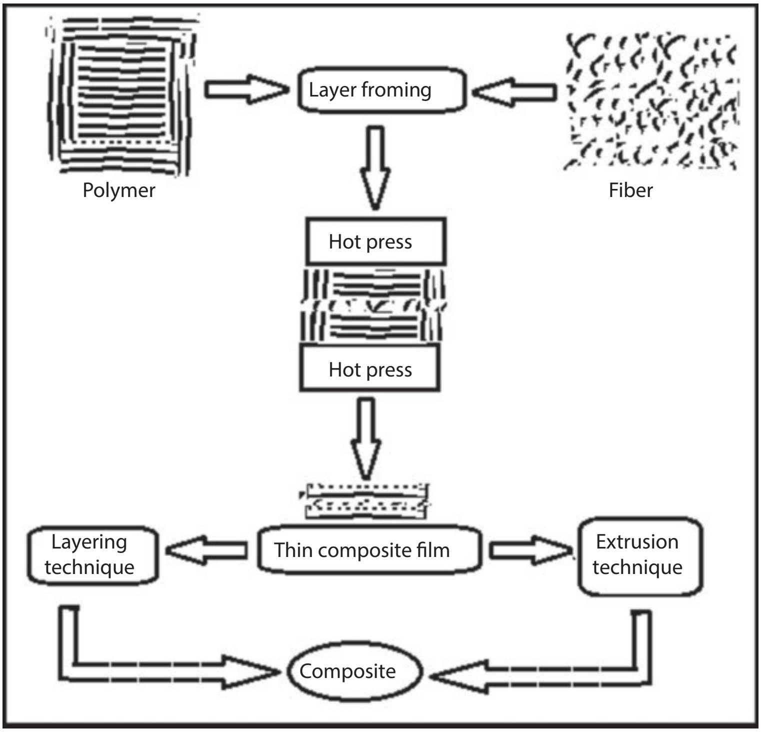

Figure 10.8 Flowchart showing the stages of the composite manufacturing process.

or imperfect impregnation. Impregnation of fiber bundles with polymer matrix takes place between individual fibers.

The higher viscosity of a thermoplastic polymer melt compared with thermosetting polymer increases the difficulty of impregnation because of the reduced matrix flow [69, 70]. For melt impregnation, the matrix needs to flow completely into the inner parts of a fiber bundle. However, this is restricted by heat transfer throughout the composite and the high viscosity of the molten matrix.

For melt impregnation, the polymer matrix needs to flow completely into the inner parts of a fiber bundle, but this is restricted by heat transfer throughout the composite and the high viscosity of the molten matrix.

Increasing the processing temperature will reduce the viscosity of matrix, but the fibers may melt at their surfaces just below their melting temperature and form a closed bundle. Thus, the penetration of matrix into the bundle will be reduced by a closed border of adhered fibers. A fine powdered matrix can be used to provide good impregnation of fiber bundles with matrix powder [71, 72]. The particle size of the powder should be in the range of the fiber diameter, which will result in an even powder distribution with some agglomerated matrix particles. In a solution method, the reinforcement and matrix would be soluble in the same solvent, which will cause a problem in producing the composite since the reinforcement will tend to dissolve in the matrix solution.

10.8.9 Compression Molding

Compression molding is a traditional process for thermosets which involves heat and pressure to process thermoset polymers. Compression molding offers better control of morphology. A hydraulic press applies continuous pressure on the powder particles in the die to induce consolidation during the heating cycle. Cartridge heaters can aid in temperature uniformity [75]. Slow heating and cooling increases tool costs. Cooling also takes place within the press platens with water or air channels and also on conduction to cool the polymer. The processing time is too high due to the large amount of time needed to heat and cool [76].

Thermoplastic polymers, which are difficult to process with injection molding due to their high viscous nature, can be processed with compression molding. Thermoplastic composites are more attactive due to their specific potential advantages such as reduced manufacturing time, less expensive storage of intermediate materials, reduced impact damage sensitivity, and possible remolding and recycling [77].

A large variety of applications has been developed based on the compression molding of fiberglass reinforced thermoplastics. Compression moldable fiberglass reinforced thermoplastic is a thermoplastic bulk molding compound (BMC). BMC is made by combining the thermoplastic and fiberglass roving in an extruder and collecting a molten charge, which is then transferred directly to a compression mold.

Stampable sheets are consolidated sheets of thermoplastic reinforced with randomly oriented, chopped and/or continuous fiberglass fibers. Prior to molding, these thermoplastic sheets are heated in an infrared oven above the melting point of the thermoplastic and then transferred hot into a cold compression mold.

Both the stampable sheet and thermoplastic BMC will yield a final part with significant increases in strength and stiffness over the thermoplastic. The random orientation of the fibers results in an isotropic composite with the same mechanical properties in all directions. In addition, the discontinuous fibers do not provide the level of reinforcement and improvement in mechanical properties as continuous fibers. Physical properties of composites vary almost directly with the density [78].

Sorbed moisture, acting as a plasticizer and crazing agent for the epoxy, deteriorates the mechanical and chemical integrity of the composite differently under certain temperature and moisture combinations. The damaging process is governed by the synergistic action of sorbed moisture and temperature leading to additional weight gains in samples exposed to cycling conditions of temperature.

Compression molding of fiberglass reinforced thermoplastic polymer uses two forms of raw materials for thermoplastic compression molding. The first form is a glass mat thermoplastic (GMT) sheet. Stampable sheets are consolidated sheets of thermoplastic reinforced with randomly oriented, chopped and/or continuous fiberglass fibers. Prior to molding, these thermoplastic sheets are heated in an infrared oven above the melting point of the thermoplastic and then transferred hot into a cold compression mold.

The second traditional form of a compression moldable fiberglass reinforced thermoplastic is a thermoplastic bulk molding compound, commonly referred to as a thermoplastic BMC. A thermoplastic BMC is made by combining the thermoplastic and fiberglass roving in an extruder and collecting a molten charge, which is then transferred directly to a compression mold.

A schematic of a heat press device is shown in Figure 10.9. The press device is equipped with a mold, a pair of steel blocks, whose temperature is controlled, and a lab jack with a pressure meter.

The melt process can be expected to alter the organization of this two-phase system from that generated by batch mixing followed by compression molding in at least two ways. The converging flow into the die followed by melt stretching will first of all affect the phase morphology by elongating the dispersed phase into long fibrils oriented in the direction of flow, whereas in the absence of this flow the dispersed phase forms domains of a more or less spherical nature.

10.8.9.1 Shortcomings

- Usual problems associated with thermal and thermo-oxidative degradation of individual polymers exist.

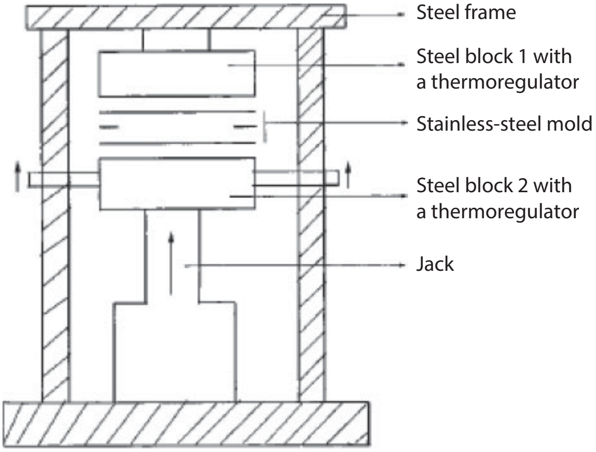

Figure 10.9 Schematic of a heat press device.

- Unexpected chemical and rheological problems can develop when certain materials are blended together.

10.8.10 Resin Transfer Molding

Resin transfer molding (RTM) is a manufacturing process for polymer composite materials, where pre-catalyzed resin is injected under pressure into the reinforcement preplaced in a closed mold. The composite part is demolded after the curing process. The actual molding operation and the design of the fibrous preform are independent, which offers engineers more freedom in designing the tooling and reinforcements. As a consequence of its flexibility, the process is regarded as one of the important processes to produce net-shape advanced polymer composites [79–81].

The RTM process offers important advantages to fabricators of fiberglass reinforced plastic parts compared to more labor-intensive processes such as hand lay-up or choppers [82, 83]. RTM permits a short cycle time with better control over mechanical properties, thickness and surface quality. There are reaction injection molding (RIM) styling panels that can serve as the exterior appearance part as well as the support for the interior headliner and overhead console/radio. RIM is chosen for several reasons.

In the RTM process, preformed fiber mats and/or woven rovings are first laid in a mold cavity. Catalyzed resin is then injected into the mold through a properly positioned injection port. The injection is stopped when the mold is completely filled with the resin, and the part is subsequently cured at room temperature. The molds for RTM usually consist of two top and bottom parts which are tightly pressed together and sealed around the edges during the injection process. Typically, the injection ports are found at the lower centers of the molds. One or more air vents are located around the mold edges. One of the important tasks in mold design is to position the injection ports and the air vents so that the molds will be filled completely without using excessive pressure. Other tasks include estimating mold distortion and minimizing required clamping forces. Successful completion requires process control and optimization [84–86] and part prices cost more than in the SMC process. The RTM process could not readily meet production volumes; and parts made from the RIM process could not meet the self-supporting requirements for large hinged panels. Neither RIM nor thermoformed parts could meet the thermal expansion limitations for the design.

Resin transfer molding (RTM) is an efficient process for manufacturing polymer composite structures. The RTM process involves liquid thermoset resin being injected into a mold cavity containing a preplaced dry fabric preform. Due to relatively low injection pressure applied during processing, this technique is expected to offer potential for cost reduction in the fabrication of large parts of complex shape. This process requires much time spent in optimizing processing parameters and in properly designing the mold in order to avoid problems such as void formation and dry spots. The useful set of parameters is the trial-error tactic based on molding experiments and on know-how. This tactic makes the process development expensive.

10.9 Wood-Polymer Composites

Most wood-polymer composites are manufactured with wood flour by injection molding or extrusion. Making composites with large particles is difficult with both processes. The influence of particle size on the mechanical strength, especially on the bending strength of WPCs, is great.

There have been problems associated with wood-polymer composites, including poor fiber dispersion caused by intermolecular hydrogen bonding [87] and wide polarity differences of the surfaces that prevent efficient polymer/fiber bonding [88, 89]. Lignocellulosic materials have been chemically modified to both increase their hydrophobicity [90] and improve their dimensional and thermal stability [91].

One of the major challenges for wood polymer is to optimize the processing operations of the wood-filled plastics to reduce costs and compete with solid wood and conventional wood composite products. Wood-polymer composites are primarily produced with high filler loading. The engineering design of extrusion operations requires proper knowledge of the flow mechanism of these highly filled melts. The formulating of wood plastic formulations also requires reliable evaluation of flow performance of the composite melts.

Wood-polymer composite (WPC) with large wood particles could be successfully prepared by a flat-platen pressing process. It shows better strength properties than that with small particles.

10.9.1 Injection Molding

Injection molding of WPC is not very different from conventional injection molding, but attention must be given to some details. Before the processing, the material must be thoroughly dried in order to avoid swelling of the product after processing.

In wood composites, the thermal degradation of wood flour deteriorates the mechanical properties. Thermal degradation changes the surface chemistry and might cause changes in the wood-polymer bonding that is responsible for the inferior properties of the composites. It also deteriorates toughness and bending strength. In polypropylene-wood composites, the loss in properties occurs after extrusion at 250 °C [92]. The volatiles at processing temperatures of 200 °C also result in thermal degradation. The volatiles lead to porous polymer products with lower densities and inferior mechanical properties.

10.9.2 Extrusion

Extrusion is by far the most common processing method for wood-polymer composites, so processors use a variety of extruder types and processing strategies. Injection or compression molding has advantages when processing of a continuous piece is not desired or a more complicated shape is needed, but the total weight is much less than that produced by extrusion.

The WPC processing is rather challenging because the increase of temperature due to shear heating, high melt viscosity, and low melt strength, leads to poor extrusion quality. To overcome this difficulty, very high molecular weight processing aids will be beneficial. However, it has been proven that their chemical composition is a critical parameter [93]. The manufacturing techniques of wood-polymer composites and wood-polymer composites are entirely different [94–102].

Extrusion is used in the manufacture of WPC products as continuous process. Manufacturing by extrusion has recently experienced dramatic growth and there has been active use of WPC [103, 104].

The manufacture of thermoplastic composites is often a two-step process. The raw materials are first mixed together in a compounding process, and the compounded material is then formed into a product. Manufacturing options for wood-thermoplastic composites include sheet or profile extrusion, injection molding, calendering, thermoforming and compression molding.

When fillers are added to either an extrusion or injection molding process, changes occur which alter the processing parameters, fiber orientation, and mechanical properties of the product. Similar to extrusion processes, filled polymers have higher melt viscosities and temperatures, increased fiber damage during mixing and molding, and a decrease in melt strength. Other issues associated with molding, such as skin-core behaviors and fiber orientation, are important issues for injection-molded filled thermoplastics [105].

The WPCs use extrusion technology as the major manufacturing process. A two-step process consisting of pelletizing the blend before extrusion persists as the most widely used method of manufacturing WPC pelletized compounds that have a higher degree of filler dispersion uniformity. It allows better control of wood fiber moisture content. Residual moisture in the fibers remains one of the biggest concerns in the manufacturing of WPCs. Drying of the fibers before processing and keeping the compounded feedstock sealed off from atmospheric moisture remain necessary steps. It is not only done to ease the manufacturing process but also to enhance the quality and mechanical performance of the products.

Vacuum drying technology is the best suited method for drying wood flour. Vaccum dryers dry wood flour more efficiently even with high moisture content. Counter-rotating twin screw extruders (both conical and parallel) and planetary extruders use a unique heating and single or dual venting system for in-line drying of the filler and venting of moisture during the extrusion process.

Direct extrusion process is claimed to have a much lower energy requirement due to lack of cooling and remelting of precompounded pellets. It has a higher degree of process variations, particularly in ensuring a constant production of fillers with low moisture content. During production, WPC products lie in cooling that has an effect on the output. Faster cooling of the product results in higher output rates. The higher specific heat of wood compared to that of polymer makes WPC products more difficult to cool than unfilled polymer. High-intensity spray cooling tanks provide a higher throughput than that obtained by adapting other cooling equipment. Spray cooling removes heat through evaporation and cools much faster than immersion cooling.

One of the technical challenges of compounding and processing WPCs is precision feeding into standard blenders or extruders due to the inconsistent bulk density and broad particle size distribution of wood flour. Gravimetric or vertical crammer feeding systems are specifically designed for the precise dosing of large quantities of polymer additives and wood flour to over feeding limitations. Screw design and element geometries meet WPC production goals to optimize mixing and shear forces to achieve the highest possible productivity. Injection molding of WPCs is proportionally smaller compared with extrusion.

10.9.3 Microcellular Foam Process

Foaming can reduce material cost and enhance sound absorption [106] and thermal insulation through making cells inside plastic matrices. It has been used in some applications, but reduced mechanical properties prevent it from being applied to the areas that require strength. This is mainly because foamed cells are too big and/or unequally distributed over the product.

Microcellular foaming is in the spotlight as a problem solver. As its name implies, the cell size is about 10 microns or smaller and nucleated cells are equally distributed over the products. Therefore, microcellular plastics have improved mechanical strength when compared with conventionally foamed polymer [107].

Foaming technology, such as microcellular foaming, enhances the ductility and impact resistance of polymer matrices while also providing a significant expansion ratio and weight reduction in plastic parts. The high expansion ratio induced by foaming generally reduces the material cost and consumption in mass-produced plastic parts without a major compromise to the required properties [108].

The microcellular foaming process dissolves an inert gas into a plastic to create a swarm of bubbles. Microcellular plastics, produced first in a batch process, involve a solid sample placed into a chamber under high pressure in an inert gas atmosphere (e.g., CO_2, N_2, etc.), wherein gas molecules diffuse into the polymer, forming a single-phase solution. Subsequently, nucleated and grown cells form by creating a thermodynamic instability (i.e., sudden pressure drop and/or temperature increase).

The basis for the continuous microcellular process lies in the concept of thermodynamic instability to promote high cell nucleation rates in a flowing polymer matrix. These high nucleation rates involve first forming a polymer/gas solution under high pressure, followed by rapidly decreasing the solubility of gas in the polymer by a rapid pressure drop and/or a rapid temperature increase [110].

Microcellular foams are characterized by a cell size less than 10 μm and a cell density greater than 10^9 cells/cm^3. Because of this unique structure, microcellular polymers offer superior mechanical properties, such as impact strength, toughness, and fatigue life, when compared with unfoamed polymers [111–117]. Microcellular foams also show a good light-reflecting ability [118].

Microcellular foams have been produced by various processes such as batch processing [119, 120], extrusion [110, 121], injection molding [122], and so on. The extrusion process has especially caught people's attention because of its high productivity compared to batch processes. Many factors affect the cell nucleation and expansion behaviors of microcellular foams. First, different types of blowing agents behave differently in the polymer matrix because of their different solubilities and diffusivities. Inert gases, such as CO_2, have high diffusivities and low solubilities, whereas long-chain molecules, such as butane, have low diffusivities and high solubilities [123]. High solubility and low diffusivity are favorable for expansion by increasing the amount of gas dissolved in the polymer matrix and retarding gas loss that occurs through diffusion out of the foam [124].

The die pressure is another important factor that affects microcellular foams. The die pressure must be higher than the solubility pressure, i.e., the pressure required for the injected blowing agent to be dissolved completely in the polymer matrix [125]. An insufficient pressure cannot form a one-phase polymer-gas solution, and this results in undesirable large voids in the foams due to undissolved gas pockets. The pressure-drop rate across the nucleation device also plays an important role in cell nucleation. The expansion behavior of foams is governed by different factors depending on the die temperature: loss of blowing agents at high temperatures and crystallization/stiffening of the polymer matrix at low temperatures.

Polymer foaming is a simple polymer processing technique (Figure 10.10) that can be used to create voids in polymer materials. Polymeric foams exhibit excellent properties, including low weight-to-volume ratios, electric resistivity, shock absorbance, heat insulation, and sound absorption [126]. Polymer foaming processes have historically involved using chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) as blowing agents for creating voids in polymers [127]. However, due to the potential

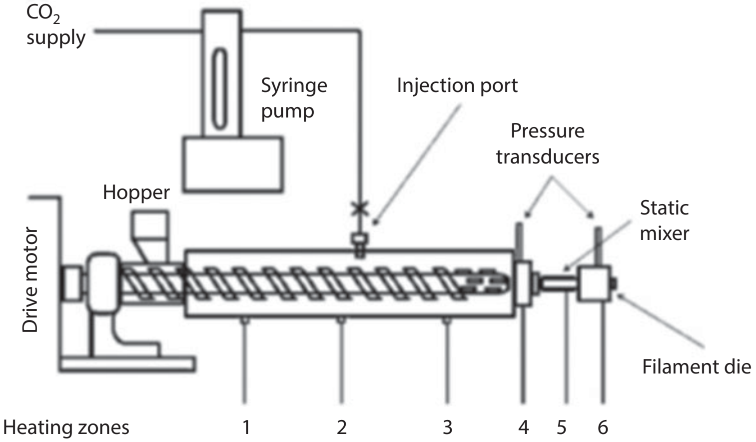

Figure 10.10 Schematic representation of single screw foam process. (Reprinted with permission from [109]; Copyright © 2010 American Chemical Society. All rights reserved)

for these compounds to deplete atmospheric ozone, the use of CFCs and HCFCs was restricted in 1987 by the Montreal Protocol on Substances that Deplete the Ozone Layer, and these agents are now monitored by the Rigid and Flexible Foams Technical Options Committee of the United Nations Environmental Program [128]. Currently, environmentally benign blowing agents are being researched by manufacturing companies.

Carbon dioxide (CO_2) has been identified as one possible candidate for replacing CFCs and HCFCs. Whereas CO_2 does not deplete the ozone layer, its solubility in polymers is low compared to CFCs and HCFCs. More specifically, the amount of pressure required to dissolve CO_2 in polystyrene (PS) at 100 °C is four times the pressure needed for the traditional organofluorine compound [129]. To achieve a high number density of CO_2 bubbles in the polymer matrix, bubble nucleation agents were used to facilitate the bubble nucleation and obtain a high number density of bubbles in the final foamed product. Several bubble nucleation agents are commercially available and have been investigated in regard to their ability to enhance bubble nucleation [130, 131].

10.10 Recycling

Research efforts to improve the compression resistance of the composite materials have mainly focused on the following areas: (i) increasing the resin modulus; (ii) enhancing the fiber-matrix interface; (iii) optimizing the fiber orientation; and (iv) introducing prestrain to fabrication processes and embedding the prestrain to leave the composite materials in tensile state [132].

Thermoset resins cannot be remelted or reformed because of their network structure. Incineration is not the best method for treating nonmetals because of inorganic fillers such as glass fiber, which significantly reduces the fuel efficiency. Disposal in landfill is the main method for treating nonmetal parts of PCBs, but it may cause secondary pollution and resource wasting. Yokoyama and Iji have carried out many studies on the recycling of fiberglass-resin powder taken from PCBs [133, 134]. In their studies, nonmetals reclaimed from waste PCBs could be used as fillers for other products such as construction materials, decorating agent, adhesives, and insulating materials. There are new methods in which nonmetal waste is used to make formative models, compound boards, or related products [135].

Thermoset polymer composites are crosslinked and therefore cannot be softened or remolded by heating again during processing and molding. Chemical additives (mostly in minor quantities) are generally incorporated into thermosets and also thermoplastic polymers. The thermoset polymer composites are processed with resins. During processing, upon complete polymerization the composite becomes infusible solids that will not soften when heated. Polymerization can be attained in two ways, namely:

- Initial application of heat;
- Use of a chemical accelerator.

Composites from thermosetting resins reinforced with high-performance fibers are replacing light metals in weight-sensitive industrial applications. Structural composites are load-bearing materials in which fibers or particles have been introduced into a matrix by improvements in methods of manufacture and enhancement in mechanical properties.

10.11 Summary

- Processing uses a mold or an extrusion die.
- The temperature of blending, screw speed, and optimum concnetation of blend is important.
- There is a physical change from solid to shapes by melting.

- During processing in extrusion or injection molding, the main cost consumption is the power consumed by the extruder in turning the screw.
- Basically, shear viscosity is indicated by melt flow index or melt elasticity during the processing.
- Fabrication into useful articles is normally done in the same melt processing machinery used with pure polymers.
- Melt filtration, melt pump, and static mixer can have significant impact on the quality of the melt stream of blend components.
- Blend with higher or lower thermal stability than the components, could lead to miscibility (interaction) or lack of interaction between the blend components, respectively.
- Product with thermal stability between the components, may indicate improvement of the properties of one of the blend components [136].
- Trial and error experiments involve the variation of processing conditions and/or mold design until the part perfection is achieved.

References

1. Liang, J.Z., *Plast. Rubber Compos. Proc. Appl. 1*8, 311, 1992.
2. Bertin, S. and Robin J.-J., *Eur. Polym. J.* 38, 2255–2264, 2002.
3. Biesenberger, J.A. and Sebastian, D.H., *Principles of Polymerization Engineering*, John Wiley & Sons: New York, 1983.
4. Paul, D.R. and Bucknall, C.B., *Polymer Blends*, Wiley & Sons: New York, 2000.
5. Lebovitz, H., Khait, K., and Torkelson, J.M., *Macromolecules* 35, 8672, 2002.
6. Keskula, H. (Ed.), *Polymer Modification of Rubbers and Plastics*, Appl. Polym. Symp. No. 7, Wiley Interscience: New York, 1968.
7. Bruins, P.F. (Ed.), *Polyblends and Composites*, Appl. Polym. Symp. No. 15, Wiley Interscience: New York, 1970.
8. Platzer, N.A.J. (Ed.), *Multicomponent Polymer Systems*, Adv. Chem. Ser. No. 99, American Chemical Society: Washington, DC, 1971.
9. Molau, G.E. (Ed), *Colloidal and Morphological Behaviour of Block and Graft Copolymers*, Plenum Press: New York, 1971.
10. Sperling, L.H. (Ed.), *Recent Advances in Polymer Blends, Grafts, and Blocks*, Plenum Press: New York, 1974.
11. Platzer, N.A.J. (Ed.), *Copolymers, Polyblends, and Composites*, Adv. Chem. Ser. No. 142, American Chemical Society: Washington, DC, 1975.
12. Klempner, D. and Frisch, K.C. (Eds.), *Polymer Alloys: Blends, Blocks, Grafts, and Interpenetrating Networks*, Plenum Press: New York, 1977.

13. Manson, J.A. and Sperling, L.H., *Polymer Blends and Composites*, Plenum Press: New York, 1976.
14. Bucknall, C.B., *Toughened Plastics*, Applied Science Publishers: London, 1977.
15. Paul, D.R. and Newman, S. (Eds.), *Polymer Blends*, vol. I and II, Academic Press: New York, 1978.
16. Cooper, S.L. and Estes, G.M. (Eds.), *Multiphase Polymers*, Adv. Chem Ser. No. 176, ACS, 1979.
17. Paul, D.R. and Barlow, J.W., *J. Macromol. Sci. Rev., Macromol. Chem. C* 18, 109, 1980.
18. Paul, D.R. and Bucknall, C.B., *Polymer Blends*, vol. 1: Formulation, 2nd ed., Wiley: New York, 2000.
19. Elyashevich, G.K., Sidorovich, A.V., Smirnov, M.A., Kuryndin, I.S., Bobrova, N.V., Trchová, M., Stejskal, J., *Polym. Degrad. Stab.* 91, 2786–2792, 2006.
20. Omastova, M., Podhradska, S., Prokes, J., Janigova, I., and Stejskal, J., *Polym. Degrad. Stab.* 82, 251–256, 2003.
21. Tadmor, Z. and Gogos, C.G., *Principles of Polymer Processing*, John Wiley & Sons: New York, 1979.
22. Rubin, R., *Injection Molding Theory and Practice*, Wiley: New York, 1972.
23. Bright, P.F., Croson, R.J., and Folkes, M.J., *J. Mater. Sci.* 13, 2497–2506, 1978.
24. Allan, P.S. and Bevis, M.J., *Plast. Rubb. Comp. Proc. Appl.* 7, 3–10, 1987.
25. Kalay, G., Allan, P.S., and Bevis M.J., *Plast. Rubb. Comp. Proc. Appl.* 23, 71–85, 1995.
26. Kamal, M.R. and Ryan, M.E., *Polym. Eng. Sci.* 20, 859, 1980.
27. Wolff, T.J., *Polym. Plast. Technol. Eng.* 11, 117, 1978.
28. Sneller, J., *Mod. Plast.* 56, 44, 1979.
29. Igarashi, T., Kondo, S., and Kurokawa, M., *Polymer* 20, 301, 1979.
30. Koroneos, E.G., *Colloid. Polym. Sci.* 256, 741, 1978.
31. Kleinemeier, B. and Menges, G., *SPE ANTEC Tech. Papers* 23, 7, 1977.
32. Han, C.D. and Lem, K.W., *J. Appl. Polym. Sci.* 28, 3155, 1983.
33. Zagal, A., Vivaldo-Lima, E., and Manero, O., *Ind. Eng. Chem. Res.* 44, 9805–9817, 2005.
34. Chuai, C.Z., Almdal, K., and Lyngaae-Jørgensen, J., *Polymer* 44, 481–493, 2003.
35. Tadmor, Z., *Polym. Eng. Sci.* 6, 185, 1966.
36. Tadmor, Z. and Kletin, I., in: *Engineering Principles of Plasticating Extrustion*, Reinhold Book Co.: Florida, 1970.
37. Gogos, C.G., Tadmor, Z., and Kim, M.H., *Adv. Polym. Techn.* 17, 286, 1998.
38. Rozant, O., Bourban, P.E., and Månson, J.A.E., *Compos. Part A: Appl. Sci. Manuf.* 32, 1593–1601, 2001.
39. Breuer, U., Ostgathe, M., and Neitzel, M., *Polym. Compos.* 19, 275–279, 1998.
40. Xanthos, M. (Ed.), *Reactive Extrusion: Principles and Practice*, Hanser Publishers: Munich, 1992.
41. Lambla, M., Reactive processing of thermoplastic polymers, in: *Comprehensive Polymer Science*, 1st suppl., p. 619, Pergamon: New York, 1992.

42. Groeninckx, G., Harrats, C., and Thomas, S., in: *Reactive Polymer Blending*, W. Baker, C. Scott, G.-H. Hu, K.S. Hyun (Eds.), Hanser Publishers: Munich, 2001.
43. Menges, G., Berghaus, U., Kalwa, M., and Speuser, G., *Kunststoffe Germ. Plast.* 79, 40, 1989.
44. Tzoganakis, C., *Adv. Polym. Technol.* 9, 321, 1989.
45. Balke, S.T., Suwanda, D., and Lew, R., *J. Polym. Sci. Polym. Lett.* 25, 313, 1987.
46. Suwanda, D., Lew, R., and Balke, S.T., *J. Appl. Polym. Sci.* 35, 1019–1033, 1988.
47. Pabedinskas, A., Cluett, W.R., and Balke, S.T., *Polym. Eng. Sci.* 29, 994, 1989.
48. Jo, W.H., Park, C.D., and Lee, M.S., *Polymer* 37, 1709, 1996.
49. Manning, S.C. and Moore, R.B., *Polym. Prepr.* 38, 390, 1997.
50. Dionisi, R.A., Villar, M.A., Failla, M.D., and Vallės, E.M., *Polym. Prepr.* 39, 134, 1998.
51. Suwanda, D. and Balke, S.T., *ANTEC '89*, 589–592, 1989.
52. Haralabakopoulos, A.A., Tsiourvas, D., and Paleos, C.M., *Polym. Prepr.* 38, 168, 1997.
53. Taha, M., Perrut, V., Roche, A.A., and Pascault, J.P., *J. Appl. Polym. Sci.* 65, 2447, 1997.
54. Guo, B. and Chan, C.M., *J. Appl. Polym. Sci.* 71, 1827, 1999.
55. Tucker, C.S. and Nichols, R.J., *Plast. Eng.* 43, 27, 1987.
56. Coudray, S., Pascault, J.P., and Taha, M., *Polym. Bull.* 32, 605, 1994.
57. Höcker, H., Michaeli, W., Grefenstein, A., Frings, W., and Ortmann, R., *Polym. Prepr.* 37, 626, 1996.
58. Paul, D.R., in: *Advances in Polymer Blends and Alloys Technology*, K. Finlayson (Ed.), vol. 4, Technomic: Lancaster, PA, 1993.
59. Plochocki, A.P., *Polym. Eng. Sci.* 23, 618, 1983.
60. Utrachi, L.A., *Polymer Alloys and Blends: Thermodynamics and Rheology*, Hanser: New York, 1989.
61. Chaudhry, B.I., Hage, E., and Pessan, L.A., *J. Appl. Polym. Sci.* 67, 1605, 1998.
62. Hsiao, S.W. and Kikuchi, N., *Comput. Meth. Appl. Mechan. Eng.* 177, 1–34, 1999.
63. Ide, F. and Hasegawa, A., *J. Appl. Polym. Sci.* 18, 963, 1974.
64. Groeninckx, G., Harrats, C., and Thomas, S., in; *Reactive Polymer Blending*, W. Baker, C. Scott, G.-H. Hu, K.S. Hyun (Eds.), pp. 44–81, Hanser Publishers: Munich, 2001.
65. Hu, G.-H. and Cartier, H., *J. Appl. Polym. Sci.* 71, 125, 1999.
66. Tan, A.-R., Hu, G.-H., Wang, W., de Souza Gomes, A., *Eur. Polym. Sci.* 35, 1979, 1999.
67. Zhou, W., Dong, J.H., Qiu, K.Y., and Wei, Y., *J Polym Sci: Part A* 36, 1607, 1998.
68. Barton, M.J., Hamerton, I., Howlin, B.J., and Liu, S., *Polymer* 39, 1929, 1998.
69. Loos, J., Hofman, T.S.J., Peijs, T., and Lemstra, P.J., *Polymer* 42, 3827, 2001.

70. Amornsakchal, T., Bassett, D.C., Olley, R.H., Hine, P.J., and Ward, I.M., *J. Appl. Polym. Sci.* 78, 787, 2000.
71. Houshyar, S. and Shanks, R.A., *Macromol. Mater. Eng.* 288, 599, 2003.
72. Thomason, J.L., *Composites* 26, 467, 1995.
73. Kitayama, T., Ishikura, K., Hamada, H., Kikutani, T., and Ito, H., *59th Ann. Tech. Conf.: Soc. Plast. Eng.* 2, 1972, 2001.
74. Hine, P.J., Ward, I.M., Jordan, N.D., Olley, P., and Bassett, D.C., *J. Macromol. Sci. Phys. B* 40, 959, 2001.
75. Upadhyay, R.K., *Adv. Polym. Technol.* 8, 243, 1988.
76. Miller, K. and Ramani, K., *Adv. Polym. Tech.* 17(3), 251–257, 1998.
77. Cinquin, J., Chabert, B., Chauchard, J., Morel, E., and Trotignon, J.P., *Composites* 21(2), 141, 1990.
78. DeBell, G.W., Plastics in aircraft construction. *Aircr. Eng. Aerosp. Tec.* 14, 254–259, 1942.
79. Johnson, C.F., Chavka, N.G., and Jeryan, R.A., in: *Proceedings of the SPI Conference*, January, 1986.
80. Krolewski, S. and Busch, J., in: *Proceedings of the 35th International SAMPE Symposium*, p. 1761, 1990.
81. Foley, M.F., *SAMPE Quarterly* (Jan.), 61, 1991.
82. Gali, E., Resin transfer molding: A cost effective alternative. *Plastic Design Forum*, 47–56, 1982.
83. Law, C., New directions for reinforced plastics. *Canadian Plastics*, 30–35, 1982.
84. Gauvin, R., and Chibani, M., *Int. Polym. Proc.*1, 42, 1986.
85. Gauvin, R., Chibani, M., and Lafontaine, P., *J. Reinf. Plast. Compos.* 6(4), 367, 1987.
86. Gonzalez, V.M., Castro, J.M., and Macosko, C.W., *Polym. Proc. Eng.* 3, 173, 1985.
87. Raj, R.G., Kokta, B.V., Maldas, D., and Daneault, C., *J. Appl. Polym. Sci.* 37, 1089–1103, 1989.
88. Maldas, D., Kokta, B.V., and Daneault, C., *J. Appl. Polym. Sci.* 37, 751–775, 1989.
89. Harper, D. and Wolcott, M., *Composites A* 35, 385–394, 2004.
90. Tronc, E., Hernández-Escobar, C.A., Ibarra-Gómez, R., Estrada Monje, A., Navarrete-Bolaños, J., and Zaragoza-Contreras, E.A., *Carbohydr. Polym.* 67, 245–255, 2007.
91. Rowell, R.M., *Forest Prod. Abstr.* 6, 363–382, 1983.
92. Takase, S., and Shiraishi, N., *J. Appl. Polym. Sci.* 37, 645, 1989.
93. Azimipour, B. and Schipper, P., Acrylic processing aids: Keys to the future. *SPE Vinyltec*, 337–343, 2002.
94. Schnieder, M.H., *Wood Fiber Sci.* 26, 142, 1994.
95. Schnieder, M.H., *Wood Sci. Technol.* 29, 121, 1995.
96. Meyer, J.A., *Forest Prod. J.* 15, 362, 1995.
97. Wang, P., *J. Chin. Chem.* Soc. 22, 77, 1975.

98. Hebeish, A. and Guthrie, J.T., *Polymer/Properties and Applications*, Springer-Verlag: New York, 1981.
99. Witt, A.E., *Radiat. Phys. Chem.* 18, 67, 1981.
100. Meyer, J.A., *Wood Sci. Technol.* 14, 49, 1981.
101. Meyer, J.A., *Forest Prod. J.* 32, 24, 1982.
102. Meyer, J.A., *Technologist* 1(3), 4, 1987.
103. Clemons, C., *Forest Prod. J.* 52(6), 10, 2002.
104. Jiang, H. and Kamdem, D.P., *J. Vinyl Addit. Technol.* 10(2), 59–69, 2004.
105. Wolcott, M.P., Production methods and platforms for wood plastic composites, in: Non-Wood Substitutes for Solid Wood Products Conference, 2003.
106. Kawai, T., *Nanotechnology*, Japanese Engineering Investment Society, Japan, 2002.
107. Okamoto, K.T., *Microcellular Processing*, Hanser Gardener Publications, Inc.: Cincinnati, 2003.
108. Martini, J.E., Suh, N.P., and Waldman, F.A., Microcellular closed cell foams and their method of manufacture, US Patent 4473665, 1984.
109. Matuana, L.M. and Diaz, C.A., *Ind. Eng. Chem. Res.* 49, 2186–2193, 2010.
110. Park, C.B., Baldwin, D.F., and Suh, N.P., *Polym. Eng. Sci. 35*, 432, 1995.
111. Baldwin, D.F. and Suh, N.P., Microcellular poly(ethylene terephthalate) and crystallizable poly(ethylene terephthalate): Characterization of process variables. *SPE ANTEC Technol. Pap.* 38, 1503, 1992.
112. Collias, D.I., Baird, D.G., and Borggreve, R.J.M., *Polymer* 25, 3978, 1994.
113. Collias, D.I. and Baird, D.G., *Polym. Eng. Sci.* 35, 1167, 1995.
114. Seeler, K.A., Kumar, V., *J. Reinf. Plast. Compos.* 12, 359, 1993.
115. Matuana, L.M., Park, C.B., and Balantinecz, J.J., *Cell. Polym.* 17, 1, 1998.
116. Matuana, L.M., Park, C.B., Balantinecz, J.J., *Polym. Eng. Sci.* 37, 1137, 1997.
117. Shimbo, M., Baldwin, D.F., and Suh, N.P., *Polym. Eng. Sci.* 35, 1387, 1995.
118. Kabumoto, A., Yoshida, N., Itoh, M., and Okada, M., Light reflecting plate, US Patent 5844731, 1998.
119. Matini, J., Waldman, F.A., and Suh, N.P., The production and analysis of microcellular thermoplastic foams. *SPE ANTEC Technol. Pap.* 28, 674, 1982.
120. Liang, M. and Wang, C., *Ind. Eng. Chem. Res.* 39, 4622, 2000.
121. Xu, X., Park, C.B., Xu, D., and Pop-Iliev, R., *Polym. Eng. Sci.* 43, 1378, 2003.
122. Xu, J., Method for manufacturing foam material including systems with pressure restriction element, US Patent 6322347, 2001.
123. Gendron, R. and Daigneault, L.E., *Polym. Eng. Sci.* 43, 1361, 2003.
124. Park, C.B., Behravesh, A.H., and Venter, R.D., *Polym. Eng. Sci.* 38, 1812, 1998.
125. Park, C.B., Suh, N.P., *Polym. Eng. Sci.* 36, 34, 1996.
126. Lee, S.-T., *Foam Extrusion*, Technomic Publishing Company, Inc.: PA, 2000.
127. Han, C.D. and Ma, C.Y., *J. Appl. Polym. Sci.* 28, 2961, 1983.
128. Ashford, P. and Guzman, M.W.Q., *J. Cell. Plast.* 40, 255, 2004.
129. Sato, Y., Iketani, T., Takishima, S., and Masuoka, H., *Polym. Eng. Sci.* 40, 1369, 2000.
130. Yang, H.H. and Han, C.D., *J. Appl. Polym. Sci.* 29, 4465, 1984.

131. Marrazzo, C., Di Maio, E., and Iannace, S., *Polym. Eng. Sci.* 48, 336, 2008.
132. Cheng, X.B., The development of advanced structural composite. *Materials Eng.* 6, 5–9, 1996.
133. Yokoyama, S. and Iji, M., Recycling of thermosetting plastics waste from electronic component production processed, in: *Proceedings of 1995 IEEE International Symposium on Electronics*, pp. 132–137, IEEE: New York, 1995.
134. Iji, M., *J. Mater. Sci.* 33, 45–53, 1998.
135. Mou, P., Xiang, D., Pan, X., Wa, L., Gao, J., and Duan, G., New solutions for reusing nonmetals reclaimed from waste printed circuit boards, in: *Proceedings of the 2005 IEEE Interantional Symposium on Electronics*, pp. 205–209, IEEE: New York, 2005.
136. Zheng, S., Guo, Q., and Mi, Y., *Polymer* 44, 867, 2003.

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11

Blends, Composites and the Environment

In polymer systems, modification is carried out with polymer-polymer blends, composites, and polymer foams. These are the three types of important modified polymer systems. The mixtures resulting from these systems are unique microstructures or macrostructures responsible for end product properties. Enhancing the properties of polymer systems and upgrading them with synthesis is an interesting solution, but it is limited by compatibility considerations.

Synthetic polymers are non-biodegradable and exist in the environment as waste polymers. The majority of polymeric materials are burned or landfilled. Recycling of polymers is limited because it is not commercially viable to sort out the waste from the waste stream. As one solution to this situation, published research states that polymer can be mixed with tar or bitumen for future use as road laying or pavement blocks. In such a case, only 1–2% polymer waste of one kind is mixed as contaminant. Life cycle analysis has not yet been done to assess the environmental impacts of these materials over their entire life time and any permanent damage done to the environment by enhancing the life of polymer with black colored tar, which already contains organic materials, without any degradation.

Household plastic wastes comprise very dissimilar generic polymers. The polyolefins are the main components; other polymers such as PS, PET and PVC make up the remaining part, possibly with minor quantities of polyamide, polycarbonate, and acrylic polymers. Even the contaminant of the waste has to be made with great efforts in order to prohibit an irreversible buildup of materials in the environment. The safety and acceptability of disposal of polymer wastes have relied upon polymer blending and composite manufacturing for a long time. No universal waste treatment or immobilization process is expected to handle all the variations in waste from polymer blends/composites in an economical way.

11.1 Recycling of Polymer Wastes

Polymer wastes generation all over the world has become a great concern due to the biological and environmental issues [1, 2]. Recycling could be a reasonable solution for overcoming the problem. Polymers wastes can offer an economic source of raw materials and can be substituted with pure polymers in some applications [3]. Polymers, such as polyethylene, occur in plastic scrap and waste. Such low-cost material affects their possible reuse [4, 5].

Polymer blends and composites meet the requirements of being a good balance between processability and properties, which allows reuse of waste polymers; however, upgrading is absolutely necessary in a recycled material. The phase behavior is considered not in terms of temperature and pressure effects, but rather in terms of chemistry.

Recycling is an environmentally friendly procedure and can be replaced with conventional routes for waste disposal such as landfilling and incineration [6–8]. However, as the volume of polymer wastes progressively increases, it is necessary to find new applications for the use of post-consumer polymers.

Polymer wastes conversion into use as polymer blends is an important factor in satisfying the needs of specific sectors of the polymer industry. In polymer wastes, the variation of melting temperature with composition has a strong positive deviation for blends. Polymer blends meet the performance demands that cannot be satisfied by the individual polymers of the blend. Polymer blends and composites increase with the increasing range of applications for the class of materials [9, 10].

Tailoring the properties of waste polymers is used in order to manufacture blends and composites. Therefore, it is used in a wide range of applications with a predetermined service life for the materials. This has become increasingly important for degradation and recycling in order to avoid the environmental burden of waste polymers.

There are four different strategies to manufacture blends and composites from waste polymers:

1. The use of cheap, synthetic, commodity bulk polymers such as PE, PP, etc.
2. Chemical modification of the main chain of synthetic polymers by the introduction of functional groups to be compatible with improvement in properties.
3. The use of biodegradable polymers, such as poly(hydroxyalkanoate) (PHA), and their derivatives in large-scale manufacture with synthetic polymers.
4. Tailor-make new hydrolyzable structures, e.g., polyesters, polyanhydrides and polycarbonates, to manufacture blends and composites.

11.2 Polymer Blends and Composites Recycling

Polymer blends and composites do not biodegrade, nor are they easy to reduce in size because of embedded reinforcing agents. They cause compaction problems in a landfill. Furthermore, they are a very stable compound, in some cases with crosslinking. Burning them produces acidic and poisonous gases.

The economy of polymer waste recycling may rely on low-cost compatibilization [11]. Polymer wastes contain a large proportion of highly inert polyolefins such as PE, PP and PS. The compatibilization of two or more of these polymers will be potentially useful for the development of a competitive recycling method [12, 13].

11.2.1 Pyrolysis

Pyrolysis is a process that has its roots in oil cracking. The heating of hydrocarbons in the absence of oxygen cracks the organic molecules into smaller hydrocarbons. The oil and gases can often be used as fuels. Polymer blends and composites are used for energy instead of being recycled through pyrolysis. They are too difficult for most recycling methods. Pyrolysis requires granulation and heat. Polymer blends are mixed with the high organic material with high fuel oil. Fibers and usable hydrocarbon oils from the polymer composites are the final result in pyrolysis. The pyrolysis process is economical but at the same time it is difficult to recycle composites subjected to pyrolysis in traditional recycling manners. There are even many composites which are not possible to subject to pyrolysis. With polymer composites, high pressure steam instead of pyrolysis releases glass, carbon fiber and filler which come out relatively clean; the polymer causes thermal degradation and may not be useful for recycling.

11.2.2 Energy Conversion

Recycling methods such as energy conversion are only significant where disposal is prohibitive. Therefore, the interest and growth of such recycling is minimal. The residual fuel value of the polymer blends and composites can be utilized as one of the several recycling streams. However, there are shortcomings such as:

- Handling and collection cost is not economical in the case of blends and composites;
- There is a high level of polymer in polymer blends and low level resin in most of the polymer composites with reinforcing agents;
- Other polymers than composites offer a higher energy from scrap.

Using polymer blends for energy conversion ends in hydrocarbons and some ash of additives or coupling agents present in them, whereas using composites for energy conversion ends in ash that must still be processed or disposed of. There are so many cleaner fuels that it is unlikely this will be the method of choice unless other recycling tactics fail.

11.2.3 Recycling of Polymer Composites

Recycling of polymer composites has significant effects on mechanical properties and blend morphology [14–17]. Composites are reduced in two stages (Figure 11.1), namely, shredding and granulation, during recycling process to be carried out.

11.2.4 Grinding

Grinding is one of the recycling strategies used to grind composite into fine powder. It can also be used in composite manufacturing. The grinding of glass is not so simple. Because it is difficult to grind, glass is used along

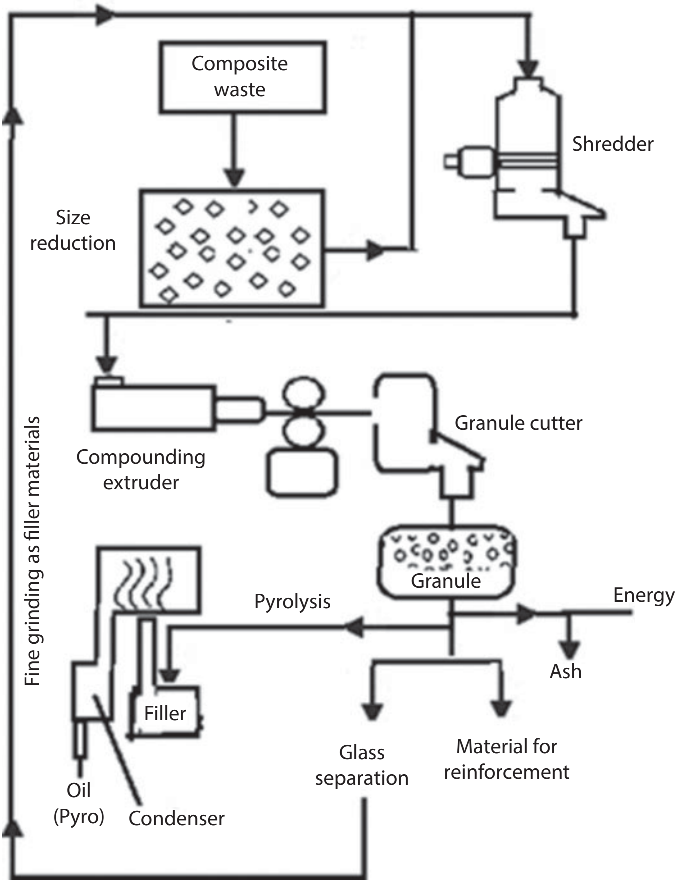

Figure 11.1 Recycling of polymer composite waste: a simple flow diagram showing the recovery of reinforcing agents.

with mineral fillers and causes resin problems to expand exponentially. The heat produced during grinding can cause the mix to burn. The reinforcing agent tends to break down rapidly without causing any burn to its original size, while the glass remains too large and with an aspect ratio that requires extra resin for wet out. This may make thermoset composites economically acceptable, but may not produce product value and process economics that will encourage post-consumer thermoset recycling.

The particulate from composite replaces mineral filler. Fibers are separated out for reuse as short fiber in further polymer composite manufacturing.

After grinding into granules, there are three ways to dispose of the composite material, as shown in the flowchart in Figure 11.1.

There are four main methods of plastic waste recycling [18]: energy recovery (incineration), feedstock recycling (pyrolysis, hydrogenation, and gasification), chemical (depolymerization), and material recycling.

Polymer composites reinforced with fillers, such as glass fibers, carbon fibers, etc., have great potential as substitutes for metals and other materials. Fiber reinforced polymers are used in applications where low weight, strength, and longevity are required. Two factors which inhibit their growth are the cost and failure to meet the recycling challenge. In the recycling of composites the shredded material is granualted and formed into small pellets. The material is cut into small chips and is reduced further in size by grinding with a grinder especially designed for the composites. The material is then sent through a compounding kneader to a granulator. There the composite material is formed into granules. The separated recycled plastic material is processed by the end user by being granulated or pelletized, melted or partially melted and extruded to form the end product. The recycled polymer may be added to virgin polymer during the process.

11.2.5 Reinforcing Agent Separation

Size reduction is one more step on the road to recycling. Upon shredding, there is an intital size reduction in thermoset composites. This is carried out by shredding or crushing or different types of milling. Scrap composite subjected to recycling first must be reduced to a size and shape that can be transported and handled with some degree of efficiency. Use of recycling or separating the reinforcing agents will provide high value if it has an aspect ratio. Fiber is removed and the remaining material is ground into fine-sized filler. The filler portion left is used in its entirety.

The key issue is that the costs of recycling operations remain economical. Recycling composites being looked at are thermoplastic lumber and reinforced composites.

11.3 Shortcomings

- Recycled quality as function of product type and design affect the efficiency of recycling processes applied to recover the material.
- Making prior prediction of recycling systems for polymer blends and composites from both an economic as well as environmental point of view is difficult within a short time.

- Life cycle analysis (LCA) methodology lacks the fundamental knowledge required to predict recycled blend and composite quality and recycling performance.
- The resulting material flows and material toxicity, economical value, quantities, etc., require expensive and time-consuming tests to collect the required details of recycling.
- The LCA methodology for the control, planning and prediction of blends and composites recycling cannot be linked to computer-aided design to predict fundamentals of recycling. The fundamentals of recycling are based on the behavior of recycling systems.

11.4 Present Needs

Recycling of polymer blends and composites is one of the methods of reducing waste stream components that have been accepted into recycling. Blends and composites are a very heterogeneous collection that encompass not only a broad range of types made from a single polymer, but also an interesting number of items that include a polymers mix, either mechanically or chemically bonded together. The varieties are made additionally diverse through the use of compatibilizers and additives to yield specific product qualities. It is technically difficult to obtain relatively pure polymers from blends and composites collected for recycling. Commercially demonstrated separation technologies are almost exclusively limited to processes. Recycling alternatives are only limited by costs, participation rates, technological or other factors which affect long-term viability.

Recovery and recycling of blends and composites are used to decrease the amount of waste disposed in landfills. It will be necessary to overcome difficulties due to their heterogeneous nature. Contaminants and separation of polymers from blends and composites are the most difficult challenges. Waste blends and composites from industrial operations are cleaner than post-consumer products. In its broadest sense, mixed plastics of blends and composites have been too broad scale for processing post-consumer waste. Mixed polymers mean a collection of a mixture of polymers or mixture.

Because of their high strength and high corrosive resistance, polymer blends and composites have shown promising results as a potential material for use in waste management and industrial applications. However, the relationship between the compatibility of polymer blends/composites and their degradability affects the crystallinity and physical properties. The compatibility of a blend therefore may influence the degradation and the properties of the blend. In the case of conventional polymers made from biodegradable polymer, the environmental problems would be reduced to some extent. As an alternative for tailoring the degradability, polymer blending has been used [19–21].

11.5 Future Commitment

As a result of the great interest in recyling, the commitment to the use of composites has greatly increased because of their durability and design advantages. New applications of composites will produce post-industrial waste streams for recycling as soon as production starts, but the challenge will be to have applications developed in post-consumer materials.

In developed countries, high temperature steam is used for composite decomposition in order to reduce landfills and minimize air and water pollution. It appears to be complicated, but offers both good economics and an opportunity for closed loop recycling in life cycle analysis of recycling. The main purpose is to minimize the volume of waste going into landfills.

In the life cycle analysis, size reduction and distribution management are used in closed-loop recycling of composites. The future will require the construction of a recycling facility to handle larger volumes. The development of thermoset composites will increase the movement towards total recyclability.

11.6 Summary

- Great interest in recycling is the requirement and commitment to the use of polymer blends and composites.
- Recycling of polymers is limited because it is not commercially viable to sort out the waste.
- Life cycle analysis has not yet been done to assess the environmental impacts of these materials over their entire life time and any permanent damage done to the environment
- Enhancing life of polymer by mixing polymer with black colored tar, which already contains organic materials, without any degradation.
- Recycling methods require energy conversion which only significant where polymer disposal is prohibitive.
- Polymer blends and composites systems are unique microstructures or macrostructures responsible for end product properties.

- Recycling of polymeric materials is an environmentally friendly procedure.
- Tailoring the properties of waste polymers is used in order to manufacture blends and composites.
- Technically difficult to obtain relatively pure polymers from blends and composites collected for recycling.

References

1. Compomanes Santana, R.M. and Manrich, S., *J. Appl. Polym. Sci.* 88, 2861–2867, 2003.
2. Shojaei, A., Yousefian, H., and Saharkhiz, S., *J. Appl. Polym. Sci.* 104, 1–8, 2007.
3. Avila, A.F. and Duarte, M.V., *Polym. Degrad. Stab.* 80, 373–382, 2003.
4. Leidner, L., *Plastic Waste*, Marcel Dekker: New York, 1981.
5. Lindsey, C.R., Barlow, J.W., and Paul, D.R., *J. Appl. Polym. Sci.* 26, 9, 1981.
6. Torres, N., Robin, J.J., and Boutevin, B., *J. Appl. Polym. Sci.* 81, 2377–2386, 2001.
7. Retolaza, A., Eguiazabal, J.I., and Nazabal, J., *Polym. Eng. Sci.* 42, 2072–2083, 2002.
8. Pracella, M., Galeski, A., Pawlak, A., and Pluta, M., *J. Appl. Polym. Sci.* 82, 1423–1436, 2001.
9. Paul, D.R. and Newman, S. (Eds.), *Polymer Blends*, vols. 1 and 2, Academic Press: New York, 1978.
10. Utracki, L.A., *Polymer Alloys and Blends: Thermodynamics and Rheology*, Hanser Publishers: Munich, 1989.
11. Bisio, A.T. and Xantos, M., How to Manage Plastics Waste: Technology and Market Oppurtunities, Hanser: Munich, 1995.
12. Hausmann, K., Recycling of incompatible plastics with reactive combatilizers, in: *Chemical Aspects of Plastic Recycling*, W. Hoyle, D.R. Karsa (Eds.), p. 170–179, The Royal Society of Chemistry: Cambridge, 1997.
13. Brandup, J., Bittner, M., and Menges, G., *Recycling and Recovery of Plastics*, Hanser: Munich, 1996.
14. Nguyen, K.T., Weber, L., and Herbert, L.P., *ANTEC* 3432, 1993.
15. Clemons, C.M. and Myers, G.E., *ANTEC* 3213, 1993.
16. Tao, W.H. and Golovoy, A., *ANTEC* 3427, 1993.
17. Rueda, D.R. and Balta-Calleja, F.J., *J. Mater. Sci.* 29, 3213, 1994.
18. Schiers, J., *Polymer Recycling*, Wiley: Chichester, 1998.
19. Cha, Y. and Pitt, C.G., *Biomaterials* 11, 108–112, 1990.
20. Yasin, M. and Tighe, B.J., *Biomaterials* 13, 9–16, 1992.
21. Tsuji, H., Mizuno, A., and Ikada, Y., *J. Appl. Polym. Sci.* 70, 2259–2268, 1998.

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12

Future Trends

Polymers are very durable and are manufactured from nonrenewable resources such as oil. The feedstocks for synthetic polymers are petroleum, coal and natural gas, which are sources of ethylene, methane, alkenes, and aromatics. Petroleum-based polymers are non-biodegradable. As fossil fuel resources dwindle, there is growing interest in developing new feedstocks for future polymers. A majority of the polymers are petroleum based and economical.

There are important fundamental scientific issues that must be addressed to render these materials competitive with their petrochemical-based cousins, and the contributors to macromolecules tackle many of the most important research questions. Research in the field of polymer science and technology has been focused on developing polymers, blends, composites, and many other industrial products from existing polymers.

Demand for sustainable materials requires thinking beyond what constitutes the best material for any application. Interest in utilization of renewable resources is increasing because of depletion of natural resources, environmental responsiveness, economic considerations, and important technological breakthroughs [1].

Due to growing environmental awareness throughout the world, new rules and regulations for the creation of a biobased economy are presenting research challenges. A new generation of environmentally friendly materials has emerged and may replace current sources in industrial applications. A dramatic increase in the use of blends and composites offers significant opportunities for improved materials without synthesis of new polymer with enhanced support for global sustainability [2, 3].

The steady growth in the use of polymer materials in many applications has encouraged industries to search for solutions for reducing the environmental impact of products at the end of their life cycle. In this framework, one of the primary objectives of product manufacturers is to completely recover the polymers [4–9].

12.1 Blends and Composites

Polymer blends and composites are inexpensive routes to modify polymer properties. The properties may be altered to have impact resistance, fatigue behavior, heat distortion and improved processability [10]. The most versatile and diverse techniques for utilization of these properties, and the utility afforded by these polymeric materials, have enabled most of the new inventions.

12.2 Blend and Composite Requirements

The following factors should be considered when producing polymer blends and composites:

- Raw materials and energy shortages, which have become the rule in recent times;
- Petroleum extracts go to the production of polymer;
- Re-evaluation toward waste materials [11];
- Disposal and proper management of the polymer waste is basically a responsibility of its original generator or entrepreneur;
- Polymer supply, product development and their costs;
- Energy conservation and environmental considerations;
- Consumer needs, safety, health and consumption of the end product in terms of public consumerism;
- Overall global competition, economy and processing of product to meet customer needs.

12.3 Future Benefits

New paradigms abound, and researchers in the area of polymer blends and composites no longer need to confine themselves to conventional materials that are merely polymers. Increased focus is required on quantifying the economics and cost to benefit aspects during the production of polymer blends and composites. It is also connected to a growing awareness of the need for standardization in the blends and composites markets.

12.3.1 Automobile Applications

In the future, polymer blends and composites will comprise a major percentage of total automobile applications [12]. The industry has already converted from steel to aluminium and from aluminium to polymer blends and composites, particularly in some automotive industries. In the near future, a valuable percentage of total industrial applications will further reduce the weight of parts and increase fuel value.

12.3.2 Aerospace Applications

Polymer blends and composites have found their way into aerospace applications and the unique properties of the materials have been discovered.

There has been explosive development in the material and process technologies areas, and the possibilities of the use of polymer-based blend and composite materials are only restricted by imagination.

12.3.3 High Strength Particle

Particle-filled polymer composites are economical and high strength. Particle-filled glass fiber reinforced polymer composite is formed by combining mineral aggregates and glass fiber with a resin system.

Because of rapid setting and high strength properties, polymer composites are being used in a variety of construction, rehabilitation, and repair applications such as bridges, pipelines, and other types of constructions [13–16].

12.3.4 Tribological Performance

Polymer composite materials are one of the most rapidly growing classes of materials. Tribology is the science that deals with the design, friction, wear and lubrication of interacting surfaces in relative motion, as in bearing or gears. These polymeric composites are increasingly used for tribological applications. Research has yet to determine the tribological performance of composites and requires consolidated information related to friction, lubrication and wear in comparison with metal and ceramic matrix composites [17].

12.4 Greener Processing

Non-biodegradable polymers pose a problem due to their end products finally ending up as waste. Burning of such waste polymers can be hazardous to human health and by equally mixing them with bituminous materials they evolve as gases from tar or bituminous materials, due to black body radiation in summer from the mix of polymer(s). Mixing of polymer(s) with tar or bituminous material creates an environmental hazard that is permanently damaging to the environment. Greener processing comes from mixing and processing waste polymers during manufacturing of blends and composites to eliminate any hazardous tendencies.

Biobased biodegradable polymers derived from renewable biomass feedstock can be powerful for sustainable development during their use in blends and composites. The mainstay of current and near-future blends and composites can be made greener in terms of their processing. Renewable resources have the potential to compete with petroleum-based products. Some problems have become evident as environmental awareness increases. Use of biodegradable fibers in composite applications will establish an entirely new value chain for the crop. Prospects have been revealed for fabrication of hybrid composites by combining all these lignocellulosics to achieve further performance improvements [1]. They are currently emerging as alternatives to traditional petroleum-based synthetic polymeric composite materials. The renewable resource-based lignocellulosic fibers are inexpensive and abundantly available. Their potential to impart high modulus and low density to composites affirms the production of lightweight and eco-friendly composites.

12.4.1 Use of Recycled Polymer Blends and Composites

Polymer blends and composites are polymer mixed with polymer, fillers, fibers and other additives to simplify processing in all phases of the product life cycle, from product design to performance. They are subjected to the above constraints in order to facilitate the product development. Therefore, they are strongly influenced by consumer and environmental considerations. It is very essential and desirable to use such blends and composites which can be readily recycled.

Polymer recycling, besides being ecologically relevant, could also be economically attractive provided that all the operations, from the material pelletizing, are optimized. The recycling of polymer is very complex because of the time requirement. A large number of different polymeric materials are often mutually incompatible; therefore, it is more important to rationalize the choice of the constitutive materials with careful consideration of their mutual compatibility.

The recycling of waste polymers needs sorting out due to cross contamination during processing. The development of polymer blends and composites should be based on reinforcing agents such as fibers obtained from agricultural resources. Therefore, blends and composites from natural renewable resources without segregation can be processed as integrated polymers waste in order to reduce the production cost.

12.4.2 Present Trends

Due to growing environmental awareness, the new rules and regulations which govern the global economy are challenging industry, academia, government, and agriculture. Within the past few years, research has emerged on a new generation of environmentally friendly materials that may replace current sources in industrial applications.

The development and commercialization of polymer blends and composites is dynamic. Increased polymer competition requires polymer systems which offer unique competitive advantages. Blends and composites satisfy changing applications with better engineered products that are more economical. They satisfy both end use requirements and are competitive for product differentiation. Continuous development is needed for specific mechanical and other properties of blends and composites in the product development environment.

Today, the commercial interest in blends and composites is due to the potential opportunities presented by combining the attractive features of different polymers to improve characteristics that are deficient in a particular material [18–21].

Present-day research in the field of polymer science and technology has been focused on many other industrial products from renewable resources, mostly the abundantly available agro-waste and lignocellulosic materials. Newer materials and composites that have both economic and environmental benefits are being considered for application in the automotive, building, furniture, and packaging industries.

12.5 Future Trends

Much of the development in science and technology has been advanced to a great extent through the new or improved systems that enable optimization of production processes and upgraded product performance. Polymer blends have been studied at both basic and applied levels in industry [22] and recent decades have seen an increasing demand for new polymeric materials. By blending, new materials can be developed that combine the physical and mechanical properties of their components, depending on the composition and level of compatibility obtained. Compatibility can be enhanced by suitable compatibilizer and processing conditions [23].

Beginning with the development of polymer materials, polymer blends and composites have reached the status of being considered an important technology. The field of polymer blends is developing rapidly, both in terms of scientific understanding and commercial utility. Future research related to polymers in combination with natural fibers with waste polymers and resins needs to be carried out in order to move from the laboratory to the manufacturing level, and at the same time to produce agricultural fiber composites at low cost.

The future direction of much polymer research will be governed by efforts to better understand these properties and to improve on them. In reviewing what has been done, and what might be done in the future, emphasis will be placed on what can be achieved by the use of polymer blends and composites.

Innovative and sustainable development is an important factor in polymer blends and composites, and the final disposal of the materials has become an issue. Hence, limitations have to be overcome in order to support the development and use of fully biodegradable blend composites in order to commercialize them in large quantities. Their physical properties need to be improved and concerns about their disposal need to be addressed in order to reduce the environmental burden.

12.6 Advantages

The economic advantages to using polymer blends and composites are:

- Lower weight than steel;
- Lower transportation costs;
- Lower assembly and installation costs;
- Little or no maintenance and better life.

The technical advantages of these materials are:

- High corrosion resistance;
- High flexibility;
- Electrical and thermal insulation;
- Low thermal coefficient of volume expansion;
- Non-slip and comfortable underfoot;
- Noise damping properties;
- Temperature resistance;
- Quick machining and assembly.

Other applications for these materials:

- Sewage treatment plants;
- Power stations;
- Chemical plants;
- Ship building industry;
- Food industry.

And many more upcoming applications.

12.7 Summary

- The feedstocks for synthetic polymers are petroleum, coal and natural gas.
- Petroleum based polymers are economical.
- Research questions on polymers are important fundamental scientific issues.
- Primary objectives polymer product manufacturers is to completely recover the polymers.
- Essential utilization of polymer properties have enabled most of the new inventions.
- Environmental factors should be considered when producing polymer blends and composites.
- Very essential and desirable in the use of blends and composites are recycling nature.
- Research has to emerge on a new generation of environmentally friendly polymer materials.
- Optimization of production processes and upgraded product performance is required in the development of polymer science and technology.
- Much polymer research will be governed by efforts to better understand polymer properties

References

1. Nagarajan, V., Mohanty, A.K., and Misra, M., *ACS Sustain. Chem. Eng.* 1, 325–333, 2013.
2. Wool, R.P., *Chemtech* 29, 44, 1999.
3. Mohanty, A.K., Misra, M., and Hinrichsen, G., *Macromol. Mater. Eng.* 276/277, 1, 2000.
4. Brandrup, J. and Bittner, M., *Recycling and Recovery of Plastics*, Hanser Publications: Munich, Vienna, New York, 1996.
5. Kahovec, J., *Macromol. Symp.* 135, 55, 1999.
6. Labana, S.S., *Polym. Prepr.* 32, 116, 1991.
7. Drake, W.O., Pauquet, J.R., Tedesco, R.V., and Zweifel, H., *Angew Makromol. Chem.* 176, 215, 1990.
8. Akkapeedi, M.K. and Van Buskirk, B., *Polym. Eng. Sci.* 35, 72, 1995.
9. Mack, J., in: *Disposal of Plastics with Minimum Environmental Impact*, STP 533, American Society of Testing and Materials, p. 1, Philadelphia, 1973.
10. Hoffman, G.H., in: *Polymer Blends and Mixtures*. D.J. Walsh, J.S. Higgins, A. Maconnachie (Eds.), NATO ASI Series, Series E, Applied Science No. 89, p. 117, Martinus Nijhoff Publishers: Boston, 1985.
11. Leidner, J., Recovery of the value from postconsumer plastics waste. *Polym. Plast. Technol. Eng.* 10(2), 199–215, 1978.
12. Mohanty, A.K., Drzal, L.T., and Misra M., *J. Mater. Sci. Lett.* 21, 1885–1888, 2002.
13. Fowler, D.W. and DePuy, G.W., ACI Committee 548, Guide for the use of polymers in concrete, *J. ACI* 83, 798–829, 1986.
14. Vipulanandan, C. and Dharmarajan, N., *Cem. Concr. Res.* 17, 219–230, 1987.
15. Guemini, G.L., *Appl. Compos. Mater.* 7, 195–207, 2000.
16. Fowler, D.W., Polymers in Concrete, *Handbook of Structural Concrete*, McGraw-Hill: New York, 1983.
17. Rohatgi, P.K., Blau, P.J., and Yust, C.S. (Eds.), *Tribology of Composite Materials*, ASM International: Materials Park, OH, 1990.
18. Utracki, L.A., *Polymer Alloys and Blends*, Hanser: New York, 1989.
19. Sweeney, F.M., *Polymer Blends and Alloys: Guide to Commercial Products*, Technomic: Lancaster, PA, 1988.
20. Olabisi, O., Robeson, L.M., and Shaw, M.T., *Polymer-Polymer Miscibility*, Academic Press: New York, 1979.
21. Paul, D.R. and Newman, S., *Polymer Blends*, Academic Press: New York, 1978.
22. Akiyama, S., Inoue, T., and Nishi, T., *Polymer Blend: Compatibility and Interface*, CMC Press: Tokyo, 1981.
23. Haba, Y. and Narkis, M., *Polym. Eng. Sci.* 44, 1473, 2004.

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