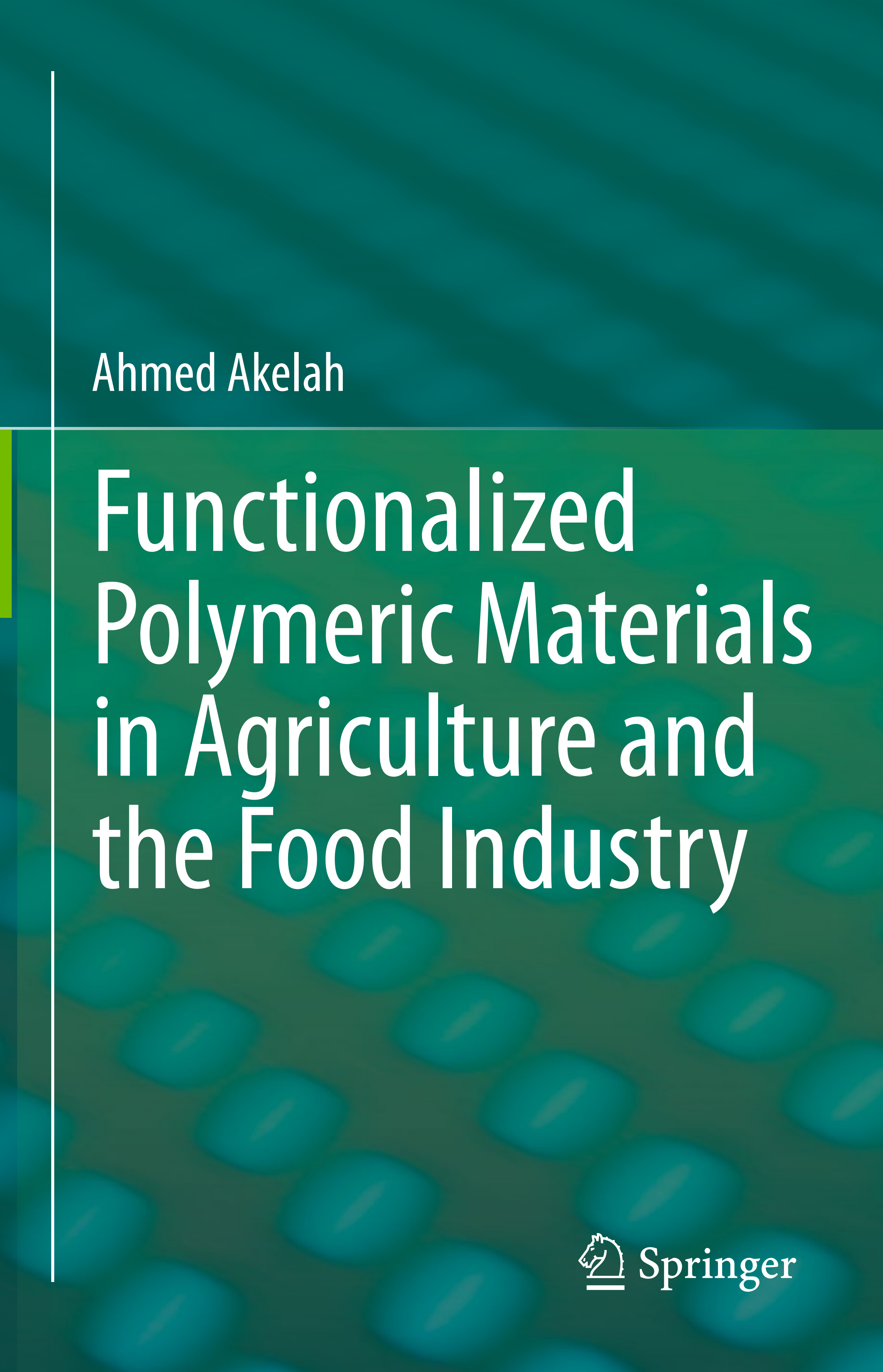

Ahmed Akelah

Functionalized Polymeric Materials in Agriculture and the Food Industry

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Agriculture in Ancient Egypt
Source: The Egyptian Museum of Cairo

Preface

Rapid progress in the development and utilization of polymeric materials and functionalized polymers in agriculture and the food industry has occurred in recent years. The growing demand for food and food safety are the main impetus behind the need for more efficient operations in growing, producing, and processing foodstuffs for higher yields and better quality, and to rid foods from possible adverse health issues. The remarkably useful combination of properties possessed by polymers make their use in this field a rapidly expanding area with respect to requirements for health, nutrition, environmental pollution control, and economic developments.

This book provides a valuable literature source on polymers that have been used in this respect. It will help to close the gap between the two fields of polymeric materials and the areas of agriculture and food development both in quality and quantity. In addition, it will be useful as a guide for systems development and solving the problems of designing polymers that may lead to new frontiers for more efficient operations in both agricultural and industrial production of foodstuffs. It aims to provide a comprehensive review of the broad spectrum of research activities currently being undertaken in the field of functionalized polymeric materials and their significant uses to improve the production quality and processing quantity of food products.

The book is composed of six chapters: the first chapter is divided into two sections that give the background knowledge of the synthesis of reactive polymeric and composite materials and their physical and mechanical properties. In an attempt to examine the utility of polymeric materials in the field of agriculture and the food industry, the first section of this chapter is concerned with fundamental and background knowledge of the types necessary for their design. A brief description is given of the conditions employed in the preparation of reactive polymers either by polymerization or by chemical modification techniques as well as an explanation of potential advantages and disadvantages of each technique. The second section is devoted to the characterization of the polymer properties. Effective utilization of a polymeric material in agriculture and the food industry depends on their properties which include their physical form, porosity, solvation behavior, diffusion, permeability, and surface properties, chemical reactivity and stability, deterioration and stability, and mechanical properties. Such properties are crucial and depend on the conditions employed during preparation and must be considered during the design of a new reactive functionalized polymer.

Part I of the book, which includes Chaps. 2 and 3, provides a general overview of the utilization of polymeric materials in a variety of agricultural fields not only as replacement for traditional materials but also as a significant improvement in technological processes in the growing of agricultural crops, in storage construction for crops and animals, and in agricultural equipment and drainage technology. These materials are used in the most diverse forms in agriculture, especially in the controlled release of agrochemicals and as useful media for plantations, as structural materials for plant protection, and in water conservation. The central aim of using polymers in agriculture is in increasing and improving crop yield in shorter time, in less space, and at lower costs. Chapter 2 covers a number of areas where polymers have been employed in growing crops and enhancing plant protection; it is divided into four areas: polymers in plantations, plant protection, farm construction materials, farm water handling and management. Chapter 3 describes the use of polymeric materials in agriculture for controlled-release formulations of agrochemicals, which are released into the environment of interest at relatively constant rates over prolonged periods of time to avoid the risk of the active agents being washed away by rain or irrigation. There are a number of agrochemical areas where polymers have been employed either as encapsulation membranes or as convenient supports to chemically attach the active agrochemical groups. In general, all principal classes of polymers have been utilized in agricultural applications of controlled-release formulations of agrochemicals.

Part II of the book, which consists of Chaps. 4, 5 and 6, provides a general overview of the utilization of polymeric materials in a variety of food processing fields. In general, polymers are not absorbed by the human body due to the size of macromolecules that prevents their diffusion across the membranes of the gastrointestinal tract. Thus, they are not of major toxicological concern with respect to low-molecular-weight food additives. The utilization of functionalized polymers in the food processing industry has a great potential for continuous industrial processes in large-scale applications. Polymeric ingredients allowed for use in the food industry are employed in three general areas: food processing and fabrication, food additives, and food protection and packaging.

Chapter 4 elaborates the basic principles of how reactive polymers can contribute to solving problems associated with conventional procedures in some areas of food processing. A broad range of polymeric applications to the food industry is covered, including various types of polymers that have a promising potential in respect to continuous processes, in particular those used in the dairy and sugar industries, the fruit juice and beverage industry, and in beer and wine production. It also covers the potential uses of polymers in tomato sauce production, and in potable water. Polymeric materials used to affect food processing and do not substantially become components of food, especially for the purification, recovery, and utilization of by-products, are not considered as food additives. In general, they are used in food processing to improve food characteristics, to aid in food processing, to make foods more attractive, or to keep food unspoiled for long periods of time under the conditions of storage. The most prominent driving factor behind the increasing need for using polymers in food products is population growth around the world. The food industry requires suitable polymers to meet the specific requirements of the food industry to simplify food production processes and to reduce food production costs, while neither deteriorating nor alterating food characteristics. Protecting health and preserving food quality are paramount. Reactive functional polymers in the form of ion-exchange resins, immobilized enzymes, membranes, and polymeric smart and nanomaterials have been utilized in various areas of the food processing and fabrication industries.

Chapter 5 describes the use of polymeric food additives such as colorants, antioxidants, nonnutritive sweeteners, nonnutritive hydrocolloids, animal feed additives, as well as indicators and biosensors in foods. Polymeric food additives are to enhance food quality, to preserve and enhance food flavor, taste, and appearance without affecting food nutritional value. They are substances other than basic foodstuffs, which exhibit their functions prior to consumption of the food products, either acting as aids in the manufacture, preservation, coloration, and stabilization of food products, or serving to improve the biological value of certain foods.

Chapter 6 focuses on the applications of polymers in food packaging and protection that include polymers in traditional food packaging, in coatings of metal cans, biodegradable and preservative food packagings, and polymeric active, modified atmospheric, and smart food packagings. Traditionally, food packages have been used to provide protection for food products and are designed to retard or delay the undesirable effects of physical, chemical, biological, and environmental factors. They are intended to extend shelf life and retain food quality by keeping the food contents clean, fresh, and safe for consumption. Their primary role in food safety is preserving and protecting the food from external contamination, maintaining food quality, and increasing shelf life. They protect foods from environmental factors, such as light, heat, oxygen, moisture, enzymes, microorganisms, insects, dust, gaseous emission and pressure, which all may lead to the deterioration of food products. Food packages are labeled to show required information regarding the nutritive value of the food and to communicate to the consumer how to use, transport, recycle, or dispose of the packages, as well as the nature of the deterioration of the product and any potential health issues that may result if the food is consumed beyond its expiry date.

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Part II Applications of Polymers in Food

Chapter 1
Polymeric Materials: Preparation and Properties

From the industrial perspective, “raw materials” are natural materials that cannot be processed directly and need to be subjected to pre-manufacturing processes for chemical modifications to form the “primary materials” used in industrial production, i.e., used in more advanced production processes.

Polymers being used as structural materials can be classified according to source into: organic or inorganic (mostly metallic) materials. They may either be purely synthetic macromolecules made of fossil raw materials (such as petrochemicals produced by cracking or refining of crude oil), or naturally occurring polymers from various vegetable or animal sources, which are of large importance for the industry and agriculture sectors [1]. Polymers can also be classified according to differences in: preparation chemistry, molecular structures, properties (mechanical, physical, chemical, geological, biological), processing, or use in different fields. Most polymers can be classified according to their application into: plastics, elastomers, fibers, coatings, adhesives etc. This classification leads to certain overlaps, as for example, polyamides and PP are used not only as synthetic fiber-forming materials but also used as thermoplastic molding materials. Other classifications are by physical properties and molecular chain structure, i.e., according to the difference of the bonding type between macromolecular chains – thermoplastics and thermosets [2]. *Thermoplastic* polymers are flexible molecular structures of linear, branched, or grafted structures having only secondary (physical) bonds between the main chains, and can be melted or dissolved and hence require heat or solvent for shaping processes. They can be reheated and reformed, often without significant changes to their properties, as for instance, PE, PS, PP, and PVC. *Thermosetting* polymers possess networked (crosslinked) structures having chemical bonds between the main chains formed via chemical reactions or polymerizations. They cannot be melted or dissolved and possess excellent thermal stability and rigidity.

Synthetic polymers have attained invaluable importance in nearly every sphere of life largely as inert structural materials and as active macromolecules. The number of different polymeric materials in our built environment increases almost daily and accordingly science and technology of polymers has received considerable

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interest and undergone explosive growth during the last years for the production of improved polymeric materials. The usefulness of a polymer in a specific application is related to its macromolecular nature whose characteristic properties depend mainly on the extraordinary large size of the molecules. Thus, the proper choice of polymer is detrimental to a successful application.

In the most general sense, all synthetic polymers offer certain properties and advantages over other structural engineering materials (natural organic, inorganic, or metallic) that can be judged quantitatively in the design of the end use in applications, such as: light weight, transparency, flexibility, economy in fabricating, self-lubrication, and decorating. In addition, the properties of polymeric materials can be modified through chemical modification or via the use of reinforcing agents, and chemical additives. Thus, polymeric materials are used in many engineering applications, such as mechanical units under stress, low-friction components, heat- and chemical-resistant units, electrical parts, high light-transmission applications, housing, building construction materials, and many others. The preparation and properties of the polymers must be thoroughly examined prior to use to evaluate the potential advantages of their utilization.

In order to understand the potential utility of polymeric materials, the first part of this chapter is devoted to fundamental and background aspects of the different types of polymers. A brief description is given of the synthesis of reactive polymers either by polymerization or by chemical modification techniques as well as an explanation of potential advantages and disadvantages of each technique.

The second part is devoted to the characterization of polymers properties. Effective utilization of a polymeric material in agriculture and the food industry depends on their physical form, porosity, solvation behavior, diffusion, permeability, surface properties, chemical reactivity and stability, deterioration and stability, and mechanical properties. Any such features are crucial and depend on the conditions employed during preparation and must be considered during the design of a new reactive polymer.

1.1 Preparation of Polymeric Materials

In general, a first step is focussing on the fundamental chemical requirements for preparation of the polymeric material. This is necessary for determining possible approaches for creating enhanced polymeric systems that combine the unique properties of high molecular weight and the functionality for a specific utilization in the desired agricultural or food application. Generally, synthetic polymers are prepared by two main routes: (1) the direct polymerization of low-molecular-weight monomers containing the desired functional groups or by (2) chemical modification of preformed synthetic or natural polymers (organic and inorganic) with the required functionality. Both approaches have advantages and disadvantages, and the one may be preferred for preparing a particular functional polymer where the other would be totally impractical. The choice of synthetic route of polymeric materials depends mainly on the potential advantages of the technique regarding the required chemical and physical properties of the polymer for its specific use. Usually the requirements of the individual system must be thoroughly examined in order to take full advantages of each of the preparative techniques.

The first section covers the basic principles and characteristics necessary for polymer preparation by polymerization, being either (a) stepwise polymerization of bifunctional monomers by polycondensation, stepwise polyaddition and ring-opening processes, or (b) chain polymerization of vinyl monomers by free radical, cationic, anionic, and coordination addition processes. Both of these polymerization techniques are used for polymer preparation from monomer. The goal of the polymerization technique is to obtain polymers with specific structures and properties – this generally requires specialized polymerization conditions. Also described are the factors affecting the rates of homo- and copolymerizations and the reactivity ratios of different comonomers.

The second section considers the basic framework and the main principles that underlie the chemistry of the chemical reactions on pre-existing synthetic or naturally occurring polymers such as polysaccharides and inorganic supports. It describes the chemical modification processes that have been applied to polymers to create new classes of polymers which cannot be prepared by direct polymerization of the monomers owing to their instability or un-reactivity, or to modify the structure and properties of other commercial or natural polymers to extend their uses over a wide range of applications [3]. Generally, the chemical reactions of polymers are of the following types: (i) reactions on side pendant groups that involve the introduction or conversion of functional groups and the introduction of cyclic units into the backbone, which result in a change in chemical composition of the polymer without affecting its molecular weight that produce functionalized polymers [4–6], (ii) reactions on the main chain that include either (a) degradation reactions which are accompanied by a destruction or a decrease in molecular weight, (b) intermolecular reactions which are accompanied by an increase in molecular weight as a result of crosslinking reactions, (c) formation of graft or block copolymers, or (d) reactions on the end groups of the main chains to form end functional groups.

1.1.1 Preparation of Synthetic Polymeric Materials

In the process polymerization the goal is to obtain polymers with specific structures and properties and these require specialized reaction conditions. Functionalized polymers prepared by the polymerization of functional monomers are of two types: polycondensation and chain polymerization polymers. The resulting polymers, either homopolymer or copolymers, can be used in the desired application as it is or after further modification. Applying such polymerization techniques bears certain *advantages*: (1) The resulting polymer is truly homogeneous with more uniform functionalization. (2) The chemical structure of the required functional group can be ascertained by analysis of the monomers prior to polymerization. (3) The degree of desired functionalization depends on the intended application of the support. In some cases, the polymer should be prepared with high loading to maximize the concentration of active group and to avoid the use of large amounts of support materials. In other cases, loadings must be limited to minimize the change in solubility characteristics. Hence it is possible to control the loading and distribution of functional groups within the support and achieve the desired degree of functionalization. (4) The polymers are not contaminated by traces of other functional groups or impurities from prior chemical transformations.

The main complications associated with the polymerization technique include: (1) The introduction of a functional group during polymerization requires an appropriately substituted monomer. A wide variety of monomers are commercially available, but most need to be synthesized for the particular purpose. The synthesis of monomers with desired functional groups is often difficult and they are generally obtained in low yields as a result of multi-steps synthesis. (2) Monomers of high purity must be prepared to obtain relatively high-molecular-weight polymer. (3) Some reactive monomers lack the required stability and display incompatibility during polymerization. (4) It is sometimes difficult to obtain polymerization of functional monomers to polymers with optimal molecular weight and of a desirable sequence distribution and compositional homogeneity of the copolymers. (5) Also, copolymerization may require the evaluation of the according parameters in order to obtain high yields and good physical properties with a satisfactory physical form of the desired copolymer.

1.1.1.1 Condensation Polymerization

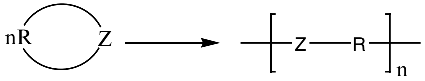
Condensation polymers, according to definition, are molecules whose main backbone chains contain heteroatoms (O, N, S, Si). Polycondensation reactions, being stepwise polymerizations, involve two reaction steps of addition and elimination of smaller molecules and are typical for compounds containing functional groups. The reactions occur between pairs of functional groups with the liberation of small molecules as by-products. Accordingly, the repeating structural units of the condensation macromolecule lack certain atoms present in the monomers from which the polymer is formed, i.e., the chemical composition of the structural units of the resulting macromolecules differs from that of the starting monomeric materials. Bifunctional groups can be contibuted by two different molecules each bearing at least two reactive groups (Eq. 1.1).

$$\mathbf{n\,A-R-A+n\,B-R-B \longrightarrow A-[-R-Z-R-]_{n-1}-B+(n-1)\,C} \tag{1.1}$$

A and **B** are the reacting functional groups, **C** is the by-product, and **Z** is the group bonding the residues of reacted molecules. Two different functional groups may be borne on a single molecule (Eq. 1.2).

$$\mathbf{n\,A-R-B \longrightarrow A-[-Z-R-]_{n-1}-B+(n-1)\,C} \tag{1.2}$$

Alternatively, the bonding functional group can be present in ring form: the two different functional groups are present within the ring in condensed form and the by-product is eliminated during ring formation. The chemical compositions of the cyclic monomers and the structural units of the polymers are essentially identical as in addition polymerization, but the stepwise nature and the rate of reaction are more characteristic of condensation polymerization reactions (Eq. 1.3).



(1.3)

Condensation polymerizations are stepwise polymerizations of functional monomers, such as polyesters (–COO–), polycarbonates (–OCOO–), polyamides (–CONH–), and polyethers (–O–). There are three types: (a) polycondensation of functional monomers, (b) ring-opening polymerization of cyclic monomers, as cyclic-ethers, lactones, and lactams which form the polymer chains via ring-opening without elimination of any small molecule, and (c) stepwise polyaddition, e.g., in polyurethanes (–OCONH–) which are formed by the addition of diol to diisocyanate without the elimination of any small molecule and their repeat units have the same net chemical composition as the two monomers. Stepwise polymerizations always proceed in stages and are reversible reactions with equilibrium properties. Moreover, each interaction is chemically identical and it is possible to interrupt or continue the reaction at any time without affecting the reactivity of the present polymer chain. The type of condensation reaction depends upon the functionality of the reactants, and the reactivity of functional groups at the ends of the oligomer chains is similar to that of the corresponding functional groups in the monomer molecules. Since most polycondensations are slow reactions, they require vigorous conditions such as high temperatures and low pressures. Polycondensation of bifunctional monomers gives linear polymers, while polycondensation of polyfunctional monomers results in crosslinking. Crosslinked polycondensation resins can be derived from condensation reactions, for example, of formaldehyde with phenol, urea, and melamine.

Although the properties of condensation polymers are often superior to those exhibited by vinyl addition polymerization, little attention has been directed toward the introduction of functional groups by polycondensation using appropriately substituted monomer. Polycondensation polymers may contain the reactive functional groups as a part of the polymer backbone or as pendent substituents.

1.1.1.2 Addition Polymerization

This is a chain polymerization through multiple bonds and may be regarded as simply the joining together of unsaturated molecules without the formation of by-products in which there is no difference in the relative positions of the atoms in the monomer and the structural unit of the polymer, Eq. 1.4.

$$\mathrm{n\,CH_2=CH—R} \longrightarrow \mathrm{—[—CH_2—CHR—]_n—}+\Delta \qquad (1.4)$$

Chain polymerization, which is generally limited to monomers possessing olefinic bonds, consists of three primary stages: initiation, propagation, and termination. Initiation is the formation of an active center by transferring the active state from the initiator to the double bond of the vinyl monomer, which becomes capable of starting the polymerization reaction of the olefinic monomer. Depending on the nature of the active center, there are four different types chain polymerization: free radical, cationic, anionic, or coordination (Ziegler–Natta) polymerization. Ionic polymerizations are used mainly in the production of rubber, such as the production of styrene–butadiene elastomers by anionic polymerization, and butyl rubber by cationic polymerization. The use of organometallic coordination catalysts to produce stereoregular polymers has added a new dimension to polymerization processes and plays an important role in the production of LDPE, HDPE, and PP. However, the most widely used in the preparation of commercial polymers is the free-radical polymerization technique.

(A) **Free-radical addition polymerization**

Free-radical polymerizations occur in three stages:

(i) Initiation occurs through two steps: the thermal dissociation of the initiator, **I–I**, into free radicals, $\mathbf{I^{\bullet}}$ (Eq. 1.5),

$$\mathbf{I-I-}(\Delta)\longrightarrow \mathbf{2\,I^{\bullet}} \tag{1.5}$$

and the addition of the formed radicals to the olefinic monomer, **M**, to give an activated species, $\mathbf{M^{\bullet}}$, capable of starting the polymerization of the monomer (Eq. 1.6),

$$\mathbf{I^{\bullet}+M}\longrightarrow \mathbf{I-M^{\bullet}}+\Delta \tag{1.6}$$

The dissociation of the initiator requires high activation energy and not every radical formed leads to the starting of a chain. A fraction of the radicals can disappear through recombination or through reaction with atmospheric oxygen or other inhibitors. The rate of the initiation reaction depends on (a) the rate of the initiator decomposition reaction which in turn depends on the temperature and the nature of the solvent and (b) the stability of the radical formed.

Free-radical initiation is induced by chemical, thermal, or radiation techniques. Chemical initiators are energy-rich compounds such as peroxides or azo-compounds. Redox initiation is used to increase the dissociation rate of the peroxide initiator at low temperatures by reducing the activation energy of the decomposition reaction, which can be achieved by adding reducing agents as activators. Such redox systems decrease the possibility of side reactions which may change the properties of the resulting polymers. Alternatively, free radicals may also be generated by light, radiation, or heat which results in the monomer itself becoming excited, i.e., the electrons are removed from the ground state to new orbitals corresponding to a higher energy and then decompose to form a biradical which leads to polymerization (Eq. 1.7).

$$\mathbf{CH_2 = CH - R} - (h\nu / \Delta) \longrightarrow (\mathbf{CH_2 = CH - R})^{*} \longrightarrow \mathbf{CH_2 - CH - R} \quad (1.7)$$

This radiation or heat technique is often useful in avoiding contamination of the polymer from initiator residues and has been successfully used for modifying polymers by anchoring organic reagents to polymer surfaces through radiation grafting.

(ii) Chain propagation is the rapid addition of the activated monomer species (I—M$^{\bullet}$) to a new monomer unit to obtain high molecular weights of propagating polymer chains. This results in a change of π bonds to σ bonds with the liberation of heat due to the difference in energies between them. In contrast with initiation, the rate of the propagation reaction is less temperature dependent and the degree of polymerization is proportional to the ratio of the rate of the propagation reaction and the rate of the termination reaction (Eq. 1.8).

$$\mathbf{I - M^{\bullet} + n\,M} \longrightarrow \mathbf{I - [-M-]_n - M^{\bullet}} + \Delta \quad (1.8)$$

(iii) Termination is the disappearance of the unpaired electron of the active center. The free radicals of the propagating polymer chains have a strong tendency to react with each other either by disproportionation leading to two chains (Eq. 1.9),

$$\begin{aligned}\mathbf{2\,I - [-M-]_n - M^{\bullet}} \longrightarrow\ & \mathbf{I - [-M-]_n - CH_2CH_2 - R} + \\ & \mathbf{I - [-M-]_n - CH = CH - R}\end{aligned} \quad (1.9)$$

or by recombination of two growing chains leading to one chain (Eq. 1.10),

$$\mathbf{2\,I - [-M-]_n - M^{\bullet}} \longrightarrow \mathbf{I - [-M-]_n - M — M - [-M-]_n - I} \quad (1.10)$$

The chains terminated by recombination are larger than those terminated by disproportionation. Deactivation of the growing chain radical always occurs through chain transfer termination, i.e., by abstraction of an atom from another molecule such as the initiator, monomer, solvent, completed polymer chain, modifier, or impurities, and thus the propagating chain radical becomes saturated. The molecule from which the atom has been abstracted will then become a free radical and may or may not start a new chain. Accordingly, the rate of polymerization does not decrease but the molecular weight decreases.

(B) Techniques of free radical polymerization

The choice of the method by which a monomer is converted to a polymer depends on the nature of the monomer, the end use of the polymer, the molecular weight, the rate of polymerization, and control of side reactions. Various techniques have been utilized in free-radical polymerizations and each method has its own pros and cons [7–9]. Different commercial polymerization processes are used in industry for the manufacture of polymers by free-radical chain polymerization and may involve one of the following methods [10–13]:

(i) Bulk (mass) polymerization is the simplest technique, economically the most attractive, and consists of carrying out the reactions on the pure monomers alone, with or without initiator, in the absence of solvents [14, 15]. The polymer is either (a) soluble in the monomer and thus there is an increase in viscosity as the polymerization progresses, or (b) insoluble in the monomer and the formed polymer is precipitated without increase in solution viscosity. The major advantages of the technique are the high purity and the high molecular weight of the formed polymers due to the decreased possibility of chain transfer.

(ii) Solution polymerization – here the monomer is diluted by inert solvent (which may or may not be a solvent for the polymer) to assist in dissipation of the exothermic heat of the propagation reaction and to facilitate the contact between the monomer and the initiator [16]. If the solvent is not compatible with the polymer, then the polymer precipitates as it is formed. However, if the reaction solvent is compatible with the polymer, then the polymer is formed in solution and can be isolated by addition of a nonsolvent which causes precipitation. The major disadvantage of this method is the possibility that the solvent can act as a chain transfer agent and hence leading to low-molecular-weight polymer.

(iii) Suspension polymerization has proved to be perhaps the most useful technique for synthesizing linear and crosslinked polymeric materials because of the extremely convenient physical form of the bead products, i.e., the regular spherical shape and surface area [17–20]. The physical state makes it easy to control any thermal and viscosity problems which are problematic in bulk and solution techniques. Crosslinked polymer beads of both swelling "*microporous*" and nonswelling "*macroporous*" types can be produced by this technique. The initiator is dissolved in the liquid monomer or comonomer mixture which is dispersed in suspending medium (water). Usually, suspending the monomer in small droplets in the suspending medium requires mechanical stirring of the reaction mixture and the use of a suspension stabilizer (suspending agent). The suspending medium acts as a heat exchanger to remove the heat of polymerization from each of the monomer droplets. Hydrophobic monomers, such as styrene or methyl methacrylate, are suspended in water using PVA as suspending agent. However, for hydrophilic monomers such as acrylamide, a "*reverse suspension polymerization*" is used in which the monomers are suspended in hydrocarbon medium using Ca-phosphate as suspension stabilizer. A free-radical initiator soluble in the monomer phase is used because it remains dissolved in the monomer during the polymerization. As the polymerization starts by heating, the liquid monomer droplets become highly viscous and then continue to polymerize to form spherical solid polymer particles "*beads*" or "*pears*". The suspending agent which does not interfere with the reaction mixture prevents the coagulation of the highly viscous droplets into gel-like precipitates by keeping the monomer in the state of small droplets. Each of the suspended monomer droplets undergoes individual bulk polymerization and kinetically the system consists of a large number of bulk polymerization units. After the polymerization, the polymeric bead product is collected by filtration and washed free of stabilizer and other contaminants. The size of the polymer beads depends on the extent of dispersion in solution and the amount of agitation. Pore dimensions can be determined during preparation by regulating the amount of crosslinking and are also influenced by the type and ratio of the solvent employed. A potential problem is associated with the presence of residual impurities from the suspension-stabilizing agents required in the polymerization procedure. Moreover, considerable difficulties are encountered when it is necessary to copolymerize a mixture of water-soluble and water-insoluble monomers.

(iv) Emulsion polymerization differs from suspension polymerization in the kind of initiator employed and in the type of particles in which polymerization occurs and their smaller size. This process has several distinct advantages. Besides being easy to control the thermal and viscosity problems of the other techniques, large decreases in the molecular weight of a polymer can be made without altering the polymerization rate by using chain transfer agents. However, large increases in molecular weight can only be made by decreasing the polymerization rate, by lowering the initiator concentration or lowering the reaction temperature. Emulsion polymerization is a unique process in that it affords a means of increasing the polymer molecular weight without decreasing the polymerization rate. The difficulty of removing all impurities such as surfactant residues from the polymer is the only disadvantage of this technique.

In conventional emulsion polymerization a hydrophobic monomer is emulsified in water with an oil-in-water emulsifier and then the polymerization is initiated with a water-soluble initiator [21–24]. Alternatively "*inverse emulsion polymerization*" can be carried out in which a hydrophilic monomer is emulsified in a hydrophobic oil phase with a water-in-oil emulsifier [25]. The main components of conventional emulsion polymerization are: monomer(s), dispersant (emulsifying medium), soap emulsifier, and water-soluble initiator. The dispersant is usually deionized water in which the various components are dispersed in an emulsion state by means of the emulsifying agent. Deionized water should be used since foreign ions can interfere with both the initiation process and the action of the emulsifier. The water-soluble initiators used in emulsion polymerization may decompose either thermally (e.g., ammonium persulfate, hydrogen peroxide) or by redox reactions (e.g., persulfate with ferrous ion). The shape of the micelles depends on the surfactant concentration, i.e., at lower surfactant concentrations (1–2 %) the micelles are small and spherical, but at higher concentrations they are larger and rod-shaped (Fig. 1.1). The emulsifier molecules are arranged in micelles with their hydrocarbon ends pointing towards the interior of the micelle and their ionic ends outwards to the water.

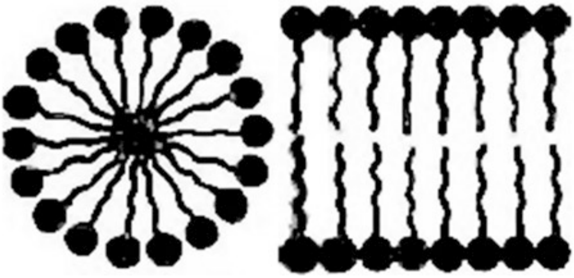


Fig. 1.1 Spherical and rod-like micelles

When a water-insoluble monomer is added a small fraction dissolves and goes into solution by the action of the emulsifier (surfactant) which has both hydrophilic and hydrophobic segments. Small portions of the monomer enter the interior hydrocarbon part of the micelles and are dissolved while the largest portion of the monomer is dispersed as monomer droplets whose size depends on the intensity of agitation. Thus, in a typical emulsion polymerization, the system consists of relatively large monomer droplets (monomer reservoir) and micelles which are the focus of the polymerization resulting from the incorporation of free radicals into the micelles. A further difference between micelles and monomer droplets is that the micelles have a much greater total surface area. The site of polymerization is the water phase where the initiating radicals are produced since the initiators employed are water soluble. Polymerization takes place almost exclusively in the interior of the micelles. The micelles act as a meeting place for the organic monomer and the water-soluble initiator. As polymerization proceeds, the micelles grow by the addition of monomer from the aqueous solution, and the concentration of monomer is replenished by dissolution of monomer from the monomer droplets. Commercial addition polymers are produced in large amounts on an industrial scale, from low-cost petrochemicals or natural gas. Examples of commercial addition polymers include PE, PP, PVC, PAA, PAN [26], PS [27–31], PAAm [32–37], PVA [38–45], PMMA. Other addition polymers are: PSMA, PEGMA, MPEGMA, PEGDMA, PHEMA [46], PIC's [47], and PU [48, 49] with a potential for biological entrapment.

1.1.1.3 Copolymerization

Homopolymerization is the reaction of a single monomeric species to produce homopolymer product with repeated structural units and simple chemical composition. The homopolymer is either a linear polymer containing the repeating structural units linked together in one continuous long-chain species, or branched polymer with the same constitutional units emerged from the main chain backbone. Copolymers, in contrast, are derived from two monomeric species and copolymerization two monomer are joined to give polymer chains containing more than one type of structural units. Each type of monomer leading to a copolymer must be separately capable of forming a homopolymer. Copolymerization allows the synthesis of an almost unlimited number of different products by variations in the nature and relative amounts of the two monomer units in the copolymer product.

The main advantage of copolymerization is in the enormous variability of polymer properties. An almost unlimited number of different polymeric products can be achieved by varying the type and relative amounts of the different employed monomer units [50, 51]. New and advanced properties can be obtained in respect to solubility, permeability, greater affinity for dyes, or good oil resistance [52]. In addition, copolymerization can be used for producing three-dimensionally crosslinked polymers, as e.g., poly(styrene-*co*-divinylbenzene).

The possible arrangements of the two structural units in the copolymer chains depend on the chemical structures of the monomers and the experimental techniques and are of the following types: (a) Block copolymer is a macromolecule which consists of blocks connected linearly. There are two possibilities for the formation of block copolymers: (i) by *living polymerization* with an anionic initiator such as PhNa or BuLi, where the chain grows in one direction, whereas with initiators such as sodium metal or sodium naphthalene the chains grow in both directions; (ii) by *end-functional group reactions* where the preformed polymer chains combine with other polymer chains with the aid of end-functional groups. Polymers with end-functional groups can be formed by condensation polymerization, addition polymerization with functional initiators, or by termination of living polymers with desired functional groups. (b) Random copolymer where the distribution of the two monomeric units in the chains is statistical, i.e., the polymerization rates of the individual monomers are greatly different. Thus, it is necessary to add the faster monomer slowly to the polymerization reaction containing the slower monomer, e.g., random copolymers of conjugated dienes as butadiene with vinyl monomers as styrene, acrylic esters, or acrylonitrile. (c) Alternating copolymer consists of alternating units in the chains. This requires that each monomer be more reactive towards the other monomer than towards its own type monomer, i.e., the radical end of the growing chain has greater affinity to react with the other monomer than with monomer of the same kind. For example, in the free radical copolymerization of maleic anhydride and styrene, the styrene radical has greater affinity to react with maleic anhydride than with styrene and vice versa. (d) Grafted copolymer is a branched polymer in which the backbone chain is chemically different from the branches. The presence of chemically different branching in the polymer usually has a large effect on many important polymer properties. The most significant property changes by grafting are the decrease in crystalline and thermal transitions, because they do not pack as easily into a crystal lattice as do linear polymers. Grafted copolymers can be prepared by different means via the use of chain transfer of polymer chains containing labile atoms which are capable of initiating polymerization of another monomer. This effect is more pronounced with polybutadiene in which the H atom of the methylene group is more labile because of the neighboring double bond. The amount of grafted copolymer formed by chain transfer is small because the chain transfer constants of the polymers are usually small. By dissolving the preformed polymer in the monomer and starting the polymerization either by adding initiator or by irradiation (X-rays, electrons or radioisotopes as Co) transfer occurs between the polymer chain and the radicals formed from the initiator to give polymer radicals which can initiate the polymerization of the monomer. The polymerization leads to a mixture of linear polymer and grafted copolymer. Grafted copolymers can also be formed by the use of polymeric free radicals or anionic initiators with the monomer to be grafted, or by chemical reactions of the polymer chains containing end-functional groups onto other polymer chains containing pendant functional groups. The pendant reactive groups present along the polymer structural units are used as sites for grafting. Polymer chains with end-functional groups used as branches can be obtained by different methods: (1) condensation polymerization, (2) free radical initiators with the desired reactive groups, e.g., azo catalyst containing carboxyl groups, (3) anionic polymerization followed by the reaction of the resulting living polymer with the desired functional reagent, e.g., carbon dioxide or ethylene oxide.

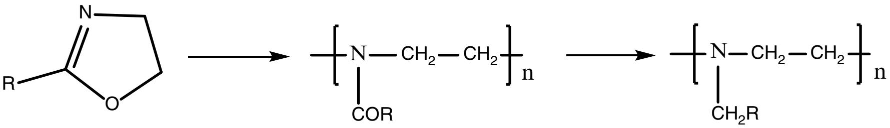
1.1.2 Chemical Modification of Polymeric Materials

Chemical modifications of preformed synthetic or natural polymers (organic or inorganic) can lead to reactive polymers having the functional groups linked to the main chain as pendant groups. The modification can be carried out either under classical conditions or by using the phase transfer catalysis technique, depending on the support reactivity and stability. While the chemical modification approach is attractive for its apparent simplicity and the fact that it ensures a product with a good physical form, it suffers from some major drawbacks such as the difficulty of purification after modification and every undesirable group that is formed by side reactions will become a part of the support chain.

The proper choice of the support matrix is important. The different available functionalized and reactive supports include: (a) cellulose as natural organic polymers, (b) PS and PMMA as synthetic polymers, (c) PS grafted onto cellulose as natural-synthetic polymers, and (d) polymer-montmorillonite nanocomposite materials as natural inorganic-organic synthetic polymers.

1.1.2.1 Modification of Synthetic Polymeric Materials

The preparation of functional polymers by chemical modification has been extensively used to modify the properties of polymers for various technological applications [53–58]. Chemical modification affords new classes of polymers which cannot be prepared by direct polymerization of monomers owing to their instability or nonreactivity. Also it is possible to modify the structure and physical properties of commercial polymers making them more suitable for specific applications [3]. For example, attempts to prepare linear poly(*N*-alkylethylenimine)s directly by ring-opening polymerization of *N*-alkylethylene imines were unsuccessful but these



Scheme 1.1 Preparation of poly(*N*-alkylethylenimine)s [59]

products were recently prepared by chemical modification of poly(*N-acylethylenimine*)s (Scheme 1.1) [59]:

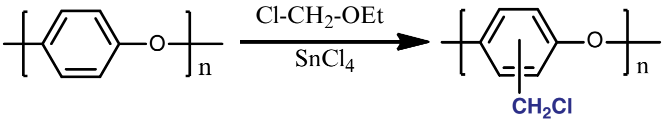
Generally, chemical reactions of polymers are of two types: (1) Reactions on the main chain that include either (a) degradation reactions which are accompanied by a destruction or a decrease in molecular weight, (b) intermolecular reactions which are accompanied by an increase in molecular weight as result of crosslinking reactions, (c) formation of graft or block copolymers, or (d) reactions on the end groups of the main chains to form end-functional groups. (2) Reactions on side pendant groups on structural units result in a change in chemical composition of the polymer without affecting the molecular weight and involve the introduction or conversion of functional groups or the introduction of cyclic units into the backbone [4–6]. Starting with an already formed polymeric material containing reactive groups and replacing them by the desirable functional groups through chemical reaction is the simplest and most frequently used technique for the preparation of high-molecular-weight polymers with functional groups. In this technique commercially available resins of high quality are normally employed and the desired functional groups are introduced by using standard organic synthesis procedures. The ease of chemical modification of a resin, and indeed the level of success in its subsequent application, can depend substantially on the physical properties of the resin itself.

While the chemical modification approach is attractive for its apparent simplicity and the fact that it ensures a product with a good physical form, it suffers some major *drawbacks*: (1) They must be carried out under mild conditions and the yield of all reactions must be quantitative because every undesirable group that is formed by a side reaction will become a part of the polymer chain. Thus the functionalization reactions required must be as free of side reactions as possible. (2) The polymer chains must not undergo degradation during the chemical modification, particularly for polymer chains which are sensitive to chemical reactions. (3) The distribution of the functional groups on the polymer matrix may not be uniform, i.e., not every repeat unit is functionalized. (4) The functional groups attached to a polymer chain may have a quite different reactivity from the analogous small molecule because of the macromolecular environment. Thus, more drastic reaction conditions may be required to reach a satisfactory conversion. (5) The density of reactive groups obtained is generally low, i.e., there is no regularity between the structure units and the functionality. (6) The chemical and physical nature of the polymer often change as a result of undesirable side reactions, such as crosslinking, dehydrohalogenation, etc. (7) The reactivity of a functional group may be low when it is directly attached to the backbone owing to steric hindrance by neighboring side groups and depends mainly on the proper choice of a swelling solvent. (8) Rate constants of reactions often decrease as the degree of substitution increases, i.e., the overall substitution reaction cannot proceed to completion. This problem of decreasing reactivity in the course of the substitution reaction on polymers can be overcome either by spacing the site group from the backbone via spacer groups or by the use of the copolymer composition. (9) The final modified polymer cannot be purified after modification because it will contain some impurities in the form of unreacted groups or other functionalities resulting from side reactions. (10) Different methods of preparation may give rise to different functional group distributions. (11) The difficult characterization of the crosslinked polymers after the reaction, since a number of analytical methods are not well suited for the study of insoluble materials.

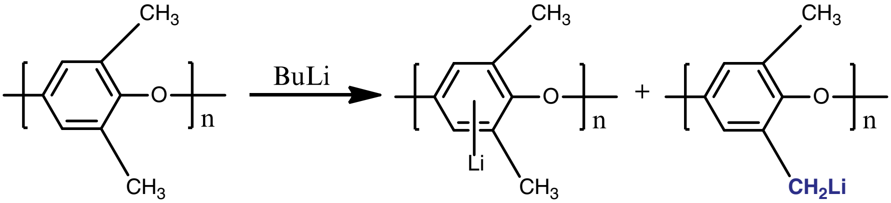
(A) **Modification of polystyrene** – Although many polymer types, including both aliphatic and aromatic organic as well as inorganic polymers, have been employed as a carrier for functional group, the most widely used as support is the PS matrix. Thus most work on the chemical modification of polymers has been centered on the introduction and modification of various functionalities on PS. The uses of polymers other than PS have met with limited success for reasons such as lack of reactivity, degradation of the polymer chain, or other unsuitable physical properties of the final polymer. In principle, PS fulfils the major requirements for a solid support because it has many *advantages* over other polymers: (1) It undergoes easy functionalization through the aromatic ring by electrophilic substitution. (2) It is compatible with most organic solvents and its functional groups are easily accessible to the reagents and solvents. (3) It is chemically stable because its aliphatic hydrocarbon backbone is resistant to attack by most reagents. Hence the polymer chains are not susceptible to degradative scission by most chemical reagents under ordinary conditions. (4) It is mechanically stable to the physical handling required in sequential synthesis. (5) Its crosslinking structure can easily be controlled during the manufacture by the type and degree of divinylbenzene crosslinker that influences the polymer swelling nature and its pore dimension. (6) PS is readily available commercially.

Polystyrene, chloromethylated PS, and lithiated PS rings are used in the modification of PS resins for the preparation of new functional polymers because they provide a method of attaching a wide variety of both electrophilic and nucleophilic species. However, the use of commercial PS beads in chemical modifications requires the removal of surface impurities such as suspending or stabilizing agents which remain from the polymerization process, since surface contaminants can prevent the penetration of reagents into the swollen beads or lead to the need for more drastic reaction conditions.

(B) **Modification of condensation polymers** – Although the mechanical properties of condensation polymers are often superior to those of PS, little work has been done on the introduction of functional groups by chemical modification of condensation polymers. For example, chloromethylation of polymers con-



Scheme 1.2 Preparation of chloromethylated poly(oxyphenylene) [60]

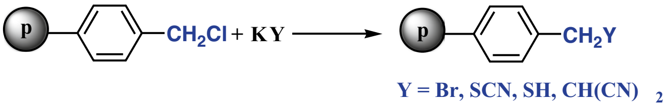


Scheme 1.3 Preparation of chloromethylated poly(2,6-dimethyl-1,4-oxyphenylene) [61]

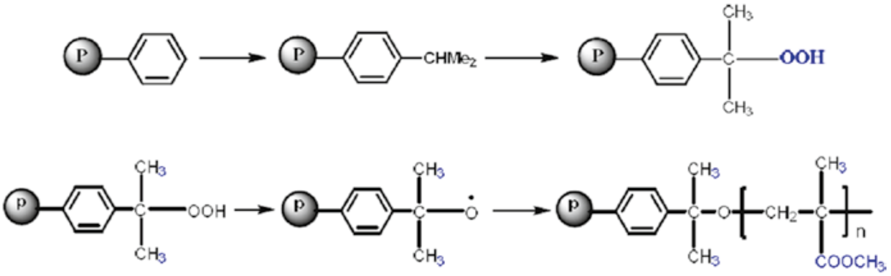
taining oxyphenyl repeat units with chloromethylethylether in the presence of $SnCl_4$ has been reported as shown in Scheme 1.2 [60].

The lithiation of condensation polymers with the aid of n-butyllithium has also been reported [61]. Poly(2,6-dimethyl-1,4-phenyl ether) was metallated to give both the ring and the alkyl group lithium product depending on the duration and temperature of the reaction (Scheme 1.3).

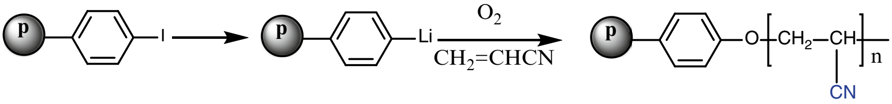
(C) **Modification under phase transfer catalysis** – A large number of functional polymers have been prepared by chemical modification under classical conditions. However, many of these reactions carried out on crosslinked polymers proceed very slowly and produce a low degree of functionalization because of hindered diffusion of the reagents through the swollen gel and the heterogeneous nature of the reaction system. These difficulties may be alleviated by using specific solvents or catalysts. Phase transfer catalysis has been found to be a valuable tool in the preparation of crosslinked and linear polymers containing various functionalities [62–70]. The application of phase transfer catalysis to polymer functionalization involves the chemical modification of polymers in a two- or three-phase system. These reactions involve mainly nucleophilic displacements on PS derivatives or reactions of polymers that have a reactive nucleophilic pendant group. In addition to the ease of reaction and work up, it has generally been found that the phase transfer-catalyzed reactions afford better results than those carried out under classical conditions in terms of both polymer purity and functional yields. These simple and mild methods have been used for the synthesis of functional polymers via, for example, chemical modifications of pendant chloromethyl groups in poly(chloromethyl styrene) by reaction with several inorganic salts [71] as well as the salts of organic compounds [72] in the presence of a typical phase transfer agent (Scheme 1.4).



Scheme 1.4 Chemical modification of poly(chloromethylstyrene) [71]



Scheme 1.5 Grafting polymerization of polymeric free radical initiators



Scheme 1.6 Grafting polymerization of polymeric anionic initiators

(D) **Modification by grafting** – The grafting functionalization technique has also been successfully used for modifying the physical and chemical properties of various polymers by several methods. (i) *Radical chain transfer grafting* is more pronounced for modification with polymer chains containing labile atoms which are easily abstracted by the attacking free radical source. Heating a mixture of a linear polymer dissolved in an appropriate functional monomer and initiator results in transfer between the polymer chain and the radical formed from the initiator. A polymer radical can initiate polymerization of the monomer and the amount of grafting achieved by this effect is usually small and depends on the magnitude of the chain transfer constant of the polymer which is usually small. Thus, this grafting method leads to a mixture of linear polymer and graft copolymer. (ii) *Polymeric initiator grafting* creates active centers in the polymer chain, e.g., peroxide or azo groups create free radicals in the polymer chain and lead to the polymerization of the monomer to be grafted (Scheme 1.5). Anionic initiators that create carbanions in the polymer chain, have been used as sites for grafting in this technique (Scheme 1.6). (iii) *Chemical reaction grafting* can aid in the formation of grafted copolymers by attaching polymer chains containing end-functional groups onto other polymers containing pendant functional groups. The pendant reactive groups present along the polymer structural units are used as sites for grafting.

Polymers with end-functional groups which are used as branches can be obtained by different methods: (1) condensation polymer, (2) free radical initiators with the desired reactive groups, e.g., azo catalyst containing carboxyl groups, (3) anionic polymerization followed by the reaction of the resulting living polymer with the desired functional reagent, e.g., carbon dioxide or ethylene oxide. (iv) *Radiation grafting* using a simultaneous method is a convenient one-step procedure for modifying polymers [72]. It is useful in particular for imparting wettability to hydrophobic polymers using hydrophilic monomers. For example, *p*-styryldiphenyl phosphine has been grafted onto PVC, PP, and crosslinked PS beads at radiation dose levels that do not affect the properties of the resulting copolymer [73, 74]. This technique is valuable for monomers and polymers that are radiation sensitive to achieve the required functional grafting. The most commonly used energy sources are ionizing radiation, plasma gas discharge, and UV-light sources in the presence of photosensitizer [75, 76]. The technique involves irradiating a solution of polymer in functional monomer with radiation that results in radical formation on the primary polymer chain, the sites of radical formation become the points of initiation for the side chains. At the same time, the radiation initiates polymerization of the monomer and thus a mixture of graft copolymer and homopolymer will be obtained. The predominant variable which influence the grafting yield include (a) the radiation dose and dose rate (time), (b) the concentration of monomer and sensitizer in the solvent, (c) the structure of both monomer and base polymer. However, for grafting the polymer surface a solvent is used. The requirements for an appropriate solvent are as follows: (1) it must a nonsolvent for the base polymer, i.e., it must not swell the base polymer, (2) slight interactions are necessary to provide reaction sites for grafting, (3) good solvent-growing chain interactions assist the propagation of the graft chain outside the base polymer surface, (4) the solvent must be inert to the triplet excited state of the sensitizer.

(E) **Functionalization of membranes –** Membranes containing functional groups, which dominate their choice and use as reactive materials, are made by (a) polymerizing styrene-divinylbenzene in sheet-shaped molds followed by further chemical reactions for incorporation of the active species, (b) copolymerization of the functionalized monomer with divinylbenzene in thin film form, and (c) mechanically incorporating powdered functionalized polymer into a sheet of some other extrudable or moldable matrix [77–82].

1.1.2.2 Modification of Biopolymeric Materials

Naturally occurring organic polymers (biopolymers) are produced by all living organisms and play an essential role for life [83]. They include polysaccharides (cellulose, starch), hydrocarbons (rubber), polyesters (polyhydroxyalkanoates, poly(glutamic acid)), and proteins (collagen, gelatin, wool, silk, hair) – all of which are also biodegradable. There are several options for chemical modification of such naturally occurring biopolymers to add desirable functionality.

(A) **Polysaccharides** are biomacromolecules consisting of monosaccharide repeating units. However, the exact placement of linkages, orientation, sequences, the configuration of the linking functional groups between the structural units, and the presence of any other substituents can cause differences in physicochemical properties. There are many different kinds of polysaccharides synthesized by plants and bacteria [84, 85]. Many of these can undergo various types of chemical modifications.

Polysaccharide-based supports prepared from cellulose, agarose, Sepharose, and Sephadex are well known gel filtration media in chromatographic procedures for the purpose of fractionation. Some of these supports have been functionalized and used widely in applications such as affinity chromatography, enzyme immobilization, [86] and ion exchangers [87]. Other supports have been employed in organic synthesis, e.g., in the binding of oxidizing and reducing anions as redox reagents [88], in the support of homogeneous transition metal complexes for use in hydrogenation catalysts [5], and for the attachment of crown ethers as alkali metal complexing species [6]. Polysaccharides are thought to play an essential role in the stabilization of soil structure [89, 90] by the adherence of soil particles into stable aggregates with polysaccharide in the soil, either as plant residues or microbial metabolites of plant tissues [91]. Recently, a number of phosphonium and ammonium salts supported on cellulose have been synthesized and employed as phase transfer catalysts [92, 93].

In spite of the nontoxic and highly hydrophilic character of polysaccharides which is particularly effective in numerous hydrophilic conditions, the main drawbacks to their wide application are that they are susceptible to microbial attack, with a high degree of adsorption on some substrates and having low capacities for functionalization. In addition, they are less mechanically and chemically stable than synthetic polymers. However, they are advantageous in applications where the degradability of the main backbone is of importance in order to prevent long persistence. Polysaccharide-based supports include: cellulose (cotton, wood), agar (agarose, agaropectin), carrageenan, alginate, chitin/chitosan, starch, pectin, gums (galactomannan, gum arabic, xanthan), Sepharose, and Sephadex.

1. Cellulose is produced by plants and isolated as microfibrils from the cell walls of cotton and wood by chemical extraction. It is a linear polysaccharide of D-β-GLUCOSE monomers joined by (1,4)-linkages (cellobiose repeating units) (Fig. 1.2) [94, 95]. The macromolecular structure regularity of the cellulose chain leads to a crystalline structure with resulting rigidity and strength due to the extensive hydrogen bonding between hydroxyl groups [96–98]. Its insolubility in

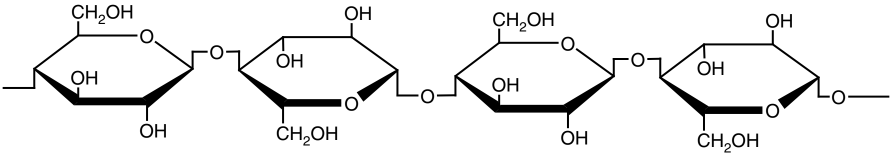


Fig. 1.2 Cellulose structure

all common solvents and infusibility prevents its processing by the melt or solution techniques and accordingly it is usually converted into derivatives to improve its processing [99]. Cellulose is not soluble in water but dissolves in highly polar solvents as *N*,*N*-dimethylacetamide-LiCl, *N-methylmorpholine-H_2O*, $Cu(OH)_2$-ammonia, trifluoroacetic acid-RCl, Ca-thiocyanate-water, and ammonium thiocyanate-ammonia.

Wood as a form of natural plant fiber is a composite material in which the cellulose fibers as reinforcing elements are embedded in the *lignin* matrix. It is used as fuel or as a construction material, for packaging, artworks, and paper. Lignins are aromatic amorphous oligomers of di- and trisubstituted phenyl propane units obtained from the wood as by-products of the pulp and paper industries by solvent extraction. Lignin can be used after fractionation as fillers or as antioxidants and can be modified by esterification [105, 106].

The properties of cellulose are closely correlated with the hydrogen bonds that produce an interchain linking, hence it is poorly reactive because the strong molecular interactions prevent the penetration of reagents. Cellulose with a wide range of functional properties can be created by controlling the degree and type of substitution [100]. It can be converted to a soluble compound via its derivatization and disruption of hydrogen bonds [95]. Acid hydrolysis of cellulose produces D-glucose, and peroxidases catalyze oxidation reactions of cellulose by free radical attack on the C2–C3 positions to form aldehyde-cellulose, which is highly reactive. Other cellulose derivatives include: (i) Ethers by reacting alkali cellulose with alkyl halide to form alkyl cellulose and with propylene oxide to form hydroxypropylcellulose [101]. (*ii*) Esters by reacting alkali cellulose with sodium chloroacetate to form carboxymethylcellulose, which is important for viscosity-forming applications [102]. Cellulose fibers can be produced from cellulose acetate by wet spinning of fibers [103]. Cellulose xanthate is obtained by treatment of alkali cellulose with carbon disulfide giving sodium cellulose xanthate which is used as a soluble intermediate for processing cellulose fiber or film forms. Then on passing into an aqueous coagulating bath (H_2SO_4, Na and Zn sulfates) loss of CS_2 produces the regenerated cellulose [104]. Treatment of cellulose with HNO_3 exchanges all the hydroxyl groups with nitrate groups yielding nitrocellulose (*guncotton*) which is an explosive component of smokeless powder. Partially nitrated cellulose (*pyroxylin*) is used in the manufacture of collodion, plastics, lacquers, and nail polish. The viscose process is used for the production of textile fibers (*viscose rayon*), and transparent packaging film (*cellophane*) [32].

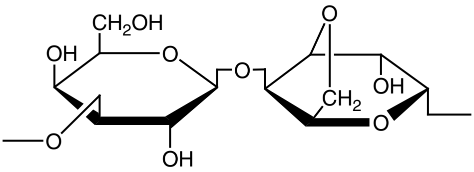


Fig. 1.3 Agarose structure

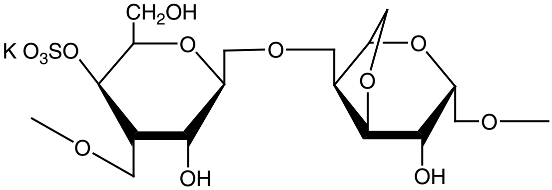


Fig. 1.4 Carrageenan structure

2. Agar is a natural gelling substance obtained primarily from the cell walls,of seaweeds. Chemically, it is a heterogeneous mixture of two classes of linear polysaccharides consisting of agarose and agaropectin, which are based on galactose-based backbones [107]. Agarose is a nonionic linear polysaccharide made up of repeating structural units of agarobiose (disaccharide of D-galactose and L-3,6-anhydro-α-galactopyranose) (Fig. 1.3). It is soluble in boiling water and the main chains are held together by hydrogen bonds. It is a gelling component which is essentially sulfate-free and has neutral charge. The beaded derivatives of agarose have many of the properties of an ideal matrix and have been used successfully in numerous purification procedures. The uniform spherical shape of the gel particles is of particular significance and can readily undergo substitution reactions. It is used in biotechnological applications for immobilization [108] and in bioreactors [109, 110]. Agaropectin is a nongelling ionic polysaccharide, slightly branched with sulfate and pyruvate acidic side-groups and sulfated, and may have methyl and pyruvic acid ketal substituents. The gelling properties of agar are improved by the conversion of L-galactose-6-sulfate (agaropectin) to 3,6-anhydro-L-galactose (agarose) or by the removal of agaropectin [111]. Agar is used as an ingredient in many foods as a gelling agent: as a thickener for soups, to make jellies, ice cream and other desserts, as a clarifying agent in brewing, and as a source of nutrition. Gels produced with agar have a crispier texture than desserts made with animal gelatin.
3. Carrageenan is obtained by alkaline extraction of red seaweeds and composed of linear sulfated polysaccharides of carrabiose (disaccharide) of repeating D-galactose units and D-3,6-anhydro-α-galactopyranose, joined by alternating β-(1-3)- and α-(1-4)-linked galactose residues present as 3,6-anhydrides (Fig. 1.4) [111–114]. It differs from agar in that it has sulfate ester groups (–OSO_3^-) in place of some hydroxyl groups of the D-3,6-anhydro-α-galactopyranose units. The three carrageenan classes are: (1) *kappa* (κ) forms strong, rigid gels in the presence of potassium ions; (2) *iota* (ι) forms soft gels in the presence of calcium ions; (3) *lambda* (λ) does not form gel. The primary differences in the

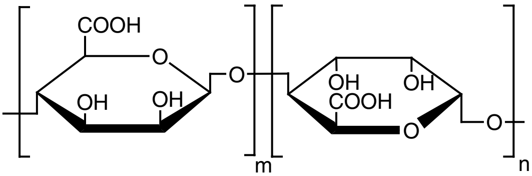


Fig. 1.5 Alginic acid structure

properties of the three types are determined by the number and position of the sulfate ester groups on the repeating galactose units. High levels of sulfate esters decrease the solubility temperature and produce low-strength gels, i.e., decrease gel formation (ι-carrageenan). Carrageenans are soluble in water and form a variety of different gels by precipitation from solution in the presence of K^+ or Ca^{2+} ions [111–114]. All types are soluble in hot water; in cold water, only the ι-form; the sodium salts of κ- and λ-carrageenan are also soluble in cold water. Carrageenans are widely used in producing gelled foods and also as thickening, suspending, and stabilizing agents, and as entrapment media [115, 116] in: (a) desserts, ice cream, cream, milkshakes, sweetened condensed milks, and sauces, (b) beer as clarifier to remove haze-causing proteins, (c) processed meats as substitute for fat, to increase water retention and volume, or to improve sliceability, (d) toothpaste to prevent separation of constituents, (e) fruit ingredients encapsulated in gels, (f) sticky foams used in firefighting, (g) shampoos and cosmetic creams, (h) soy milk to emulate the consistency of whole milk, (i) diet sodas: mouth feel and sustended flavor, (j) personal lubricants, (k) sexual lubricants and microbicides, (l) to thicken dairy products, and (m) in air freshener gels and for marbling of ancient paper and fabrics [111, 112, 117–120].

4. Alginate is present in the cell walls of brown algae as the calcium, magnesium, and sodium salts of alginic acid. It is a linear block copolymer of (1-4)-linked β-D-mannuronic acid and α-L-guluronic acid units, linked in different ways (Fig. 1.5) [121, 122]. Alginate forms gels with divalent Ca^{2+} ions [123], in which chemical and physical crosslinking takes place via carboxyl and hydroxyl groups, retaining the random-coiled shape or crosslinked structure [124]. An increase in gel strength can be achieved by Al^{3+} ions [125].

Alginate is water-insoluble because of crosslinking caused by the divalent cations. It forms a gelatinous, cream-colored substance by adding aqueous $CaCl_2$ to aqueous sodium alginate. The alginate beads are generally suitable for immobilizing enzymes and for entraping all sorts of cells, such as bacteria, yeast, and fungi [126]. Alginate beads [127] were used for immobilization [128] of yeast cells [129], phenol oxidase [130], ethanol produced by fermentation [131], production of acetone–butanol–ethanol [132, 133] and isopropanol–butanol–ethanol [134] in fermentation [135], and β-glucosidase [136–139]. Alginate film immobilizes bacteria in both milk acidification and inoculation depending on the surface area of the immobilized biocatalyst and the bioreactor volume [140, 141]. Calcium alginate is used in: (a) plant tissue cultures to produce insoluble artificial seeds, (b) to produce edible substances, (c) and is incorporated into wound dressings. It absorbs water and is used as a gelling agent, and for

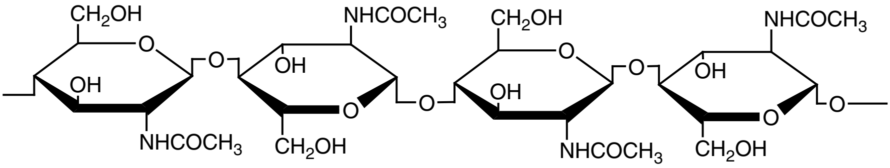
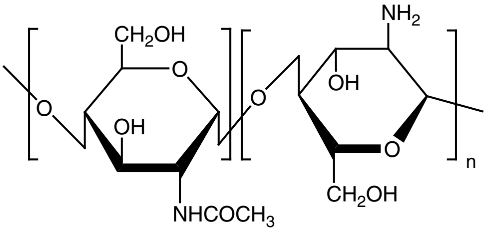


Fig. 1.6 Chitin structure: *N*-acetyl-D-glucosamine

Fig. 1.7 Chitosan structure: poly-D-glucosamine



thickening drinks, ice cream, and cosmetics, in the preparation of dental impressions, prosthetics, life casting, and in the food industry for thickening soups and jellies. It is also used in the weight loss industry as an appetite suppressant. Sodium alginate is a flavorless gum, used as an additive by the foods industry to increase viscosity as in the production of gel-like foods. Potassium alginate is also widely used in foods as a stabilizer, thickener, and emulsifier.

5. Chitin/Chitosan: Chitin is natural poly(*N*-acetyl-D-glucosamine) (Fig. 1.6) obtained from the exoskeletons of arthropods (e.g., insects, crabs, lobsters, shrimp, and other crustaceans), mushroom tissue, the cell walls of fungi, and the radulas of mollusks by extraction via chemical treatment with alkali solution followed by decalcification and demineralization [142–147]. Chitin occurs in three forms: α-, β-, and γ-chitin. The α-form is a three-dimensional, hydrogen-bonded network, rendering its swelling and dissolution difficult. The β-form lacks hydrogen bonding between the main chains, which allows its easy hydration and high reactivity; it is biodegradable, hard, and insoluble in most common solvents but dissolves in *N*,*N*-dimethylacetamide–LiCl, *N*-methyl-2-pyrrolidone–LiCl, and trichloroacetic acid-chlorinated methanes or ethanes. It has some unusual properties as a flexible and strong material, depending on the presence of other cellular materials such as glucans, proteins, and $CaCO_3$.

   Chitosan (Fig. 1.7) is obtained from deacetylated chitin by chemical treatment (via a strong alkali solution) or by enzymatic (deacetylase) treatment, consisting of 50–70 % *N*-deacetylated chitin. Repeating the hydrolysis can lead to extented values of *N*-deacetylation of up to 98 %. Its solubility in water depends on the degree of *N*-deacetylation, the molecular weight, and media pH. It is biocompatible, biodegradable into harmless products, and suitable to chemical modifications to form chitosan derivatives through modification of the primary (C-6) and secondary (C-3) hydroxyl groups and amine (C-2) groups. Reactions

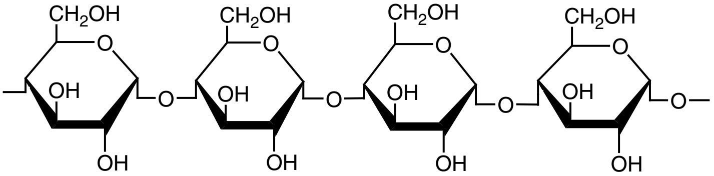


Fig. 1.8 Amylose structure

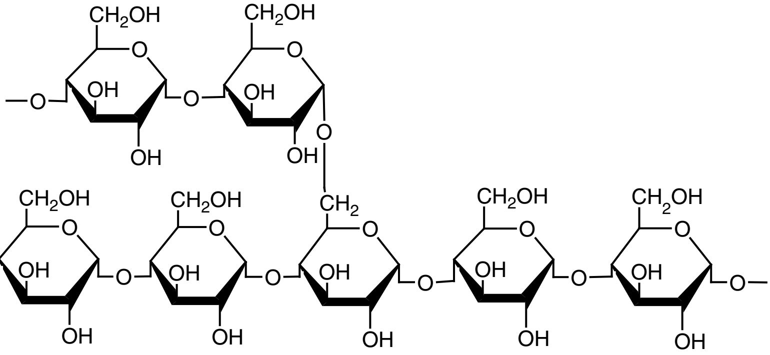


Fig. 1.9 Amylopectin structure

of hydroxyl and amine groups include: acylations leading to acid chlorides, urethane, and ureas; amine quaternization by alkyl iodides; imine formation by aldehydes/ketones that can subsequently be reduced to *N*-alkylated derivatives. Carboxymethylated chitin and chitosan are commonly produced by the reaction of their salts with sodium chloroacetate. Chitin or chitosan can also be chemically modified by graft copolymerization using a variety of monomers (styrene, methyl methacrylate, methyl acrylate, acrylic acid, and acrylamide) initiated by a redox free-radical, γ-irradiation, or by chemical grafting with preformed polymers via end-functional groups, e.g., PEG or poly(2-methyl-2-oxazoline).

6. Starch is the major form of stored carbohydrate in plants (e.g., potatoes, corn, rice). It consists of a physical combination of two polysaccharides: amylose and amylopectin. Amylose is a linear polysaccharide in which the glucopyranoside repeating units are linked together by α- or β-1,4-glycosidic bonds (Fig. 1.8). Amylopectin is a branched polysaccharide in which the α-glucopyranoside repeating units are linked together by 1,6-linkages (Fig. 1.9) [148].

   Amylose (20 % wt) is crystalline and soluble in boiling water, whereas amylopectin is completely insoluble. Starch can adsorb water, can be easily chemically modified, and is resistant to thermo-mechanical shear [149, 150]. Acetylated starch has several advantages as a structural fiber or film-forming polymer, is hydrophobic, and has better retention of tensile properties in aqueous environments. Corn syrup is obtained by the chemical hydrolysis of starch that breaks

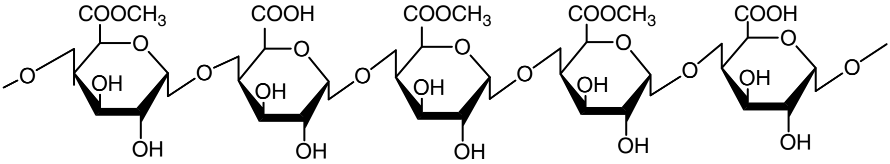
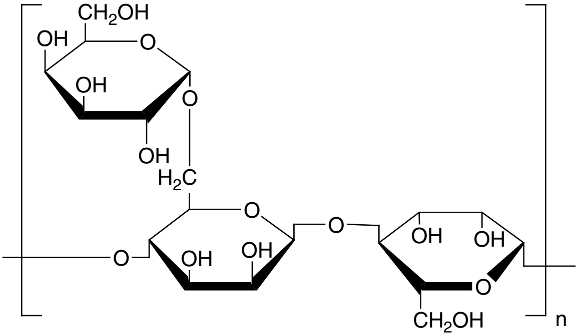


Fig. 1.10 Pectin structure

Fig. 1.11 Guar gum structure



the main chains into maltodextrin (not sweet), then to dextrins (oligosaccharides), and finally to glucose. Fructose corn syrup is made by treating corn syrup with enzymes to convert the glucose into fructose, which is commonly used to sweeten soft drinks. Hydrogenated glucose syrup is made by hydrogenating the corn syrup to produce sugar alcohols like maltitol and sorbitol. Polydextrose is a highly branched polymer with many types of glycosidic linkages created by heating dextrose with an acid catalyst and purifying the resulting water-soluble polymer. Starch is used as a raw material to produce films that possess low permeability useful for food packaging and for making agricultural mulch films because they degrade into harmless products on contact with soil microorganisms [148].

7. Pectin is a polysaccharide that acts as a cementing material in plant cell walls. It is the methylated ester of polygalacturonic acid consisting of α-galacturonic acid units joined by 1,4-linkages (Fig. 1.10). It is an important ingredient for fruit preserves, jellies, and jams.
8. Gums are of different types: (a) Galactomannan gums are plant fiber polysaccharides consisting of β-mannose backbones with α-galactose side groups. The mannopyranose units are linked via 1,4-bonds to which galactopyranose units are attached with 1,6-linkages (Fig. 1.11). There are four types of galactomannan gums according to the ratio of mannose to galactose: fenugreek gum (1:1), guar gum (2:1), tara gum (3:1), locust bean gum (4:1) [151–155].

Galactomannan features high water absorption, gelling action due to intermolecular hydrogen bonds, high thickening power, and is extensively used in the food industry to increase the viscosity and the stabilization of food products. It is

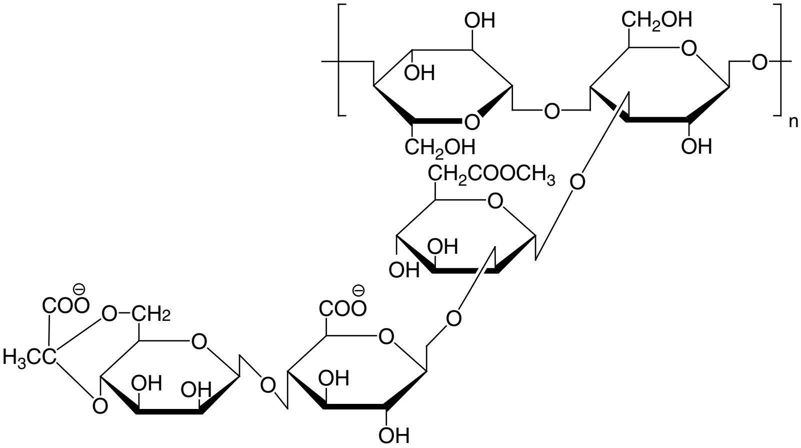


Fig. 1.12 Xanthan gum structure

used as a hunger suppressant because it produces a feeling of fullness by creating highly viscous solutions that retard absorption of nutrients in the gastrointestinal tract. (b) Gum arabic is a resin obtained commercially from acacia trees. It is a complex mixture of polysaccharides and glycoproteins. It is used in the food industry as a stabilizer and as important ingredient in soft drink syrups. (c) Xanthan gum is a polysaccharide of β-D-glucose structural units, but every second glucose unit is attached to side chains of trisaccharides consisting of mannose, glucuronic acid, and mannose (Fig. 1.12). The mannose unit near the backbone has an acetate ester on C-6, and the mannose at the end of the trisaccharide is linked through C-6 and C-4 to the second carbon of pyruvic acid. It forms viscous fluids on mixing with water due to the negatively charged carboxyl groups on the side chains and on mixing with guar gum the viscosity of the combination is increased. Thus it is used as a thickener for sauces, to prevent ice crystal formation in ice cream, and as a low-calorie substitute for fat. (d) Gum rosin, also called colophony, is a solid form of resin obtained from pines and other conifers, produced by heating fresh liquid resin to vaporize the volatile liquid terpene components. It is semitransparent in appearance and varies in color from yellow to black. At room temperature rosin is brittle, but it melts at stove-top temperatures. It chiefly consists of different resin acids, especially abietic acid.

9. Sephadex is a three-dimensional network in which soluble dextran chains are crosslinked by glycerol ether bonds or reaction with epichlorohydrin in alkaline solution. Dextran is a branched-chain polysaccharide composed of D-glucose units which are jointed mainly by means of α-1,6-glycosidic bonds and is branched by 1,2-, 1,3-, and 1,4-glycosidic linkages. Sephadex is stable to chemical attack by, for example, alkali and weak acids and can be heated without any change in properties.

(B) **Specific polymeric materials of animal origin.** Animals obtain polymeric proteins from plants or other animals that they use as foods. They digest the proteins into amino acids and then manufacture their own specific proteins (including enzymes) from these [148]. Specific animal proteins are collagen, gelatin and keratin. (1) Collagen is derived from connective tissues such as skin and cartilage and can be extracted by organic solvents. It is widely used as a support for enzymes and is cast into membrane form. Collagen spherical beads can be structured by dehydrating suspensions of collagen fibers and stabilized by crosslinking of the gel beads with formaldehyde or glutaraldehyde vapors [156–160]. (2) Gelatin is manufactured by refining processed collagen. It dissolves in warm water and forms an elastic physical hydrogel upon cooling. Gelatin and its copolymers with agarose and alginate crosslinked with glutaraldehyde have been used as suitable immobilization supports to sustain more stable invertase activity for the fermentation of glucose or sucrose [161–163]. Gelatin is used as a thickener and gelling agent in the food industry and used for the production of microcapsules that enclose active agents, bacteria, and adhesives [164–166]. The application of natural animal biopolymers can be extended via their chemical modification, by grafting that serves the dual purpose of utilizing renewable biopolymers, as replacements for petroleum-based polymers, and as biodegradable compositions which can be tailored for degradation, e.g., grafting MMA onto gelatins by radical initiators.

1.1.2.3 Modification of Inorganic Polymeric Materials

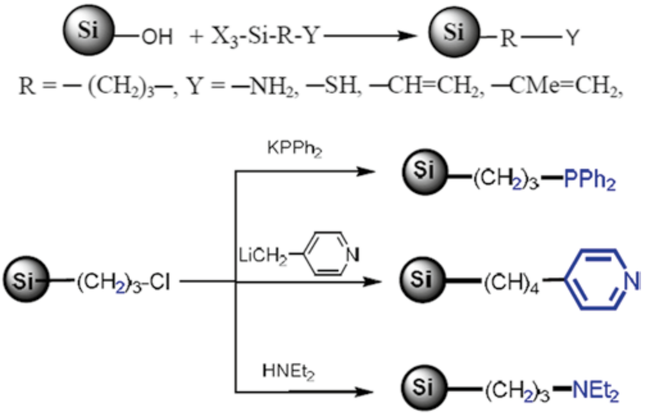
Inorganic polymers whose backbone chains are devoid of carbon atoms essentially include metal oxides such as polysiloxane, polysilane, polygermane, polystannane, polyphosphazene, *o*-alumina, zeolites, glass, and silica (silicate). Modified silica is rigid and not subject to swelling and the choice of the solvent is of little effect regarding its physical and chemical behavior since most of the functional groups are located on the surface. Physical adsorption of reagents and catalysts on inorganic supports, by hydrogen bonding between oxygen functions of the support surface and polar groups on the reagent or catalyst, have been used in many heterogeneous modification [167]. A quite interesting approach for modification of silica supports has been introduced in the form of chemical binding of reactive molecules to the surface hydroxyl groups, owing to the small average pore diameter [168]. Modification of the surface hydroxyl groups often leads to condensation of additional silica material in the pores. Several difficulties arising when using organic polymers and that can be overcome by using modified inorganic support material, include: (1) All reaction rates are unfavorably controlled by diffusion since functional groups are uniformly distributed throughout the organic polymeric resin. This distribution cannot be overcome by using resins with a lower concentration of functional groups. (2) The use of different solvents during the reaction and washing steps causes different swelling of resin particles, and thus affects reaction rates, yields, and purity of the synthesized products [169, 170]. (3) Variable swelling of the polymer particles by the different solvents is necessary in a solid phase synthesis, but also causes some difficulties in the automation of the processes, hence batch procedures must be used instead of column procedures.

However, the properties of modified inorganic supports, such as the localization of reactive groups to the surfaces, the chemical and dimensional stabilities, the ease of filtration, and the use in continuous-flow column operations, all serve to overcome the difficulties involved in the use of organic supports. Additionally, inorganic supports offer several advantages: (1) prevent any ion exchange mechanism before or after the coupling step in multistep synthesis, (2) have high thermal stability and mechanical strength, (3) are stable in solvents and acids, (4) resistant to microbial attack, (5) can be used under high-pressure operation, (6) do not require special equipment for most procedures.

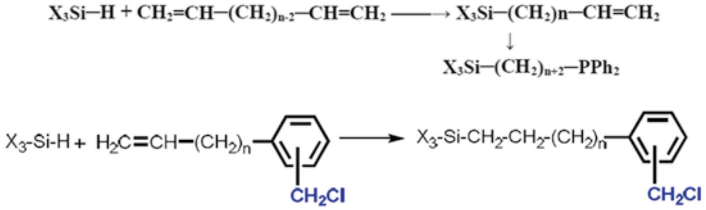
Despite these advantages, the main disadvantage of using modified silica as a support in organic synthesis is that the Si—Z—C bond (Z = O, N) is highly polarized and thus highly sensitive to attack by all reagents containing free hydroxyl groups, especially water, which results in removal of the synthesized molecule from the silicate polymers. This difficulty can be overcome by constructing a short aliphatic chain between the three-dimensional silicate network and the functional group by bonding organic molecules to the siliceous surface through Si—Z—Si—C bonds which are more stable against an attack by electrophilic or nucleophilic agents than the Si—Z—C bonds. Another significant drawback to the use of inorganic supports is the degree to which they can be functionalized. Inorganic matrices have an upper limit of functional groups so that loadings of 1–2 meq/g are difficult to achieve, whereas organic matrices can carry up to 10 meq/g matrix. Thus, although the specific activity of inorganics may be lower, their potential for monocoordination and site isolation is greater than that of organic matrices. Nevertheless, limits to the range of applications of functionalized silica occur because of the chemical stability of the silica oxygen bond in an alkaline medium.

The most useful technique for modifying silica involves the reaction of surface silanol groups with organosilanes of the kind X_3—Si—R—Y, which are able to markedly improve the bonding between functional groups and silica particles. Silane coupling agents either contain the desired functional group or can be subject to later modification (Scheme 1.7). Y is a reactive organic group, such as amino, mercapto, phosphino, vinyl, or epoxy, which is bound via an alkyl or aryl to the silicon (R). X represents an hydrolyzable group OMe, Cl, NH_2, or OCOMe.

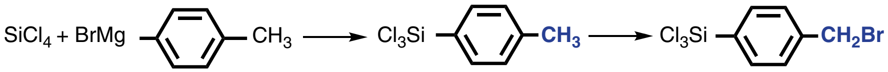
The activation of a silica surface and the successive covalent binding of active groups is normally realized by treatment of silica particles or gel with hydrochloric acid to afford a sufficient number of silanol groups to be reacted with different organosilane derivatives [171]. In general, functionalization of all surface hydroxyl groups is difficult to achieve and those remaining without modification can give rise to adsorption problems. Thus, it is necessary to silylate the unmodified hydroxyl groups by reacting the modified support with excess hexamethylene disilazane in order to minimize the adsorption of substrates or reagents. This type of modification has been employed successfully to anchor different functionalities. It has the



Scheme 1.7 Silica functionalization with organosilanes and chemical modification



Scheme 1.8 Preparation of organosilane derivatives [174–176]



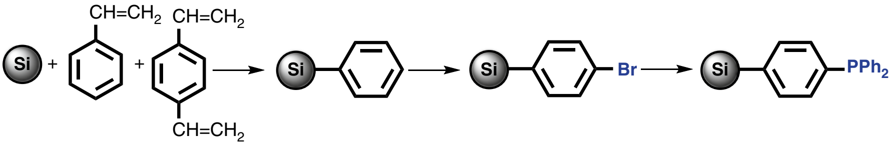
Scheme 1.9 Preparation of organosilane derivatives by Grignard reagent [179]

advantage of being a one-step reaction, simple to perform under mild conditions, and a wide range of X_3—Si—R—Y compounds are commercially available. These modification reactions have been used for the formation of chemically bonded layers of organic molecules on the surface of siliceous materials in the field of gas and liquid chromatography [172, 173].

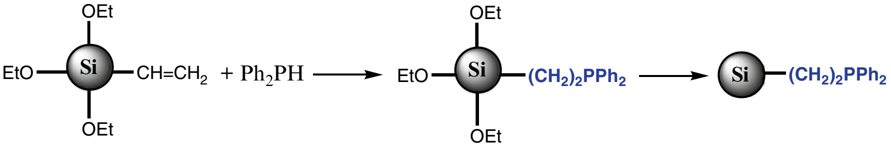
Organosilanes, X_3—Si—R—Y, can be prepared by hydrosilylation, i.e., by the addition of silane, $HSiX_3$, to an olefin derivative in the presence of catalyst such as dipotassium hexachloroplatinate or palladium. The addition is anti-Markovnikov because of the unusual polarization in the silicon hydrogen bond (Scheme 1.8) [174–176].

In addition, organosilanes can be prepared by the reaction of Grignard reagent (Scheme 1.9) [175, 177, 178]:

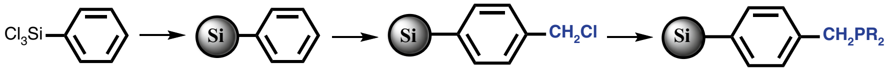
The nature of X in X_3—Si—R—Y affects the extent of anchoring, i.e., the concentration of functional groups anchored to silica decreases with increasing steric requirement of the hydrolyzable group X [179]. This is probably due to the reaction



Scheme 1.10 Preparation of phosphinated silica [180, 181]



Scheme 1.11 Preparation of phosphinated silica from silane derivatives [183]



Scheme 1.12 Phosphination modification of polyphenylsiloxane [183–185]

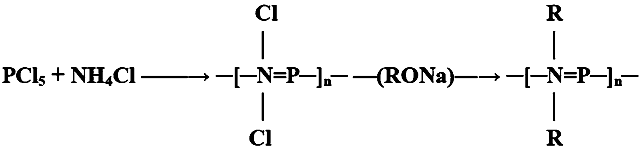
of a single hydrolyzable group with a surface hydroxyl, leaving two groups free to block other sites from reacting with other X_3—Si—R—Y compounds.

Another type of silica-supported functional group has been prepared by coating silica gel with PS via free radical polymerization of styrene and divinylbenzene in the presence of silica gel which can in turn be further functionalized by the bromination and reaction with $KPPh_2$ to give silica gel coated with phosphinated PS (Scheme 1.10) [180, 181]:

A totally different approach for functionalization of silica has been developed in which the functional group is built into trialkoxysilane and then polymerized to produce a nonlinear polymer based on Si—O—Si backbone [182]. For example, 2-(diphenylphosphine)ethyltriethoxysilane was treated with $Si(OEt)_4$ and a trace of HCl to give silica containing phosphorus (Scheme 1.11) [183]:

Furthermore, inorganic polyphenylsiloxane has been prepared by hydrolysis of $PhSiCl_3$ and subjected to further functionalization [183–185]. After initial formation of a prepolymer, the polymer formed in the presence of KOH catalyst [183], is subjected to chloromethylation with chloromethylmethylether and $ZnCl_2$ catalyst, and phosphination by reaction with $LiPR_2$ (Scheme 1.12) [184, 185]:

Other inorganic supports, such as γ-alumina [186, 187], zeolite [188], clay [189], glass, and silica (silicate) which are essentially metal oxides, have network structures and hydroxyl groups on the surface that can be used as the point for attaching functional groups [190]. Zeolite known as "molecular sieve" is a crystalline hydrated aluminosilicate whose framework structure encloses cavities (or pores) occupied by cations and water molecules, both of which have considerable freedom of movement, permitting ion-exchange and reversible dehydration. The pores in dehydrated



$$PCl_5 + NH_4Cl \longrightarrow -[-N{=}\overset{Cl}{\underset{Cl}{P}}-]_n- \xrightarrow{(RONa)} -[-N{=}\overset{R}{\underset{R}{P}}-]_n-$$

Scheme 1.13 Preparation of polyphosphazenes [191]

zeolites are generally about 6 Å in size, while those of a typical silica gel average about 50 Å. Polysiloxanes are the most common inorganic silicone polymers, $-[-SiR_2-O-]_n-$, in which the bond between silicon and oxygen atoms is strong, yet flexible. So silicones can stand high temperatures without decomposing, but they have very low glass transition temperatures, as e.g., rubber. Polysilanes, poly(dialkyl silane), $-[-SiR_2-]_n-$, are polymers with backbones made entirely from silicon atoms by reacting dichlorodialkyl(aryl)silane (R_2/Ar_2SiCl_2) with sodium metal to form either homo- or copolysilanes. Polysilanes are interesting because they can conduct electricity for use as electrical conductors and are highly heat resistant, but by heating them to very high temperatures silicon carbide can be formed, which is a useful abrasive material. Polygermanes, $-[-GeR_2-]_n-$, and Polystannanes, $-[-SnR_2-]_n-$, are polymers with backbones made entirely from metal atoms of germanium or tin. Polyphosphazenes, $-[-N = P(OR)_2-]_n-$, are polymer chains of alternating phosphorus and nitrogen atoms and made in two steps: (1) phosphorus pentachloride reacts with ammonium chloride to give a chlorinated polymer, (2) treating with sodium alkoxide gives an ether-substituted polyphosphazene (Scheme 1.13) [191]. The backbones are highly flexible, so polyphosphazenes make good elastomers, and are excellent electrical insulators. Graphite has stacked parallel sp^2-hybridized (aromatic) C sheets with each C atom bearing a π electron with charge transfers occurring between the intercalate and the host [191].

Although investigation of the employment of modified inorganic beads is limited, the fundamental simplicity of this technique seems attractive. The major applications of modified silica, as an example of inorganic polymers containing covalently attached functional groups, in solving some organic synthesis problems have been investigated in several fields. In addition to the specific utilization of modified silica as a support material for liquid chromatography and for immobilization of biologically active materials [192, 193], it has been used as a catalyst or reagent in the field of organic synthesis reactions [168]. It has also been successfully used as a support for peptide synthesis [179, 194], for oligonucleotide synthesis [195], for immobilizing transition metal catalysts [196] and other applications.

1.1.3 Advanced Polymeric Materials

Traditional polymeric materials are used in a number of important engineering areas involving mechanical, electrical, telecommunication, aerospace, chemical, biochemical, and biomedical applications. These engineering polymers possess physical properties enabling them to perform for prolonged use in structural applications, over a wide temperature range, under mechanical stress, and in difficult chemical and physical environments. The usefulness of advanced polymeric materials in advanced applications is related to their special properties linked to their extraordinary large size or on the potential advantages of particular chemically attached active functional groups. Advanced polymeric materials with special properties are classified into three groups: reactive functionalized polymeric materials, smart materials, and nanomaterials/nanocomposites.

1.1.3.1 Reactive Functionalized Polymers

A functional group attached to a polymer chain may have a different reactivity from an analogous group on a small molecule due to the surrounding macromolecular environment. Thus, more drastic reaction conditions may be required to reach a satisfactory conversion. The design of a new reactive polymer must be planned by considering important factors affecting its activity. These include (a) the type of solvents and reagents to which the polymer must be subjected during the course of its functionalization or subsequent reactions, and (b) the thermal behavior of the support which depends on its physical form, crosslinking density, the flexibility of the chain segments, and the degree of substitution.

Since the functional groups on the resin are not free to move, the surrounding low-molecular-weight substances must diffuse to the fixed reactive sites in the rigid-gel structure, essentially by using solvents with good swelling properties. The primary function of the solvent is to affect the degree of swelling of the polymer lattice, which is also an important factor in determining the chemical reactivity of immobilized molecules [197]. In fact, poorly swollen resin retards the rotation of unattached molecules imbibed in the matrix. The swollen polymer exhibits a high internal viscosity and the crosslinks restrict the long-range mobility of chain segments, thus the collision frequency of substituent's attached to different chain segments is reduced substantially.

The role of a solvent in the application and reaction of a functionalized resin is complex. An ideal solvent should meet the following requirements, it should: (1) interact with the polymer matrix to optimize the diffusion mobility of reagent molecules, (2) have the correct solvating characteristics to aid any chemical transformations being carried out, (3) not limit the reaction conditions which are to be applied, (4) enhance translucence rather than opacity. Certainly, it is difficult to satisfy all these criteria simultaneously and the selection of a solvent often involves compromise.

Gel polymers are usually found to be slightly less reactive than linear polymers, as restrictions will be limited by diffusion of the reagent within the resin pores. The reaction yields can be affected by the degree of crosslinking, i.e., highly crosslinked resins result in lower yields. Thus resins with very low degrees of crosslinking will be the most suitable, as increased swelling will result in higher accessibility through enhanced diffusion properties. In addition, swellable polymers are found to offer the advantage of achieving higher loading capacity during functionalization.

The reactivity of a functional group may be low when it is directly attached to the main chain. This may be a result of steric hindrance by the polymer backbone and neighboring side groups. In addition to the microenvironment of the functional groups, surface impurities on the polymer beads have marked influence on the apparent lack of reactivity of a functionalized polymer. An additional cause for the apparent lack of reactivity may be that the structure of some of its functional groups is different from that which is assumed from the reaction sequence leading to it, i.e., the polymer may contain interfering functionalities introduced during its preparation or chemical modification.

The capacity of a polymer support is also important in terms of reactivity. A polymer with a very high capacity may only react partially due to a lack of accessibility of the functional sites. Since the size of the molecules which are attached to the polymer may increase during a synthesis and result in other changes such as variations in polarity of the medium, the accessibility of the polymer–substrate bond may become restricted and result in partial or difficult cleavage when the synthesis is complete. In contrast, a polymer with a very low capacity may not be useful for a synthesis on a practical scale. Furthermore, the reaction rate of the functional group depends on the nature of the functional group, the concentration of the low-molecular-weight species in solution in contact with the resin, the diffusion rate of the low-molecular-weight species, the diameter of the resin particles, the temperature of the reaction, and the mixing rate.

1.1.3.2 Nanocomposites

It is normally difficult to have in the same material both properties of high strength to sustain high loads and high toughness to absorb a large amount of energy during fracture which occurs by breaking of primary and/or secondary bonds, depending upon the structure of the material [198]. Inorganics are originally introduced into polymer systems as fiber or fine solids to act either as fillers or as reinforcing agents. Inorganic *fillers* are used to dilute and hence to reduce the amount of the final polymers used in the shaped structures, thereby lowering the economically high cost of the polymer systems. However, inorganic *reinforcing agents* are used to enhance the the properties of polymers which show an increase in modulus, hardness, tensile strength, abrasion, tear resistance, and resistance to fatigue and cracking [199]. The properties of reinforcing agents such as particle size and structure (degree of aggregation and agglomeration), chemical composition of the particle surface, level of hydration and surface acidity, adhesion between particle and polymer, play an important role in the improvement of the service life of polymeric products. For improvement of vulcanized rubber properties, large amounts of carbon black can be incorporated as reinforcing agents. Carbon black produces a remarkable reinforcing effect on vulcanized rubber because it has a variety of active functional groups such as carboxyl, carbonyl, phenolic, and quinone groups on the surface of the particles that result in strong mutual action with the rubber chains. Although carbon black is still a major reinforcing agent for vulcanized rubbers, however, it has the disadvantage of raising the viscosity of the compound and impairing the processability of the compound when it is incorporated in large amounts into rubber. Grafting of polymer chains onto the surface of carbon black particles has been developed to solve the problem of poor processability of carbon black-filled systems.

Although some improvements of the lack of strength shown by many polymeric materials have been achieved particularly by the incorporation of some inorganic reinforcing agents, there is still significant need for producing polymeric materials with extremely high levels of stiffness and hardness in order to become widely accepted as structural engineering materials. There are a number of disadvantages to reinforcing polymers by the usual technique of blending finely divided inorganic reinforcing agents into a polymer. Unfortunately, the incorporation of inorganic minerals into the organic polymers results in a brittle composite material because of the very poor bond strength between the polymer matrix and the inorganic mineral, i.e., the bonding between them is not sufficient to provide the desired reinforcing effect. In addition, the amount of an inorganic material that can be incorporated is limited. Consequently, inorganic minerals are not uniformly dispersed in the organic polymer. The efficiency of the inorganic mineral to modify the properties of the polymer is primarily determined by the degree of its dispersion in the polymer matrix, which in turn depends on its particle size. However, the hydrophilic nature of the inorganic mineral surfaces impedes their homogeneous dispersion in the organic polymer phase. Thus, it is necessary to make the mineral surface hydrophobic in order to enhance its compatibility prior to compounding with the molecular chains of the polymers. Inorganic additives of spherical (granules) particles often coalesce into larger, irregularly shaped aggregates. Such aggregates are most frequently united into larger agglomerates by attractive forces of the van der Waals type. The extent of aggregation and agglomeration has a marked influence on their reinforcing properties.

The key to the development of cracks is the stress distribution around indigenous flaws. The simplest way of using the filler particle as a retarder of crack propagation is by lengthening the crack's paths, since the crack has to move around the particle, thereby dissipating more energy. The aggregated particle chain is clearly more effective than single spherical filler particles. With fillers poorly bonded to the matrix, dewetting and vacuole formation occurs upon a significant deformation, initiating cracks. Therefore, a strong bond between inorganic particle and polymer matrix contributes to overall strength. Factors which absorb or dissipate energy turn the potentially destructive energy of an impact into a more harmless form, such as heat. Besides, hystersis of the matrix is caused by uncoiling of chains (change in molecular conformation) and the frictional resistance to deformation, the breakup of transient filler structures, alignment of polymer chains and particle aggregates, strain crystallization, and stress relaxation which dissipate potentially destructive stored free energy.

Clays are naturally most abundant minerals and available as inexpensive materials that have high physical and mechanical strengths as well as high chemical resistance. Because of the small particle size and intercalation properties of clays, they afford an appreciable surface area for the adsorption of molecules. Clay–polymer materials have received considerable interest because the interactions between them have effects on the properties of both the clay and polymer [189, 200]. Polymers have been added to clays in order to enhance the physical and colloidal properties of clays because of their agricultural potential as conditioning and stabilizing agents. The beneficial effect of polymer on clay and natural soils is related to the improvements observed in their structure and stability, which are basically due to aggregation and water stability of the aggregates formed.

Attempts have been made to graft organic polymers onto clay layers for creating new organic-inorganic materials to improve the accessibility of clay in polymer matrices by appropriating the dimensions of molecules under microscopic observation. Composite materials composed of inorganic and organic units are used for structural modification of polymer backbones, for creating new functions within an inorganic network, and for constructing new types of organic polymeric chains. The molecular dispersion of polymers within inorganic phases, i.e., the incorporation of the polymer matrix into the space between layers of clay minerals, which are harder and more rigid, leads to improvement of the physicomechanical properties of the polymers. But at the same time, such composites lose their rheological properties.

The ultra-small size of the building blocks of nanostructured materials is on the order of nanometers. Nanostructured materials often exhibit combinations of physical and mechanical properties that are not available in conventional materials [201, 202]. Their special properties are determined by a complex interplay among the building blocks and the interfaces between them. The properties are improved when the grains are reduced in size to 100 nm, which are further improved at sizes down to 1 nm. Thus, nanocomposites offer a major opportunity for creating a nearly infinite array of new materials that offer new potentially useful combinations of properties. These include multilayered sandwich-like materials in which polymer chains are located between ultrathin sheets of clay silicates. The chemistry and crystal structure in each layer of a multilayer can be quite different from those located just a few atoms away, because the nanosized gaps that exist between the clay layers are infused with polymers. The layers in the resulting structure are extremely thin and the confinement of the polymer molecules in these two-dimensional spaces isolates them and forces them into a more orderly arrangement, which, in turn, has a major effect on the properties of the nanocomposite. When polymers are intercalated between silicate sheets, they do not behave the way bulk polymers do upon heating. Intercalated polymers do not undergo the same transitions as amorphous and crystalline polymers do, because the molecular confinement hinders their translational and rotational motions. Furthermore, melting is a behavior of crystallites, which require more space to grow than is available in the nanosized gaps of the silicate lattice. Thus, the intercalation of polymers in silicates increases their thermal and oxidative stability because the clay lattices protect the polymer's internal molecular confinement from engaging in degradative behavior. This approach allows the design of materials that combine high strength and thermal stability of clay with the processability and crack-deflecting properties of a polymer because of frequent, periodic interlayer boundaries.

1.1.3.3 Smart Materials

The properties of conventional standard materials cannot be significantly altered, e.g., if oil is heated, it will become thinner, whereas smart materials can exhibit volume, shape, and size changes or phase transitions in response to environmental conditions, such as temperature [203], pH [204], pressure [205], electric or magnetic fields [206], light [207], or moisture. A smart material with variable viscosity may turn from a nonviscous fluid to a solid. Smart materials recently have been used in a wide range of applications, such as coffee pots, cars, eye glasses, etc.

(A) **Types of smart materials**. Several smart materials already exist, each with different special properties which can be further altered, such as viscosity, volume, and conductivity. The type of application of smart materials depends on the specific features intended to be altered. There are a three general types of smart materials: (1) *Piezoelectric materials* have reversed properties that give off a measurable electrical discharge on deformation, i.e., the material produces a voltage when stress is applied and vice versa, whereas the application of a voltage across the sample will produce stress (bend, expand, or contract) within the material. Alternately, when an electrical current is passed through a piezoelectric material, its size is significantly increased (change in volume), i.e., stress results when a voltage is applied, and this effect also occurs in the reverse manner. Suitably designed structures from piezoelectric materials can therefore be made that bend, expand, or contract when a voltage is applied. They are often widely used as sensors in different environments to measure fluid compositions, fluid density, fluid viscosity, or the force of an impact. An example of a piezoelectric material in common use is the automobile airbag sensor. The materials sense the force of an impact on the car and send an electric charge deploying the airbag. (2) *Shape memory alloys and polymers* are thermoresponsive materials where deformation can be induced and recovered through temperature changes. (a) *Magnetic shape memory alloys* are materials that change their shape in response to a significant change in the magnetic field. (b) *pH-sensitive polymers* are materials which swell/collapse when the pH of the surrounding media changes. (c) *Temperature-responsive polymers* are materials which react to temperature changes. (d) *Halochromic materials* change their color in response to acidity variation; they can be applied in paints that can change color to indicate corrosion in a metal surface beneath. (e) *Chromogenic systems* change color in response to modification of electrical, optical, or thermal properties: these include *electrochromic materials*, that change their color or opacity on the application of a voltage; *thermochromic materials* change in color depending on their temperature; and *photochromic materials* which change color in response to light, e.g., light-sensitive sunglasses that darken when exposed to bright sunlight. (3) *Electro- and magneto-rheostatic materials* are fluids that can dramatically change their viscosity in response to an applied shear rate, i.e., the liquid will change its viscosity under an applied force or pressure. These fluids can change from a viscous fluid to a solid substance when exposed to a magnetic or electric field and the effect can be completely reversed when the applied force is removed. Magneto-rheostatic fluids change their viscosity when exposed to a magnetic field, while electro-rheostatic fluids change their viscosity in an electric field. The composition of each type of smart fluid varies widely. A magneto-rheostatic fluid consists of tiny iron particles suspended in oil, while electro-rheostatic fluids consist of milk chocolate or corn starch and oil. Magneto-rheostatic fluids are being developed for use in car shock absorbers, damping of washing machine vibration, prosthetic limbs, exercise equipment, and surface polishing of machine parts. Electro-rheostatic fluids mainly have been developed for clutches and valves, as well as engine mounts designed to reduce noise and vibration in vehicles.

(B) **Smart hydrogel materials** are temperature-responsive materials and exhibit unique thermo-shrinking properties, e.g., poly(*N*-isopropyl acrylamide) and PVME [208–210]. Heating the polymer aqueous solution beyond the lower critical solution temperature causes the the polymer to shrink leading to phase separation. Thus, below the lower critical solution temperature the polymer is soluble in the aqueous phase as the chains are extended and surrounded by water molecules, while above the lower critical solution temperature the polymer becomes insoluble and phase separation occurs. This gel can be used like tweezers to pick up a target compound in aqueous solution by simply raising the temperature above the lower critical solution temperature and to release the compound below the lower critical solution temperature. Poly(*N*-isopropyl acrylamide) and its copolymer hydrogels have been synthesized for this purpose [203]. Polymer substrates grafted with *N*-isopropyl acrylamide monomer initiated by electron beam, irradiation, or UV cause special modifications of polymer surfaces, e.g., *N*-isopropyl acrylamide has been grafted onto porous polymer films as LDPE, PP, or polyamide films in order to prepare films or membranes for separation of liquid mixtures [211, 212]. The solubility of poly(*N*-alkyl acrylamides) can change completely towards insolubility as the size of the alkyl side group increases [213]. The lower critical solution temperature of poly(*N*-isopropyl acrylamide) can be shifted either up or down by varying the copolymer composition range with *N*-alkyl acrylamides, i.e., by the variation of the smaller or larger *N*-alkyl group than *N*-isopropyl [213, 214]. Moreover, a lower critical solution temperature can be obtained with a small amount of highly hydrophobic comonomer (*N*-Dec) or high fraction of less hydrophobic comonomer (*N*-*t*-Bu). Poly(*N*-isopropyl acrylamide) gels as an inexpensive alternative to ultrafiltration [215, 216] have been used for removing low-molecular-weight contaminants from soy protein [217], water from gasoline or fuel oils [218], and as a urine absorbent [219], while PVME gels crosslinked with γ-ray irradiation have been used in wastewater sludge dewatering [220].

1.2 Properties of Polymeric Materials

There are a number of considerations in the choice of the polymeric materials to be used in a specific application. Particular properties of a polymeric material can be achieved either by the initial selection of monomers for the organization of the structural elements of the macromolecules or by the polymerization technique and by applying optimum conditions. The chemical reactions of polymers always represent changes in the repeating structural units (type and sequence) that are subsequently transmitted into changes in the structural organizations and of the properties of modified polymers. The solid-state properties are determined by the structural organization of the macromolecules that depends on: (a) chain length (molecular weight), symmetry and branching of chains, (b) intramolecular conformational flexibility of chains, which depends on internal rotation in the backbone, (c) intermolecular cohesion energy determined by the influence of the polarity and the size of the side groups that hinder the packing of chains. Variations in the polymer structure are alteration in main-chain structure leading to changes in their properties. These variations in turn depend on the degree of crosslinking and the conditions employed during polymer preparation.

Regularity in the organization of macromolecular chains is an important physical parameter that influences the chemical and thermal resistance and mechanical strength of polymers. Crystallinity depends mainly on the symmetry of the elements of a polymer chain. The linkage of the macromolecules impedes their independent translation and reduces the crystallinity. The conformational flexibility of the chains is diminished by crosslinking, the entropy change is reduced and the melting temperature increases. The degree of crystallinity depends on the distribution, the polarity, and the volume of the substituent groups. The presence of strong intermolecular forces promotes the interaction of the chains, which increases crystallinity. Thus, linkage of polar groups to the chains increases the hardness of polymers and lowers their creep under load. The glass transition temperature T_g is determined by cohesion energy, conformational flexibility and length of the macromolecule. Crosslinking that increases network density, increases T_g by restricting the mobility and reducing the free volume. Branched polymers provide large free volume, hindered chain mobility, and decreased T_g.

1.2.1 Physical Forms

The structure of the polymer macromolecule is determined by the spatial arrangement of the atoms and by the constitution of the bonds. Polymer structure is often rationalized in terms of microscopic and macroscopic elements. Depending on the chemical arrangement of the repeating structural units relative to one another, the conditions of the polymerization reaction, and the macromolecular structure arrangement, polymers can be classified into different types. Each type has pros and

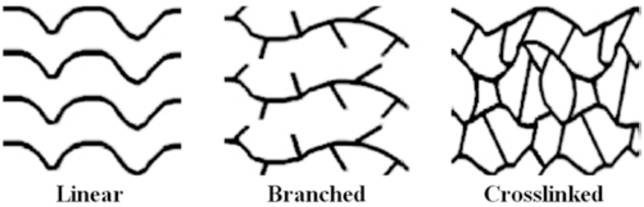


Fig. 1.13 Structure of polymer macromolecules

cons regarding their final utilization. Polymers are either linear homo- or copolymers, branched (grafted), or crosslinked macromolecules (Fig. 1.13). Crosslinked polymers are network structures and commonly referred to as resins. The physical form of a polymer must be carefully studied in order to maximize its success of application while minimizing any potential problems.

1.2.1.1 Linear Polymers

A linear polymer is a long-chain species in which the monomer molecules have been linked together in a continuous straight line. Linear polymers can be derived from a single species of monomer, in which the repeating structural units have a chemically consistent composition (homopolymer) or derived from more than one monomer species, i.e., the repeating structural units contain more than one chemical composition. Thus, copolymerization is a reaction that joins two or more monomer units to give polymer containing more than one type of structural units in the chain. Copolymerization allows the synthesis of an almost unlimited number of different products by variation in the nature and relative amounts of the two monomer units in the copolymer product. The possible arrangements, i.e.,, distribution, of the two structural units in the copolymer chains depend on the monomers structure and the experimental techniques and are of three types: block, random, and alternating copolymers. In the solid state the linear polymer molecules have a thread-like shape and occur in various conformations. Linear polymers are usually in crystalline or amorphous form. In the *crystalline state* the molecules are oriented in a regular manner with respect to each another (Fig. 1.14). The degree of crystallinity depends on the structure of the polymer chains and the amount of chain flexibility, and can be increased by appropriate thermo-mechanical means. In the *amorphous state*, maximal possible entropy determines the most probable shape. Linear polymers are capable of forming a molecular solution in a suitable solvent, in which an individual chain is not usually present as an extended chain but adopts a random-coil conformation. The coil density is usually influenced by (a) the structure of the polymer chains, (b) the extent of solvation, (c) the molecular weight, (d) temperature, and (e) ionic groups and their degrees of dissociation. Polymer coils readily expand in a good solvents and contract in poor ones.

The use of functionalized linear polymer is of growing interest especially when separation of the polymer is not necessary or when the polymer must be soluble to

Fig. 1.14 Crystalline polymers: regular domains, amorphous polymers, coiled irregular domains

permit working in an homogeneous phase to perform its function. Soluble polymer substrates are useful for some chemical reactions in food and agricultural applications and as a soluble substrate for kinetic studies because they are not limited by diffusion control problems.

The *advantages* associated with the use of linear soluble polymers include the following: (1) Reactions can be carried out in homogeneous media, minimizing diffusion problems. (2) Functional groups are of equal accessibility. (3) Problems arising from the pore size distribution and reactions which involve substrates of large molecular size that are not able to penetrate all the pores of a crosslinked polymer can be overcome by the use of soluble polymers. (4) Reactions are not affected by the size of the polymer backbone and usually proceed to a high extent. (5) High conversions can be achieved which give yields comparable with those in the homogeneous phase. (6) Characterization at the various stages of the functionalization is easy.

In some applications, the use of linear soluble polymers may give rise to some *disadvantages*, e.g., the separation of the polymer from low-molecular-weight contaminants can be difficult. Separation can be achieved by ultrafiltration, dialysis, or precipitation. However, the recovery of the polymer by these methods may not be easy and is not quantitative. Moreover, low-molecular-weight species are sometimes insoluble in the precipitating medium and thus complete removal of impurities from the precipitated polymer may not be achieved. Gel formation is yet another potential problem with the use of linear polymers.

1.2.1.2 Branched Polymers

Branched polymers are homopolymers containing branches with the same constitutional units emerged from the main chain backbone. In contrast, "star polymers" have branches that radiate from a central atom or groups of atoms. Grafted polymers are branched copolymer in which the backbone chain is chemically different from the branches. The presence of branching in a polymer usually has a large effect on many important properties. The most significant property changes by branching are the decrease in crystalline and in thermal transitions, because they do not pack as easily into a crystal lattice as do linear polymers. Branched and grafted polymers can be prepared by different ways such as chain transfer, polymeric initiation (polymeric free radical initiators, polymeric anionic initiators), and chemical reactions of the reactive groups present along the polymer chain with the end-functional groups on the polymers used as branches.

1.2.1.3 Crosslinked Polymers

Crosslinked polymers are formed by polymerization techniques in the presence of a crosslinking agent, or are subsequently crosslinked in a post-polymerization process, in which all the main chains are effectively interconnected to form an infinite network. Such a system can no longer form a true molecular solution and may be regarded as insoluble in a strict thermodynamic sense. Crosslinked polymers exhibit considerable differences in properties depending on the degree of crosslinking and the method of preparation. They can be conveniently characterized in terms of their total surface area (internal and external), total pore volumes and average pore diameter. In general, the degree of crosslinking determines the solubility, extent of swelling, pore size, total surface area, and mechanical stability of the polymer.

The use of crosslinked polymers in chemical applications is associated with some *advantages*: (1) Since they are insoluble in all solvents, they offer the greatest ease of processing. (2) They can be prepared in the form of spherical beads which do not coalesce when placed in a suspending solvent and can be separated from low-molecular-weight contaminants by simple filtration and washing with various solvents. (3) Polymer beads with low degrees of crosslinking swell extensively, exposing their inner reactive groups to the soluble reagents. (4) More highly crosslinked resins may be prepared with more porous structures which allows solvents and reagents to penetrate the inside of the beads to contact reactive groups.

However, there are also a number of *disadvantages* arising from the use of crosslinked polymers: (1) The reaction rates and kinetic course in solid-phase synthesis show that the reaction sites within the polymeric matrix are not equivalent neither chemically nor kinetically, which makes quantitative conversions almost impossible. (2) The difficulty in accessibility of insoluble polymers appears to limit a more general application of these materials in chemical reactions. (3) The rate of diffusion and pore size may restrict the reactions, especially in the case of larger substrates which may only be able to react at some of the more accessible sites located on the surface of the beads or within the larger pores. (4) The accurate loading of the resin is often very difficult to control. However, it is possible to cause a reaction to occur at a fraction of the available sites by controlling the swelling of the polymers. Such reactions on partially swollen resins give functional polymers in which the reactive sites are not distributed evenly throughout the bead but are concentrated in the more accessible sites only. (5) It is difficult to characterize adequately the structural changes which take place, since a number of analytical methods are not well suited for the study of insoluble materials. (6) Not all reagents can penetrate with ease into the crosslinked network. (7) The introduction of any functional group onto a resin may remove some of the original pore volume, whether this be in the form of permanent macropores or in the form of gel porosity of solvent-swollen lightly

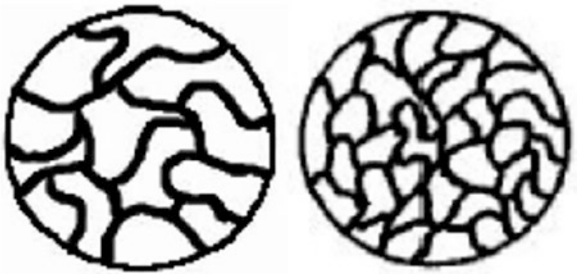


Fig. 1.15 Microporous and macroporous beads

crosslinked materials. (8) The generation of a polar environment in an originally nonpolar support, and vice versa, by the introduction of appropriate functional groups can alter the solvent compatibility of the system significantly. (9) In some instances, ionic groups generated on a lightly crosslinked nonpolar support can actually aggregate or cluster into charged nuclei, considerably increasing the rigidity of the resin matrix. (10) Crosslinked polymers exhibit considerable differences in properties depending on the degree of crosslinking and the method of preparation.

Crosslinked polymers are classified into different types, each physical form possessing its own distinct enhanced properties:

(a) Microporous (gel-type) resins are generally prepared by suspension polymerization using a mixture of vinyl monomer and small amounts (0.5–2 %) of a crosslinking agent containing no additional solvents (Fig. 1.15) [221, 222]. The growing polymer chains are solvated by nonincorporated monomer molecules, but as higher conversions are reached this solvation diminishes and finally disappears. The resulting nuclei tend to aggregate as the more extended portions of the polymer chains slowly collapse, eventually forming a dense glass-like material in the form of spherical beads. The crosslinking sites are usually randomly distributed, producing a heterogeneous network structure. In the dry state, the pores of a gel resin are small, and hence they are often referred to as microporous resins. However, on the addition of a good solvent, extensive resolvation of the polymer chains causes considerable swelling with the formation of a soft gel and results in the reappearance of considerable porosity that depends on the degree of crosslinking.

Swellable polymers offer advantages over nonswellable polymers, particularly their lower fragility, i.e., lower sensitivity to sudden shock, and their potential to achieve a higher loading capacity during functionalization. However, a decrease in crosslinking density will increase the swelling but will also result in soft gels which generally have low mechanical stability and readily fragment even under careful handling. Gels with lower density of crosslinking are difficult to filter and under severe reaction conditions can degrade to produce soluble linear fragments. In addition, gel-type resins that are lightly crosslinked may suffer considerable mechanical damage as a result of rapid and extreme changes in the nature of the solvating media and cannot be subjected to steady and high pressures.

Microporous resins with less than 1 % crosslinking generally have low mechanical stability and readily fragment even under careful handling. Thus, in chemical applications, resins with a crosslink ratio of approximately 2 % provide a satisfactory compromise, generally allowing adequate penetration by most reagents and yet retaining sufficient mechanical stability to provide ease of handling. Some examples of porous polymer beads are: styrene-DVB [223], 4-vinylpyridine-DVB [224], N-vinyl-carbazole-DVB [225], methacrylamide-styrene-DVB [226], acrylonitrile-DVB [227], glycidyl methacrylate-ethylene glycol-dimethacrylate [228, 229], methacrylic acid-triethylene glycol dimethacrylate [230, 231], acrylic acid-triethyleneglycol dimethacrylate [226], acrylamide-ethylene glycol dimethacrylate [232], 4-vinylpyridine-ethylene glycol dimethacrylate [233].

Hydrogels are hydrophilic polymers with three-dimensional networks that absorb water. The extent of volume change due to water absorption varies with the degree of ionization of the gel and the degree of crosslinking. The volume change is a phase transition which results in the competition among three forces on the gel: the positive osmotic pressure of counterions, the negative pressure due to polymer–polymer affinity, and the rubber elasticity of the polymer network [234]. The balance of these forces varies with changes in temperature or solvent properties. *Superabsorbent hydrogels* such as polyacrylamide are partially hydrolyzed (ionic groups) and lightly crosslinked polymers with large volume change during swelling and are prepared by free-radical polymerization of acrylamide in the presence of *N,N-methylenebisacrylamide* as crosslinking [234].

(b) Macroporous polymers are also prepared by suspension polymerization using higher ratios of the crosslinking agent and in presence of an inert solvent as diluents for the monomer phase (Fig. 1.15) [182, 221, 235–242]. The diluents "*porogens*" consist of two constituents: (1) a nonsolvent diluents part: a good solvent only for the monomer but a nonsolvent for the growing linear polymer chains, as aliphatic hydrocarbons, and precipitate the polymer (noncrosslinked) from the initially homogeneous polymerization solution. (2) a solvent diluents part: a thermodynamically good solvent, as toluene, for both the comonomers and the resulting growing linear polymer chains which remain solvated throughout the entire time of polymerization.

As the polymer growing chains are solvated by the good solvent, fully expanded crosslinked networks are formed with a considerable degree of small pore porosity, whereas poor solvents lead to large pores. Proper pore size can be achieved by the ratio of the diluents. With macroporous resins the growing chains remain fully solvated in a good solvent during polymerization and do not collapse as the comonomer is consumed. Crosslink ratios of about 20 % are most common, so that the matrix formed has sufficient mechanical stability in the solvent state and a large volume of solvent is retained. The resulting polymer contains cavities filled with the solvent, the pores may collapse partially when the solvent is removed because of the much larger extent of the solvated network during polymerization, but this collapse is reversible and if the polymer is placed again in a good solvent the initial macroporous structure is regenerated. Macroporous resins will also absorb varying quantities of bad solvents and remain in a fully expanded form, i.e., removal of solvent yields a residual network with a permanent system of macropores.

With increasing the diluents in the course of the polymerization reaction, the apparent surface area of polymers tends to decrease, whereas the pore volume increases. As the pore volume expands the pore size distribution shifts towards large pore diameter and the mechanical strength of the beads in the dry state decreases. The porosity of the polymer is controlled by the amount and type of porogen and crosslinking [182, 243–265]. Pore volume of beads is increased by increasing the amount of porogen, the ratio of nonsolvent to good solvent in porogen, and with increasing pore volume, the pore size distribution shift towards larger pore diameter [182, 247–264]. The porogen has an effect on the distance between crosslinks and the permanent pores, i.e., macroreticular porosity [266–268]. The porous structure, characterized by the specific surface area and pore volume, varies over a wide range with the amount of crosslinker used and the type of inert solvent. Porous polymers are obtained with maximum surface areas of around 750 m^2/g by suspension polymerization.

(c) Micro- and macroreticular polymers**.** *Microreticular resins* are prepared by solution polymerization using smaller amounts of the crosslinking agent in the presence of diluents for the monomer phase. When the diluents are removed at the end, the polymer matrix shrinks showing no pores in the dry state, but the polymer may still have large spaces between polymer chains and crosslinks, i.e., microreticular porosity, which may reappear upon swelling with good swelling.

Macroreticular resins are also prepared by solution polymerization using higher ratios of the crosslinking agent but with the inclusion of an inert solvent as diluents for the monomer phase [241, 269–272]. When the solvent employed during polymerization is a good solvent for the monomer but precipitant for the polymer (noncrosslinked), the term macroreticular is generally employed to describe the product. When the diluents are removed, the permanent pores or macroreticular porosity is left behind, which is the void space between microsphere agglomerates. Pore volume in the dry state of the polymer is a measure of its macroreticular porosity. Macroreticular resin is nonswelling, rigid material with a high crosslinking ratio, and retains its overall shape and volume when the precipitant is removed. The method adopted for the synthesis of this type of resin consists essentially of the usual homogeneous solution phase process modified by inclusion of a nonsolvent for the expected polymer. The ratio of nonsolvent in the reaction mixture is critical and must be carefully adjusted to cause the crosslinked particles to precipitate at the desired stage of polymerization. Control of particle size can be accomplished by adjusting the rate of stirring, but the nature of the solvent, nonsolvent, and crosslinker components mainly determines the physical characteristics of the final product.

The structure of these resins is quite different from that of the previous two. They have a large, definitive, and permanent internal porous structure with an effective surface area larger than that of swollen beads. Macroreticular resins are generally much less sensitive to the choice of solvent and can absorb significant quantities of both solvents and nonsolvents, which probably fill the available voids. In general, the whole structure is not susceptible to the dramatic changes when the nature of the surrounding medium is changed. The dimensional stability of macroreticular resins makes them resistant to high pressure in column applications where better solvent flow rates can be achieved than would be the case with gel polymers. Macroreticular resins usually display negligible change in volume during their use. Moreover, they have further *advantages* in chemical applications: ease of filtration from the reaction medium and minimal effects of surface impurities. The main *disadvantages* of these resins include: (a) a lower reactivity than the swellable polymer, (b) a lower loading capacity, (c) brittle nature, i.e., they may fracture under sudden stress during handling with the formation of fine particles, and (d) static electricity causes difficulty in handling.

(d) Popcorn polymers are prepared by gently warming a mixture of vinyl monomer and a small amount of crosslinking agent, 0.1–0.5 %, in the absence of any initiators or solvents [273, 274]. Popcorn polymer is a white glassy opaque granular material, fully insoluble and porous, with a low density. It is not swellable in most solvents but easily penetrated by small molecules and has a reactivity comparable with that of solvent-swellable beads but it is often more difficult to handle.

(e) Macronet polymers are also referred to as hyper-crosslinked, post-crosslinked, or isoporous [275–278]. These are three-dimensional crosslinked networks obtained by linking the main chains of linear, micro-, or macroporous polymers through crossbridges by chemical transformation reactions with a bifunctional reagent such as α,α-dichloro-*p*-xylene, 4,4-bis(4-chloromethyl)biphenyl, or 1,4-bis(4-chloromethylphenyl)butane [279–283]. They are usually produced in the presence of a solvent such that the resulting material has a relatively floppy structure and is capable of reabsorbing large quantities of solvents. As a result, it has the disadvantage of poor mechanical stability.

The post-crosslinking reactions lead to the formation of permanently porous structures with high surface area and the crossbridges introduce reinforcing structures and separation of the polymer phase and heterogeneous permanently porous structure which is stable in the swollen state as well as in the dry state. Hypercrosslinked polymer networks represent another class of polymeric networks displaying a special type of porosity [284–291]. They are rigid, highly crosslinked networks, and highly porous materials with different, more fine porosity than that of traditional macroporous polymers, and have high sorption capacity towards both polar and nonpolar organic compounds. Their structures are characterized by permanent porosity with very high apparent inner surface area, S_{app}, up to 1,000–1,500 m^2/g for the networks with a degree of crosslinking of 100–200 %. The porous structure of hypercrosslinked networks differs from that of macroporous polymers where its porosity results from microphase separation in the course of free radical polymerization of comonomers, caused by the presence of inert diluents and crosslinking agent.

1.2.2 Porosity and Surface Properties

Porosity: Pores represent voids between loosely packed polymer chains. The porosity of the crosslinked polymer beads produced by suspension polymerization in the presence of inert organic liquid as diluents depends mainly on the amount of crosslinker and on the type and quantity of the porogen used [244, 250, 267, 292]. In the swollen state, a crosslinked polymer has a certain porosity in which the size and shape of the pores may continuously change owing to the solvating effect of a good solvent and hence the mobility of the polymer segments. Dry solid supports can be conveniently characterized in terms of their total surface area (internal and external), total pore volumes, and average pore diameter. These physical parameters are not independent of each other but are generally interrelated by the simple geometrical equations (Eq. 1.11) and (Eq. 1.12):

$$P = \mathbf{n\pi r^2 l} \tag{1.11}$$

and

$$\mathbf{S = 2n\pi rl} \tag{1.12}$$

where P is the pore volume, S is the surface area, r is the average pore radius, n is the number of pores, l is the average pore height, and nl is the effective total pore length. These equations illustrate that as the pore diameter increases, the number of pores becomes relatively small and the total interior surface area is also restricted. Conversely, as the total interior surface area increases, the number of pores increases and the radius of each pore diminishes.

Gel-type supports usually have relatively small pore diameters and a large effective surface area which gives rise to high loading capabilities, up to approximately 10 mmol/g. Macroporous and macroreticular supports have large pore diameters but relatively small surface area. Chemical modification of these resins occurs largely on the pore surfaces, and the entangled polymer chains are not readily available for functionalization with loading capabilities of the orders of 3 mmol/g. A resin of high surface area (~500 m^2/g) can be prepared by using a good solvent as a porogenic agent.

Total pore volumes can be obtained simply by measuring the volume uptake of an appropriate liquid. The total pore volume and pore size distribution depend upon the type and relative amount of the diluents, the degree of crosslinking, and the reaction conditions. The pore volume PV of the polymers can be calculated from Eq. 1.13.

$$\mathbf{PV} = \mathbf{1} / \rho_{\mathrm{ap}} - 1 / \rho\left(\mathbf{ml} / \mathbf{g}\right) \tag{1.13}$$

where ρ_{ap} is the apparent density (g/ml) and ρ is the skeletal density (g/ml), which are measured by the picnometric technique. Electron microscopy and small angle X-ray scattering can be employed to measure the average pore diameter D which can also be estimated according to Eq. 1.14.

$$\mathbf{D} = 4\mathbf{PV} / \mathbf{S}_{\mathbf{BET}} \times \mathbf{10}^{4} \tag{1.14}$$

The high porosity of the matrix has two desirable effects. It leads to good flow properties, and it does not hinder the penetration of molecules of high molecular weight. The polymer porosity (*%P*) can be calculated according to Eq. 1.15 [59]:

$$\%\mathrm{P} = 100\left(1 - \rho_{\mathbf{ap}} / \rho\right) \tag{1.15}$$

It should be noted, however, that solvent–polymer interaction significantly determines the porous structure of the networks [60].

The pore volume of the polymer defines the porous structure and mechanical properties of polymers [258] and the porosity can be determined by: (a) diluents: increasing the proportion of nonsolvating diluents in a mixture of solvating and nonsolvating diluents increases the pore volume, (b) crosslinking: the pore volume can be decreased by increasing crosslinking [293] and is determined in the dry state by the BET method (Brunauer, Emmett, Teller) or by mercury porosity [267, 294, 295]. The pore volume can be calculated from the density of the dried beads by BJH mathematical model [258]. The total porosity and pore size can be controlled either by the gel type and grade or by the osmotic potential of the solution used to swell the gel [182, 251–258, 296, 297].

Surface properties: In the interaction of polymers with other materials (liquid or solid), surface properties are critical. (a) *The interaction of polymer surfaces with liquids*: in this case, the important phenomena are the wetting and spreading and these affect the adhesion of polymer surfaces applied in the liquid state. When a liquid is brought into contact with a polymeric solid, the extent of wetting is described by the contact angle θ which a liquid droplet makes with the surface at the three-phase contact line. When a liquid wets a polymeric solid to the extent that the contact angle becomes zero, the equilibrium spreading coefficient S is defined as in Eq. 1.16:

$$\mathbf{S} = \gamma_{\mathbf{SV}} - \gamma_{\mathbf{SL}} - \gamma_{\mathbf{LV}} \tag{1.16}$$

where γ_{SL} is the interfacial tension, and γ_{LV} is the surface tension. For good adhesion to a substrate the contact angle of an adhesive or coating must be zero so that the liquid will spread. (b) *Modification of nonpolar polymer surfaces*: Variation in the chemical structure of the polymer surface by chemical modification affects the surface energy of polymers and alters all the surface properties. The introduction of polar groups into the surface layers of a hydrophobic polymer enhances its surface tension and the angle of wetting by polar liquids is reduced. Polymer surface modification can either be reached by substituting the nonpolar groups of the polymer by polar groups or by grafting the polar monomer to the polymer surface, and vice versa. Changes of the surface energy of polymers after modification and the surface properties originate from the changes in the chemical polarity of the surface structure which can be evaluated quantitatively for their performance in a particular application from nitrogen adsorption-desorption isotherms BET (Brunauer, Emmett, Teller) technique [298]. (c) *The interaction of polymer surfaces with solids*: in this case, the important phenomena are contact adhesion, hardness, scratching resistance, friction, and wear. The chemical treatment of the polymer surface improves the properties of the polymer to interact with other solids in numerous applications such as in the membrane permeability and the strength of adhesive joints.

1.2.3 Solvation Behavior: Swelling and Solubility of Polymers

The solubility of a polymer is a property determined by the enthalpy ΔH_{mix} which expresses the change in intermolecular interactions on transfer of a polymer into solution in a given solvent. In general, a polymer dissolves when a chemical and structural similarity exists between the polymer and the solvent molecules, i.e., when the cohesion energies of solvent and of polymer are identical. Solubility of the polymer indicates that a large volume of solvent is necessary to dissolve the polymer and the polymer dissolution process is relatively slow and characterized by (1) swelling due to the slow penetration of the solvent into the interstices of the polymer matrix and the interaction between the solvent and the polymer, (2) the solvated polymer molecules lead to loosened polymer molecules that diffuse out of the polymer segments and disperse in the solvent phase resulting in a completely homogeneous solution. The process of dissolution and hence the extent of swelling and solubility depends on: molecular mass, crystallinity, degree and nature of the substitution, density of crosslinking, and polymer–solvent interactions. Thus, the reduction in the molecular mass, crystallinity, and the crosslinking density of the polymer determine the changes in the polymer solubility.

The solvent has a significant influence on the physical nature and the chemical reactivity of immobilized molecules. An organic linear macromolecule can dissolve in an appropriate solvent to form a true molecular solution in which the concentration of polymer can be made to approach zero. Dissolving a polymer is a slow process that can take place if the polymer–polymer intermolecular forces can be overcome by strong polymer–solvent interactions in which the gel gradually disintegrates into solution. In solution, the polymer chain generally exists as a random coil which can be highly expanded or tightly contracted depending on the thermodynamics of polymer–solvent interactions. Generally, a highly compatible or good solvent, where polymer–solvent contacts are highly favored, will give rise to an expanded coil conformation, and as the solvating medium is made progressively poorer the coil contracts and eventually precipitation takes place. The conformations of the randomly coiling mass occupies many times the volume of its segments alone. The random coil arises from the relative freedom of rotation associated with the chain bonds of most polymers and the large number of conformations accessible to the molecule. The ability of a given solvent to dissolve a linear polymer depends on: (a) the chemical nature of the polymeric backbone, (b) molecular weight, (c) crystallinity, (d) the nature of the solvent, i.e., the polymer–solvent interaction forces, and (e) temperature.

However, the absence of solubility does not imply crosslinking, but other features, such as crystallinity, hydrogen bonding and a high molecular weight give rise to sufficiently large intermolecular forces to hinder solubility. A crosslinked system can be solvated by a suitable solvent and remains macroscopically insoluble. In this case, swelling rather than solubility is the required property, the polymer can be solvated homogeneously only to a limited extent, beyond which addition of more solvent will not increase salvation. Swelling of resin beads is very important as it brings the polymer to a state of complete salvation and thus allows easy penetration of the network by molecules of the reagent. The crosslink ratio controls the behavior of a resin in contact with a solvent and is inversely proportional to the degree of swelling. When a good solvent is added to a crosslinked polymeric network, solvent molecules slowly diffuse into the polymer resulting in swelling and gelation and it becomes highly expanded and extremely porous. If the degree of crosslinking is low, then such gel networks can consist largely of solvent with only a small fraction of the total mass being polymer backbone. As the degree of crosslinking is increased, or if strong polymer–polymer intermolecular forces are present because of crystallinity or strong hydrogen bonding, then the ability of the network to expand in a good solvent is reduced and penetration of reagents to the interior may become impaired. With poor solvents, crosslinked matrices display little tendency to expand and movement of reagents within such an interior can become somewhat analogous to a diffusion process in the polymer solid. Solvent compatibility with the resin can be adjusted by mixing monomeric units in the polymer chain, i.e., by the use of copolymers.

Information on the degree of swellability of the polymers can be determined either from the measured density of the dry resin and the weight of imbibed solvent using the centrifugation technique [52–55, 299] or from the proportion of the specific gel bed volume to the bulk volume [57]. The volumetric swelling coefficient B can be calculated using Duesek's equation (Eq. 1.17) [58].

$$\mathbf{B} = \rho_{\mathbf{ap}} / \rho + (\mathbf{w} - 1)\rho_{\mathbf{ap}} / \rho_{\mathbf{solv}} \, (\mathbf{ml} / \mathbf{ml}) \tag{1.17}$$

where ρ_{solv} is the solvent density (g/ml), w is the swollen polymer weight divided by the dried polymer weight, and w−1 has the same meaning and value as the measured solvent uptake coefficient.

1.2.4 Permeability and Diffusion

Membranes (homogeneous or heterogeneous) are generally described as permeable, semipermeable, or perm-selective depending upon the nature of the penetrants.

A homogeneous membrane is defined as one which has uniform properties across all its dimensions, while a heterogeneous membrane has some anisotropy due to either molecular orientation during the manufacturing process or fillers, additives, voids, or reinforcing materials. The permeation behavior (permeation coefficient P) depends on both the diffusivity D which is a kinetic parameter related to polymer-segment mobility, and the solubility coefficient S which is a thermodynamic parameter that is dependent upon the strength of the interactions in the polymer permeant. Thus, the permeability coefficient P is the proportionality constant between the flow of penetrant per unit area of membrane per unit time and the driving force per unit thickness of membrane. It is given by a combination of the diffusivity of the permeant D dissolved in the polymer and its concentration gradient, which in turn is proportional to the permeant solubility S in the polymer.

The diffusion and permeability are closely interconnected with the solubility of a polymer. The permeation of the permeants through polymeric membrane film occurs in three stages: (1) *Sorption* includes the initial adsorption, absorption, penetration, and dispersal of penetrant into the voids of the polymer membrane surface and cluster formation. The distribution of permeant in the membrane may depend on penetrant size, concentration, temperature, and swelling of the matrix as well as on time. The extent to which permeant molecules are sorbed and their mode of sorption in the polymer depends upon the enthalpy and entropy of permeant–polymer mixing, i.e., upon the activity of the permeant within the polymer at equilibrium. When both polymer–permeant and permeant–permeant interactions are weak relative to polymer–polymer interactions, i.e., dilute solution occurs, Henry's law is obeyed. The solubility coefficient S is a constant independent of sorbed concentration at a given temperature. (2) *Diffusion* includes the transfer of the penetrant through the polymer membrane which depends on: penetrant concentration that leads to a plasticization effect, penetrant size and shape, polymer T_g, time, and temperature. The diffusion coefficient is determined by Fick's first law of diffusion. (3) *Desorption* includes release of the penetrant from the opposite side of the membrane face.

Factors affecting permeation properties of polymers include: (a) *Permeant size and shape*. An increase in size of permeants leads to an increase in their solubility coefficient due to their increased boiling points, but will lead to a decrease in their diffusion coefficients due to the increased activation energy needed for diffusion. Shapes of flattened or elongated permeants have higher diffusion coefficients than spherical permeants of equal molecular volume. (b) *Permeant phase*. Weak interactions of the permeant with polymers lead to minimal sorption and hence to little swelling of the polymer. Permeant, which is a good solvent for the polymer, swells and plasticizes the polymer, and gives rise to increased mobility of the polymer chain segments and leads to enhanced permeation rates. (c) *Polymer molecular weight*. Its increase leads to decrease of the number of chain ends. The chain ends represent a discontinuity and may form sites for permeants to be sorbed into glassy polymers. (d) *Functional groups* present in the polymer which interact weakly with permeants can decrease the permeability as the cohesive energy of the polymer increases. Functional groups which have specific interactions with a permeant act to increase its solubility in the polymer. This leads to plastization and hence enhanced permeability. Removal of a functional group which strongly interacts with a permeant from a polymer will reduce its permeability to that permeant. (e) *Polymer density and structure*: reduction in polymer density, which may be regarded as a guide to the amount of free volume within a polymer, results in an increase in permeability. The increasing of the polymer rigidity and the decreasing free volume available for the diffusion of permeants are main causes of the decrease in the permeability due to the decrease in permeant diffusivity. The substitution of bulky groups in the side chains has a stronger influence on decreasing the diffusivity than substitution of bulky groups in the polymer backbone. An increase in the rigidity of the structures can lead to increases in permeability. The interchain separations in the rigid bulky polymers permit free movement of permeants below pore size. (f) *Crosslinking, orientation, and crystallinity*: in noncrystalline polymers, diffusion coefficients decrease linearly with crosslink density at low to moderate levels. Crosslinking reduces the mobility of the polymer segments and tends to make the diffusivity more dependent on the size, shape, and concentration of the permeant molecules. Crystalline polymers act as impermeable barriers to permeants. Permeant solubility is proportional to the product of the amorphous volume fraction and the solubility S of the permeant in the amorphous phase. Orientation of amorphous polymers can result in a reduction in permeability.

The permeation process is characterized by the permeability coefficient P, as the product of the diffusion coefficient D, and of the solubility coefficient S (Eq. 1.18).

$$\mathbf{P = DS} \tag{1.18}$$

The diffusivity D is a kinetic parameter related to polymer mobility, while the solubility coefficient is a thermodynamic parameter which is dependent upon the strength of the interactions in the polymer–penetrant mixture. Chemical modifications of polymers affect the coefficients of diffusion and of solubility. Changes in material structure have a greater effect on diffusion coefficient, whereas the solubility coefficient depends mainly on the character of the low-molecular-mass compound. Permeability is determined by factors such as the magnitude of the free volume, and crosslinking which reduces the segmental mobility and the free volume and diminishes the permeability coefficient. A reduction of interchain cohesion and of crystallinity increases the permeability coefficient. The transition from the amorphous to the crystalline state usually decreases the permeability. A decrease in crystallinity may increase the permeability. The permeability of polymers is determined primarily by the amount of the amorphous phase [62, 300, 301].

Permeation of relatively small molecules through a membrane may occur by one of the following processes: (i) *Flow mechanism*. This involves flow through pores or capillaries in a nonhomogeneous membrane. The size of the permeant relative to pore size and the viscosity of the permeant are the controlling factors governing permeability [63, 64]. The simplest type of flow mechanism is viscous flow, in which the volume q of penetrant passing through a capillary of radius r and length Δx in unit time is given by Poiseuille's equation:

$$\mathbf{Q} = \pi \mathbf{r}^4 \Delta \mathbf{p} / 8\eta \Delta \mathbf{x} \quad (1.19)$$

where η is the viscosity of the permeant and Δp is the pressure difference across the capillary. Accordingly, the permeability coefficient P corresponds to:

$$\mathbf{P} = \phi \beta \mathbf{r}^2 / \mathbf{8}\eta \quad (1.20)$$

where β is a tortuosity factor which increases the effective length from Δx to $\Delta x/\beta$ and Φ is the volume fraction of capillary in the membrane. For all penetrants that do not interact with the membrane, i.e., for which Φ and r are independent of the penetrant, the permeability coefficient is inversely proportional to the viscosity of the penetrant.

(ii) *Diffusion mechanism.* This involves diffuse flux of molecules dissolved in a membrane which has no pores or voids. In this process the penetrant dissolves and equilibrates in the membrane surface and then diffuses in the direction of lower chemical potential. If the boundary conditions on the two sides of the membrane are maintained constant, a steady-state flux of the components will be established which can be described at every point within the membrane by Fick's first law of diffusion, Eq. 1.21:

$$\mathbf{Q}_\mathrm{i} = -\mathbf{D}_\mathrm{i} \mathbf{dc}_\mathrm{i} / \mathbf{dx} \quad (1.21)$$

where Q_i is the mass flux ($gcm^{-1}s^{-1}$), D_i is the local diffusivity (cm^2/s), c_i is the local concentration of component i (g/cm^3), and x is the distance through the membrane measured perpendicular to the surface. The measurement of permeability is carried out by two basic methods: the transmission method and the sorption-desorption method [65, 302–304]. The factors affecting permeation include: penetrant size and shape, penetrant phase, polymer molecular weight, functional groups polarity, polymer density and structure, bulky side groups, chain mobility and rigidity, interchain interactions, crosslinking, orientation, and crystallinity. In the transmission method a concentration gradient of the penetrant is applied across the membrane and the rate of penetrant transmission passing through the membrane in unit time can then be determined by a number of techniques such as the refractive index method or interferometry, thermal conductivity, chemical analysis or colorimetry, gravimetric techniques, mass spectroscopy, gas chromatography or pressure-volume-temperature measurements of gases.

The diffusion and permeation properties are important for using the polymers in a wide range of applications as protective coatings and packing, especially in impermeable food packaging. *Food and drinks packaging*: polymers have widely supplemented metals and glass as containers in the food and drinks industry because of their low cost, light weight, and controllable permeation properties. Polymers having the desired permeation properties in combination with strength, toughness, clarity, and easy processability have been developed to achieve this application. In order to attain the necessary combination of desired properties, multiple layers of different polymers are used. Protection of foods against oxygen is necessary in order to reduce oxidation which can cause flavor or color changes. In order to prevent rancidness due to oxidation, the packaging must be impermeable to oxygen and moisture, e.g., packings consisting of nylon-6 laminated to a low-permeability coated PE film. The retention of carbon dioxide in carbonated drinks, by PET, for instance, can easily be detected by both taste and observation of the lack of sparkle in the drink, since it loses 10 % or more carbon dioxide. For beer, preventing access of oxygen is necessary since its flavor can be affected by oxygen. Low water-vapor permeability is also important [305]. *Coatings*: polymeric coatings that provide a surface protection with good resistance to corrosion must fulfill several functions. Since corrosion occurs at the metal surface only in the presence of water, oxygen, and ionic impurities, the coating must be highly impermeable to all of these agents. Consequently, the polymers used for coatings are highly crosslinked and contain a high concentration of filler particles to reduce oxygen and water permeability. Additionally, the polymers should not contain polar or ionic groups which could interact with water and subsequently lead to swelling of the polymer and so increase its permeability. Furthermore, low permeability to ions is also achieved by the polymer having few easily polarizable groups, thus ensuring a low dielectric constant. The relative importance of water, oxygen, or ionic permeability through the coating, and the adhesion between the coating and the metal surface are often of decisive importance.

1.2.5 Adhesion

Adhesive materials are applied as thin layers of polymeric materials capable of transmitting stresses between two substrates. They can be classified according to their functions into physical or chemical adhesive forms. Adhesives must behave as fluids before they set and become solid. Thus, the solid adhesive is formed from (a) its solution by solvent evaporation, (b) hot-melting by cooling and (c) reactive liquid precursor by in-situ thermosetting reactions. The purpose of adhesives is the transmission of forces from one adherent to the other. Thus, adhesive performance is always described in terms of mechanical adhesion in which the strength of the polymer interface with the adherents is evaluated. The distribution of stresses in bonded joints depends on the overall bond geometry and on the loads applied to the bonded structure. The initiation and development of failure is most certainly associated with stress distribution.

Cooling a hot-applied adhesive or solvent removal may result in shrinkage of the polymer adhesive. Interface cracks resulting from applied loads lead to high stresses that generate bond cracks and the propagation of the crack for total failure to occur. Besides the chemical interaction of the adhesive with the adherents, the physical properties determine its performance that is evaluated by measuring the safe response of an adhesive bond to loads. The properties relating to contact formation include: (1) the viscosity during the bond formation process, related to high temperature or solvent staging, (2) the contact angle of an adhesive in the liquid state, as a measure of the adsorptive affinity of the adhesive to the adherent surfaces, (3) the rigidity and strength of a bonded joint, as characterized by the relaxation modulus or creep compliance in tension and in shear, (4) contact and flow properties of the polymer to make adequate contact with the adherents, (5) thermomechanical and mechanical properties related to polymer rigidity or deformability.

The glass transition temperature T_g of amorphous polymer indicates for each polymer a narrow temperature range in which the polymer undergoes a change from soft leathery behavior to a solid. A polymer at a temperature a few degrees below T_g will exhibit pronounced time-dependent behavior over long periods of time or under very slow deformation rates (creep), although under normal deformation rates it may appear stiff and hard. In crystalline polymers, the crystal T_m lies above T_g and softening of the polymer normally results from crystal melting. Large volume changes are associated with crystal formation and melting, which would lead to large cool-down stresses in bonded joints. Thus crystalline polymers are usually poor candidates for adhesive purposes. The expansion/contraction behavior occurring in the case of temperature changes is one of the important properties of adhesives because it is associated with the development of stresses. Thermal contraction results from slow temperature changes; heating or cooling generates the same thermal contraction. When polymers are cooled above T_g, or lose solvent, they shrink, with the shrinkage continuing over prolonged periods of time. Associated with this shrinking is a continual change in the mechanical properties of the polymer in the direction of stiffer material characteristics.

1.2.6 Polymer Deterioration and Stabilization

Chain degradation is generally possible both in the presence and in the absence of oxygen at higher temperatures. It may be caused by thermal, hydrolytic, or mechanical effects. The mechanical stability of networks varies considerably from one material to another, and also depends on the nature of the mechanical stress and on the crosslink ratio. Lightly crosslinked materials are extremely fragile, particularly when in contact with a good solvent, and even conventional stirring techniques can cause considerable mechanical degradation of the support. Increased physical stability can be achieved with increased crosslinking but there always exists a balance between the required mechanical properties and the porosity of the network. Macroreticular resins can be employed in high pressure conditions and present some flexibility in the use of solvents. Gel-type resins are readily compressed and are not suitable for high pressure applications but can show marked mechanical resilience and ability to absorb shock because of their elastomeric properties in the swollen state. However, sudden dramatic shear will cause considerable damage. Similar effects can arise from osmotic shock if the nature of the solvent is changed dramatically, and rapid evaporation of solvents from the interior can also cause excessive rupture of the structure due to the sudden increase in volume.

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Part I
Applications of Polymers in Agriculture

The application of polymeric materials in agriculture and horticulture has increased considerably in recent years, not only as replacement for traditional materials but also as a significant improvement in technological processes in the growing of agricultural vegetables and crops, in storage construction for crops and animals, and in agricultural equipment and drainage technology. The aims of using polymer engineering technology in agriculture and horticulture is concerned with growing more and better plants faster in less space and at lower cost [1–49]. A first chapter here is concerned with the utilizations of polymeric materials in plantations and plant protection as is divided into four parts: polymers in plantations, polymers in plant protection, polymeric farm construction materials, and polymers in farm water handling and management. The second chapter is devoted to the effective utilization of polymeric materials as reactive macromolecules in controlled-release formulations of various agrochemicals to reduce the amount of these chemicals released to the environment.

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Chapter 2
Polymers in Plantation and Plants Protection

This chapter is devoted to polymers employed in agricultural applications for various purposes in growing crops and in plant protection. It is divided into four parts: the first part is concerned with the utility of polymeric materials in suitable media for enhancing crop growth under poor weather conditions and to minimize water and nutrient requirements of plants. The second part covers the various aspects of effective utilization of polymeric materials in plant protection against poor weather conditions and birds to increase crop yield, and shortening the crop season. The third part discusses the utilization of polymeric materials as engineering structural components in farm building constructions and machinery and other engineering tools. The fourth part is devoted to the use of polymers in farm water handling and the management of irrigation to control water distribution and conservation.

2.1 Polymers in Plantations

Polymeric materials are extensively used in agriculture for improving the mechanization of farming and growing crops, to enhance the cultivation of plants under adverse weather conditions, and for effecting more favorable conditions for plant development. They are used in agricultural plantations in steadily increasing amounts to obtain higher yields of harvests and for improving the quality of plants in a shorter time and using less space at lower costs [1, 2]. Polymers are used in such agricultural applications as soil conditioners, planting and transplanting gels, seed coatings for controlled germination, soil aerators, and in soil sterilization.

Polymers can benefit plants in the various stages of development: germination, growth, evapotranspiration, flowering, and fruit formation. Their successful application in agricultural plantations includes more rational plant spacing and improved economization, especially regarding plant containers, films for soil sterilization, and as coverings and sheetings for protective structures. They are employed in mulching and as low tunnels, windbreaks, and protective nets; as protective structures in

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greenhouses where an artificial microclimate can be precisely controlled. Conventional cultivation schemes are now being superseded by soilless culture on an extensive scale, which now makes use of gullies formed from plastics with the nutrient solutions being circulated through plastics pipes and applied directly to the root system [3–7].

2.1.1 Soil Conditioners

Soil management is aimed at effectively maintaining or increasing agriculture production for the benefit of society and preserving or improving the environment.

Soil factors include soil type, thickness, compaction of soil layers, and ground water conditions. Soil provides a medium to support plants, and is a reservoir for water and plant chemical nutrients made up of a mixture of solids, liquids, and gaseous materials. The solid materials of agriculturally productive soils are variable mixtures of mineral particles (95 %) and organic matter (5 % of animal, plant, fungal, and bacterial origin), capable of supporting plant life and determining the soil type. The mineral portion contains particles differing in size, shape, and chemical composition, and is the final product of the weathering action of physical, chemical, and biological processes on Earth. The liquid portion of the soil consists of water that fills part or all of the spaces between solid particles. It is crucial because it contains nutrients that plants need for growth and survival, some of which have entered through the soil surface. The remaining pore space between the soil particles that is not filled with water is occupied by air. The topsoil is the top layer with maximum biological activity and contains most of the organic matters. The subsoil receives organic matter, nutrients, and clay particles through leaching from the topsoil. Soils exhibit a large variety of characteristics that are used for their classification for various purposes. Soil characteristics include: strength, soil particle size, permeability, degree of maturity, and soil composition. Soil texture is classified according to increasing particle size into: clay, silt, sand, gravel, and rock. The voids between the larger particles are entirely filled by smaller particles, i.e., sand fills the space between particles of gravel, silt between particles of sand, clay between particles of silt. The finer grained soil particles, silt and clay, are powdery, hard, and impenetrable in the dry condition, but exhibit spongy and slippery characteristics when wet and become fluid when mixed with water. It is difficult to find a soil that is in perfect physical condition for agriculture plantation purposes. Humid *tropical soils* exposed to heavy rain intensities suffer from the decrease in aggregate stability and increase in bulk density. Consequently, water intake and storage are reduced while surface drainage and laminar erosion increase. Tillage operation in these soils is difficult and retaining the soil around the growing plants is almost impossible. In *sandy soils*, low water-holding capacities and high infiltration rates are the major problems in establishing a successful plants irrigation system. In *clayey soils*, crust formations cause problems for seedling emergence. Thus, there is a great interest in soil reclamation to overcome these problems.

Polymeric materials are being added to soils for reclamation and to improve soil composition and structure. These polymeric materials improve the soil grain structure by forming cloddy soil suitable for vegetation for improving plant growth [8–26]. They reduce water demand especially in sandy soils via increase of water-holding capacity, reduction of water stress, preventing soil erosion by altering soil mechanical structure, improving friability, enhancing the establishment of seedlings, and increasing crop yields [20].

2.1.1.1 Soil Conditioner Types

There are various natural and synthetic materials used for soil reclamation. They are added to the soil surface or around the seedling roots at the time of planting, thereby improving the soil's physical properties [21].

(A) **Natural organic matter.** Animal manure, crop residues, organic compost, sawdust, and various other materials such as food, textile, and paper processing wastes are used for soil reclamation to increase infiltration and retention, promote aggregation, provide substrate for biological activity, improve aeration, reduce soil strength, and resist compaction and crusting, and surface sealing. These are particularly important for improving the crop-growing potential of sandy soils. The use of these materials for the purpose of soil improvement also contributes positively to solving the problem of waste materials disposal from the full range of human activities.

(B) **Mineral materials.** These can modify the chemical or physical characteristics of soils by increasing soil base saturation (reducing soil exchangeable sodium percentage), increasing flocculation of primary particles and stabilizing aggregates, and reducing dispersion and sealing. In *saline soils*, calcium sources are applied to reduce water sodium adsorption ratio and soil exchangeable sodium percentage. They are important for management of *arid* or *tropical soils* where high temperatures promote rapid bio-oxidation of incorporated organic material. Iron oxides have been used to promote aggregation in soils with low organic matter [27–29]. Inorganic materials such as modified silica are used as soil conditioners for improving soil properties [22–26].

(C) **Synthetic polymeric materials.** These are designed to produce specific physical and chemical effects in soils for improved agricultural performance; only very small amounts of material are added [30–36]. The mode of action of these synthetic amendment materials can be targeted to a particular physical property of the soil: (1) *Surfactants* affect the surface tension of soils to water and are most commonly used to enhance the wetting and infiltration of treated soils. (2) *Flocculants* enhance the cohesive attraction among dispersed fine particulates and lead to formation of aggregates (flocs) in aqueous media that achieve sufficient size and weight. These materials enhance the existing structural stability of the soil and increase shear strength and reduce detachment.

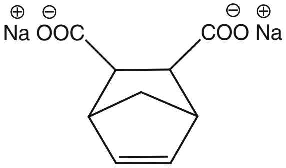
There are three major classes of synthetic polymeric materials used as soil conditioners to improve agricultural production:

(a) **Water-soluble polymers** are linear soluble hydrophilic or ionic polymers used as wetting agents leading to more effective water-holding capacity and more stable soil aggregates [37]. The most commonly used water-soluble synthetic polymers effective in soil reclamation especially of sandy soils, include: PEG [38], PVA [39–56], CMC, H-PVAc [57, 58], H-PAN, PiBMA, NaPAA, PVAcMA [33, 59], and water-soluble PAAm [60]. PVAcMA and H-PAN are used for preventing soil surface crusting [61] and for moisture retention [62]. Polyelectrolytes improve the chemical, physical, bacteriological, and agronomical aspects of soils aside from supporting reclamation of saline and alkaline soils [63–65]. Linear PAAm and cationic guar derivatives (polysaccharides) have been applied in sprinkler irrigation water to sandy soils to maintain stability, infiltration, and preventing surface crusting [66]. However, the use of water-soluble polymers in reclamation of clayey soils reduces root growth of plants as a result of inadequate aeration.

(b) **Hydrogels** are insoluble crosslinked hydrophilic polymers and have the ability to hold water many times their own weight depending on their structures, i.e., water-absorbent polymers, and have the ability to release the absorbed water as the environment becomes dry. Polymers aggregate in different states: solution, gel, viscoelastic, and glassy-crystalline states. The macromolecular solution state depends on the coil density and is characterized by the absence of the physical interaction between the macromolecule chains, i.e., they do not form secondary valence bonds between the chains, but form secondary valence bonds between chains and solvent. As the solvent is removed, the dilute solution changes to a gel in which the chain segments of the coils penetrate each other, i.e., become entangled. The gel state represents a transition between the solution and the solid states. The gel state can be distinguished from the solution state by the fact that the coils no longer move as units or interchange their positions. A general characteristic of gels is their swelling power (the amount of solvent in cubic centimeters taken up by 1 g of crosslinked polymer), which is an indication of the effective pore diameter.

Hydrogels are classified in two categories with respect to the nature of linkages between the coils: (i) the *physical gel* which occurs through secondary valences and undergoes reversible gelation by externally induced topological interaction of polymer chains, either in the melt or in solution. The linkage caused by secondary valences is not of long duration and requires a certain minimum size of the macromolecule to ensure a gel formation upon solvation. Depending upon the differences in the strength of intermolecular forces, there are polymer systems which have either weak or strong tendency to form secondary valence gels. The secondary valence gels usually become liquid again on warming, i.e., they are thermoreversible, and the physical entanglement networks dissolve to form a polymer solution.

Fig. 2.1 Sodium humate



The formation of weak secondary valence gels occurs in poor solvents, which will not prevent all secondary valence bonds between the polymer coils by solvation. The solvation equilibrium is temperature dependent, i.e., it increases at higher temperatures. (ii) The *chemical gel* is a network structure (crosslinked) formed by covalent links between polymer chains. Chemically crosslinked materials are formed by copolymerization, chemical modification, or radiation of linear polymers. The crosslinked network will swell but not dissolve, because the covalent crosslinks cannot be broken by any solvent and the swelling depends on the degree of crosslinking.

Superabsorbent hydrogels are used for the renewal of sandy soils and can reduce irrigation water consumption, improve fertilizer retention in soil, lower the plant death rate, and increase the plant growth rate [66, 67]. Most polymeric superabsorbents are based on sodium polyacrylate, but they are not suitable for saline water and soils [68]. Superabsorbent composites have been made by incorporating mineral into hydrogels to reduce production costs and improve salt resistance [69, 70]. Incorporating fertilizers into a superabsorbent network may thus be an effective way of increasing the utilization efficiency of both water and fertilizer [71, 72]. Superabsorbent composites containing **sodium humate** (Fig. 2.1) release the fertilizer over a long period, depending on the sodium humate content. Superabsorbent composites based on P(AAm-NaAA) crosslinked with MBAA has been shown to improve the water-retention capacity of the soil, regulate plant growth, accelerate root development, improve soil cluster structures, and enhance the absorption of nutrient elements [72].

1. **Physical properties of hydrogels**. The swelling capacity of hydrogels to retain water in their fully swollen state is an important characteristic. The equilibrium moisture-retention capacity of a hydrogel above about 55 % facilitates the diffusion of large ions into and out of its structure. The degree of hydrogel swelling, “hydrogel volume,” at the equilibrium represents a balance between the osmotic pressure force that drives water into the polymer (driving expansion) and the tension within the elastic contractability of the stretched polymer network that tends to expel the water from the swollen polymer (resisting expansion). The swelling pressure of the hydrogel at equilibrium is equal to zero. Hydrogels undergo reversible swelling and shrinkage which are a consequence of the affinity of their chemical structure, i.e., ionic form, to interact with water and also affects the moisture-retention capacities of hydrogels. The water-holding capacities of hydrogels allow spraying or blowing slurries of them with other agromaterials in soil reclamation [8, 60, 73, 74]. Hydrogels in the dry state are glassy with a

tendency to become soft, rubber-like after swelling in water or other polar solvents in which they are thermodynamically compatible. The ability of hydrogels to swell with water is governed by the free energy of their mixing and by the density of crosslinking [75]. Water penetration into the free spaces between the macromolecular chains of the hydrogel causes stresses which are then accommodated by an increase in the radius of gyration of the hydrated macromolecules. The entrance of the water into the free regions within the polymer favors the elongation and expansion of the polymer chains, and is increased by the strong hydrogen bonding interactions between the water and the polar functional groups on the polymer chains [60]. The water amount in the hydrogel can be regulated by suitable shrinkage or expansion, i.e., by the distance between crosslinks with the macromolecular segment chains. The swelling water within the hydrogels can affect their properties [76–81]. The equilibrium water content measured by gravimetry is the ratio of the weight of water in the hydrogel to the weight of the swollen hydrogel at equilibrium hydration [8, 13, 60, 73, 82, 83]. The equilibrium degree of swelling of a hydrogel is determined by the factors influencing coil density: hydrophilicity and concentration of ion-exchange groups on polymer chains, density and nature of the crosslinking, nature and degree of dilution solvent during polymerization, polymer chain mobility, branching, stereoregularity, as well as the type, concentration, and dissociation degree of solutes in solutions.

2. **Mechanical properties of hydrogels**. Gel coils are not hard, but soft and easily deformable, due to the large freedom of segment movement, which are not able to move as units and thus not able to flow and the extent of the segment movement is dependent on coil density, solvent content, constitution of the chains, and the degree of crosslinking. With increasing crosslinking, the gels become hard and brittle because the chain segments between crosslinking points become short and the possibility for movement become small. The coils of gel are forced to a less probable state on deformation and with a decrease in the entropy of the system. Thus, the elastic retractive force of the gel (elasticity) is a characteristic property of the gel at low degree of crosslinking, in which the deforming force is not sufficient to bring a permanent deformation after removal of the deforming forces (stress), i.e., the gel returns completely to its original state before deformation of higher entropy. The gels have lower mechanical strength than solvent-free polymers, because the solvent isolates polymer chains from each other. In the swollen state, a hard, brittle gel becomes soft and rubber-like with low tensile strength and modulus. This solvent effect on mechanical strength has a profound effect on the lifetime of the gel in use. The elasticity and rigidity of hydrogels are governed by their chemical structures and affect their mechanical properties, such as the modulus of elasticity, degree of swelling, permeability and diffusion, and optical properties, which can be governed by the polymerization technique and conditions, the diluents, monomer structure, crosslinking density and hydrogen bonding structures, ionic and polar interchain forces, and the water-binding properties of the hydrogel [3–7, 84].

3. **Hydrogel application methods**. There are two methods for applying hydrogels as soil conditioners to stabilize the surface of soils to inhibit crust formation and improve water-holding capacity or to improve poor structure at greater depths by aggregation and to enhance plant growth. (1) *Dry method to subsoil*. Dry polymer such as PAAm or PVA is applied to the subsoil by mixing with the sandy soil into depths of about 15–25 cm and then subjecting to wetting for swelling prior to cultivation. After the polymer has swollen the soil structure is improved and the water penetration and retention capacity increases, decreasing water runoff and erosion. This method is applied for long-term intentions as the polymer has to absorb water prior to becoming beneficial, it is not recommended for immediate sowing. (2) *Wet method to topsoil*. The polymer solution is sprayed onto initially wetted topsoil, followed by drying to create water-stable aggregates that resist erosion [85–87]. This method is particularly well adapted to sowing immediately afterwards and can also be adopted to reduce water consumption in irrigation systems where water losses occur due to the soils' poor ability to retain moisture. These wet polymer methods can also decrease soil erosion by being applied to topsoil or to driveways of irrigation [88, 89]. Surfactants have positive effects on aggregate stability [90, 91], hydraulic conductivity [92, 93] and the distribution of conditioners [94].

2.1.1.2 Hydrogel Applications

The application of polymeric soil conditioners as additives to soils to improve their aggregate conditions can be extended into other areas: to reduce soil erosion and to prevent crust formation and general stabilization.

(a) **Soil fixation** treatments of poorly structured soils are to improve stabilization and solidification of soils by varying the physical and chemical features of soils for construction and other structural applications where soil movement must be reduced or eliminated. The process generally requires the use of more than one additive. Polymers can be used to fix soil particles into aggregates by incorporating a crosslinking agent with them in the soil. They can be incorporated to improve water retention in the soil and provide a better growth medium. This technique is designed to allow crop cultivation without irrigation in areas where natural rainfall is inadequate due to drainage and evaporation losses or long dry seasons. Polymers can enable the existing water supply to be used more efficiently.

(b) **Soil conditioning** aids for increasing the available water content of soils, for improving plant growth, and reducing irrigation requirements due to reduction of water loss and evaporation, thus, allowing the intervals between irrigations to be increased. The improved water retention in the soil will protect the plants against hydric stress. This is particularly suitable in arid areas where agriculture is marginal due to infrequent rainfall. Polymers can be incorporated in the soil to improve soil structure and water retention by reducing leaching and increasing water supply to the roots. Hence they improve germination percentages and early growth, and reduce plant mortality during transplantation and simplification of transportation of plants. *Sandy soils* may allow good aeration but fail to retain sufficient water. They may not be able to meet the water demands of a plant, resulting in plant dehydration and wilting stress. Repeating this hydric stress during the growth period can seriously inhibit plant growth. In these soils, the polymers can agglomerate the sandy particles and hence increase the water retention capacity. *Clay soils* inhibit plant development by inadequate oxygen levels, excess of carbon dioxide, and lack of drainage. These soils have the tendency of forming compacted crusts that inhibit seedling germination and emergence and restrict early root growth, which may be compensated by overseeding and excessive irrigation during germination. Polymers can also be employed to improve the structure characteristics of clay soils, where the swelling of the polymer particles breaks apart the structure of the soil and leads to an improvement in aeration, better drainage, and provide a stable aggregate in the soil thus reducing the crusting effect. This dual action of improving water infiltration and reducing erosion enhances seedling emergence and accelerate early growth.

Hydrogels are of great interest in soil reclamation as (1) soil amendments to modify the water status of growth media, (2) seed amendments, and (3) transplant aids [8, 60, 75–77, 95–118]. Hydrogels used as soil conditioners for improving soil properties [8, 119–121] include: plastic foams [122, 123], PS [124], H-SPAN copolymers, crosslinked P(KAA-AAm) gel [125], P(KPA-PAm) [126], and PAAm gel [21]. Hydrophobic conditioners, such as bitumen [122], are also employed in emulsions for reducing soil runoff and saving water in subsoils, especially for in tropical rainy zones [8, 128]. They decrease crust firmness of sandy and a clay loams, decrease infiltration rates, and increase water retention. Incorporating hydrogel polymers as polymeric plant growth media by spraying onto soil surfaces as a thin soil layers results in: improved plant growth and size [66], improved crop yields, superior water relations of plants growing in soils [129, 130], improved moisture retention in the root zones during plantation, more healthy transplants, i.e., reduced growth retardation after transplanting, increased water-holding capacity, reduced soil compaction [131], and improved nutrient retention, efficiency, and uptake. Nutrient-amended polymers serve as effective seedling growth media for short-term seedling production [129, 132], reduce nutrient leaching losses [133], improve soil fertility and prevent soil erosion [95, 129], increase time of leaf wilting that improve root development and increase yield [134], decrease irrigation frequency [73, 74, 135], and provide adequate aeration to seedling roots by pore creation between gel granules upon hydration. The combination of hydrogels and wetting agents produces more effective water-holding capacities, which are influenced by the type of irrigation method (overhead sprinkler, trickle emitter, flood and drain trays, capillary mat, etc.) [136].

Naturally aggregating polymeric agents in soils such as polysaccharides and protein are formed as a result of chemical and fungal reactivities [137–140] or due to the interaction between clays and organic matter in soils [141], e.g., cationic starch-grafted copolymers possessing diethylaminoethyl- and 2-hydroxypropyl trimethylammonium ether groups have been shown to be effective stabilizers of surface soils [142]. In addition to the use of H-SPAN-containing carbamoyl and carboxylate groups in seed and root coatings and thickening agents, the former have the potential of increasing the water-holding capacity of soils, especially of sandy soils [13]; it is insoluble in water and, when wet, produces gel sheets of large surface area [143] and has been used as a soil conditioner in agriculture to increase the soil water-holding capacity of sand and delays moisture stress because it can absorb high amounts water [60, 144–147]. The addition of this material to soils has a reducing effect on the water-retention properties and the infiltration rates of soils [148].

PAAm gels are useful in stabilizing unstructured sandy soils and in forming water-stable aggregates in soils, preventing surface crusting [61, 149, 150] and reducing soil splash and runoff [151, 152] besides settling and consolidating soils and dust against wind [153, 154]. They are effective in improving the physicochemical properties of sandy soils that have favorable effects on water infiltration and decrease the erodibility of soil, thus reducing the requirement for irrigation and increasing crop yields [155]. Structural improvements due its hydrophilicity results in a better infiltration and drainage by increasing the holdup of water and reducing water evaporation from the soil. PAAm has successfully been used in treating water repellency [156] in alluvial soils and has improved seed germination, plant growth, and crop yields [62]. The erodibility of silt loams and dune sand are reduced by PAAm addition. However, it increases soil aggregation, porosity, aeration, and imparts friability, which lead to an increase in the infiltration rate and storage of water in the subsoil. Besides soil reclamation by use of PAAm as soil conditioner, it imparts improved chemical and bacteriological fertility that increases the yield of crops. These have been attributed to the continuous supply of nitrogen, increasing nitrification or nitrate content in the soil, and enhancing soil bacterial growth and microbial populations, and imparting friability which results in increasing rooting. PVA has also a stabilizing effect on soil surfaces and its distribution is determined by: method of application, application rate, and the polymer's molecular weight [88]. PVA is more effective in stabilizing the soil surface at very low application rates than root exudates and soil organic matter, due to its strong adsorption. Soil conditioners used for soil reclamation and aggregating and stabilizing soils have been comprehensively reviewed previously [157–165].

(c) **Soil erosion control.** Soil erosion and runoff are serious land degradation problems in arid and semiarid regions caused either by rain or wind. It is a significant environmental problem for agricultural lands that results in destruction and eventual abandonment of the land and the loss of civilization itself. Sediment in runoff from agricultural landfills in reservoirs and rivers endangers aquatic life and reduces soil productivity. Chemicals transported with the sediment may cause water quality problems in lakes and streams. Land classification is based on the capability of crop production, as determined by the degree of limitations and hazards, and involves the following parameters: soil type, erosion degree, drainage extent, presence of rocks and stones as impediments to cultivation, water-holding capacity, and the amount and distribution of rainfall. These soils are characterized by relatively high levels of salinity and low structural stability, and irrigational erosion reduces the productivity of irrigated soils, the yield of grain, forage, and industrial crops, and lowers the quality of the produce. Soil erosion by water can be reduced or controlled by varying the irrigation technology and its mechanism. This can include the ability of a water flow to detach and move particles along the surfaces and the resistance of the soil to the force of irrigation water, and by providing adequate supplies of the irrigation water for agricultural and crops uses and removing excess water from the soil surface. Long-term control of soil erosion is usually achieved by growing plants. However, until the plants are fully established soil erosion will continue, thus reducing the efficiency of the early cover. Polymers can be applied to aggregate the soil by surface treatment and hence to provide surface stabilization during the early phase of crop growth. Thus, hydrogels act to reduce erosion from water and wind by stabilizing the surface layers, reducing runoff and soil losses, decreasing the infiltration rates of water into the soil, and increasing the hydrophilic nature of the soil surface which aids seed germination and emergence. The combined effects of reducing runoff and promoting a higher level of moisture to be retained in the soil reduce erosion and improve plant growth. In addition to their use as straw mulch, hydro-seed hydrogels are used to reduce erosion by increasing soil strength by aggregating the soil particles, absorbing the impact of raindrop energy, and promoting plant growth by protecting seeds and seedlings, maintaining aggregate stability, and increasing soil moisture [37, 166, 167].

(d) **Seepage control** can be achieved by certain polymeric hydrogels which form water-impermeable layers or membranes in the soil and can be efficiently used to control the movement of water and dissolve salts through their interactions with charged sites on the surface of the soil particles. Thus, hydrogels are used for seepage control by the formation of membranes in the soil that restrict the movement of water thereby protecting crops from salt damage. This technique can be used to save irrigation water, to control salt damage to crops caused by irrigation in arid soils and finally to prevent the seepage of such water into rivers and reservoirs.

2.1.2 Container and Pot Plantations

Cultivation in containers (flower pots) is charactzerized by features that differ from those in open field cultivation. The volume of soil available to the plant is smaller and less deep than in an open field. This results in a reduced reservoir of water and nutrients available to the plant. To compensate this deficiency, regular watering and fertilizing is required in order to obtain acceptable growth rates. In the open field, plant roots can grow freely towards water sources, which is not possible in the containers. The roots in a container tend to grow in circles which is detrimental to the overall aeration and drainage. In all types of soil the amount of water decreases with compaction, this means that the deeper compacted layers contain less available water than the surface porous ones. Soil conditioner is added to prepare the container soil for improving its physical properties by reducing its density, increasing its porosity, and thereby increasing the amount of air and water. Most bedding plants are grown in small containers that make them highly susceptible to water stress. Avoidance of water stress and protection against possible plant injury would be of significant value to growers and retailers.

Containers and pots for plants made from molded PS or PP have almost completely replaced the traditional clay pots both for commercial undertakings and for the private gardener. Plastic pots have the advantage of being easy to clean, of lighter weight, and losing less water by evaporation through the sides. Black PE film containers are cheaper and consequently have become accepted as the norm by the majority of nurserymen. Small containers and cylindrical pots of varying sizes formed in PS are widely used commercially for exporting and transporting young plants. With more people living in multistorey apartments there is an increasing demand for plant troughs which are designed from molded PP so that there is a constant supply of moisture available to the plant roots. PE film bags are used for the cultivation of mushrooms in underground quarries [168]. Various efforts to reduce water loss and increase market life of larger container-grown plants involve the use of hydrogels that act as rechargeable reservoirs holding many times their dry weight in water. Several beneficial results of hydrogels include greater nutrient availability, improved aeration and drainage, increased market life of container-grown plants [135], reduced watering requirements, improved top growth and flowering, better root development, and increased yields [169]. Hydrogel incorporated in the growing media of bedding plants grown in different size containers generally increased time to wilting as demonstrated by the reduction in internal water tension under stress due to hydrogel incorporation in the growing medium. High rates of hydrogel incorporation were as effective in increasing time to wilting in small containers as was doubling container size [73]. Various forms of soil amendments and antitranspirants have been used for many diverse crops [135]. In floriculture with hydrogels, their effects on water-holding capacity of media in pot-grown crops [73] improve aeration and drainage of the medium [169], improve market life of container grown plants [170], and reduce watering requirements. A delay in wilting and moisture stress can be decreased by incorporation of a hydrogel into the medium [73]. Film-forming antitranspirants and hydrogels affect net photosynthesis and water loss during water stress [88]. When plants are transplanted into medium with a hydrogel, such as PEO, water loss is lowest for plants where both the foliage and medium are treated. As water stress developed, net photosynthesis decreased, reaching a zero rate at wilting. Crosslinked PAAm, P(KPA-PAm), polyamide and cellulose-ether containing $FeSO_4$ are used for greenhouse pot plants, to improve the storage of available soil water and are effective in supplying Fe to plants [26, 171].

Water retention in potting soil is an important factor in irrigation management of potted plants and may be influenced by amendments soil conditioner: hydrogels or wetting agents [172–176].

2.1.3 Gel Planting and Transplanting

Hydrogel applications in agriculture include their addition to soils as gel planting [3–7], incorporation into hydro-seeding or hydro-mulching systems where they serve as tackifiers for seeds and as germination aids, and are added to water as a gelling agent for fluid drilling of pregerminated seeds [60, 75]. There are two types of *transplanting* to beds: (a) trees and shrubs are normally transplanted with a dry root structure. This results in a requirement for constant watering while the root system becomes reestablished. This water problem is obviously more severe in dry regions with sandy soils. (b) annuals are transplanted as cuttings and seedlings. During plant transportation over long distances there is a problem of provisioning adequate water supplies to the plants. Polymers can be used to provide water without any spillage.

2.1.4 Seed Coating Germination

Planting seeds is one of the most important steps in the process of propagating plants [177]. The most critical phases in the growth and development of plants are those of germination and establishment. The successful establishment of agricultural crops from seed is often restricted by poor soil moisture levels, especially in arid or semiarid regions. Improvements in soil-water relations should enable more even and predictable germination and establishment. Water uptake by seeds and subsequent germination rates are strongly influenced by moisture potential at the seed-soil interface [178, 179]. Polymers with binding tensions for water in the plant-available range have the potential to increase moisture levels around germinating seeds. Amendment of plant growing media with hydrogels often increases water-holding capacity and improves plant growth [180, 181]. Thus, plants grown in hydrogel-amended media require irrigation less frequently than plants in nonamended media, due to the effect of hydrogels on the surface properties of soil particles [148]. The influence of hydrogel-amended soil on the growth of transplants of some vegetables shows increased yields over other growing media [182]. Application of the gel slurry to the root zone of plants before transplanting prevents roots from drying, reduces wilting and transplant shock, and improves plant survival especially under poor field conditions. However, the more important application of hydrogels is in coatings for seeds to absorb water and is coated directly onto the seed surface. After planting, the hydrogel absorbs water thereby increasing the rate of germination as well as the percentage of seeds that germinate. The type of hydrogel seed coatings can be adapted depending on the application, to delay germination, inhibit rot, control pests, fertilize, or to bind the seed to the soil [183–188]. Seeds have also been coated to increase the size of small seeds to permit machine planting [3–7] to greatly reduce the waste of seed, and the cost of thinning the excess plants is eliminated. In such cases, the primary objective is to increase the bulk of the seeds and to include pH buffers, fungicides, trace nutrients, or other beneficial constituents to enable better plant establishment and growth [118] and to supply plant-available water [114] and reduce evaporation rates [108].

Seed coating can improve germination, reduce the germination time, improve root development in the early stages of growth and accelerate the harvest. By coating seeds with hydrogel by homogeneous mixing, moisture supplies can be improved in soils. This application method is commonly used with starch copolymers because the coated seeds have small particle sizes when dry and form a gel mass upon hydration. The gel adheres easily to the seed and the coating allows high water potentials to be maintained both inside the seed and within the protective layer [183–186]. This also enhances imbibitions of water prior to germination [9]. Powder polymer can adhere to the surface of the seeds by electrostatic attraction. When the polymer becomes wet it will loses its ability to stick to the seed and cause considerable difficulties of handling, hence the coated seeds are kept in an airtight container. In agricultural plantations and plant growth development, polymeric wetting agents have been used either as soil amendments for gel planting of germinated seeds [189, 190], for coating the root zone of seedlings before transplanting [3, 34], or as seed coatings for germination [185, 191]. However, there are some problems associated with seed coatings: (1) the coatings often do not stick to the seed well and can chip and crack, (2) thick coatings impede the rate of the flow of seeds in planters.

Hydrogels such as PAA and PVA are more commonly applied by mixing them dry into the growing medium and then irrigating to allow full hydration and the formation of a gel. In such cases seed and gel are not in direct contact as they are with the coating method [187, 188]. Polymeric wetting agents used in seed coatings include: PVA, H-PVAc, PVME, P(VME-MA), poly(vinyl pyrrolidone), agar, H-SPAN, starch copolymers, PAAm copolymers and water-soluble cellulose ethers, such as carboxymethyl- and hydroxymethylcellulose. However, clay seed coatings decrease germination because coatings reduce oxygen movement into the seed [9, 191]. In addition to the use of H-SPAN for increasing the water-holding capacity of sandy soils, its potassium salt results in viscous solutions which have a wide variety of applications like seed and root coatings and thickening agents. The gel absorbs water and holds it at the seed surface, thus increasing both the germination rate and the percentage of the total number of germinated seeds. H-SPAN coatings have been used as seed coating to enhance stand establishment and plant growth of sweet corn [184], soybeans, cotton, corn, sorghum, sugar beets, and leafy vegetables [85]. Elastic PU foam containing soil has been used as an effective plant growth medium supporting the root structure of a plant placed in the substrate foam [178, 179]. An example of a plant growth medium suitable for use as a matrix material to support the root structure of a living plant is foamed synthetic polymeric material impregnated with finely divided mineral particles and microorganisms suitable for rendering the minerals available for plant use and which may additionally contain a seaweed concentrate for supplying additional vitamins and minerals to the plant [192]. Additionally, plant growth media can be improved by using hydrogels for seed coatings that may incorporate other additives such as insecticides, nematocides, fungicides, repellents, herbicides, growth regulators, nutrients (N, K, P fertilizers), and bacteria capable of exerting a favorable effect on the germination and growth of plants.

2.1.5 Soil Aeration

A good soil for growing plants should have air gaps for proper gas circulation and exchange. Earthworms are significantly involved in aerating the soil through digging through the soil allowing gases to pass. Losening of heavy soil can be effected by the addition of foamed plastics in granular or chip form. Expanded PS as a waste product is now being used as a soil additive to improve soil structure and stimulating root formation, applied for plant propagation and potted plants. It is also used for drainage in place of conventional drains. Urea-formaldehyde foam is also used for this purpose having the advantage of moisture retention, unlike PS, and decomposing only slowly in the soil and supplying nitrogen to the plants [193].

2.1.6 Soil Sterilization

Soil sterilization has many benefits which provide secure and quick relief of soils from organisms harmful to plants such as: metabolites, bacteria, viruses, fungi, nematodes, and other pests, and killing of all weeds and weed seeds. *Soil heat sterilization* is often performed by heating the soil when covered with PE sheets by solar radiation during summer or during periods of intense sunshine and clear skies [191]. The process raises the soil heat and temperature, killing soil-borne pathogens and pests that would lower the yield of field crops. This nonchemical management of soil pathogens is an eco-friendly and inexpensive technique to control pests and diseases in the soil for a profitable yield. *Soil steam sterilization* (fumigation) is a farming technique that sterilizes soil and plants with steam or agrochemicals in open fields or greenhouses [194]. It consists of injecting into the soil, to a depth of several centimeters, steam or volatile chemical products while the area is covered with a sheet buried at the edges. Fumigation involves injecting into a well-prepared plot, covered with PE film stuck down at the edges, a toxic liquid which evaporates only slowly so that the vapor is maintained in contact with the soil for sufficient time to destroy all the unwanted plants and animal parasites. For preparation, all roots should be eliminated and the soil watered for several months in advance, in order to speed up the decay processes. Fumigation allows crops of high profitability to be grown without interruption on the same ground from year to year [192]. Fumigation cleanses the ground getting rid of weeds and pests such as nematodes, insect larvae, and microorganisms responsible for plant diseases. Harmful pests and weeds are also killed by induced hot steam. Steaming is the most effective way for a quicker growth and strengthened resistance against plant diseases and pests. Different types of steam application are available including substrate steaming and surface steaming. Several methods are used for surface steaming such as area sheet steaming, hood steaming, sandwich steaming (combined surface and depth injection of steam), plow steaming, and vacuum steaming with drainage or mobile pipe systems. Particular factors are considered in chosing the most suitable steaming method such as soil structure, plant culture, and area performance.

2.2 Polymers in Plant and Crop Protection

Polymeric materials have extensively been involved in the mechanization of farming and for the protection of plants and crops [195–215]. Covers are placed over growing plants for protecting them against adverse weather conditions and for stimulating an artificial microclimate for precisely controlled cultivation. Greenhouses, tunnels, direct covers, windbreaks, mulching films, and protective nets against birds are all examples of such action taken for plant protection. Such measures are also taken for shading not only to provide protection against weather damage but also to control photosynthesis. Polymeric windbreaks and protective nets play important roles in as antifrost measures. The use of films, set around the plants is more effective to create a channel for plant protection against damage by cold weather, excessive insolation, and animals. The purpose of protection is to increase the crop and accelerate maturation, or to extend the cropping season. The main form of protection is achieved through regulating the temperature and moisture levels, and eliminating wind and possible damage from the adverse weather conditions as high temperature, hail, or wind. Such protection can also modify the spectrum of light reaching the plants which modifies their growth. The mechanics of this type of protection primarily involves a covering of film, but netting is used when shading is required to reduce temperature. Windbreaks are a permeable barrier rather than a covering. Additional advantages of greenhouses and tunnels are that they provide shelter for the workforce. The other form of protection is to prevent pests from reaching the plants, which is generally achieved with netting or mesh. While a film covering could protect against birds, preventing other pests is usually more cumbersome as the artificial environment suits the pest as much as it does the crop. The most widely used protection is for vegetables but is also used for fruit, flowers, and nursery stock. Covering protection can be effectively applied in a relatively cold climate where cropping may not even be possible without protection, and can also be applied in a relatively warm climate where improving is more effective and important especially in economic terms.

2.2.1 Creation of Climate

The fate of plants is determined by microclimates occurring within an area to a limited extent. Such environments can be artificially created by means of various types of plastic coverings, such as mulch and greenhouses, in which temperature, humidity, and radiation are controlled. The air temperature inside and outside a covered structure varies during the course of a day and the external temperature depends on the region and the time of the year. Films are used to create microclimates in the form of mulching, low tunnels, various shelters, and greenhouses. They are also used in soil sterilization by fumigation, and also in the handling of fertilizers and their distribution in the soil in association with water. In general, under *transparent film*, the temperature of the soil rises during the day according to the season and type of soil and also according to the level of sunshine and the water content, while under *black film*, the soil temperature is only slightly higher than the control. Under *white film*, the soil temperature is always lower than for uncovered soil; these are used either in regions with a high levels of sunshine, where it is necessary to reduce the transmitted radiation and soil temperature, or in regions of low luminosity, where there is a need to increase the amount of reflected light on the lower and middle leaves. Thermal insulation is characterized by the specific heat and the thermal conductivity in relation to the specific gravity and the thermal diffusivity.

2.2.1.1 Mulching

Mulching is a protective covering on the soil around plants for plant protection with the aim of helping growth and crop earliness, productivity, and partial protection of the produce by suppression of weeds [214, 216–218]. Mulching plays a major role in plant cultivation by creating at the soil surface some protection and microclimate which is favorable in respect to temperature distribution and retention of humidity, surface fermentation, and the supply of carbon dioxide to the plants. Prolonged dry periods have an adverse effect on the growth and development of crops particularly in light textured soils. Therefore, it is essential to minimize the losses due to evapotranspiration in order to ensure adequate water supply to the crop during dry periods. Mulching is particularly important where water needs to be conserved, when it is necessary to heat the soil lightly in order to obtain growth, and also when there are many weeds. Mulches are used for plant protection with the advantage of easy application over hydrogels that are used as binding agents for soils [219–221]. The main objectives and benefits of mulching protection for plant growth and yield include: elimination or reduction of weed growth problems through radiation control, control of insect infestation, better retention of moisture in the soil [195], avoidance of soil compaction [222], avoidance of leaching [223], improvement of microclimate temperatures and humidity [224], increased plant growth by carbon dioxide retention under the film, soil protection from erosion and leaching of nutrients, action as thermal insulation for the roots in cold climates (in winter), protection from frost and the action of torrential rain, saving and retention of irrigation water, saving in labor, increase in root growth; earlier fruiting; reduction in the unfavorable effect of possible soil salinity [203], reduction of evaporation by insulating soil surface against direct solar radiation and by obstructing vapor diffusion, suppression of transpiration losses without reduction in photosynthesis. Effective fumigant mulches require reduced-porosity films which reduce the escape of volatile chemicals, i.e., nematocides, insecticides, herbicides, etc., and therefore allow for lower application rates. The use of polymers for hydro-mulching is particularly beneficial in areas with water deficiency and in sandy soils with rapid drainage. The plastics used for mulching soil surfaces are of various types.

Mulch film types. The advantages of plastic film mulching over traditional mulching are in its light weight, that it covers a much greater area per volume than natural mulches, its being amenable to mechanized installation, and its lower cost. The most widely used plastic film is PE. Several specialized types of PE film include heat-resistant film, heat-retaining film, water-absorbing antistatic film, and photodegradable film. A heat-resistant PE film for warming the soil will enhance absorption in the long wave region of radiation that enables the temperature under the film to be higher than when under normal PE film. In order to facilitate the passage of the plants through the film, it can be perforated at the time of sowing, but slit film is used extensively. Moisture-absorbing antistatic PE film with enhanced permeability to UV radiation is used primarily for seed beds, as it does not become dusty and therefore creates better conditions for growing plants inside hothouses. The film's surface characteristics also prevent the deposition of condensed droplets, increasing the yield of vegetable crops as compared to normal PE film. PE-film tunnels and perforated flat PE film allow better use of natural resources such as solar energy, water, and soil. Shrinkable PE films are used for sheet steaming in horticulture. The quality of the used film for mulching with satisfactory term service can be distinguished by the film color. Mulch films are classified into the following types:

(a) ***Transparent film mulching*** enables rapid heating of the soil as well as conserving moisture and protecting the soil. The use of transparent film increases the soil temperature during the day according to the season, type of soil, the level of sunshine, and the water content, thereby increasing the activity of the volatile fumigants within the enclosed area. Clear PE film which is an effective heat trap is commonly used as mulch and soil fumigation in the production of food crops. However, weeds will grow under clear film and soil temperatures may increase under the film. The film transmits most of the incoming radiation which warms the soil and the moisture droplets that collected on the underside of the film block; much of the radiation is emitted as the soil cools at night. Most of the heat loss from the soil is trapped under the clear film and a greenhouse effect that stimulates and forces plant growth is maintained under the cover. Mulching with LDPE has been described for various plants [198, 200, 204, 213]. Transparent PE is more effective in trapping heat than black or smoke-gray films. Soil temperatures may rise under clear films, as compared to black films.

Heat loss at night, as the soil cools, is lessened by polymer films. Weed control has been reported because of solar heating of the PE mulches.

The use of transparent films does not prevent weed growth and their short life requires the use of high quality PE film containing UV stabilizer for long durability. Special photoprotective systems as UV-light absorbers, quenchers, radical scavengers, and hydrogen peroxide decomposing agents are added to the films to delay the effects of these environmental factors. UV-light absorbers as benzophenone and benzotriazole are frequently used in polymeric films. While the addition of UV absorbents increases the service life of the film, they have the disadvantage that their effectiveness is dependent on the thickness of the film to be protected. Quenchers are photoprotective compounds that can take up and dissipate energy that has been absorbed by chromophores, such as hydrogen peroxide, which are present in PE film. Organic nickel compounds are quenchers that also act as decomposing agents of hydrogen peroxide. Hindered amine light stabilizers as photoreactive compounds are referred to as scavengers, they absorb light and do not act as UV absorbers or quenchers.

(b) ***Black and colored film mulching*** is opaque to incoming radiation and hence it is effective in preventing weed growth. The increase in crop yield by using black PE mulch is based on the elimination of weeds and the avoidance of soil compaction. Thus, the use of black plastic mulch eliminates the need for mechanical cultivation often associated with root damage and stunting or killing of plants. The film used in mulching should retain in position for several years. Opaque films reduce maintenance work. Films and sheets used in mulches are generally opaque LDPE, PVC, PB, and PEVAc. PE films for agricultural applications need to have high strength and elasticity, resistance to wind forces, and a long service life. Since PE mulch cannot be reused and does not degrade between growing seasons, it must be removed from the field and disposed of, or mostly produced from combination of PE with PEVAc. In addition to black and transparent PE films [225], black paper coated with PE [226], aluminized PE, and other opaque films made of EVA and PVC are used. Black films are used extensively for strawberry cultivation, for humidity control, and suppression of weed growth [195, 209].

Colored mulching is effective for a range of vegetables (cucumbers, melons, peppers, corn, cabbages) but a single color mulching is not suited to all crops nor effective against all pests. Red mulch gave best results for tomatoes for growth whilst silver mulch controlled whitefly. Similarly, colored mulch has reduced thrips on leeks. UV light reflected by silver mulch repels insects whilst a plant may be stimulated by the colored light reflected giving the impression of there being competitive plants nearby. Reflective films, whether opaque, white, or metallized, can be used in low light conditions to concentrate sunlight onto the plants to increase photosynthesis. Blue mulch produced best results for peppers [227] due to the reflection of photosynthetically active wavelengths and raised soil temperature, whilst black mulch on inclined beds gave improvement of pineapple yield and sugar content [228]. Yellow-brown films delayed the incidence of tomato yellow leaf curl [229]. The use of black mulch in temperate climates has some advantages for asparagus cultivation [230]. Colored mulch made of rubber from recycled tires avoids the need for otherwise frequent replacement [231, 232].

(c) ***White film mulching*** lowers soil temperature in relation to uncovered soil. This type is used either in regions with high levels of sunshine, where it is required to reduce the transmitted radiation and soil temperature, or in regions of low luminosity, where there is a need to increase the amount of reflected light on the lower and middle leaves.

(d) ***Photo-/biodegradable film mulching*** is significantly used in agricultural mulch as it is completely degraded in a short time when buried in the soil at the end of the crop season. Conventional films can cause problems during harvesting or during cultivating operations and their removal and disposal are costly and inconvenient. Therefore, there is a growing interest in the development of biodegradable or photodegradable films with short service lifetimes. A large number of polymer types have been designed for controlled biodegradation by soil microorganisms and that contain light-sensitizing additives for photodegradation. Coated starch-based films withstand weathering conditions commonly associated with crop production; after a period of time, depending on the amount of coating, they will become brittle and rapidly deteriorate. The amount of coating needed depends upon the crop application. Starch-PVA film is coated to yield a degradable blend film that resists weathering conditions associated with its use as agricultural mulch for controlled periods and then rapidly deteriorates into small particles which mix with the soil; the time at which decomposition occurs depends upon the thickness and amount of coating [233]. Another approach for the preparation of biodegradable film is by inserting biologically labile compounds as starch into normally stable PE chains. The labile starch component is then rapidly consumed by soil microorganisms, leaving the resistant PE in a porous state that is more easily accessible. However, the compatibility between starch and PE is poor due to their difference in hydrophilicity, but starch can be compounded successfully with various proportions of LDPE and PE containing carboxylic groups as PEAA to form starch-PE films. PEAA acted as a compatibilizer between starch and PE. By soaking starch-PEAA mulch films in urea solution, the leached urea would enter the soil and be available as a nitrogen fertilizer. Replacing a part in these formulations with PVA increases tensile strength values while it reduces percent elongation. Three polymeric gels based on starch-PEAA-LDPE [127, 234], starch-PVA [235, 236], and starch-PVC [237] have designed as biodegradable films that possess clarity, elasticity, and water resistance for the use as agricultural mulch [234]. Polylactone and PVA films are readily degraded by soil microorganisms; the addition of iron or calcium accelerated the breakdown of PE. Degradable mulches should break down into small brittle pieces which pass through harvesting machinery without difficulty and do not interfere with subsequent planting.

Photodegradable PE film is used for mulching the soil in vegetable growing. The film breaks down as a result of solar radiation and the degradation products combine with the soil [238]. A particularly interesting photodegradable system consists of a mixture of ferric and nickel dibutyldithiocarbamates, the ratio of which is adjusted to provide protection for specific growing periods. The degradation is tuned so that when the growing season is over the plastic will begin to photodegrade. Another additive system for this application includes a combination of substituted benzophenones and titanium or zirconium chelates. The principal commercial degradable mulch is photodegradable poly-1-butene. PE films suffer from decomposition by environmental influences such as light and atmospheric oxygen, hence the problems encountered with the collection and disposal of the used films have been overcome by the use of photodegradable film [213].

2.2.1.2 Growing Enclosures

Polymeric materials are extensively used in constructing materials for growing enclosures as for: (a) *Greenhouses* – for crops and flowers out of season, starting plants for early transplanting, and controlling the environment for forcing and early maturing of plants. (b) *Row covers* – are small, temporary, field greenhouses, used to protect field plants against damage and to force earlier maturing. (c) *Hotbeds and cold frames* – accelerate the growth of plants to be used for transplanting. Economy of construction was a major factor leading to the use of plastic films as greenhouse glazing.

Among the polymeric materials used as growing enclosures are the cellulosics, rigid and flexible PVC, PE, PET, PMMA, glass-reinforced polyesters, PSAN, and PS. Clear films or sheets transmit solar radiation. PVC, polyesters, and PE effectively block the passage of radiation absorbed by soil, plants, and frames inside the greenhouse during the day to the outside air as the soil and greenhouse contents cool. This provides a small heat reservoir during the cool night hours, i.e., it reradiates radiation as heat energy at night, and therefore reduces heating costs. Condensed moisture on the inside of the film assists in trapping the radiation.

(A) **Greenhouses** are large structures in which it is possible to stand and work. Traditional greenhouses were wooden or metal framed with glass panes. Use of clear, flexible, light-weight plastic covers has made possible the design of new types of greenhouses. The idea of growing food at controlled temperatures all year round and the ability to extend the growing season has led to the wide use of greenhouses in agriculture to create protection to the plants grown. The greenhouse is a structure with a covering and walls, either flat or curved, transparent or translucent, in which it is possible to maintain an atmosphere more or less conditioned as regards temperature, humidity, and radiation energy, so as to encourage crop earliness, improve the yield, safeguard the crop, and make more effective use of water. The control and possibly the variation of the artificial climate thus created are suitable and seasonable as a result of using satisfactory automation and that the manual or mechanical operations are made easier by the topography and the arrangement of the sites. Greenhouses attract heat because the electromagnetic radiation of the sun warms the plants, soil, and other components within a greenhouse. Air is warmed from the hot interior area inside the structure through the roof and wall. Thus, the main objectives of greenhouses are the ability to extend the growing season and sowing, control of growing conditions (temperature, light, and moisture) for plants inside the greenhouse to produce the desired new kinds of plants, protection from birds and animals, facility in controlling pests and diseases, less physically demanding than fields and open crop spaces, and the possibility of reducing gardening costs. The main advantages in using plastic greenhouse covers include lower maintenance costs, less shadowing of the plants by rafters, maintenance of higher humidity which results in faster growth of plants, and ease of replacement, better control of the internal atmosphere, and lower heating costs. However, the disadvantages in the use of plastic greenhouse covers are associated with heating, heat distribution, disease control in a highly humid atmosphere, moisture condensation on the underside of the plastic film, and the tendency of films to crack during extremely cold weather.

The parts of a greenhouse include: framework (wood or aluminum frames), glazing (safety glass, plastic wall or roof), foundation (concrete foundation, wall, slab/tile), and accessories (benches, shading, heating, air circulation, misting system). A detailed design and construction of plastic-film greenhouses involves consideration of the specific imposed forces generated by outside weather conditions of storm, rain, hail, and snow as well as crop and structural loads [239]. The standards for designing plastic-film-covered greenhouses provide rules for structural design, including requirements for mechanical resistance and stability, serviceability and durability, and the scope extends to cover the foundations.

Properties of Plastics for Greenhouses. Inherent limitations of greenhouse films are their modest strength and working lifetimes, although considerable improvements have been made by chosing adaquate combinations of film and frame construction needed to ensure satisfactory performance in a given situation. The desired properties of covering films include the following: (i) *Density*: the framework can be lighter for plastic greenhouses than for glasshouses and the shading zones will be less in plastic greenhouses than in glasshouses. The light weight of plastic greenhouse construction and the resistance to impact make them easy to move for crop rotation while the rounded form helps to make them air-tight. (ii) *Transparency*: the permeability to solar radiation leads to effective heating during the day and is followed by rapid cooling at night, although this effect is compensated by the presence of condensed water on the internal wall or by the use of a double wall of film. The light transmittance of the covering films is high when they are new but there is considerable loss of light transmittance with ageing and if cleaning is not undertaken. (iii) *Heating*: this is more expensive for a glasshouse than for a double-walled plastic greenhouse. (iv) *Air humidity*: plastic greenhouses permanently maintain a higher degree of humidity resulting from evapotranspiration due to their low permeability to water vapor [197]. (v) *Ventilation*: it is necessary to ventilate the greenhouses by low-speed fans early in the morning before the temperature rises. (vi) *Airtightness*: plastic greenhouses, particularly those with flexible film coverings have the advantage of superior airtightness as compared with glasshouses. (vii) *Resistance to hail*: plastic greenhouses are resistant to hail hazards.

Plastic films for greenhouse coverings act as filters, selectively allowing radiation of different wavelengths to pass. Visible light covers the photosynthetically active range of the spectrum which is essential for plant growth. When other requirements of water, temperature, carbon dioxide, and nutrients are satisfied, growth will depend on the amount of light received. In sunny conditions the covering needs to diffuse the light; this reduces shadows and the light is more efficiently used, plus that scorching is prevented. At night, the longer-wavelength IR emitted by plants and soil causes the cooling of the greenhouse. The lower the transmission of radiation through the covering the better is the heat retention, and the greater the “greenhouse effect” [240–242]. Adding fluorescent or phosphorescent molecules to a covering film allows certain wavelengths to be absorbed and re-emitted at more photosynthetically efficient wavelengths and the film becomes photoselective [243]. Both photochromic and thermochromic additives in greenhouse films accelerate growth and increase yield also effecting photodegradation [244, 245]. Water condensing in droplet form on the inside of the greenhouse covering reduces light transmission; drops falling onto the plants can encourage diseases and the drops act as lenses and may cause scorching. Films having antidripping properties have lowered surface tension so that water tends to form a film layer rather than drops and such materials are clearly advantageous. However, a disadvantage of antidripping films can be the attraction of dust in dry weather, but this can be alleviated in multilayer films by having antidripping characteristics on the inside [246].

Greenhouse Types. There are many different types of plastic greenhouses, each type having its own advantages and disadvantages. The classification of greenhouses depends on many factors such as cost, space area, the plant and crop type, the climatic conditions, terms of temperature control (hot, warm, cool), and the structural design [201, 202]. Greenhouses can be classified according to the materials from which their framework structures are made into the following types [209]:

1. **Flexible plastic greenhouse**: Most consideration of greenhouses is directed towards conditions in the temperate climates, but simple, cheap wooden frames with film or net coverings have been developed for warmer climates [239]. They are popular due to their low cost and can absorb sufficient heat. PE films have good mechanical properties and are used almost similarly as the covering material for flexible plastic greenhouse structures because of its lightweight and inexpensive cost; however, it deteriorates during summer

when exposed to the sun. Its breakdown due to UV rays can be avoided by using UV stabilizer. Soft, flexible, transparent PVC films are relatively stable but they attract dust and dirt from the air, and hence they must be washed from time to time. Reinforcing the PVC films with nylon or polyester fibers tends to overcome the deterioration of its mechanical properties. The use of thin, rigid PVC in greenhouses provides a significantly longer service life than flexible PVC or PE. However, improvements in the light stability and fungus resistance of flexible PVC have extended its service life beyond that of stabilized PE film for greenhouse covers. PEVA films are widely used as double-walled structures, while PP films are rejected because of the high rate of dirt pickup which considerably reduces the light transmission. The framework structure can be made of wood or metal which is necessary to hold the film in position in order to prevent it from flapping in the wind from the greenhouse [209]. The films can be attached to wooden framework structures with metal nettings or wire strands to form light-weight constructions that can be used in regions where there is no heating for during early growth or where wood is cheap. Metal frameworks are usually consist of galvanized metal tubes with hoops, ridge pieces, diagonal braces, and foundation tubes for receiving the ends of the hoops. The assembly of the metal framework is quickly carried out. Tensioning wires are also fitted, and the entrances at the two ends are of timber construction. The film is stretched over and secured to the framework, the edges being buried in a shallow trench running alongside the structure. The structure frames clad with PVC must be firmly closed at night to keep the heat in and so that during the flowering period good ventilation can be maintained. The hoops are often made of PVC tubes and are connected with ropes. The hoops are set in steel tubes which are partially buried, the film used being LDPE [247]. The use of double-layer film coverings separated by an air space reduce the heat loss from plastic protective structures and hence reduce the cost of fuel for heating [199]. The distance between the layers should maintain a dead air space for maximum insulation. The double film reduces light transmission but since the structural strength is greater, fewer supporting members are required [248]. Air-supported greenhouses are usually semicylindrical structures, maintained in shape by using air pressure, often provided by fans [249] and have the advantage of not requiring structural supports, they have improved luminosity and can be accessed with mechanical equipment. However, the disadvantage of this structure is its collapse in the event of an electricity failure.

2. **Rigid plastic greenhouses** have the advantage of strength but are an expensive option and much less often used than film. However, they are popular because of safety compared to glasshouses. These constructions are generally based on using sheets of fiber-reinforced polyester, rigid PVC, or PMMA. These materials have been used for greenhouse structures of conventional glasshouse design with a metal framework structure. Because of the high coefficients of thermal expansion, PMMA and rigid

PVC must be fixed to the framework at a minimum number of points [205, 206]. The other option is twin-wall polycarbonate which offers exceptional energy saving where the greenhouse is heated. This is also used for the ends of large commercial greenhouses because of its structural integrity and thermal efficiency [250].

Fiber-reinforced polyesters – Their properties depend on the composition of the resin and the amount and distribution of the fibers. The composite composition determines the penetration of light as well as its mechanical and chemical properties. Thus, the use of tetrachlorophthalic acid increases the refractive index whereas the use of PMMA in place of styrene lowers the diffusion power and increases the transparency and stability of the product. Polyesters are slightly transparent to UV radiation and the penetration is further reduced or eliminated by UV absorbers. Transparency of reinforced polyesters to solar radiation is low and hence gives rise to a reduced temperature build-up. The greenhouse effect results from the opacity of this material to radiation emitted by the soil.

Rigid PVC – Its light transmission varies appreciably according to the used stabilizers and lubricants in their compositions. The opacity of transparent PVC sheet increases with exposure to outdoor weathering and the development of a yellow to dark brown color reduce light transmission to such an extent that replacement ultimately becomes necessary. Degradation is accelerated at those points where the sheet is in close contact with the supporting structure and consequently local hot spots are created. Rigid PVC must be fixed to the framework at a minimum number of points.

PMMA – This is a rigid transparent plastic material and has a high transmission to radiation and does undergo some yellowing on prolonged outdoor exposure but this can be reduced by the incorporation of UV absorbers. PMMA must be fixed to the framework at a minimum number of points due to the high coefficient of thermal expansion of the metal framework. The superior light transmission of PMMA does not exert a great effect upon the crop growth [205].

3. **Glasshouses** are the most traditional coverings used and may be constructed with slanted sides and straight sides. Aluminum–glass buildings provide low maintenance, are aesthetic and weather-tight structure. The ease breaking and the high costs are the main disadvantages of this type.

(B) **Direct covers.** These are frameless low tunnels and are virtually unsupported row covers. Interestingly, if perforated films and nonwoven fleece are used plants can strongly grow under such direct covers even if they are holding up the protecting cover themselves. The film or fleece is generally several meters wide and is laid very loosely with the edges held down with earth. The covering films will then float in the wind and expand as plants grow (floating cover). Growth under direct covers is often very fast, and at low cost. The covering is generally perforated PE because it needs to be lightweight and allow the passage of water for irrigation and air for ventilation. These covers provide the same function as low tunnels in that they act to conserve heat, prevent excessive transpiration, protect from wind and heavy rain, and exclude pests, but the level of protection is different because of the intrinsic ventilation and the absence of a frame. If the cover is made of a very fine mesh it will be particularly effective for excluding pests such as carrot fly but allow good ventilation and passage of water. The effectiveness of nonwoven covers alone and in combination with black/white and brown PE mulch on growth of squashes has been investigated [251, 252]. The effects of different combinations of spun-bonded fabric covers, perforated and unperforated PE microtunnels and black PE mulch on growth and yield of muskmelons, insect populations, and soil temperatures have been evaluated [253].

(C) **Tunnels.** Low tunnels provide an inexpensive means of protection and are useful as covers for low-growing crops. The most widely used tunnels consist of double hoops with the film held between them so that it can be slid upwards to allow ventilation. The labor required for adjustment of the ventilation is the only disadvantage of this tunnel type. Tunnels with single hoops are set up by stretching the film out over the hoop and then burying the two edges. Ventilation is introduced simply by making holes in the sides, depending on the climatic conditions. Another method involves two films used over metal hoops that are fixed at the top by clips to a steel wire which is stretched along the length of the hoops. The plants can grow upwards between the two films by opening the clips. This type of low tunnel can be easily ventilated and maximum ventilation obtained by removing one of the films. Film coverings without the need for support can be used for semiforcing by employing perforated and permeable films. These give protection to early crops grown in the open in spring [195]. This type of covering has similar advantages to the low tunnels, i.e., earlier crops, better quality produce, staging of production, and protection against birds. The cultivation of different varieties of vegetables and crops in plastic tunnels has the main advantage that crops can be produced earlier than in the open, with improved yields, by protecting them against frost and wind [254].

Low tunnels or row covers could be thought of as an improved development from the glass cloche or structure frame traditionally used in market gardening, being much more efficient though. In fact, PE films has made row covering highly economic on a large scale. Small tunnels are much less expensive than greenhouses, but more expensive than direct covers, and essentially do the same job. They are highly effective in the right circumstances, e.g., for short-term cover of low-growing crops. Construction size varies, but essentially a simple frame of hoops, stakes, and wires supports a film covering to give a typical cross-section of 50 cm high and about 100 cm wide. The edges of the film may be buried in soil or pinned down. The restricted volume and access means that care has to be taken with ventilation to avoid overheating and high humidity by opening the tunnel when necessary. Consideration also has to be given to providing the plants with sufficient water. Obviously, the small size restricts the material that can be grown and very often the tunnel does not remain in place for the whole growing period of taller species. The film covering is usually PE, essentially the same as used for larger tunnels. Similar tunnels on a smaller scale are also cloches and frames with rigid or semirigid plastic construction. Cold frames are also quite popular and can still be seen in nurseries. Plastics used include PVC and twin-wall polycarbonate.

Large tunnels are simply a particular form of construction in which a high level of control of temperature, moisture, ventilation, shading, can be achieved and suitable for tall-growing plants. Their structures can be made with simple tubular metal framing and a flexible film covering and this has been the most popular commercial approach. However, a great variety of constructions have been developed including inflated double-skin roofing, multispan houses, and the use of rigid or semirigid plastic end covering. The different requirements in different climates and for different crops include construction details such as the need to insulate the film covering from metal supports to avoid its local overheating, the need to avoid anything that hinders the runoff of water droplets and the ratio of ventilation area to floor area.

Tunnel structures of LDPE, PVC, and EVA films can be used for semiforcing so as to grow without heating but with an increase in yield. LDPE and transparent plasticized PVC have comparable qualities regarding flexibility, lightness, and radiation permeability to short-wave light which penetrates into the interior of structures and heats up the soil and the plants. During the night, PE is equally permeable to the long-wave radiation emitted by the soil, thereby giving rise to a high thermal loss. PVC is impermeable to long-wave radiation, so that heat losses during the night are less and the temperature is therefore higher under PVC than under PE. However, with PE a temperature inversion becomes possible in the cooled region, i.e., lower inside a structure than outside. Thus, crops grown under PVC are earlier than those grown under PE. PEVAc film has improved permeability characteristics regarding radiation so that it competes with PVC in the production of early crops grown.

2.2.1.3 Nets for Plant and Crop Protection

An increase in the damage to plants and crops caused either by adverse weather or by birds has increased efforts for improved protection. Birds can be considered a pest in agricultural terms and the damage caused them can be excessive. In addition to potentially spreading transmittable diseases, birds can also damage and cause unsightly problems to fruit and vegetables. Protection of vegetables and fruit trees from bird damage is desirable especially before or upon ripening of fruits. There are various different ways that can be used to protect and control fruit tree from birds and the damage they can cause: (1) Chemical repellants are useful in fruit tree pest control, often helping to protect fruit trees from birds and while keeping other pests away. Pest control by the chemical repellants, e.g., by methyl anthranilate, must be repeated if the bird damage is continuing and after a heavy rain. (2) Electronic bird protection devices will keep the birds away from fruit trees by emitting a sound that frightens them. (3) Nets made from filaments of various polymers such as HDPE, PP, and nylon are stretched over the trees to give the desired bird protection. Nets play essentially two roles in: (a) plant protection and (b) crop protection. The nets have effects on: fruit size and yields, fruit maturity and color, quality parameters, fruit sunburn and cracking [255–263].

(A) **Plant protection nettings** are used as anti-bird and anti-butterfly nettings to stop pests on the wing and to protect plants against weather damage. In winter, the increase in the damage to plants caused by frost and winds presents a problem for loss of crop production that results in an increase in total crop costs, hence *antihail nettings* are used to protect plants against frost damage [264] and *shade and windbreak nettings* are very useful to provide wind resistance and shade. The increase in damage to crops caused by adverse weather has led to the use of *climatic protection nettings* as efficient tools for crop protection to prevent the loss of crop production that results in an increase in total crop costs. The effect of plant protection nettings on an orchard's climatic conditions (temperature, light, and humidity) [262, 265–271] can be explained by: (1) reduction in direct incident light and radiation by interception [255, 266, 272–275], reduction in maximum orchard temperatures [255, 266], increased minimum orchard temperatures, and increased humidity [276]. This indicates shading by the nets which lowers the temperature and the intense solar radiation as the main causes of sunburn and increases skin quality [265, 266]. (2) Air circulation interception that increases humidity and leads to decrease in plant water stress thus reduces irrigation needs due to decrease of evaporation. The shading resulting from the use of nets leads to: reduced number of fruits affected by sunburn incidence, decreased temperatures that decrease fruit cracking and favor appealing fruit color, decreased exposure to light leads to lower fruit sugar content [255, 263], and decreased photosynthesis caused by the interception of radiation results in reduced fruit size [266]. Increased shading leads to reduction of the radiation reaching trees, decreased soluble solid content of fruits, delayed fruit ripening, reduced fruit color due to the decreased direct sunlight on the fruits, and reduction of the evapotranspiration level. A reduction in plant water stress is favored by a reduction in maximum temperatures, increase in orchard humidity, and an increase in photosynthesis.

(B) **Crop protection nettings** are used as crop gathering and fruit cage nettings to protect fruit and vegetables from both aerial raids and ground attacks from larger animals. Crop protection netting is also used as side netting on all manufactured fruit cages and is an ideal deterrent to birds, rabbits, and other similar pests, but has a large enough mesh size to allow invaluable pollinating insects to pass through. Heavy-duty protection netting of a high strength and durability consists of a high-quality square mesh knotted net, and a thicker gauge for superdurability. It can be used as a crop protection net on any fruit or vegetable cage, and used as any general-purpose garden netting. Fruit tree netting is lightweight, cost effective, and offers protection for fruit trees and gardens from birds and other predators. There are many different types of crop protection nettings: (1) *Crop-gathering nettings* can be used for the rapid gathering of crops allowing the trees to be shaken without any great damage. Nets supports for fungicide or insecticide form a protective trellis which prevents mildew from the net growth stage of vines right up to leaf-fall [277]. (2) *Fruit cage nettings* will protect fruit and vegetables from both aerial raids and ground attacks from larger animals. High-strength and long-lasting knitted fruit cage nettings are used in the construction of fruit cage frames. (3) *Anti-bird nettings* are used for fruit trees to prevent the birds from reaching the fruits by trapping the birds. Wire can help to keep the bird control netting away from the fruits to prevent damage while providing adequate pest control. Anti-bird nettings can provide complete exclusion of birds over a long period of time and are of different mesh sizes and choosing the correct mesh size is important in order to prevent either large or small birds from getting inside the netted off area and becoming stuck or trapped. There are several types of netting available to exclude pest birds such as knotted PE netting manufactured using UV-treated flame resistant material that is long-life and heavy duty. Bird PP netting is strong, lightweight, and easy to install and used to protect crops and orchards from pest birds. This type of netting is ideal for use in homes, gardens, warehouses, airplane hangars, canopies, overhangs, and other large areas where pest birds are to be excluded. Bird control netting is used to: protect valuable crops from all kinds of pest attacks, repel the smallest of birds without trapping them in the net, and to repel small and large birds, animals, deer, rabbits, foxes, insects (including butterflies) and partially shield off wind.

2.2.2 Windbreaks

In exposed areas barriers against wind can have a significant effect on cropping. An artificial barrier against wind has obvious advantages over natural materials of consistent permeability. Windbreaks are used as barriers against wind for lowering the wind speed which reduces mechanical effects. Thus, they are effective as modifiers of the microclimate and have beneficial effects on the growth of plants. Windbreaks of plant rows of trees serving as shelterbelts have been effective in reducing wind erosion. Plastic snow fences have also served as windbreaks. Growing crops and postharvest residues can reduce wind erosion. Closely spaced crops are more effective than row crops. The establishment and subsequent growth of vegetation is crucial to stabilize dune areas. Sand dunes have also been stabilized with surface treatments, such as spray-on adhesives and soil stabilizers. Plastic windbreaks of PE or PP, essentially as meshes or grids supported vertically and fixed firmly between supports, are used in place of hedges, lines of trees, and bamboos [196]. The use of other forms of plastics for this purpose has been reported [213]. Adequate strength and stabilization against UV light of plastic windbreaks is essential. The inconvenience of these windbreaks is their cost of manufacture, maintenance, and the area lost for cultivation that provides a habitat for certain pests.

2.2.2.1 Benefits of Windbreaks

Windbreaks reduce the temperature of an irrigated crop and the vertical and horizontal transfer of heat, reduce the transfer of water from the plant to the air that leads to a reduction in the potential evapotranspiration, reduce the speed of the wind which is accompanied by a reduction in the amount of mechanical damage, lower the temperature during the night and reduce the air temperature of the irrigated crops that creates better conditions for plants growth, reduce the exchange of carbon dioxide and water vapor between the vegetation and the atmosphere that lowers the evapotranspiration, and hence increase the growth of plants and crop yields [215].

2.2.2.2 Mechanism of the Functioning of Windbreaks

When air meets an impermeable barrier it is directed upwards, and the width of the layer, as represented by the height of the windbreak, is reduced. Therefore, there is an increase in air speed and this reduces the pressure. Thus, air is drawn into the stream from downwind of the windbreak so that the air stream quickly regains its original dimensions and the static pressure increases. The air which is drawn into the stream thereby creates a turbulent zone immediately behind the windbreak. The flow of the air returns to ground level fairly quickly, so the area of the protected zone is relatively small. With a permeable windbreak the volume of air which is deflected over the top is less; consequently, the increase in speed is less and the pressure effects which lead to the formation of a turbulent zone are reduced. The deflected zone returns more slowly to its original course and hence the protected zone is longer. Thus, the wind speed can be less reduced as the porosity of the windbreak increases.

2.2.2.3 Factors Affecting Windbreak Protection

Various factors influence the efficiency of windbreaks, i.e., the efficiency of soil protection provided by a windbreak depends on: the permeability of the windbreak over the entire height of the films or sheets i.e., the effect of air flow through a permeable windbreak, the roughness of the smoother ground in front of the windbreak, successive windbreaks located behind another over a shorter distance, the climate of the used windbreaks region, the extent of the wind speed.

2.2.2.4 Soil Erosion

Loss of soil structure is often associated with a reduction in organic matter, which can reduce the resistance of soil to erosion. Thus, soil erosions due to the low capacity of topsoil to retain water are mainly due to the low content of organic matter in the topsoil. The organic matter in soil has a particle-aggregating effect, which converts dust into heavy clumps [278–283]. Soil erosion is one of the most serious natural environmental problems, especially where arable land resources are limited and light and poor soils are present. Soil erosion involves physical detachment and removal of soil materials from one place to another and represents a primary source of sediment that pollutes streams and fills reservoirs. The two major types of erosion are geological erosion and accelerated erosion. (a) *Geological erosion* involves long-term soil-eroding and soil-forming processes and generally maintains the soil in a favorable balance having caused the many topographical features on Earth. Such soils are usually suitable for the growth of plants. (b) *Accelerated erosion* results from human or animal activities from tillage and removal of natural vegetation that leads to a breakdown of soil aggregates and accelerates removal of organic and mineral particles.

The major factors affecting soil erosion include: (1) Climate conditions: humidity, temperature, wind, solar radiation, precipitation. (2) Soil characteristics: soil structure, texture, organic matter, water content, clay mineralogy, density, as well as soil chemical, biological, and physical properties which affect the infiltration capacity and the extent to which particles can be detached and transported. Soil detachment increases as the size of the soil particles or aggregates increase, and soil transport rate increases with a decrease in the particle or aggregate size. Clay particles are more difficult to detach than sand, but clay is more easily transported. Tillage is intended to provide an adequate soil for preparing a seedbed and water environment for cultivated plants and reducing weed competition. Excessive tillage can damage soil structure, leading to surface sealing and increased runoff and erosion. (3) Vegetation results in reducing erosion by the effects of: (a) interception of rainfall by absorbing the energy of the raindrops and thus reducing surface sealing and runoff, (b) decreasing surface velocity, (c) physical restraint of soil movement, (d) improvement of aggregation and porosity of the soil by roots and plant residue which protect the surface from raindrop impact and improve the soil structure, (e) increased biological activity in the soil, (f) transpiration, which decreases the amount of soil water, resulting in increased water storage capacity and less runoff. (4) Topography is the degree, shape, and length of slope, size, and shape of the watershed. However, the most common factors for soil erosion of the accelerated erosion type are water and wind.

(A) **Water erosion** is soil detachment and transport of the detached sediment resulting from the impact of raindrops or water flow directly on the particles of the soil surfaces. Raindrops break down and detach soil particles and the detached sediment can reduce the infiltration rate by sealing the soil pores, which increases runoff and sediment transported from the field. The impact of raindrops increases turbulence of streams, providing a greater sediment-carrying capacity. The soil losses by water erosion (eroded soil) reduce the productivity of irrigated soils, the crops yield, and the quality of the produce due to a decrease in the amount of water available to the plant, which can be overcome by higher fertilization. Sediments from erosion are the most serious pollutants of surface water and can deposit in streams and lakes and alter stream channel characteristics and adversely affect aquatic plant and terrestrial life. The erosion effects of water can be minimized by mechanical control, varying the employed irrigation technology, reducing the water flow rates, by waterway vegetation or lining by concrete, stone, or plastics. These factors decrease the ability of a water flow to detach and move soil particles along surfaces, and increase the resistance of the soil surfaces to the force of the water flow.

(B) **Wind erosion** causes soil movement by wind turbulences that damage land and crop plants. The eroded dust in the atmosphere is harmful to human health, specifically affecting the human respiratory tract. The quantity of soil moved is influenced by the particle size, density, gradation, wind speed, direction and distance across the eroding area. Surface encrusting caused by wetting and drying will reduce wind erosion for most soils as does an increase in the amount of plant residues. Tillage reduces soil water and wind erosion thus decreasing soil erodibility and increasing surface roughness. Water conservation in agricultural use is favorable for soils as it increases surface roughness and reduces runoff.

2.2.3 Polymers in Crop Preservation and Storage

A wide range of polymeric materials are used in packaging of agricultural products (fruits and vegetables) such as plastic crates and boxes that are produced from various polymeric materials for food and agricultural produce handling [26]. A wide range of trays, crates, and product boxes, molded from polymeric materials such as PP and HDPE are available. Thin PP sheets with folding qualities are being used as a replacement for carton board in packaging. Strong, ventilated crates may be produced economically for harvesting, handling, and transporting agricultural products of fruits and vegetables. Boxes produced from PP material are suitable for cut flowers since they provide good protection for the blooms. Boxes are also produced from structural foam material as HDPE reinforced with glass fiber. A system has been developed for producing and circulating collapsible and reusable plastic crates such as PP to replace traditional cardboard and wooden crates for transporting fruit and vegetable products. Despite their light weight, these containers that are compatible with standard container specifications are capable of holding a high load of produce and can be easily stacked. Films are extensively used for the packaging (preservation and storage) of vegetable and fruit products for direct sale to the consumers. The most common form of produce wrapping is that of stretch wrapping using highly plasticized PVC. The film is wrapped around the produce contained in a tray (formed from expanded PS sheet) by stretching over the pack and sealing on the underside. Films used for shrink wrapping are usually plasticized PVC, PE, or PP for packaging of vegetables and fruit. The technique requires that the film is applied directly to the produce, and then passed through a heated tunnel when the film shrinks and holds the produce firmly in position. The degree of shrinkage depends on the amount of orientation introduced into the PE film at the manufacturing stage. Storage of fruit may be greatly improved by using wrappings and sacks with diffusion windows. These wrappings make use of the selective gas permeability of PE films and special silicone elastomer membranes so that the fruit is kept in a controlled atmosphere with optimum concentrations of oxygen and carbon dioxide. Plastic wraps have been used to protect tree trunks against damage by freezing, sun, and animals [211].

2.2.3.1 Polymers in Protection Against Pests

Various types of covers can be employed against birds, but for shielding off small flying pests one needs to use fine mesh as direct covers for exclusion to be effective. Insects can readily infest greenhouses and low tunnels. In fact one of the problems of using plastics for protection is that the conditions suiting the plants also suit the pests. Red spider and whitefly, for instance, are usually more of a problem under cover than in the open, because the closed environment of a greenhouse supports their development. The use of mulches in repelling insects can be highly effective. While netting is widely used to protect fruit, particularly soft fruit, from birds, polyolefin nettings with suitably small mesh size are being used attached to a frame forming a cage and covering the plants for protection against flying insects. Netting is also used on a small scale to protect fish in ponds from herons. Spun-bonded fleece used as wind and frost protection can also be effective in keeping insects out. PEVAc can prevent insect attack by interfering with insect behavior [284]. Effective tree guards can be made from recycled PVC and used in tree plantations [285].

Protective sleeves. Thin-gauge pigmented blue PE film sleeves have been introduced as a loose covering for protecting banana bunches during the growing season. PE is preferred to flexible PVC because of its lower price; the covers are used for only one season. An unusual application of PE sheet is to apply it as a sleeve around trees to prevent mealy bugs from climbing up [286].

2.2.3.2 Polymers in Shading

Shading can be achieved either with pigmented films or PE mesh screens on either the interior or the exterior of greenhouses. Black PE film mounted in the form of an easily movable tunnel is used to control the day length in cultivation out of season. Several techniques mainly using film have been used as shading to protect a cultivated area from excessive sunshine. A low-cost and easily erected shaded area can be made by tying pieces of black PE sheeting to strings or wires stretched above the crop. Shading is mostly important in exceedingly hot countries to prevent plants from becoming overheated. The use of porous mesh in tropical conditions can allow the cultivation of a broader range of vegetables. It has also been used to help establish newly planted areas in parks in tropical areas. Nurseries without natural shade can protect their stock with shade netting. Such artificial shading material has all the advantages over natural shading, and it can be employed temporarily by season. Even in temperate climates protection is needed for shade-loving plants such as ferns and rhododendrons in nurseries. Greenhouses are often shaded with “paint,” the use of netting, or various blinds. Applying different degrees of coverage by netting and choosing appropriate colors it is possible to cater for different conditions and even different plants. PE shading netting and fabrics give coverage with a large variety of colors and are treated to prevent rotting and to repel insects [287].

2.2.3.3 Polymers in Harvesting and Crop Storage

Polymers are employed in crop harvesting in the form of containers: nets, bags, and crates. Their advantage over traditional materials is light weight and ease of cleaning and disinfecting. Plastic crates can be molded to particular forms to suit the crop and are reusable. The containers used at harvest are in many cases suitable for transporting the crop to store or market without damage. Film can be used in several ways for the storage of grain to line existing pits or silos, cover sacks stacked on a dry base or to directly produce storage containers, depending on the low permeability to air and moisture and low cost. The use of film as a covering for sacks in the open is expedient in times of exceptional harvest. Recently, there has been a large increase in the use of PE bags for grain storage [288]. The bags are essentially tubes in which the grain and can be stored outside and alleviating the problem of limited on-farm storage at low cost. The trend for plastics to replace metals applies to conventional grain silos and here consideration has to be given to the electrical insulating nature of most polymers and the danger of dust explosions. Ensilage is an anaerobic fermentation process of storing and fermenting green fodder in a silo that requires air-tight containmentfor fodder preservation (silage). The object is to produce a material when a crop is plentiful that can be stored for feeding in the winter when food is scarce. Ensilaging has been carried out in steel or concrete structures, a difficult and expensive process. The other method of preserving fodder is by making hay which is seriously reliant on the weather or by introducing plastic film containment for silage to replace hay making. Haylage is made by essentially the same process as for silage but the grass has been allowed to dry before being baled and is wrapped in the same manner as silage. Initially, large bags were used while stretch wrapping now serves for large bales [289]. PE film is most commonly used but it has relatively low air permeability; thus, coextruded materials are being used which improve the permeability. The color is usually black but sometimes white or a black/white bi-extrusion is used, particularly in sunny climates. A white film outwards reflects light and helps avoid extreme heating of the fodder.

2.2.3.4 Polymers in Containers and Packaging

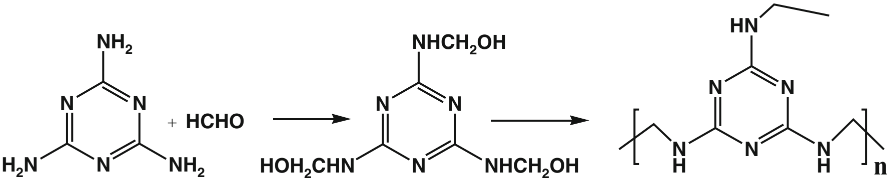
A wide range of shapes of plastics are allowing an enormous freedom in design and performance of agricultural containers and packaging. This applies to containers for plants and seeds, troughs, pans, and buckets, packaging for fertilizers and plant protection chemicals, packaging of foodstuffs, tanks, and pits. PP plant pots in a large range of sizes are lighter than clay pots with considerably more efficient drainage. Their low cost and convenience are ideal for containerized plants that can be marketed and transported at any time of the year. Plastic pots serve for carrying and shuttling market tray systems for transport and display, having relatively high rigidity but low material usage. There are also specialized containers for the relatively new market of plug and young plants. Simple seed trays have been augmented/replaced with multicell plug trays and tray insert systems that cater to all possible plant raising needs. Plant containers are made in a variety of designs and sizes and have enabled container gardening under conditions of limited space availabilty at relatively low cost. Specialist containers have been developed for strawberry towers, hanging baskets, pond planting baskets, and potato growing. A variety of simple plastic buckets are used as troughs, pans, and drink-and-feed dispensers in animal husbandry. In domestic use, polyolefin compost bins, water butts, and watering cans are extensively used. Large carrying bags of PP or PE are used for horticultural rubbish and to package fertilizers, composts, soil improvers, lawn sand, providing efficient handling with good protection at low cost. Additionally, compost-filled grow-bags used for vegetables offer a pest- and disease-free starting environment. In agriculture, most everything nowadays comes in packaged form, including shrink-wrapped film that encases the pallets of bags of potting or seed compost and the foam to protect farm machinery parts during transit. Produce shipped by the agriculture industry after processing will in most cases be packaged when route to the retail market. Food packagings are highly sophisticated now; multilayer films with selective gas and moisture permeability suit the requirements for preserving any particular product. Milk, vegetable oils, and fruit juices sold in markets no longer come in glass bottles but usually in plastic bottles. Perhaps upsetting to the purist, plastic corks are now being used for sealing wine bottles and it has been demonstrated that screw tops with plastic insets are be even more efficient. As an indication of the care taken with packaging, PE has been proven to be the best option for maintaining the taste and quality of produce [290]. Animal waste can be channeled from buildings and contained in GRP tanks or polymer-lined pits/ponds constructed as reservoirs. Tanks made of plastic or glass fiber-reinforced polymers and lined with PVC can be used in fish farms [291].

2.3 Polymers as Building Construction Materials

In addition to the utilizations of polymeric materials in plantations and crop and plant protection, they are also successfully used in agricultural building constructions [234]. They are utilized as engineering structural components for farm buildings and agricultural machinery and other engineering tools and operations. The successful applications of polymeric materials as structural components in buildings include: (a) farm building constructions such as wire and cable covering, as moisture and vapor barriers, thermal insulation, pipe work and fittings, adhesives, sealants, siding materials, roof lighting, tub and shower enclosures, as paints for protection of traditional substrates, polymer cements, concrete reinforced by polymers, suspended roofs, (b) semipermanent structures such as animal shelters, silage containers, equipment shelters, (c) plastic tubing for use in the dairy industry, collecting the sap of maple trees, heating and ventilating livestock barns, (d) liners for water impoundments and canals, (f) plastic pipe for water transport and control in above- and below-ground use in irrigation and drainage.

2.3.1 Polymers in Farm Buildings

Polymeric materials are widely applied in building and construction operations. This transformation from traditional materials due to economic and demographic changes has created increased opportunities for polymers products [292–296]. The use of polymers for protective structures in animal and farm buildings is often in association with other materials such as concrete, steel, wood, and aluminum. Polymers often replace glass, brick, ceramics, iron, steel, and wood. The high potential of polymeric materials for use in construction is the rapidly growing market for various building parts replacing traditional building materials, as by resident consumer request. Polymers are used in a wide range of farm building construction applications, such as extruded gutters, siding, imitation wood beams, room dividers, window and door frames. Polymeric materials used as structural components in agricultural settings must have the property to withstand external mechanical load influences, i.e., possess good mechanical strength and stiffness. This behavior is primarily determined by the microscopic structure at the molecular level, i.e., by the macroscopic response to physical, chemical, and mechanical properties. All classes of polymeric materials such as plastics, elastomers, coatings, fibers, and water-soluble polymers have been utilized in this area of agricultural applications. In the construction of farm buildings, metal roof sheeting shows signs of deterioration after short periods due to condensation of water vapor produced by animals. Hence PE sheeting can be used to provide relatively cheap farm buildings, particularly animal shelters. HDPE and PVC have been used in rigid piping and tubing, in sanitary sewer lines, storm water lines, and potable water mains. Unsaturated PEs, PS, and PVC are other significant plastics predominantly used as construction materials. PVC is also used for siding, accessories, windows and doors. The thermosets of urea-, melamine-, and phenol-formaldehyde resins (Scheme 2.1) are used for resin-bonded woods such as plywood, particle board, and oriented strand board in buildings. Agricultural buildings can incorporate plastics in a number of ways which include PE damp-proof materials, PVC cladding, rainwater goods, and PU foam insulation. Plastic wall linings are easily cleaned and nonabsorbent and hence hygienic for wall linings in milking parlors. PVC has been found to be a practical and cheap option for flooring because of corrosion resistance and strength, not causing damage to stock, and ease of cleaning and disinfecting [291]. Foam mats from



Scheme 2.1 Formation of melamine-formaldehyde resins

recycled polyolefin have been shown to nicely serve as creature comforts to milk cows when used to cover floors [297]. PVC has been shown to resist kicking of horses when used as separating walls in stables.

Glass fiber made from spinning of molten glass, as reinforcing material impregnated with polymer as epoxy resin are used in the preparation of glass fiber-reinforced polymer composites, which improve the mechanical properties of the resulting reinforced polymer. Glass fiber-reinforced polyester sheets have a long service life and are unaffected by acids and alkali solutions and used as cladding materials in pressure tanks to provide the highest strength composition. Glass fiber-reinforced epoxy resins are used to produce structural panels. PU and PS foams are used in laminated panels between two layers of a surface material such as plywood. Glass reinforced-plastic bars are used in place of steel bars in reinforced concrete.

There is an important interrelationship between material selection, processing (convenience, design), and performance (shape, appearance, durability, quality, and cost). The acceptance of polymeric materials application in the construction of agricultural buildings over traditional materials is due to the following advantages: (a) *Processing*: the opportunity of optimizing the design of products; convenience of fabrication: (one-step process). (b) *Performance*: according to macromolecular properties and characteristics; convenient and inexpensive due to light weight, ease of use and handling; pigmentation and appealing appearance; elimination of repeated painting; durability and stability due to resistance to degradation and low maintenance requirements. In summary, the successful application of polymeric materials as components in farm building includes: ceiling and roofing, flooring, windows and siding, pipe work and fittings, thermal insulation (wire/cable covering, thermal barriers), polymer-impregnated concrete, polymer-cement-concrete, polymer concrete, reinforcing steel in concrete, building soil stabilization.

2.3.1.1 Ceiling and Roofing

Ceiling panels are fabricated from moisture-resistant polymers that can be used as a protective film over conventional ceiling tiles. Polymers have a distinct advantage over competitive materials because of their low density, moderate cost, ease of pigmentation, and low energy requirement in fabrication into final products. Polymer films are widely used for waterproofing purposes in building insulation as damp-proof membranes and vapor barriers. The basic parts of a roof are the deck, the thermal insulation barrier, and the impervious roofing membrane that seals the roof complex structure. The built-up roofing membrane is made of (a) bitumen or asphalt, (b) the roofing felts for reinforcement, and (c) the aggregates for protection of bitumen against UV light and oxidation. The molten asphalt used for waterproofing is a mixture of mineral fillers and bitumen. The physical and mechanical properties of bitumen can be improved by chemical treatment and blending with rubbers or polymers. There are various polymer-bitumen mixtures, such as PE-bitumen, poly(styrene butadiene)-bitumen. Waterproof roofing membranes based on elastomer-bitumen mixtures especially preferred in cold climate and other materials such as PEPD, chlorosulfonated PE, and plasticized PVC are commercially used in roofing systems, depending on their ease of installation and handling, their durability, and resistance to weathering, chemicals, and ozone.

2.3.1.2 Flooring

A number of polymers are used as flooring materials, such as PVC tiles, PVCVAc, vinyl–asbestos tiles, PVC welded sheet, fiber-epoxy polymers, PP, and PU. All are inexpensive materials for use in flooring applications. Polymeric materials applied as domestic floor surfacing materials, where appearance and glazing are necessary, provide other advantages as being easily installed, durable, lightweight, flexible, slip and dent resistant, scratch and scuff resistant, stain and dirt resistant, fungus resistant, heel-mark resistant, exerting superior chemical resistance, and having decorative effects for seamless floors. However, for industrial floors where appearance is not critical, sanding and glazing are not necessary. Laminated PVC products made of several sheets of varying thickness are widely used as flooring materials, offering a wide range of colors and patterns, ease of cleaning, good cushioning, insulation, and reasonable price. PP flooring provides heavy-duty, easily cleaned work platforms, increasing operator comfort and safety, and resistance to corrosion and bacteriological attack. Epoxy flooring is used only for industrial flooring purposes due to its low level of sound insulation and lack of pleasing appearance. Epoxy flooring systems can be used as floor coverings over a subfloor of concrete, wood, or steel, and can also be used for remedial work and applied over existing floors. PU flooring can also produce durable, attractive seamless floors and imaginative effects by embedding a variety of different colored fillers into the PU resin.

2.3.1.3 Windows and Siding

Window frames are usually made of PVC formulations with PEVAc, chlorinated PE, or acrylic exhibiting the particular requirements of impact strength and weathering resistance needed under conditions of different climates. Bonding of acrylic to PVC allows window production with a wide range of colors and designs. Both production and precision in window extrusion have been improved with the development of new screw designs, better dies, and microprocessor control of production parameters. PVC is used widely as siding for houses, competing with wood and aluminum. It can be extruded as siding in long, uniform panels as required, and either applied directly over sheathing in new construction or over deteriorated wood siding. Resilience of PVC siding minimizes damage by impact and stability to biodegradation especially in humid areas, which is another advantage of PVC siding. The insulating value, the relatively low cost, and the simple installation are all in favor of polymers over competitive materials in this application. The technology for producing self-frosting glass windows depends on a liquid crystal polymer film that is produced by dispersing liquid crystal droplets in a polymer matrix sandwiched between two conductive-coated polyester films. The film allows for windows that can be either frosted or cleared on demand. To clear the window, one flicks a switch, which causes the crystals to “line up.” To frost the window, the charge is broken, thus returning the crystals to their random, unaligned state. An optical film has been designed to be used in windows to create a reflecting screen capable of returning the image like a conventional mirror, while preserving the transparency and visual properties of glass. It consists of a single-layer film with a polyester base of high optical quality, i.e., treated for UV rays, on which aluminum oxide particles of controlled density are deposited using a complex vaporization process and a second polyester crystal layer to protect the metal coating. The film is coated with a UV-resistant and pressure-sensitive acrylic adhesive that can be reactivated in water. Once applied to the window, the film becomes an integral membrane, forming an authentic laminate.

2.3.1.4 Pipes

The main factors contributing to acceptance of use of plastic pipes in buildings include their low cost relative to conventional materials, excellent corrosion resistance, and ease of installation. Plastic pipes are fabricated from PVC, PE (principally HDPE), PP, chlorinated PVC, polybutylene, ABS terpolymer, and other polymeric composite materials such as fiber-reinforced epoxy and polyester. Perforated drainage pipes are not as fragile as ceramics, and long pipes can be extruded easily. Cutting into desired lengths is easy and joining is relatively simple. However, in those applications in which the pipe must withstand high pressure, metal pipe is still superior.

2.3.1.5 Insulation

Major uses of insulation in the construction industry are in roofing, residential sheathing, and walls. In these applications, polymeric foams offer advantages over traditional insulation such as glass fiber, and these include higher insulating value per inch of thickness and lower costs. The use of polymeric foam for insulation increased markedly due to increased awareness of the need for energy conservation. Foams are available as rigid sheets or slabs which are used in the majority of roofing systems, as beads and granules which are used in cavity wall insulation, and also as spray and pour-in applications. PU foams, particularly polyisocyanurate products and expanded PS are used on commercial scale. PS foam holds much of the sheathing market. In masonry and brick walls, PS foams are mainly used because of their better moisture resistance. In cavity walls, loose-fill PS is used, while exterior wall applications use low-cost expanded PS. PU–polyisocyanurate products are the leading products in plastic foam, as sheets and slabs and have higher insulation value and good flammability ratings. A shift toward single-ply roofing as compared to built-up roof systems has an important influence on the type of foam being utilized. Thus the lower cost of expanded PS has promoted its use in preference to PU foam and extruded PS in single-ply applications. This is facilitated by the fact that the problems of damage to expanded PS foam from hot pitch when used in built-up roof systems are not encountered in single-ply systems. As wiring insulation, PVC is favored because of its greater resistance to burning. Because of its flame resistance, it competes effectively as insulation for inside wiring, particularly in constructions where weight is an important factor.

2.3.1.6 Polymer-Modified Concrete

The improved useful physical and mechanical properties of concrete in addition to the corrosion stability of reinforcing steel are the main reasons for the continuous interest shown in polymer-modified concretes. Polymer concretes are materials obtained by the addition of monomers, prepolymers, or polymers to conventional concrete, either during the mixing process (premixing) or by impregnation of the mature concrete (postmixing). The addition of polymers will lead to improved mechanical properties, in particular regarding durability of the concrete and its ability to prevent corrosion of the reinforcing steel. There are the following polymer–concrete composite types:

(A) **Polymer-impregnated concrete** is composite prepared by impregnating dry precast Portland cement-concrete with liquid monomer and polymerized by radiation, thermally, or chemically. Some of the most widely used monomers for this type of cement composite include: MMA, S, BA, VAc, AN, MA, and TMPTMA as crosslinking agent. With impregnation by an appropriate monomer, the main effect after polymerization is the filling of the continuous capillary pore system, which reduces the porosity. The reduction of porosity reduces the effect of stress concentrations from pores and microcracks, thereby increasing the strength of the composite. The largest improvement in the strength and durability properties obtained with this composite is strongly dependent on the fraction of the porosity of the cement phase that is filled with polymer. It exhibits an increase in the compressive strength and the modulus of elasticity, reduction of the water and salt permeability, improvement of the freeze-thaw resistance, and zero creep properties. The film already formed by curing on the surface retains its moisture necessary for full hydration of the cement. The improved specific characteristics of this composite material place it in a position between traditional concrete and other groups of engineering materials as metals and ceramics. The important applications of polymer-impregnated concrete composite are in pipes, underwater habitats, dam outlets, and underwater oil storage vessels. The attractive property of blocking the pores in the concrete and restricting the permeability of moisture and oxygen not only prevent corrosion but also increases the wear resistance of the resulting concrete. Incorporated polymer has been used to improve the durability of concrete, to make the concrete behavior more ductile, and reduce short-term deflections because of the increased elastic modulus and the reduced creep. The improvement in properties that can be achieved depends on the initial quality of the concrete and the amount of impregnated polymer. Polymer impregnation increases the shear capacity of beams without shear reinforcement. Although styrene is an attractive candidate for properties and economical reasons, MMA is preferred because it polymerizes readily and is a suitable impregnating material. TMPTMA and DAA are better suited for high temperature applications. Components of such materials are suitable for underwater structures, desalination plants, bridge decking, and concrete pipes for high pressure gas.

(B) **Polymer-cement concrete** is a modified concrete in which a part of the cement binder is replaced by organic polymer. It is produced by incorporating a monomer, prepolymer, or dispersed polymer latex into a cement-concrete mixture. The process technology used is similar to that of conventional concrete and has the advantage that it can be cast in place for field applications. Most of the polymer-cement-concrete composites are based on different kinds of lattices obtained especially by emulsion polymerization. The lattices are aqueous emulsions containing polymer particles such as SBR, NBR, PVAc, copolyesters of AA-MAA, and PAA-PMAA-SBR. The compatibility of SBR, PVAc, and acrylic lattices with Portland cement produces particular characteristics that led to wide use of this component as polymer-concrete composites.

The polymer latex used for making a polymer-cement-concrete must be able to form a film under ambient conditions, coat cement grains and aggregate particles, and form a strong bond between the cement particles and aggregates. Polymer-cement-concrete has a higher corrosion resistance as compared with ordinary concretes and can effectively be used for floor coating in a moderately aggressive atmosphere, at milk-processing factories and breweries. However, the presence of cement in polymer-cement-concrete is a source of corrosion destruction under the action of more aggressive and concentrated chemical media at sugar refineries and meat-processing enterprises. In such cases, polymer-cement-concrete may be recommended only for under floors. The problem may be radically solved by producing floor coatings with a purely polymeric binder. For example, the use of epoxy alkyl resorcinol-based polymer concretes for floor coatings in production shops at food industry enterprises increases the corrosion resistance of the floors to a great extent [298]. Reinforcing conventional concrete with PP filaments has been used for concrete pile shells where resistance to breakage drastically reduces down time and costs. The material results from the addition of PP filaments to foamed-concrete is easier to handle, resists frost damage, has better aggregate distribution, and can be decorated with three-dimensional effects.

(C) **Polymer concrete** may be considered as an aggregate filled with a polymeric matrix without any cement, i.e., it can be described as a concrete containing polymer as a binder instead of conventional cement. The aggregate of small particles is used in producing polymer concretes to minimize void volume in the aggregate mass so as to reduce the quantity of the polymer necessary for binding the aggregate. Aggregates commonly used include quartz, silica, fly ash, and cement. Thus, by careful grading, it is possible to wet the aggregate and fill the voids by the use of a some polymer and to obtain high degrees of packing with high compressive strength. A wide variety of monomers, prepolymers, and aggregates have been used to obtain polymer-concrete composite such as epoxy prepolymer, unsaturated polyester–styrene system, MMA, and furane derivatives. To obtain the best chemical resistance, complete curing of the polymer is necessary by using an appropriate crosslinking agent. In order to improve the bond strength between the macromolecular matrix and the aggregate, a silane coupling agent can be added to the hydrophobic monomer before the polymerization process. The nature of the aggregate influences the hydrothermal stability of polymer-concrete composites.

The product of the mixture of unsaturated polyester with fine aggregate has higher compressive strength and bonding strength than conventional concrete, permitting thinner and lighter components. The applications of this material include: boundary markers, windowsill units, drainage gullies, effluent pipes and sumps in chemical plants. The products of PU foam and unsaturated polyester foam which fill the spaces between aggregate particles of expanded glass and clay aggregates offer fire resistance materials that are used in prefabricated pod bathrooms and external wall panels. Polymer-concrete composites based on unsaturated polyester and wet aggregates of cement and silica result in significant strength improvements. The chemical bonding between cement particles and carboxylate anions of unsaturated polyester brought on by a hydrolytic reaction is a crosslinking reaction. The addition of MMA to unsaturated polyester–styrene provides a hard, clear mirror finish, improves the workability without reducing the strength, and enhances durability. Polymer-concrete composites offer several advantages such as fast curing, impermeability to moisture, very little cracking of the concrete caused by freezing and expansion of moisture within the cured mix, resisting salts and other agents that cause corrosion of the reinforcing steel within the reinforced concrete. These properties have led to the use of polymer-concrete composites in water treatment and sewage treatment plants. They can be used in thinner layers than conventional concrete to give the same strength at lower volume, thus allowing a weight and cost reduction. The excellent resistance to chemicals allows many applications in the construction of sewer systems, sewage treatment plants, animal stables, and high-resistance floors.

2.3.1.7 Steel-Reinforced Concrete

Corrosion of the reinforcing steel in conventional concrete by moisture and oxygen is a very costly problem in the construction sector. This corrosion problem can be solved by the use of polymers which fill the pores in the concrete, restricting the permeability of moisture and oxygen that cause and accelerate the steel corrosion. The successful application of epoxy coatings on underground transmission pipes has received considerable attention, and fusion-bonded epoxy-coated reinforcement can significantly extend the durability before deterioration of reinforced concrete with uncoated steel bars in areas with a high level of salinity. Epoxy-coated reinforcements have shown relatively little steel corrosion and concrete deterioration in structures of service [299], while in other cases there has been unsatisfactory performance of epoxy-coated reinforcements in regular maintenance, where the coating was found to be completely disbonded from the steel. Epoxy coatings are effective in preventing corrosion of reinforcing steel in highly corrosive environments. These observations have brought into focus the need to study damage morphology in terms of coating characteristics, i.e., the adhesion, integrity, and thickness of coatings. If there are no defects, the corrosion protection barrier is effective, but if there are defects in placed epoxy-coated reinforcement, the coating resistance is disbonded from these defects. To improve the long-term adhesion of epoxy coatings to reinforcing bars other approaches need to implemented which include chemical treatment of blasted steel surfaces prior to coating application, and developing a strong quality assurance for coating application industries [300].

2.3.1.8 Building Soil Stabilization

Building soils are the basic structural materials on which constructions are built. The design of a foundation depends on soil factors: the soil type, the soil layer thicknesses and their compaction, groundwater conditions. Soils consist of different layers with varying thicknesses and of different particle sizes (clay, silt, sand, gravel, and rock). The voids between the larger particles are entirely filled by smaller particles. The finer grained soils become fluid when mixed with water and exhibit spongy and slippery characteristics and in a dry condition, clay becomes hard and impenetrable, silt becomes powdery. They exhibit elastic properties, i.e., deform when compressed under load and rebound when the load is removed. The elasticity of soils is often time dependent, i.e., the deformations occur over a period of time. Because of these properties, a building which imposes on the soil a load greater than the natural compaction weight of the soil can shift because the soil may settle in time.

Hardcore, aggregate bases or layers of drainage gravel, often to which polymers as polyester fibers are added, stabilize the soil and prevent objects from sinking into the subsoil.

2.3.1.9 Polymer Properties in Building Construction

The use of commercially available polymeric materials with their distinct advantages over other competitive materials in the building construction sector depends on their cost and their physical and mechanical properties. The properties of polymer used in buildings include: (1) *Physical properties*: the low density of polymers provides important advantages over metals and ceramics in those applications in which the weight-volume ratio is critical. Low density can be altered in the desired direction by various means. Polymers have a high tensile strength-to-density ratio, which allows reduction of the material mass, enabling to build strong structures of the least possible weight. Polymers have excellent dielectric properties, i.e., can be used for electrical insulation. Both the dielectric constant and the surface resistivity of polymers are influenced by moisture. For use in dielectric applications, water resistance filler is preferred to provide the best possible combination of properties for electrical wire insulation and cable jacketing. The ease of fabrication and flexibility of polymers are important factors favoring their use as ideal materials in rigid insulator applications. However, polymers have unfavorable electrical breakdown strength, so they are less widely used in high-voltage applications. In addition, polymers are good heat insulators, and have favorable features for sound proofing, and possess good optical properties i.e., are colorless and transparent, and are good adhesives. (2) *Mechanical properties*: many polymers have a high tensile strength-to-density ratio. However, some polymer composites have strengths well within the competitive range of metals and have the ability to damp mechanical vibrations. Polymers are usually materials of choice when low density and ease of fabrication are required but the high strength can be enhanced by the introduction of reinforcing agents which enable polymers to compete effectively with metals in certain applications. (3) *Morphology*: polymers exist in a semicrystalline state having advantages regarding strength in the ordered crystalline regions and flexibility in the disordered amorphous regions. Polymers can be applied in engineering solutions when strength is combined with flexibility, i.e., toughness, in the same copolymer or blend of polymers, or orientation of the polymer chains at the macrolevel to maximize strength in polymers. In general, polymers exhibit higher strength in tension than in compression. (4) *Processability*: polymer fabrication into final products in many processes requires less energy than the energy required for fabricating the same product from metals. Polymers have further advantages regarding ease of pigmentation and ease of fabrication as a result of their low melt flows that can be used to manufacture complex products with a high degree of detail, allowing workability and weldability. (5) *Deterioration*: vinyl polymers degrade when exposed to high temperatures or UV radiation, but they are resistant to breakdown by hydrolytic degradation and biodegradation by microorganisms. In contrast to metals, polymers are ideally suited for applications in the presence of high humidity or moisture. Their high durability and corrosion resistance make them suitable for use in situations with required long service life in aggressive media, e.g., in underground structures, for water proofing various constructions, for making chemically resistant articles and structures. (6) *Scrap reuse*: the separation of recovered polymer scraps from waste stream mixtures can expand their reuse and remove some serious problems in respect to environmental pollution.

2.3.2 Semipermanent Structures

PVC and PE films have been used extensively for protecting silage stored in bunkers, trenches, and stacks. They are used as caps in conventional and trench silos. These polymeric films exclude oxygen from the anaerobic atmosphere developed by the fermenting silage, reduce spoilage losses, and maintain the palatability of the ensiled material [175, 176]. Silos have been constructed of flexible glass-reinforced polyester sheets bonded to PP [213]. PE and PVC sheeting is also used as cover for agricultural equipment, for harvested crops such as grain, and for other commodities that need protection from moisture damage. Plastic film and panels are used as building materials in rearing animals and poultry and for winter shelter or summer shade for livestock. Inflatable plastic structures and light-weight, prefabricated portable houses made of foamed polymeric materials have been used for temporary, seasonal storage facilities. For increased egg and milk production in environmentally controlled houses, foamed plastic insulation is used in farm buildings. Polymers have also been used in other areas such as: (a) *Growing trays and troughs*: potted seedlings are grown in trays carried on free-standing pillars in the greenhouse. Trays and troughs are molded from PP and HDPE and can be easily handled on trolleys for transporting. Double-wall PP-extruded sheet is light, rigid, and used for canal systems and for forming gullies lined with black PE film in cultivation. (b) *Baler twine* is a special application mainly based on PP; ageing has been improved by incorporating UV stabilizers. (c) *Animal protection* by small coats and jackets made from PE film especially for young animals (lambs) often required because of high losses by exposure to a combination of wind, rain, and excessively low temperatures.

2.3.3 Polymers in Agricultural Equipment and Machinery

Plastics are used for components such as covers and bearings in agricultural equipment. PP and nylon can be molded to give high strength components, while extruded sheet can be vacuum-formed to produce covers and boxes. The range of plastics and rubber-based components used in agricultural machinery parts includes polyamide gear wheels and bearings, PP and glass-reinforced polymer covers, electrical wiring, and various synthetic rubber seals. The biggest use of rubber in agriculture is for tractors tires, which have large tires especially as the engine power has increased [301–303]. Polymers are extensively used in dairy equipment including hoses, storage tanks, and rubber liners. High impact PP is successfully used in lawn mowers, e.g., as an under deck to improve grass collection and reduce noise [304]. Spraying equipment uses PP tanks, rubber seals and many components are molded plastics. Polymers are prevalent in tools; PP has even replaced steel for the trays and wheels of some wheelbarrows with the obvious advantages of strength to weight ratio and no rusting. Plastics were increasingly replacing metals in engines of garden machines and that polyamide was being used in handles, as described in the review of lawn and garden injection molded products [305].

2.4 Polymers in Water Handling and Management

Rainfall distribution is geographically and seasonally extremely variable and in many areas there are periods in which the amount of water is insufficient for growing crops. The demand for water is increasing. Agriculture is the main consumer of water and only 50 % of water used in agriculture actually reaches the plants [306]. In consequence, proper water management for agricultural and horticultural use is of paramount importance. Clearly, water needs are greatest in arid regions but water can also be a limiting factor in temperate regions and using less water would reduce the needs. The use of plastic materials in irrigation technology has contributed to a real change in irrigation in many ways, from the actual irrigation equipment to the control of water by changing of soil characteristics [307]. Films, tubing, and reservoirs provide improved means for making water available to plants through: (a) water storage by reservoirs and lakes, the construction of dykes and the control of streams; (b) controlled distribution of irrigation water and removal of excess water by drainage. The adequate management of water in a most effective way can help to reduce environmental stress. Water conservation can be improved by increasing the rate of water movement into the soil by appropriate drainage and irrigation practices.

Plants need water and carbon dioxide along with sunlight for photosynthesis. Shortage of water in the soil and low insolation slow down photosynthesis. Crop yield depends also on the availability of minerals (fertilizer). The utilizable water available to the plant is the difference between the retention capacity of the soil and the limit of extraction, and this capacity is dependent on the type of soil. In arid zones, the water which is available to the plant is only a fraction of the water received by the soil because the latter ends up in different places, for instance, as runoff water, seepage water lost or diverted, or water which is a constituent part of the soil and is not extractable by the roots. If the water extracted by the roots is insufficient, the plant will wilt and may eventually reach the permanent wilting point. Each plant requires a certain depth of soil for occupation by its roots and the water requirements must be satisfied for each period of plant growth, which depends on the season that determines the quantity of water required to the plant and the amount lost by evapotranspiration.

2.4.1 Water Types

The only practical source present for a continuous water supply for all agricultural, industrial, and domestic uses is rain which is the source of water for lakes and rivers. Desalination of salt water can supply water for high-value uses in some countries. Water problems, involving water distribution, and water demands by agriculture are continually increasing because of population growth and the necessary development of additional irrigated land. The development of water resources involves storage and transport of water from the place of natural occurrence to the place of beneficial use. Natural water sources are of three types:

2.4.1.1 Surface Water (Rivers, Lakes)

Surface water predominantly results from rainfall that continuously feeds streams, rivers, and lakes. Rainfall characteristics include: rainfall amount and intensity, the depth of rainfall, and the frequency of occurrence. Relatively high intensity and long duration result in a large total amount of rainfall that causes soil erosion damage and may result in devastating floods. Rainfall intensity varies greatly with geographic location and the duration of occurrence. Water from rainfall will infiltrate the soil and some will flow to runoff and stream channels, lakes, and oceans. Soils higher in clay will have greater runoff, whereas sandy soils have less runoff. The total annual runoff volume from storms is of interest when flood-control reservoirs are to be designed for irrigation or water supply. Waterways are often located where there is a low flow over long periods of time and they can be established by vegetation. If establishment is difficult because of poor soils or an adverse climate, organic fiber or plastic meshes with seeds in the fabric are used to improve germination by making more water available to the seeds and offers some erosion protection. Soil stabilizers and asphalt mulches assist in fixing the soil and increase channel erosion resistance. Accumulation of sediment in waterways may restrict channel capacity and the best method of minimizing sediment problems in waterways is by reducing erosion within the upland watershed. Sediment may deposit at the lower end of the waterway if the slope decreases. Accumulated sediment may be removed or the channel reshaped to minimize damage to the vegetation, and to prevent localized erosion.

2.4.1.2 Groundwater (and Wellwater)

Groundwater predominantly results from rainfall that has reached the zone of saturation in the bottom soil layer through infiltration and percolation. This subsurface water is developed for use through wells, springs, or dugout reservoirs. It is an important source of water supply and is being withdrawn much faster than it is being replenished from infiltration and percolation of precipitation. Groundwater supplies may be at the soil surface near lakes, swamps, and continuously flowing streams, or primarily obtained from artesian wells, which are present when water is confined under pressure between upper and lower impervious layers. Wells are holes drilled downward from the soil surface into the groundwater aquifer. A casing is installed during the drilling process to stabilize the hole allowing water, but not aquifer particles, to move into the hole. The lower portion of the casing is the well screen. The openings in the screen should be properly sized to minimize the movement of sand into the well.

2.4.1.3 Wastewater

Municipal sewage contains oxygen-demanding materials, sediments, grease, oil, scum, pathogenic bacteria, viruses, salts, algal nutrients, pesticides, refractory organic compounds, and heavy metals. Several characteristics are used to describe sewage, which include: turbidity, suspended solids, dissolved solids, acidity, and dissolved oxygen. The cost of wastewater treatment depends on many factors such as plant location, environmental control regulations, and type of wastes produced. Overall costs can be minimized by utilizing professional services of highly qualified and experienced engineering firms. The capital and operating costs of wastewater treatment increase with increasing efficiency of required contaminant removal.

2.4.2 Polymers in Water Treatment

Water quality may be improved by the proper selection and management of the water sources and delivery methods. Water purity is determined by the presence of contaminants: (a) *Physical contaminants*: result from suspended sediment in irrigation and runoff water. Sediment occurs because of soil erosion and disposal of man-made objects. Sand may be obtained during pumping from wells. Sediment must be removed from water used in microirrigation systems to prevent plugging. Sands may cause excessive wear to pump impellers and to the nozzles in sprinkler irrigation systems. If sediment is deposited on sandy soil, the textural composition and fertility may be improved. Sediments derived from eroded areas may reduce fertility or decrease soil permeability. Sedimentation in canals or ditches results in higher maintenance costs. (b) *Chemical contaminants*: result from chemicals that enter the water supply from industrial processes and agricultural use of fertilizers and pesticides or introduced during water movement through geological materials. (c) *Biological contaminants*: result from microorganisms as bacteria and viruses that enter the water supply from human and animal wastes and can create serious health problems.

The natural water from rivers or wells and wastewater can be treated by several physical, chemical, and biological means to produce clear, safe, and tasty water that presents no hazards to the human and animal consumer. While river water may be polluted with mud and bacteria, well water is often hard and may contain high levels of dissolved ions as iron and magnesium. The type and degree of treatment are strongly dependent upon the source and use of the water. The treatment of water is usually divided into three major categories: (1) *Purification for domestic use* in which water must be disinfected to eliminate disease-causing microorganisms. (2) *Treatment for industrial use.* For water to be used in boilers it must be quite free of salts because the minerals form deposits on heating and reduce heating efficiency. (3) *Treatment of wastewater* for agricultural reuse and wastewater being discharged into rivers may require less rigorous treatment. As world demand for water resources increases, more extensive means will have to be employed to treat water. The process of wastewater treatment occurs in three stages:

2.4.2.1 Primary Treatment

The first step in wastewater treatment is the removal of water-immiscible liquids and insoluble solid matter from the untreated wastewater by several physical processes via density separation such as screening, sedimentation, flotation, and filtration. Screening consists of the removal of large objects as well as grit, grease, and scum from wastewater. The removed solids are collected in screens and scraped off for subsequent disposal. Small-size particles as sand and other small objects may be separated by subjecting to settling under conditions of low flow velocity, and scraped mechanically from the bottom of the tank. This removal process may reduce the amount of particulate matter preventing their accumulation in other parts of the treatment system, reducing clogging of pipes, and protecting moving parts from abrasion and wear. Solid colloidal particles are removed by settling and filtration, whereas the solid suspended matter is coagulated by flotation with polyelectrolytes and the sedimented solids by aggregation are removed by fine screening. Dense suspended matter in wastewater can be separated by settling, while some other solids contain higher surface area relative to their density and thus float to the surface and can be skimmed off there. Air dissolved in wastewater under pressure and then released at atmospheric pressures is generally used to effect flotation of suspended solids. Sedimentation removes settable and floatable solids by aggregation of flocculent particles (grease) for better settling by the addition of chemicals. Grease consists of oils, waxes, fatty substances, and insoluble soaps containing Ca and Mg. Flotation and sedimentation generally reduce the solids into sludge. Flotation requires less retention time than that required for sedimentation to remove solids. Screening is an economical and effective means of rapid separation of relatively large-sized suspended solids from the remaining wastewater.

Colloidal solids are small enough to remain stable, but interfere with the passage of light, and therefore cause turbidity. They do not settle unless destabilized and flocculated into larger masses with sufficiently high density by coagulants. (a) *Coagulation* involves the reduction of the electrostatic repulsion of the negative surface charge surrounding colloid particles via neutralization by binding with positive ions as *aggregating agent* which results in precipitation of aggregated colloids. This kind of aggregation by neutralization of the surface charge on the particles results in precipitation. (b) *Flocculation* depends upon the presence of polyelectrolytes as bridging compounds, which form chemical bonds between charged colloidal particles and aggregate the particles in relatively large masses. The flocculation process induced by anionic polyelectrolytes is greatly facilitated by the presence of metal ions capable of forming bridges between the anionic polyelectrolytes and the negative surface charge surrounding the colloidal particles. Coagulants as normal electrolytes $Al_2(SO_4)_3$, or polyelectrolytes with a strong positive charge are added to stimulate coagulation and appear to react with the negative colloidal particles in the wastewaters forming clusters that settle out with gelatinous $Al(OH)_3$ and can later be removed. The aggregation and settling of microorganisms (bacterial cells) is essential to the function of biological wastewater treatment systems for the removal of organic material and its oxygen demand.

2.4.2.2 Secondary Treatment

Because of the high pollution density of wastewaters by organic constituents, and the rapid industrial development for water, there is a great need to treat wastewater in a manner that makes it suitable for reuse. Organic constituents such as toxic substances, volatile solutes, and other odorous substances can be removed by several procedures: (1) they can be removed by air and steam stripping. (2) Dissolved oxygen in wastewater is suitable for microorganism degradation by biological processes that allow the biodegradation of organic matter. The waste is oxidized biologically under conditions of optimal bacterial growth which does not affect the environment. Wastewater treatment processes employ biological means by activated sludge, trickling filtration, rotating biological contractors, oxidation-pond treatment, or sorption by activated carbon. The organic contaminants removed by these processes include suspended solids and dissolved organic compounds. (3) Trickling filtration is a biological waste treatment process in which wastewater is sprayed over a solid medium (rock, plastic, or glass) covered with microorganisms for biological oxidation degradation of organic matter. (4) Rotating circular biological reactor consists of groups of large plastic discs (HDPE, PS) mounted close together on a rotating shaft, in which half of each disc is immersed in wastewater and half exposed to air. The discs accumulate thin layers of attached biomass that build biological growths on their surfaces, which degrades organic matters in the sewage by oxidation. The advantage of this process is its low energy consumption because it is not necessary to pump air or oxygen into the water. (5) Activated-sludge treatment consists of aerating biological flocculent growths within the wastewater. The surface for biological oxidation is created on the flocculent growths. Microorganisms in the aeration tank convert organic material along with nitrogen and phosphorus in the wastewater into microbial biomass and carbon dioxide, nitrate, and phosphate. Recycling of active organisms provides optimum conditions for waste degradation present in the aeration tank. This process is the most effective of all wastewater treatment processes. Oxidation-pond treatment is less effective, requires large land areas, long detention time, emanates odors, but is not expensive to build and operate.

2.4.2.3 Tertiary Treatment

Heavy metal elements and excess inorganic salts which are often contained in wastewater are potentially hazardous and can cause disease and discomfort, cause scale in pipelines and equipment, accelerate algal growth, increase hardness of water, and enhance metal corrosion. Water hardness is caused by Ca and Mg salts which are froming insoluble curd by reaction with soap that adversely affects detergent performance. Hard water causes formation of mineral deposits on heating units, coating the surface of hotwater systems, clogging pipes, and reducing heating efficiency. Inorganic salts can be removed by several processes such as ion exchange, membranes (reverse osmosis, hyper- and ultrafiltration), evaporation, and distillation. Water softening by removal of inorganic ions can be achieved by: (a) *Lime-soda ash treatment*, (b) *Ion exchange* by strong cation and anion exchanger resins; the deactivated resins require regeneration for their reuse, (c) *Reverse osmosis* consists of forcing water through a semipermeable membrane that allows the passage of water but not of other materials. It depends on the sorption of water on the surface of the membrane (porous cellulose acetate or polyamide) and the sorbed water is forced through the pores in the membrane under pressure.

Disease-causing pathogenic organisms require disinfection in cases where humans may later come into contact with the water. Chlorine and ozone are commonly used to disinfectant water other than drinking water for killing pathogens in water from sewage treatment plants, and to control viruses and bacteria in food processing. Chlorine dioxide is also effective water disinfectant, it does not produce trichloromethane as impurity in treated water, but it is explosive when exposed to light and does not chlorinate or oxidize ammonia or other nitrogen-containing compounds.

2.4.2.4 Immobilized Microorganisms for Water Treatment

Water originating from food or agricultural industrial processes can be contaminated with nitrate, that can be removed by denitrification methods generally employ special beads for immobilized biosystems, i.e., physical or physicochemical bonding of denitrifiers to the surface of insoluble carriers (sand, plastic, or ceramic particles). However, immobilized microorganisms, adsorbed by weak hydrogen bonds or by electrostatic interactions with the carrier, can be easily washed from the support into the treated water, resulting in microbial pollution [308]. Although an alternative method of immobilization by enzyme entrapment has been used, microorganism containment is a recent approach to wastewater treatment [309–312]. Cellular structures formed as a result of drying gels serve as matrices for the immobilization of denitrifying isolates. The dried beads have physical properties similar to those of porous, sponge-like matrices, with apparent air spaces within and around hydrocolloid-matrix walls. The beads revealed a matrix structure with variously sized pores that enabled gas release without matrix damage. The incorporation of starch granules within the matrix strengthened its structure. The dry matrices sustained their biological activity over a prolonged period, meaning that the drying process did not damage the bacterial activity [313]. The starch incorporated into freeze-dried alginate beads can serve as a carbon source and filler. Freeze-dried beads containing high concentrations of starch were found to have better mechanical and denitrifying properties than beads containing low concentrations of filler [313].

2.4.2.5 Treated Water Uses

(A) **Agricultural uses.** Water is a basic component of all plants and is taken up from the soil via the root system, flowing up the plant by the osmotic gradient between the soil and the air. The water consumption of a crop can be broken down into three parts: (1) *Constituent water*, which is retained as a constituent part of the plant matter and used in combination with carbon dioxide to produce carbohydrates (photosynthesis), and to assist the uptake and transport of nutrients from the soil. (2) *Transpiration water*, which is taken up by the plant and lost as water vapor through the process of transpiration to provide cooling for aerial structures. (3) *Evaporation water*, which is lost by evaporation from the surface of the plant.

Water is available in soils from the evaporation and precipitation cycle that generates rain. The factors that affect agriculture are: soil type, rainfall distribution during the growing season, and climatic characteristics such as temperature and wind. The soil structure retains water in several different ways that will determine water availability to the plant: (1) *Drainage water* runs freely through the soil displacing air; it penetrates by gravity, is nonpermanent in the soil, and lost by percolation. (2) *Capillary water* makes up the majority of water in the soil and is the source of water for plants. This water is held in the soil by surface tension both on the surface of soil particles and in the capillary spaces between the particles. The capillary water capacity of a soil is lower for a sandy soil than for clay-containing soil. (3) *Interstitial water* is bound within the colloidal particles remaining from the gradual evaporation of both drainage and capillary water. The majority of this water is not available to the plant. (4) *Water vapor* within the soil pore spaces establishes equilibrium between its liquid state and the vapor level in the air, which is a negligible source of water to plants.

As water demands grow, treated wastewaters will increasingly be employed in agriculture. The direct application of wastewater to soil has yielded appreciable increases in soil productivity. Wastewater may provide the water that is essential to plant growth, in addition to the nutrients usually provided by fertilizers. All of the waste materials which are essential for soil fertility, may be absorbed by soil or degraded in soil. Soil is the natural habitat for a number of organisms (microorganisms, fungi, worms, etc.) that are active decomposers of wastes. The degradation of organic wastes in soil provides carbon dioxide for plant photosynthesis. Soils as natural filters for wastes have physical, chemical, and biological characteristics that can enable wastewater detoxification, biodegradation, chemical decomposition, and physical and chemical fixation. A number of soil characteristics are important in determining their usability for land treatment of wastes, these include: physical form, water retainability, aeration, organic content, acid–base characteristics, and redox behavior.

(B) **Industrial use.** Water is used in various industrial applications, as for instance as boiler feed water and cooling water. Cooling water may require minimal treatment, though removal of corrosive substances and scale-forming solutes may be necessary. Water used in food processing must be free of pathogens and toxic substances. Improper treatment of water for industrial use can cause problems, such as corrosion, scale formation, reduced heat transfer in heat exchangers, reduced water flow, and product contamination. These effects may cause reduced equipment performance or product deterioration. Obviously, the effective treatment of water at minimum cost for industrial use is an essential aspect of water treatment. Numerous factors must be taken into account in designing and operating an industrial water treatment facility: water requirement, quantity and quality of available water sources, sequential uses of water (water recycling), and discharge standards. The various specific processes employed to treat water for industrial use are: (a) *external treatment* by aeration, filtration, and clarification to remove suspended or dissolved solids, hardness, and dissolved gases from water that may cause problems, (b) *internal treatment* which modifies the properties of water for specific uses by: (i) reaction of dissolved oxygen with hydrazine or sulfite, (ii) addition of chelating agents to react with dissolved Ca^{2+} and prevent formation of calcium deposits, (iii) addition of precipitants for calcium removal, (iv) treatment with dispersants to inhibit scale, (v) addition of inhibitors to prevent corrosion, (vi) adjustment of pH, (vii) disinfection for food processing uses or to prevent bacterial growth in water.

2.4.3 Polymers in Irrigation

Irrigation is necessary to supply to the plant the water necessary for its needs that it otherwise would not receive by natural means. Although irrigation greatly increases the availability of food supplies and reduces their cost, failure to irrigate or excess irrigation is associated with adverse effects on crop production. Thus, irrigation is desirable or even required for economic crop production and for field crops grown in low water-holding capacity soils as well as for dry land farming where water is not available or costly. Irrigation has other significant effects on the environment resulting from the applied chemicals. Dissolved salts remain in the soil after irrigation and require drainage to remove excess salts from the plant root zone. Irrigation is usually provided by underground or surface reservoirs, as decrease in the irrigation table may lead to water stress that slows the growth of leaves and stems. Advantages resulting from proper irrigation include: (1) increased crop yield and quality, (2) controlled time of planting and harvesting, (3) reduced damage from freezing and high air temperature, (4) increased efficiency of fertilizers and reduced cost of application, (5) a stabilized farm income. However, disadvantages of irrigation include increase in: (1) fertilizer requirements, seed costs, and more field operations, (2) weed growth that calls for use of herbicides, higher requirement of pesticides, and associated field operations, (3) water-borne diseases to animals and humans, (4) chemical contaminants in the root zone, (5) need for artificial subsurface drainage and leaching requirements, (6) detrimental effects on groundwater and downstream water quality, (7) conflicting demands on limited water resources.

2.4.3.1 Irrigation Water Quality

The chemical quality of water largely determines its suitability for irrigation and the most important characteristics of irrigation water are: (1) concentration of toxic elements, (2) concentration of soluble salts, i.e., water salinity, indicated by the electrical conductivity of the water (dS/m); the major ions causing water salinity are Na, Ca, and Mg cations. The rate of water flow is determined by its movement through the soil and is directly proportional to the soil pore space. Leaching is the only way to remove salts in the soil; this can be done by irrigation water. By frequent application of sufficient water excess salts can be dissolved and removed from the root zones by subsurface drainage.

Irrigation management needs to take into account: irrigation period, total irrigation water quantity and quality, soil salinity, effect of rainfall, and the efficiency of the irrigation system. The total seasonal irrigation requirement is the total amount of water that must be supplied over a growing season to plants. Irrigation is intended to provide optimum or maximum yield of crops; excess irrigation is undesirable because it decreases yields by reducing soil aeration and by leaching fertilizers away. Critical parameters include: (1) atmospheric conditions such as evaporative demand, radiation, temperature, wind, and humidity, (2) soil water retention, (3) the kind of crop and the rate of growth, (4) rainfall amount and intensity. During the early stages of growth the water needs are generally low, but they increase rapidly during the peak growing season to the fruiting stage, while during the later stages of maturity water use decreases as the crops ripen.

2.4.3.2 Irrigation Methods

Irrigation systems are categorized as flooding, soil surface spraying or sprinkling, and drip irrigation, which are all referred to in detail in the following:

(A) **Surface irrigation.** Application of irrigation water by flooding the soil surface is the most widely used method in spite of the associated adverse effects caused to the land. Surface irrigation is the application of water to the soil by allowing the water to flow over the soil surface. Efficient surface irrigation requires grading of the land surface to control the flow of water. It is the least efficient but predominantly used irrigation method in large irrigation areas, under conditions of: (1) flat soil land, (2) soils having high water-holding capacity and moderate infiltration rates, (3) large streams to cover the soil area quickly, (4) balance between soil and flow characteristics for optimum efficiency. The farm water supply is normally delivered either by conveyance ditches from surface storage or from irrigation wells. In surface irrigation systems, water is fed from a main channel into a series of ditches which are constructed to control the flow and aid in distributing the water over a field. The flow of water from the main channel into the gullies can be controlled by using PE siphon tubes. Gullies made from glass fiber-reinforced polyester have replaced concrete channels.

(B) **Spray irrigation.** Water taken from the source (river, lake, well, or reservoir) is pumped through a distribution network system to feed sprayers or sprinklers which are spaced at regular intervals over the ground to be watered. Distribution irrigation systems are designed to distribte the water by means of a network of pipes using a variety of filters for the removal of solid matter. Pipes with slip joint connections have been commonly used for water distribution. Permanent systems are suitable for high-income crops because of the high labor cost in moving these systems. (a) *Spray irrigation systems* do not necessarily involve the transport of the water by pressure through a water-main for a small plot, since these can be readily watered by simpler means. An automatic pumping station is required for a system covering large areas of ground. Regular pipework systems are not designed for irrigation requirements subject to pressure surges due to the opening and closing of the valves. The overloading and reduction of pressure appears to accelerate the aging and deterioration of plastic pipes.These systems can be fully automated, fertilizer can be added to the water, nozzle holes are not to be liable to blockage by colloids. Drip or trickle irrigation does not cause leaching or compaction of the soil in contrast to other methods. (b) *Sprinkler irrigation systems* are automatic-timed systems and provide uniform application of water and can be used for lowering the temperature of plants by the cooling effect of evaporation. It is appropriate for circumstances where the soil infiltration rate exceeds the water application rate. It can provide a high efficiency of water application and its rate can be easily controlled. With this method, water is sprayed into the air and falls on the crop and soil, surface ditches are not necessary, prior land preparation is minimal, and pipes are easily transported and provide no obstruction to farm operations when irrigation is not needed. It is also well suited for sandy soils in which surface irrigation may be inefficient and expensive, or where erosion may be hazardous. Low amounts and rates of water may be applied, such as are required for seed germination, frost protection, delay of fruit budding, land application of wastewater, and cooling of crops in hot weather. This method can be used as a convenient means for the application of fertilizers, soil amendments, and pesticides to the soil or crop. It reduces energy and labor costs, and improves the effectiveness and timelines of the application. However, it is not suited for windy conditions that reduce efficiency and uniformity and the use of salty water may result in reduced yields because salts remain on the leaves as the water evaporates.

(C) **Trickle/drip irrigation.** This microirrigation system consists of small-bore flexible plastic pipe with connectors and drip heads and is used for irrigation of sandy soils in open fields and greenhouses with saline water and is effective for making the best use of the water fed to the plants [314–318]. The distribution pressure of the water is reduced at the point where it is fed to the roots of the plant at a very low rate as a trickle or series of drips. This can be accomplished by the use of small tubes branched from the main feed pipe. The quality of water can be controlled so that optimum results are obtainable with any particular crop under different climatic conditions. For crops grown at wide spacing, tubes fitted with drippers are used. Layflat hose systems are used for crops grown fairly closely together. The layflat irrigation tubes may be installed over the soil surface with a tractor or applied below the soil surface, to avoid attack by rodents and blockage of the jets by evaporation of the water drops at the tip and to allow water to move up through the root zone by capillary action. Surface application of PE film improves the plant performance and is also capable of being used with a dilute fertilizer solution. Significant improvements in the yields are obtained, particularly with low-growing plants. The gain in the earliness of the crop is not so pronounced with taller-growing plants. The main difficulty to the greater use of the drip irrigation technique lies in the difficulty in removing the suspended colloids from the water with anticolloid filters. Trickle or drip systems that apply water at very low rates provide an opportunity for efficient use of water because of minimum evaporation losses and because irrigation is limited to root zones. Since the distribution pipes are usually at or near the surface, operation of field equipment is difficult. Such systems of microirrigation are well adapted to application of agricultural chemicals of fertilizers and pesticides with the irrigation water. It is a low-pressure distribution system and delivers slow, frequent applications of water to the soil near the plants, i.e., to individual plants or rows of plants. Drip irrigation systems can be used for watering and fertilizing plants in greenhouses and open fields. It has been accepted mostly in arid regions for watering high-value crops, commonly coupled with plastic film mulch to prevent evaporation losses. PVC pipes are used for permanent underground networks to carry water for drip irrigation to the field and PE pipes are widely used in surface networks which may be moveable or not to feed spray and sprinkler heads. PVC is used for spray line pipes, networks for sprinkler systems, mist systems in greenhouses and sprinkler systems. There are also various molded plastic components such as pipe connectors, spray-, drip-, and mist heads.

The drip irrigation technique has many advantages such as: (1) supplying water only to the root zones of the plants, (2) increasing crop yields and improving quality; (3) adequate to meet evapotranspiration demands, (4) reducing labor, energy, and equipment requirements and costs, and require only low pressures, (5) reducing water consumption use, i.e., delivering water directly to the needed area; (6) facilitating use of saline water; because the water does not contact the plant, less stress and damage occurs to the plant, (7) ease of crop harvesting there is no watering between the rows, (8) decreasing disease and pests due to the reduced moist environment, (9) minimizing deep percolation losses, (10) decreasing water loss by soil evaporation because only a portion of the surface area is wet, (11) ease of control of weeds, (12) decreasing rates of water use, (13) reducing the use of fertilizers and pesticides, (14) reducing chemical leaching to the groundwater.

Drip irrigation also has some disadvantages such as: (1) relatively high installation costs but favorable in the long term; (2) blockage of holes and pores of system components; (3) attack by rodents and animals if it is installed over the soil surface but this attack can be avoided by application below the soil surface, (4) salt tends to accumulate along the fringes of wetted surface strips, (5) restricting plant roots to the soil volume near each emitter, (6) result in dust formation from tillage operations and subsequent wind erosion in dry soil areas between the emitter lateral lines, (7) requires highly skilled labor for operation and maintenance of the filtration equipment.

2.4.3.3 Evapotranspiration

Evaporation is the removal of free water from the soil surface, while evapotranspiration is the removal of water from plant leaves. The soil is a reservoir for water and chemical plant nutrients and provides a substrate to support the plants – water is removed from this soil reservoir by evaporation. The rate of water removal from the soil by plants and the amount of rainfall or irrigation water stored in the soil is determined by the type of plants, on plant spacing and yield, and general management criteria. For irrigation, the water-holding capacity and the rate of water removal by plants must be considered.

2.4.4 Polymers in Drainage

Plants need air as well as water in their root zones and the presence of excess water in the subsurface generally retards plant growth because it fills the pores in the soil and restricts aeration. Soils with excess irrigation water are not suitable to the majority of plants due to the lack of oxygen; this can lead to reduced yield or death of the plants. Soil permeability for the excess water depends on the soil structure and composition (sand, silt, clay, humus). The fine particles can fill the spaces between the larger particles, thereby preventing the flow of water through the soil. Under such conditions the roots can become anaerobic and water will be collected on the surface. The rate at which water seeps away depends on the type of soil and is expressed as the amount of seepage water in a given time per square meter of surface. Consequently, drainage is essential to reclaim land for agriculture or desirable to improve yields. Traditionally, ditches and clay pipes have been used in field drainage. However, clay pipes are brittle, heavy, and the laying process is labor intensive; ditches became blocked, requiring annual maintenance. Use of plastic pipes has eliminated the disadvantages of clay tiles and pipes in the agricultural sector such as heavy weight, allowing the installation on reverse slopes, and improving the ease and efficiency of field drainage. They do not become disconnected, even with settlement of the ground, which occurs particularly in peat bogs. Rigid PVC pipes have been used but they are not totally satisfactory regarding lack of strength and flexibility. Flexible pipes of any length can be machine laid very rapidly and their use is much more efficient. Pipes made from PE, PP, and plasticized PVC have excellent strength and stiffness-to-weight ratio i.e., ensuring that pipes will not fracture under soil loading, and are suitable for the design of drainage systems.

2.4.4.1 Surface Drainage

Undesirable salts can be removed from the soil surface by providing excess water using constructed open ditches, land grading, and related structures. This application is for land that has insufficient natural slope to provide adequate drainage for good agricultural production. In arid regions under irrigation, drainage ditches are necessary to dispose of excess rainfall. Surface drainage generally gives a greater benefit than subsurface drainage. In surface drainage it is sufficient to provide drainage channels by cutting through the impermeable layer and running off the rainwater from the shallows where it collects. Drainage of natural wetlands is associated with adverse effects on migrating birds and other wildlife as well as on aquatic organisms as well as other environmental concerns.

2.4.4.2 Subsurface Drainage

The water content of root zone areas is lowered in subsurface drainage, thus increasing the pore space that allows greater infiltration and storage of water in the soil. It reduces erosion and sediments by reducing surface runoff rates and volumes. Adequate surface drains are needed to remove excess water, but subsurface drains are also required to remove excess water from soils with high water content and poor internal drainage, thus reducing wetland areas and making them available for agriculture. Subsurface drainage is required for many irrigated arid lands to prevent salinity build-up in the soil. Soils that do not have an impermeable layer below the root zone but have adequate internal drainage do not need pipe drains. Subsurface drainage increases crop yields by (1) removing the excess free water, (2) increasing the soil volume from which roots can obtain nutrients, (3) increasing the aeration, (4) permitting the soil to warm up faster, (5) increasing the bacterial activity that makes nutrients available in the soil, (6) reducing soil erosion, (7) removing soluble salts, high concentrations of which retard plant growth, (8) reducing labor operations, (9) reducing the loss of nutrients and pesticides.

2.4.4.3 Deep Drainage

If a topsoil lies on an impermeable compact layer with practically no slope, a drainage system will be required. The use of plastic pipes (formerly metal and clay drainage tiles) is required; these are light weight, flexible, and corrosion resistant. The use of plastic piping systems requires deep drainage and must take into account the topography of the subsoil, the filtration speed, the water content and the impermeable zone, and must consider drainage spacing, the length of drains and their location in relation to the outflow and the collector.

2.4.5 Polymers in Water Collection and Storage

The systems for collection and storage of water are mostly shared by industry, domestic households, and agriculture. In addition wells and reservoirs specifically serve agricultural purposes. Polymeric materials as structural components in water collection, storage, transport, and control for water conservation are in steadily increasing demand for successful crop production. They are used in plastic piping systems for above- and below-ground irrigation and drainage, for harvesting containers, and for purposes of conveyance and storage [173]. The need to prevent losses by seepage has put focus on the use of polymeric films and membranes to line storage ponds, irrigation and drainage canals, reservoirs, and waste lagoons [174]. Because of their water impermeability, flexibility, puncture resistance, ability to suppress weed growth, and good durability, sheets of PE, plasticized PVC, and butyl rubber have increasingly used as replacements for, and supplements to, rolled earth, clay, concrete, and asphalt in the building of water impoundments and canals. Butyl rubber and PVC liners have been used as water-seepage barriers. Polymeric materials used as water barriers are usually black to provide the necessary protection against sunlight. Plastic membranes placed under concrete liners in irrigation canals help to keep seepage losses to a minimum. Thin-walled collapsible polybutylene tubing, rigid and flexible PVC, and PE pipes have been used for conveying irrigation water.

2.4.5.1 Groundwater Reservoirs

Groundwater reservoirs are supplied primarily by water percolating from the surface, and provide evaporation-free storage. Water conveyance losses from canals and ditches can be greatly reduced through reduction or elimination of seepage. Concrete linings, as well as asphalt, fiberglass-reinforced asphalt, and plastic linings, are frequently placed in irrigation canals and ditches to reduce seepage. Chemical additives that tend to deflocculate the soil are successful. If carefully selected according to soil characteristics they can reduce the infiltration capacity by causing soil particles to swell, making the soil hydrophobic, e.g., clays swell and seal soil pores to reduce infiltration rates. Storage of water in groundwater reservoirs can also reduce evaporation losses.

2.4.5.2 Surface Water Storage

Surface water, runoff from land and roofs, as well as groundwater from wells and springs, can be stored in streams, lakes, ponds, excavated reservoirs and pits, cisterns, above-ground reservoirs, and tanks. A requirement for adequate water collection and conservation is to line the excavated site of the reservoirs with concrete, sheet metal, or asphalt. Successful water harvesting requires attention not only to the collection of water, but also to the conveyance and storage of the collected water. Storage ponds or reservoirs may require soil smoothing and removal of vegetation, application of chemicals that disperse the soil aggregates and greatly reduce infiltration, or application of plastic film. Uses for stored water include irrigation, livestock, pesticide spray water, fish production, recreation, fire protection, milk house sanitation, and domestic purposes. All surface water and some well water need to be filtered from sediment (turbidity) and purified from chemicals and bacteria for domestic and milk house use, which need to meet the according sanitary standards. Water stored in the open without a tight cover and accessible to wildlife and animals must be treated for domestic use. Reduction of evaporation losses from free-water surfaces can be accomplished by: (a) minimizing the free-water surface area-to-volume ratio of reservoirs by making reservoirs deeper; (b) protectiong the free-water surface; though being uneconomical, this can be achieved by reducing the exposure of the free-water surface using films, floating plastic membranes, or floating particles.

2.4.5.3 Ponds, Lakes, and Reservoirs

Polymeric films and sheets can be used to control seepage in larger bodies of water for improved availability for plants Irrigation reservoirs are excavated and lined with polymeric sheeting made of PVC, EVA, HDPE, LDPE, PEPD, butyl rubber, or thick PE sheets [318].

2.4.5.4 Water Storage Requirements for Reservoirs

The water storage capacity of a reservoir depends on the anticipated water needs, evaporation from the water surface, seepage into the soil or through the dam, storage allowed for sedimentation, and the amount of water carryover from one year to the next. Water needs include the volume required for the intended uses and the desired depth and surface area to satisfy recreation or fish and wildlife requirements. Evaporation can be reduced by selecting sites having a small surface area and adequate depth. Sedimentation can be reduced with good vegetative cover in the watershed especially in waterways and the area surrounding the water surface.

2.4.5.5 Cisterns and Tanks

Cisterns and tanks are increasingly being used for handling corrosive aqueous solutions especially for fertilizers and herbicides; they are generally produced from glass-reinforced polyesters, although blow molding of thermoplastics has enabled larger sized vessels to become available using PP and HDPE. Such structures are suitable for water storage in rural areas and are useful in areas where the surface soil is seriously polluted, for situations where water needs are minimal, well yields are low, or groundwater quality is poor. Cisterns used for water storage are usually located on rooftops, whereas tanks may be buried below ground level or located on high ground to provide the stored water by gravity flow. Cistern and tank size and location depend largely on: the rate of water usage and availability, automation of the power source, the source of the water, and proximity to the point of use. Tanks are smaller than cisterns and provide much less water storage capacity than cisterns. Cisterns and tanks made of glass-reinforced polyesters have also been used for the storage and processing of fruit juice concentrates, wine, edible oils, and aqueous solutions on the farm. Open tanks are commonly used for livestock water.

2.4.5.6 Pipes and Hoses

Watering systems for irrigation consist of the main supply pipes which are buried, while secondary pipes feeding the water to the actual distributors are laid on top of the soil. Valves and flowmeters regulate the water supply. Polymeric pipes are being increasingly used in agriculture for drainage and irrigation to transport water from the storage facility by pipe or open channels but pipe clearly has the advantage of no contamination or loss. The improved strength and greater crack resistance of PE has allowed the wall thickness of such pipes to be reduced and their diameters increased. PE has been irradiated to produce crosslinks thus giving it improved strength. Drip irrigation for row crops uses such irradiated LDPE tubing. Polymeric pipes compete with numerous traditional material pipes with considerable success. PE pipes are being more frequently used for drainage and irrigation of soils. PVC pipes are used to transport water from the water-storage source and film or sheet can be used in channels to divert water to storage positions. The materials generally used in polymeric pipes are PE (LDPE, HDPE), PVC, and glass-reinforced polyesters. Polymeric pipes are also used for the transport of fluids because they are unbreakable and do not corrode and are more durable than cast iron or asbestos pipes, and replacing various alloys because of their light weight and ease of installation. Plastics are now being used in a variety of ways to replace metal components in different irrigation systems. PVC pipes have been used in sprinkler irrigation systems as a replacement of brass, gunmetal, or zinc alloys. Plastic hoses used in irrigation are made of PE. Flexible hoses that can be rolled up are used in spraying and sprinkling machines. Hoses reinforced with a rigid spiral are being used with machines to introduce chemicals into the soil for the protection of plants. Plastic tubing and piping are used particularly for portable and wastewater, for irrigation and drainage, and also for beverages (milk, wine, beer, cider) and various solutions (fertilizers, pesticides).

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Chapter 3
Polymers in the Controlled Release of Agrochemicals

Polymeric materials are increasingly [1] being used in controlled-release formulations of agrochemicals. Controlled release refers to the use of polymer-containing agents of agricultural activity which are released into the environment of interest at relatively constant rates over prolonged period of time to avoid the risk of the reagents being washed away by rain or irrigation. A different strategy for controlled release is based on polymer permeability or hydrolysis and degradation. Polymers have been employed either as encapsulation membranes for active reagents or as convenient supports to chemically attach the active agrochemical groups. All principal classes of polymers have been utilized in agricultural applications for the controlled release of pesticides.

3.1 Principals of Controlled Release Formulations

Agrochemicals are usually applied to targets systemically or topically by conventional means such as broadcasting, spraying, etc., which may lead locally to concentration levels that are too high or too low for effective action. High concentrations may produce undesirable side effects either in the target area that lead to crop damage, or in the surrounding environment. When concentration levels and activity decrease, additional applications may become necessary at periodic intervals to guarantee continued efficiency of controlling pests throughout the growing season. Also, administration of the active agent at a distance to the actual target may lead to ineffectiveness (Fig. 3.1a). Both cases, in addition to increasing treatment costs, will produce undesired side effects on target and environment.

During the past years, controlled release formulation (CRF) technology has emerged as a promising approach for solving problems associated with the application of agricultural chemicals. Rapid advances have been made in the use of polymers for CRFs of agrochemicals, including pesticides, growth regulators, fertilizers, and others [2–21]. Controlled release is a method by which smaller quantities of

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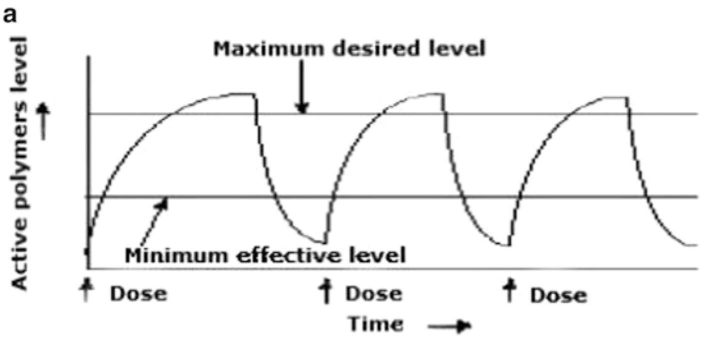
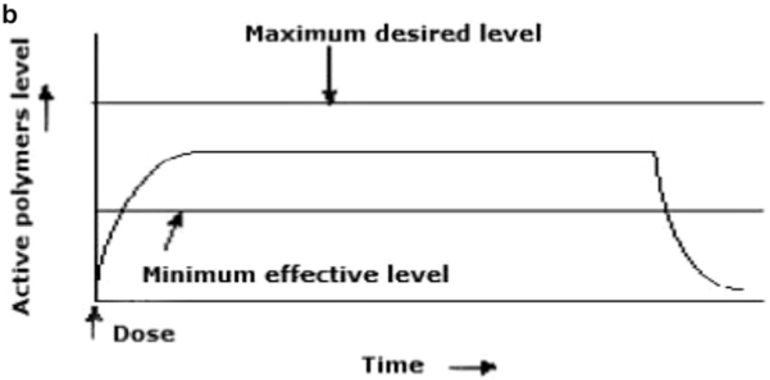
DOI 10.1007/978-1-4614-7061-8_3,



Traditional delivery system



Controlled-release delivery system

Fig. 3.1 (**a**) Traditional delivery system, (**b**) controlled-release delivery system

agricultural chemicals maintain effectiveness to a target species at a specified concentration and for a predetermined period of time (Fig. 3.1b). Thus, the aims of CRFs are: (a) to protect the supply of the active agent, (b) to allow the continuous release of the agent to the target at controlled rates, and (c) to maintain the agent concentration in the system within optimum limits over a specified period of time. This results in the use of smaller quantities of active agents and produces a great increase in specificity and persistence of the biocide. There is also promise for reducing the undesirable side effects of agrochemical losses by leaching, volatilization, and degradation. The macromolecular nature of polymers is the key to limiting chemical losses and serves primarily to control the rate of delivery, mobility, and period of effectiveness of the active components.

Controlled-release polymeric systems can be divided into two broad categories based on the concept of combining biologically active substances with polymeric materials to achieve a desired release profile. These systems are either a physical combination in which the polymer acts as a rate-controlling device or a chemical combination in which the polymer acts as carrier for the agent. The choice of the best system to release the active agent in sufficient quantity for achieving the desired biological effect with minimum biological or ecological side effects depends on many considerations. These include the biological and chemical properties of the active compound and on, its physicochemical interactions with the polymer, the nature of the polymer (thermoplastic or thermosetting), thermal behavior (T_g or T_m) and compatibility with the bioactive agent, stability of the combination, processing conditions, desired shape and size of the final product, cost, seasonal conditions, desired release rate, duration, ease of formulation and application.

3.2 Polymers in Physical Combinations of Agrochemicals

The physical combinations of active agents with polymeric materials are categorized according to different approaches for the design of controlled-release devices. The selection of a particular device to provide the controlled-release dosage depends on, the route of administration and other manufacture factors, in addition to composition and structural factors. For CRFs in which the active ingredient is adsorbed on inert carriers such as silica gel, mica, or activated charcoal, the active agent is released by desorption, and it is difficult to determine the desired release rates. In other physical systems, the release of the active agent is generally controlled by diffusion through the matrix from a membrane-controlled reservoir or a monolith, or by chemical or biological erosion for biodegradable systems. Some other devices release the active agent by a combination of both diffusion and erosion. In general, natural polymers such as starch, cellulose, chitin, alginic acid, and lignin are often insoluble in solvents suitable for encapsulation and dispersion formulations, hence they can be used after modification [22–28].

3.2.1 Encapsulations

The first approach to physical combinations is membrane-regulated formulations, in which the active agent is released by diffusion through a surrounding membrane. Ideally the active reagent encapsulated in the reservoir of a polymeric membrane or in a strip as a saturated solution with excess in suspension, allows diffusion through the membrane at constant rate without loss of activity. Alternatively, the reagent may be dispersed in a polymer matrix and released into the environment by diffusion or extraction. A variety of membrane and matrix devices are commercially available [25]. Microencapsulation is the application of a uniformly thin polymeric coating around the active agent that results in reservoir systems with rate-controlling membrane. Macrocapsules are greater than 2,000–3,000 µm. Several methods have been used for microencapsulated active agents with rate-controlling membranes, which consist of a series of steps carried out under continuous agitation: (a) formation of three immiscible chemical phases (solvent, active agent, coating),

(b) deposition of the coating, and (c) rigidization of the coating. Such methods include phase separation methods, interfacial reactions, multiorifice centrifugal and electrostatic methods. Microcapsules can be produced by solvent-evaporation processes in which the active ingredient and the polymer are dissolved in a single solvent that is immiscible with water. This solution is emulsified in water and the temperature is raised to evaporate the solvent, the polymer solidifies at the aqueous interface of microdroplets, forming a polymeric shell around a core or reservoir of active ingredient [29, 30]. Because the active ingredient must diffuse through the polymeric shell to be released, the release rate is controlled by the permeability of the microcapsule wall to the active ingredient and the inside and outside radii, and this will be a zero-order (constant) rate.

Microcapsulation may also involve initial dispersion of pesticide into a polymer matrix, e.g., PVA or a starch paste, followed by coagulation through crosslinking or adduct formation. The resulting products contain pesticide entrapped as tiny spheres within the polymer matrix [31]. Microcapsules of pesticides within a starch matrix are produced by (a) dispersing the active agent in an aqueous starch paste that has been formed from alkali-treated starch or starch xanthate, followed by crosslinking with bifunctional reagents as epichlorohydrin or by oxidation [32]; (b) dispersing the pesticide in alkali-treated starch followed by coagulation with multivalent metal ions such as $CaCl_2$ or boric acid [33]. In addition, microcapsule formulations can be made from polymers that have relatively low permeability, relatively high mechanical strength, and the advantage of being sprayable with conventional application equipment. The microencapsulation process has been used to encapsulate insecticides [34–40], e.g., methylparathion and insect pheromones that are released at a zero-order rate [41–45].

Polymeric membrane devices function by permeation of the water through the coating to form an aqueous solution of the active agent within the structure. This solution permeates from the reservoir into the environment medium. Hence, the outflow of active agents is a function of: (a) the film thickness, area, composition, and permeability to water and to the aqueous saturated solution of the active agent, (b) the solubility of the encapsulated active species, and (c) the given environment. As long as the thermodynamic activity of the agent, i.e., the concentration of the agent, is maintained constant within an inert polymer membrane, the release rate will be constant and independent of time (Eq. 3.1).

$$\mathbf{dMt/dt = k, Mt = kt} \tag{3.1}$$

This zero-order type of release is maintained if the reservoir contains a saturated solution and excess solid agent. This potential for zero-order release makes reservoir systems the most efficient of any type of controlled-release device. However, when the reservoir contains no excess solute the internal concentration falls with release of the agent, first-order release then results (Eq. 3.2).

$$\mathbf{dMt/dt = k\left(M - M\right)} \tag{3.2}$$

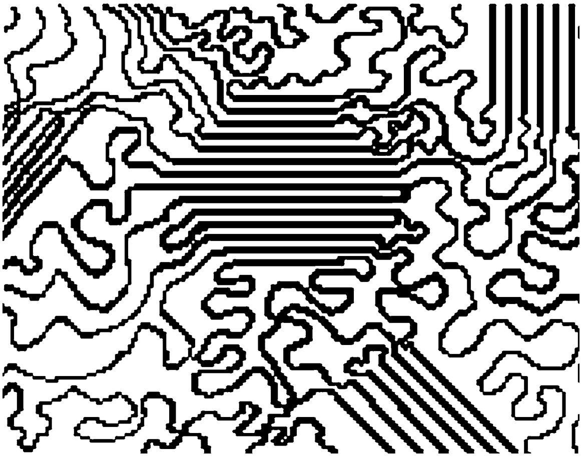


Fig. 3.2 Semicrystalline LDPE

They have the additional advantage that the active agents represent a high percentage (90 %) of the volume of the device. However, the presence of spots or pinholes that could lead to failure of a reservoir system represents its main disadvantage. This type of release applies for all geometries of the device, e.g., spheres, slabs. A wide variety of film-forming polymers are used as coating materials for microencapsulations [46] including modified cellulose and starch such as cellulose acetate [32, 47–49], carboxymethylcellulose, ethylcellulose, nitrocellulose, propylhydroxycellulose, gelatin, succinylated gelatin, and waxes. Synthetic film-forming polymers [50] are the most useful materials for controlled-release devices with rate-controlling membranes such as natural and silicone rubbers [51–53], PE [54, 55], PEVAc [56], flexible PU elastomers [57–59], polyamides [60–62], plasticized PVC [63], aminoplasts, PVA, hydrogels [64, 65], PMMA, and polysulfones.

The high permeability level of silicone rubber membranes that results in easy passage of the diffusing species, is due to the great magnitude of the diffusion coefficients resulting from the high segmental chain mobility of the rubber, and represents a disadvantage. Because of the high permeability of silicone rubber, it is desirable to select less permeable membrane materials in order to retain control of release within the delivery system. LDPE (53 % crystallinity, Fig. 3.2) has lower permeability than silicone rubber. The introduction of extremely low vinyl acetate levels into the basic HDPE structure reduces the crystallinity which approaches LDPE, but at higher vinyl acetate levels the crystallinity, stiffness, tensile strength and softening temperature decreases while toughness, permeability, flexibility, and solubility parameter increase. As a result, both the diffusion coefficient and partition coefficient change markedly with monomer ratio. Thus, the permeability is a function of PEVAc comonomer ratio. Poly(ether-*co*-urethane) membranes permeability is intermediate between silicone rubber and PE.

In microcapsules the release of the active agent is controlled by Fickian diffusion through the micropores in the capsule walls. However, the polymer phase in the microcapsule walls are often not homogeneous and have cracks and pores, therefore, in some field applications, microcapsules have been found to follow 1st order release. In microcapsules with erodible membranes, the release can be the erosion and rupture of the barrier membrane. Fick's first law states that the transfer rate of diffusing substance through unit area of a section is proportional to the concentration gradient measured normal to the solution. Thus the rate of diffusion $\boldsymbol{R_d}$ depends on the dimensional factors $\boldsymbol{A}$ and $\boldsymbol{h}$, which involve the geometry or dimensions of the device, and the diffusion factors $\boldsymbol{D}$, $\boldsymbol{C_s}$, $\boldsymbol{K}$, and $\boldsymbol{C_e}$, which involve active agent-polymer interactions (Eq. 3.3).

$$\mathbf{R_d = dM/dt = A/hD\left(C_S - KC_e\right)} \tag{3.3}$$

where $\boldsymbol{A}$ is the surface area of the membrane, $\boldsymbol{h}$ the thickness through which diffusion occurs, $\boldsymbol{D}$ the diffusion coefficient of the active agent in the membrane in centimeter, $\boldsymbol{C_s}$ the saturation solubility of the active agent in the polymer, $\boldsymbol{K}$ the partition coefficient of the active agent between the polymer and the medium which surrounds the device, and $\boldsymbol{C_e}$ the concentration of released active agent in the environment.

3.2.2 Reservoir Systems

These systems without rate-controlling membranes include agrochemical impregnated porous plastics, hollow fibers [66], foams and hydrogels [67–69], and ultramicroporous cellulose triacetate. In these devices, the rate of release is proportional to t. With these systems, a large amount of the agent is released initially, and substantially smaller and decreasing amounts are released during the last half of the life of the device.

Hollow fibers hold the active agent in tiny open tubes from which the agent escapes to the outside by diffusion through the air layer above it. Release rates of hollow fibers depend on the internal diameter for a cluster of the fiber, the number of fibers in the cluster, and the composition of the fiber. The diffusion step is rate controlling. Hollow fibers are limited by (a) an intrinsically low mass capability, (b) a high ratio of fiber weight to active material weight, and (c) the requirement for specialized application equipment. Hollow fibers are exclusively used in controlled release of insect pheromones and insecticides [70, 71]. In impregnated porous plastics such as porous PVC or PP, the active agent is retained by capillary action or physically embedded in the pores. Release also occurs by diffusion to the outside through the air layer above the liquid that fills the pores. The amount of agent released is proportional to the square root of time, i.e., the release is linear with the reciprocal of time. The rate is given by Eq. 3.4.

$$\begin{aligned}\mathbf{dMt/dt} &= \mathbf{k/t},\\ \mathbf{Mt} &= \mathbf{kt}\end{aligned} \tag{3.4}$$

Ultramicroporous cellulose triacetate is crystalline, noncrosslinked material with very large internal surface area because the pore dimensions are extremely small. It can strongly retain large quantities of liquid by capillary action where the release is diffusion controlled. Anionic and cationic hydrogels have been used containing atrazine, 2,2-dichloropropionic acid [72], and cetylpyridinium chloride [73] as sustained-release pesticidal compositions. Transport across a hydrogel membrane is largely a function of the water solubility of the agent and involves primarily the entrapped aqueous phase rather than dissolution of the agent in the polymer itself.

3.2.3 Monolithic Systems

Monolithic systems consist of a physically homogeneous dissolution or heterogeneous dispersion of the active agent within a nonporous polymeric matrix, which later are fused together. Methods used to prepare these devices include: (a) dissolving the polymeric (plastic or elastomer) matrix and the active agent in a solvent until saturation is reached, evaporating the solvent, and press-melting the residue to produce a film [74]; (b) physically blending the active agent with the ground polymer powder. The mixture is then fused together by common processes in the plastic industry, such as compression molding, injection molding, screw extrusion, calendaring, or casting into films or pellets. Alternatively, the active agent is blended with elastomeric materials in the mixing step as is done with the other additives. This uniform dispersal of the active agent in an inert polymeric matrix is the simplest and least expensive means of controlling the release of an active agent.

As the agent evaporates or is removed from the surface of the monolithic device, more of the agent diffuses out from the interior to the surface in response to the decreased concentration gradient leading up to the surface. The release rate in physically dissolved, nonerodible plastomeric or elastomeric matrix is proportional to t until 60 % of the active agent is released. Thereafter, the release rate is related exponentially to time (Eq. 3.5).

$$\mathbf{dM_t/dt = ke^{-kt}} \tag{3.5}$$

where $\boldsymbol{k}$ is constant. Thus, the release rate above 60 % drops exponentially. This first-order release is also observed in reservoirs in which the solution of active agent within the enclosure is less than saturated.

If the polymer used is soluble or degrades during its use, the monolithic device is erodible, and the active agent is released by a combination of diffusion and liberation due to erosion. Pure degradable and erodible systems release their contents by diffusion, osmotic bursting, leaching, and other controlled-release mechanisms, but in addition they chemically or biologically degrade after expiration of the useful life of the device. In monolithic erodible systems, the speed of chemical or biological erosion controls the release rate of the active agent. The release by erosion will be zero-order as long as the surface area does not change during the erosion process. This is true for slab-shaped devices, but cylindrical or spherical devices give delivery rates that decrease with time owing to decreasing surface area, even though the kinetic process providing the rate-determining step is zero-order. This results in a decreasing release rate unless the geometry of the device is carefully manipulated or unless the device is designed to contain a higher concentration of the agent in its interior than in the surface layers. In polymers which have a period of very slow erosion, the degradation rate increases rapidly later (due to autocatalysis) and the bulk then erodes over a comparatively short period. If the polymer is swellable by an environmental agent, the system involves ingression of an environmental agent into the device plasticizing the polymeric matrix, thereby allowing physically bound active agent to diffuse outward. Such systems include: starch xanthate, hydrogels, and modified lignin.

Release by erosion is a surface area-dependent phenomenon, and the general expression which describes the rate of release $\boldsymbol{R_r}$ by an erosion mechanism is (Eq. 3.6):

$$\mathbf{R_r = dM_t/dt = K_E C_0 A} \tag{3.6}$$

where $\boldsymbol{K_E}$ is the erosion rate constant, $\boldsymbol{A}$ the surface area exposed to the environment, and $\boldsymbol{C_0}$ the loading of the active agent in the erodible matrix. Polylactic acid and copolymer of lactic-glycolic acids have been used as useful erodible matrices in the preparation of controlled-release devices for pesticides [75], fertilizers, and insecticides [76–81].

The release pattern in physically dispersed nonporous plastomeric or elastomeric matrix depends on the geometry of the system, the identity and nature of the polymer, and the loading of the agent. If excess solid reagent is present, an agent-depleted zone forms at the surface of the device, which leads to square-root of time release kinetics. Thus, the release rate is proportional to time as long as the concentration of the active agent present is higher than the solubility of the agent in the matrix. Thus, these dispersed systems are similar to the dissolved systems, except that instead of a decreased release rate after 60 % of the agent has been released, the relationship holds almost over the complete release curve. For a system containing no solid agent, the concentration profiles change with time, which leads to a complex declining release rate expression.

The advantage of the ease with which dispersions can be made lowers fabrication costs and can outweight the frequently less desirable declining release rates of monolithic systems. Monolithic PVC (nonerodible) devices have been prepared from a mixture of PVC, plasticizer, and active agent, which is liquefied and followed by solidification through cooling [82]. In the monolithic dispersal of an insecticide (dimethyl-2,2-dichlorovinyl-phosphate) in PVC, the agent is released through diffusion [83, 84]. Monolithic rubber devices have also been prepared from uncured prepolymers of silicone rubbers.

3.2.4 Laminated Structures

A specialized form of the monolithic device consists of several adhered or laminated polymeric layers, which has the active ingredient impregnated in a central layer (active agent reservoir layer) between two outer plastic layers. The inner layer which contains large amounts of the active agent and is made of porous or nonporous polymeric material serves as a reservoir for the active ingredient. The outer layers which control the rate of release of the agent are usually made from a rigid polymer. The active agent can be insecticides, sex attractants, or insect pheromones [85–89]. The active agent migrates continually, due to an imbalance of chemical potential, from the reservoir layer throughout layers to the exposed surface. At the surface, the active agent is removed by volatilization, degradation, hydrolysis, or mechanical contact by insects, wind, or rainfall. The release rate is controlled by the concentration of the stored active agent and the composition and construction of the plastic layer components. Silicone rubber, PE, PVC, and nylon films are used as nonporous, homogeneous polymeric films (solution-diffusion membranes). The release through the membrane in the absence of pores or holes is achieved by a process of absorption, solution, and diffusion down a gradient of thermodynamic activity, and desorption until desorbed and removed. The transport of the active agent is governed by Henry's law and Fick's first law.

The structural and the molecular size and shape of the polymer and active agent plays an important role in regulating the release rate of agents, which include the free rotation energies (flexibility), free volume (the degree of polymer crystallinity), and intermolecular interactions that are a function of the diffusion coefficient [90, 91]. In the case of membrane transport, the permeability constant is the product of the partition coefficient and the diffusion coefficient. The partition coefficient is an additive property of the functional groups present in a molecule and is extremely sensitive to slight changes in molecular structure [92]. If the distribution coefficient of the active agent between the reservoir layer and the barrier membrane is much smaller than unity, the system approximates zero-order release (reservoir system with rate-controlling membrane) and the amount released is independent of time, i.e., the release rate can be maintained constant for extended periods of time. If the distribution coefficient is close or larger than unity, the system forms a single homogeneous polymeric film and approximates 1st order release (monolithic, physically dispersed system). If the reservoir nears depletion or initially contains less than saturated solution of active agent, the amount of agent released varies as a function of time, i.e., first-order release.

Other factors affecting the transport of active agents through the membrane include: (a) *reservoir concentration*: increasing the concentration of the active agent in the reservoir does not increase the amount of the agent release, but deviation is pronounced because intermolecular interactions of the agent molecules increase with concentration, (b) *membrane thickness*: the amount of the active agent released is inversely proportional to the thickness of the barrier membrane, (c) *polymer stiffness*: the amount transported into the membrane becomes smaller as the membrane material varies from flexible to rigid, because the reorientation of the segments of the polymer chains which is necessary to allow the diffusant passage becomes more difficult, (d) *active agent compatibility*: the active agents which have the ability to swell, soften, or aid in the dissolution of the polymer matrix, are capable of altering the polymer stiffness and hence have a pronounced effect on their diffusion that facilitate their transport through the membranes, (e) *diffusant molecular weight*: the release rate decreases with increasing molecular weight because it is inversely related to diffusivity, (f) *solubility*: the presence of functional groups in the active agent and membrane, that lead to hydrogen bonding or polarity, has varying effects on the extent of membrane solubility and hence on the release rate. As the difference of the solubility parameter, which is a measure of the cohesive energy densities of the same molecules, between the active agent and membrane decreases, the solubility of the membrane is increased which increase the distribution coefficient.

The design of the physical combination is not necessarily influenced by the structure of the active agent, i.e., there is no need for a specific structural moiety within the biologically active agent molecule. Thus, this technique has general applicability for the controlled release of a wide variety of agrochemical materials. It is also not influenced by the structure of the polymer matrix and a broad range of polymeric matrices can be used, such as plastics, rubbers, laminates, fibers, coatings, and membranes. However, in some cases there are requirements on the polymer such as (a) compatibility with the active agent in which there are no undesirable chemical or physical interactions; (b) low softening point to prevent thermal degradation of the active agent during mixing of an agent with a molten polymer; (c) low crystallinity to avoid the alteration of the release rate of dissolved materials caused by the highly ordered matrix; and (d) mechanical stability, ease of fabrication, and low cost.

Such deposit systems have been investigated and their use has attained some importance in their technical applications. The use of polymers physically combined with the active agents has been investigated for most classes of agrochemicals [93] such as herbicides [94], insecticides [95, 96] and insect sex attractants [82, 97–101], antifoulants [102, 103], fungicides, molluscicides [104–106], rodenticides, nematicides, algicides, and repellants [107] and a number of commercial products have already been introduced. However, these combinations have considerable disadvantages due to the drawbacks in their production, the limitations on their period of effectiveness, and the large amount of inert polymer employed as carrier, thus leaving residual polymer when the biocide has been exhausted.

3.3 Polymers in Chemical Combinations of Agrochemicals

In the chemical combination type of controlled release technology, the active agent is chemically attached to a natural or synthetic polymeric material either as pendant side chains through an ionic or a covalent linkage, or as part of the macromolecular backbone. Obviously, only those active ingredients that contain a structural moiety with at least one reactive functional group suitable for use as a link to the functionalized polymer can be used in this technique. Polymers which chemically bond active agents can be prepared by two synthetic methods: (a) Polymerization of monomers containing the active ingredient leads either to polymers with the active groups as repeat units in the main backbone, $-[-R-Z-]_n-$, through the polycondensation technique or to polymers that contain the active group as a pendant side chain through the addition or condensation polymerization. The major advantage of the polymerization technique lies in the ability to control the molecular design of the polymer and the active agent-polymer ratio. (b) Chemical modification of a preformed polymer with the desired active agent via a chemical bond leads to a polymer with the active group linked to the main chain as a pendant, $-[-R(Z)-]_n-$. Chloromethyl, carboxyl, thiol, hydroxyl, or amine-containing polymers have been used in this method because these compounds bear functional groups appropriate for formation of hydrolytically or biologically labile bonds, i.e., esters, amides, ureas, urethanes, and acetals.

Ionic combinations prolong the effect of the active agents, based on the principle that positively or negatively charged bioactives combined with the appropriate ion exchange resins yield insoluble polysalt resinates. The loading of bioactive groups into an ion exchange resin may be accomplished by two methods: (a) a highly concentrated bioactive solution is eluted through a bed or column of the resin until equilibrium is established (column process), or (b) the resin particles are simply stirred with a large volume of concentrated bioactive solution. In this batch process, equilibrium will occur resulting in a reduced yield, while in the column process the liberated cation is driven downwards, thus avoiding competition.

The active material, which is attached to the polymeric substrate by a definite identifiable chemical bond, is released by slow degradation of the polymer itself or through cleavage of the active agent-polymer linkage. The cleavage is often governed by the surrounding environmental reactants via hydrolytic, enzymatic, thermal, or photochemical reactions and is a function of polymer microstructure. In this combination, the rate of release of the active group from the polymer matrix and the consequent efficacy and duration of the effective action are influenced by: (1) Chemical characteristics of the active agent structure. (2) Strength and type of the active agent-polymer bonds. (3) Environmental conditions as sunlight, moisture, microorganisms effect the rate of chemical, biological, or environmental breakdown of the polymer-active group bonds. (4) Chemical nature of the polymer backbone: a nondegrading active polymer could maintain its activity for a long period of time but could create, in some cases, new environmental problems. (5) Polymer hydrophilicity: the chemical nature of the neighboring groups surrounding the active groups effects the release rates. Hydrophobic groups offer protection against rapid hydrolysis, whereas hydrophilic groups assist hydrolysis and hence result in shortening the period of protection. (6) Spacer groups: an increase in the length of the pendant side chain would enhance the hydrolysis of the bioactive-polymer bond since it would be removed from the hydrophobic backbone and less sterically hindered. (7) Dimensions and structures of the polymer molecule as governed by the degree of polymerization, comonomers, solubility, degree of crosslinking, and stereochemistry. A crystalline polymer or stereoregular is less susceptible to hydrolytic attack than an amorphous or atactic polymer and an uncrosslinked polymer is much more susceptible to hydrolysis than a highly crosslinked one. (8) Release condition: as the temperature and pH of the surrounding medium.

3.3.1 Release Mechanism

The persistence of activity of a particular formulation is determined by measuring the time until the release of the active agent fails to make up the loss. When the active agent is chemically bonded to the polymer, the most common cleavage reaction employed is hydrolysis induced by water in the surrounding environment. The kinetic expressions which describe the rate of release of active agent by the hydrolysis depend on the type of the linearity or crosslinking structure of the polymer backbone, i.e., on whether the cleavage reaction occurs on the surface of an insoluble particle or in solution. Thus, the release rate depends on the reaction kinetics, the rate of diffusion of the active agent through the polymer, and the boundary layer effects.

The heterogeneous systems, i.e., surface reactions, are similar in nature to the erodible matrix systems and zero-order release is obtained for slabs. The rate of release is also governed by the geometry and size of the active agent-polymer combination. Owing to geometry, i.e., changing of surface area as reaction proceeds, spherical or cylindrical systems have nonlinear release characteristics with time. Small particles have high surface-to-volume ratios, and hence the smaller particle, the faster the release rate. The rate of biocide release for a **heterogeneous** reaction on the surface of insoluble spherical particles follows ***zero-order kinetics*** and is given by Eq. 3.7 [108]:

$$\mathbf{dM_t/dt = nK_h 4\pi r^2 C_0} \tag{3.7}$$

where $\boldsymbol{n}$ is the number of spherical particles of average radius $\boldsymbol{r}$ at time $\boldsymbol{t}$, $\boldsymbol{K_h}$ is the reaction rate constant for hydrolysis, and $\boldsymbol{C}_0$ the concentration of active agent-polymer linkages, which is constant because, as one active agent molecule escapes from the surface, the water finds another combined active agent behind.

A water-soluble polymer undergoing homogeneous hydrolysis with no boundary layer effects follows first-order kinetics, and the reaction rate limits the release rate. The reaction and the diffusion play important roles in the hydrolysis of the polymer and the rate of release of pendant active groups follows first-order kinetics. When the active agent moiety is present as a comonomeric unit in the backbone and the release of active group occurs through depolymerization, the chemical system may be of zero order if the mechanism of release comprises unzipping of the polymer chains. For water-soluble polymers $\boldsymbol{C}$ is constant because as one active molecule is removed from the surface, another active agent-polymer bond comes in contact with water. For water-soluble delivery (**homogeneous**) systems, the rate of release of pendant active groups follows conventional first-order kinetics (Eq. 3.8).

$$\begin{aligned} \mathbf{-dC/dt} &= \mathbf{k_2C} \\ \mathbf{-dC/C} &= \mathbf{k_2dt} \\ \mathbf{ln(C_0/C)} &= \mathbf{k_2t} \end{aligned} \tag{3.8}$$

where $\boldsymbol{C}$ is the concentration of active agent per unit weight at time $\boldsymbol{t}$ and $\boldsymbol{k_2}$ is the degradation rate constant. The release rates depend on the degree of substitution, the pH of the hydrolysis medium, the geometry, microstructure, and size of the system.

However, in the case of natural polymers, the pattern of active agent release has been explained on the basis of microstructure and unequal reactivities of the hydroxyl groups on each anhydroglucose unit toward esterification. α-Cellulose fiber contains 50–70 % dispersed crystalline and 30–50 % amorphous regions and hence the esterification does not take place uniformly. The amorphous regions are preferentially esterified in nonpolar, nonswelling reaction media, and the primary hydroxyl group reacts faster than the adjacent secondary hydroxyl groups as shown from the tosylation reaction [109] and kinetic studies [110]. Thus, the density and pattern of substitution varies in the α-cellulose backbone. As the degree of substitution is increased, the hydrophilic character of the active agent-polymer combination decreases and water cannot effectively permeate the system and start the hydrolytic release of the agent.

Homopolymers in which the active agent is bonded directly to a polymeric backbone exhibit extremely slow rates of hydrolysis. Increasing the distance between the active agent and the main chain by extending the pendant chain length would enhance the rate of hydrolysis and hence the rate of active agent release. Incorporation of a hydrophilic neighboring group in the backbone would also enhance the hydrolysis of active agent [111]. Swelling of crosslinked polymers is accompanied by auto-acceleration of the hydrolysis rate.

3.3.2 Ion Exchange Resins Containing Biocides

The liberation of the active agents from ion exchange resins occurs slowly by exchange with the ions present. The rate of ion exchange depends upon various factors that can influence the releases kinetics: (a) the resin characteristics such as the type and strength of ionogenic groups, i.e., acid-base strength, the degree of crosslinking, porosity, and particle size, (b) the nature of the bioactive group, and (c) the release conditions, e.g., the ionic strength of the dissolution medium, pH, competing ions, and electrolyte concentration [112].

Quantitative releases by ion-exchange processes are mainly concerned with equilibria rather than kinetics. With the exchange of small ions, the equilibrium is reached fairly rapidly, but for large organic ions the equilibrium is reached only very slowly and kinetic considerations become important. In the exchange process one counterion must migrate from the solution into the interior of the ion exchanger, while another must migrate from the exchanger into the solution. The rate-controlling step has been shown to be diffusion either in the resin particle itself or in an adherent stagnant film. As particle and film diffusion are sequential steps, the slower of the two is rate controlling. In the case of particle diffusion, the concentration gradients in the resin particles will level out with no re-immersion, so the exchange rate will be higher than at the moment of interruption. The adsorptive forces of the ion-exchange resins can decrease the release of an ionic species through an equilibrium favoring the resin's adsorption sites, but renewal of the medium can result in very fast release [113]. With film diffusion, control of the rate depends on concentration differences across the film and these are not affected by the interruption. Hence there will be no effect on the rate. If all resin particles are uniform spheres of radius $\boldsymbol{r}$, and under conditions where particle diffusion is the rate-controlling step, the fraction $\boldsymbol{F}$ of bioactive released as a function of time is given by Eq. 3.9:

$$\mathbf{F = Q_t / Q_\infty = 1 - 6 / \pi^2 \sum_{n=1}^{\infty} exp\left(-n^2 Bt\right) / n^2} \tag{3.9}$$

where $\boldsymbol{Q_t}$ and $\boldsymbol{Q_\infty}$ are the amounts released at time $\boldsymbol{t}$ and at time ∞, $\boldsymbol{B} = \pi^2\boldsymbol{D}/r_2$ and $\boldsymbol{D}$ is the effective diffusion coefficient of the exchanging ions in the resin particle. This equation holds only for conditions of infinite solution volume obtained when a solution of contact composition is continuously passed through a thin layer of beads or in a batch experiment if the solution volume is very large. The rate of exchange will be inversely proportional to the square of the particle radius.

3.4 Polymeric Agrochemicals and Related Biocides

Agriculture needs to comply with international requirements for nutrition, environmental pollution control, health, and economic development. The rapidly growing demand for food is the main impetus behind the need for more efficient operations in both agricultural and food industrial production to afford higher yields and better quality.

Synthetic and natural polymers play an important role in agriculture as structural materials for creating a climate beneficial to plant growth, e.g., mulches, shelters, or greenhouses, for fumigation and for irrigation in transporting and controlling water distribution. However, the principal requirements for polymers used in these applications concerns their physical properties, such as transmission, stability, permeability, or weatherability, as inert materials rather than as active molecules. Starch [25–28, 114], cellulose (saw dust, bark) [115], chitin [115, 116], alginic acid, and lignin are modified natural polymers used in controlled-release systems. These have the advantages of being abundant, relatively inexpensive, and biodegradable. However, they have one significant disadvantage of being insoluble in solvents suitable for encapsulation, dispersion formulations, and chemical reactions. This generally limits the amount of bioactive agent per unit weight of polymer.

Agrochemicals are substances used to control either plant or animal life in an adverse way to improve the production of crops both in quality and quantity by reducing the competition to the crop that would interfere with harvesting [117]. Hence a major increase in the quantities of these costly and toxic chemicals will be necessary for achieving any substantial increase in farm production of foodstuffs. However, the potential hazards of agrochemicals to public health and wildlife result in stringent limitations on their use. Depending on the method of application and climatic conditions, as much as 90 % of the applied agrochemicals never reach their objective and result in nonspecific and periodic applications. Both factors, in addition to increasing the cost of the treatment, produce undesired side effects on either the plant or the environment. Controlled-release technology emerged as a means of reducing and minimizing problems associated with the use of several types of agrochemicals.

In spite of the considerable potential of using agrochemicals chemically bonded to polymeric materials, only a few have been studied in these combinations. In addition to improving the efficiency of some existing pesticides and eliminating the problems associated with the use of other conventional biocides, the chemical combination method has several advantages: (1) Prolongation of activity, by providing continuous, low amounts of biocides at a level sufficient to perform its function over a long period. (2) Reduction of the number of applications by achieving a long period of activity duration through a single application. (3) Reduction in cost by eliminating the time and cost of repeated and over-application. (4) Convenience because it converts liquids to solids and hence results in easily handled and transported materials with the reduction of their flammability. (5) Reduction of environmental pollution by eliminating the need for widespread distribution of large amounts of biocides at one time. This reduces the undesirable side effects of agrochemical losses by evaporation and degradation by environmental forces or leaching by rain into the soil or waterways because of the macromolecular nature of the agrochemical polymer. (6) Alteration or modification of the activity by extending the activity duration of less persistent or nonpersistent biocides which are unstable in an aquatic environment by protecting them from environmental degradation and hence enhancing the practical applicability of these materials. (7) Mammalian and phytotoxicity reduction by lowering the high mobility of the biocides in the soil and hence reducing their residues in the food chain. (9) Extension of herbicide selectivity to additional crops by providing a continuous amount of herbicide at a level sufficient to control weeds but without injuring the crop.

3.4.1 Polymeric Herbicides

The cultivation of plants for economic purposes requires a permanent struggle against losses from weeds, which reduce yields by competing for sunlight, water, and soil nutrients. Weeds can be controlled by many techniques such as mowing or tilling the soil. However, weed seeds remain dormant in the soil and are unaffected by these techniques. Herbicides contribute significantly to weed control by selectively killing weeds without crop damage.

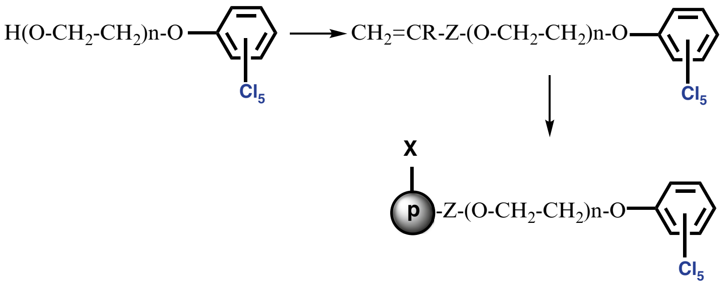
The main problem with the use of conventional herbicides to produce a desired biological response in plants at a precise time is the use of a greater amount of herbicide over a longer period than that actually needed to control the pest because of the need to compensate for the herbicide wasted by environmental forces. These forces include photodecomposition, leaching and washing away by irrigation, rain and evaporation, or biodegradation by microorganisms which act to remove the active agent from the site of application before it can perform its function. The application of large amounts of persistent herbicides is undesirable because of their frequent incorporation into the food chain. In addition, they result in a major contamination of the surrounding environment which may be hazardous for humans. For these reasons many of these persistent herbicides have been phased out. However, the application of less persistent herbicides that have greater specificity are ineffective in controlling herbs for a prolonged time because they are unstable in an aquatic environment. These herbicides have other disadvantages such as high exposure of operators and farm workers and are very costly because of the expense for their synthesis and the expense of multiple applications necessary in view of their lower persistence. Furthermore, the effective lives of conventional herbicides are shortened by leaching into subsoil and then into underground water sources and lakes, with subsequent damage to aquatic and wildlife. Hence their practical application is impossible.

Thus, the achievement of improved production of crops using smaller amounts of herbicides with little or no detrimental effect on the surrounding environment but with high biological activity is necessary for agriculture. Recently, interest has grown in using controlled-release technology that allows delivery of the herbicide to the plant at a controlled rate in the optimum quantities required over a specified time [3–10, 117–123]. In most of these formulations, the polymers containing the herbicide moieties as pendant groups were prepared by chemical modification of preformed natural or synthetic polymers.

Linear and crosslinked polymeric pesticides containing the pentachlorophenol (PCP) moiety linked via ester bonds either directly or through oxyethylene as spacer group prepared by polymerization (Scheme 3.1) [124, 125]. Investigation of the release of PCP showed that the rate of hydrolysis depends on the degree of crosslinking, the hydrophilicity, and the spacer group as well as on environmental conditions such as pH, time, and temperature.

A series of polyherbicides containing active moieties, such as 2,4-dichlorophenoxyacetic acid (2,4-D), 4-chloro-2-methylphenoxyacetic acid (CMPA), PCP, and 2,4-dinitro-6-methylphenol (DNMP), linked via ionic bonds to ammonium salt groups was prepared by the chemical modification technique (Scheme 3.2) [126]. The amounts of herbicides released from these modified polymers through ion exchange at different pH values indicated that the degree of divinylbenzene (DVB) as crosslinking agent and the hydrophilicity of the ammonium salt appear to be the main factors affecting the hydrolysis rates.

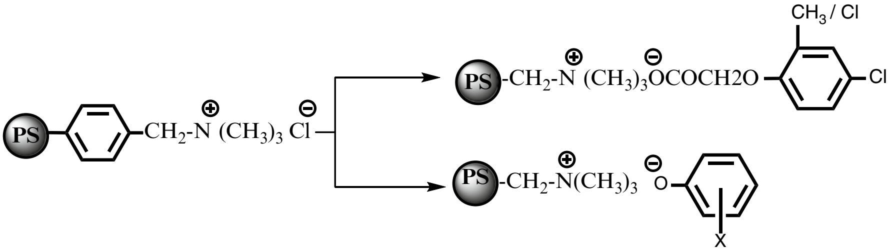
Polymeric herbicides were prepared with 2,4-D and CMPA covalently or ionically bound to oligoethylenoxylated polystyrene resins at different degrees of crosslinking. These adducts were formed by ion exchange, by nucleophilic displacement on chloromethyl groups, and by esterification of hydroxyl groups (Scheme 3.3) [127]. Herbicide release from polymer beads loaded with herbicide was monitored in aqueous solutions buffered at pH 4, 7, and 9. For covalently bound herbicides, a release of



n = 0, 1,
R = H, Me,
Z = -CO-, $-C_6H_4-CO-$,

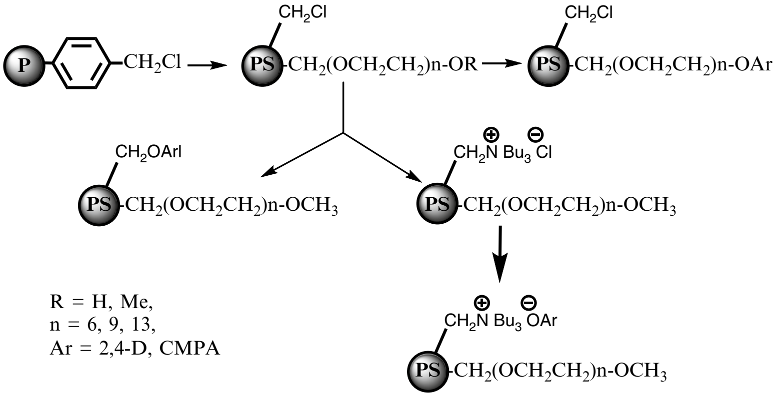
X= H-, Ph, $-CO(OCH_2CH_2)_2-OH$,
$-CO(OCH_2CH_2)_2-OH$ + 2% DVB,
$-CO(OCH_2CH_2)_2-OH$ + 5% DVB,
$-CO(OCH_2CH_2)_2-OH$ + 10% DVB

Scheme 3.1 PCP monomers and their polymers [124, 125]



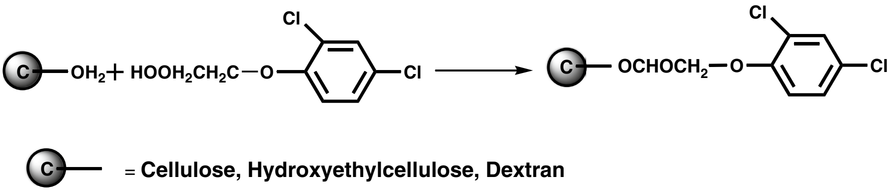
linear, 4% DVB
X = C_6Cl_5-, 2,4-$(NO_2)_2$-6-Me-C_6H_2-

Scheme 3.2 Preparation of polymeric herbicides [126]



R = H, Me,
n = 6, 9, 13,
Ar = 2,4-D, CMPA

Scheme 3.3 Synthesis of polystyrene-bound herbicides [127]



Scheme 3.4 2,4-D modified crosslinked polysaccharides [128]

20–30 % at best was detected after 3 months under acidic and neutral conditions, whereas much faster rates and higher extents of release were detected at pH 9. The ionically bound herbicide systems appeared to be less affected by pH.

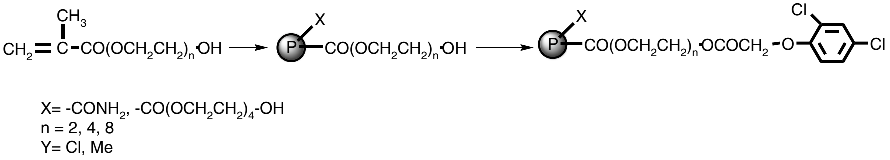
Although delivery of herbicides by polymers offers ecological and economic advantages, the major drawback to their economical use is connected with the excessive amounts of inert polymer that must be employed as a carrier. The residual polymeric material, once the herbicide content has been exhausted, becomes harmful to the soil and the plants. An attempt has been made to reduce this problem by attaching the herbicides to biodegradable polymeric carriers such as cellulose. However, these polymeric carriers will only bind an extremely low concentration of herbicide, because of their insolubility in common solvents suitable for modification. Hence, excessive amounts of such natural polymer are necessary for weed control. Further, the hydrophilic and noncrosslinking nature of the polysaccharide leads to a faster rate of hydrolytic cleavage of the pendant herbicide. Another factor is its rapid deterioration in soil by microorganism biodegradation and the subsequent destruction of the polymeric matrix within a short period of time, which leads to a shorter period of effectiveness of the herbicides.

Hydroxyethylcellulose and dextran, crosslinked by reactions with epichlorohydrin, were loaded with 2,4-D by direct esterification in the presence of carbonyldiimidazole (CDI) (Scheme 3.4) [128]. The modified polysaccharide was obtained with low loads of 2,4-D groups per glucose unit. The release rates of 2,4-D were investigated in buffered aqueous solution at different pH values (4, 7, 9) and evaluated with respect to the nature of the polymer matrix, the extent of crosslinking, and the herbicide loading. A fairly slow release, ranging from 10 % to 25 % after 4 months, was recorded under neutral and acid conditions, whereas at pH 9 an initial burst in the release profile reaching almost 90 % release of 2,4-D loading was observed.

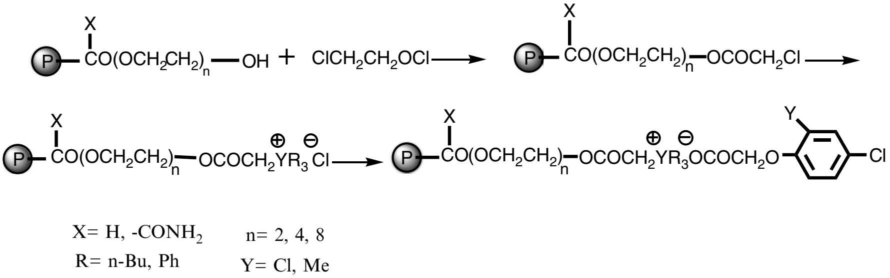
In an attempt to eliminate or at least to reduce the disadvantage of using excessive amounts of inert polymers as carriers in the controlled-release formulations of herbicides, two forms of dual combinations have been recently introduced [19, 20, 129].

3.4.1.1 Polymeric Herbicide-Water Conservation Combinations

This combination is based mainly on the concept of attaching the herbicides to polymeric hydrogels for achieving both the controlled release of the herbicide and water conservation. In addition to the primary function of these polymers to control the rate of



Scheme 3.5 Preparation of hydrogels containing herbicide [130]



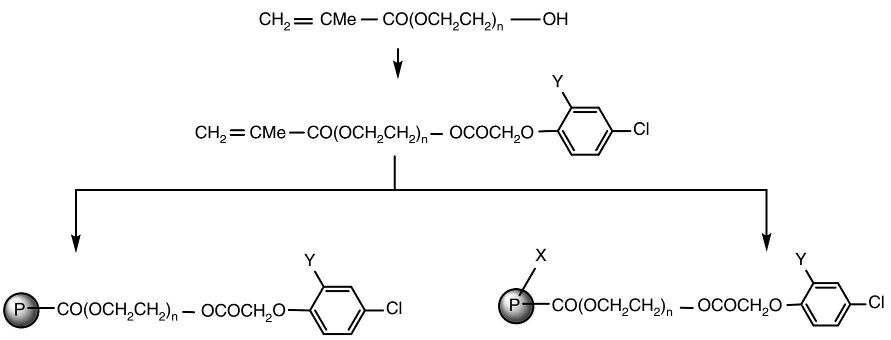
Scheme 3.6 Polyherbicides of OEGMA hydrogels [131]

delivery of herbicides, they play also an important role as soil conditioners in increasing the water retention by sandy soils. These polymers can contribute positively to change conventional agricultural irrigation, especially to alter the basic character of sandy soils.

A series of polymeric hydrogels containing systemic herbicides covalently bound to oligoether side groups and having different amounts of crosslinking agent or hydrophilic comonomer were reported and their swelling capabilities in water were measured. Kinetic release profiles of herbicides in water were tested in vitro and in experimental soils at different moisture contents. Polymeric hydrogels containing different oxyethylene oligomers were prepared by the polymerization of oligooxyethylene methacrylates in the presence of different amounts of *N*,*N*′-methylenebisacrylamide (MBAA) as crosslinking agent and hydrophilic comonomer as acrylamide (AAm) [130]. The herbicide moieties were covalently supported on the hydrogels by esterification of the side chain hydroxyl groups (Scheme 3.5). Swelling in water depends mainly on the length of the oligooxyethylene side chains, the content of hydrophilic comonomer and the degree of crosslinking. The herbicide loading produces a substantial drop in the water uptake by the polymer. The release of herbicides, investigated at room temperature in water at different pH values, is very much affected by alkalinity and the polymer structure.

In addition, polyherbicides consisting of CMPA ionically bound to hydrogels based on oligooxyethylene monoacrylates, containing quaternary onium groups were reported (Scheme 3.6) [131]. The modified polymers displayed typical moderate to strong hydrogel character. The herbicide release, performed in water medium at controlled pH and saline content, reached after 3 months a 55 % value at best.

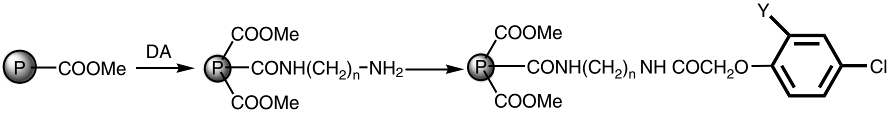
A number of oligooxyethylene methacrylates containing 2,4-D and CMPA covalently bound via an ester bond to oligoether side groups were prepared (Scheme 3.7)



Y= H, Me R' = H, Me

X= $-CONH_2$,$-CO(OCH_2CH_2)_n-OH$

Scheme 3.7 Polyherbicide derivatives of OEGMA [132]



DA= $NH_2(CH_2)_nNH_2$, n = 0, 2, 6

Y= Cl, Me

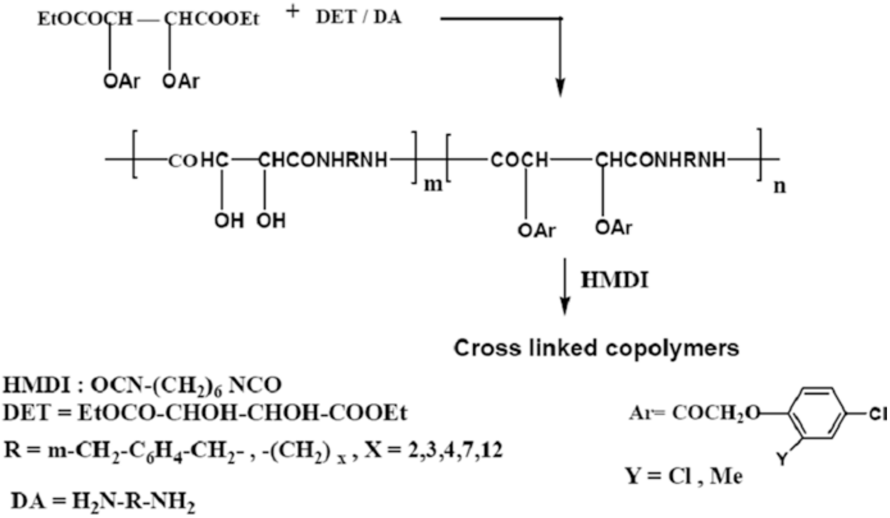
Scheme 3.8 Polyherbicides of aminated PMMA resins [133]

[132]. Two of the corresponding homopolymers exhibited a water uptake lower than 50 %. Hydrogels containing herbicides were also prepared by copolymerization of the CMPA-containing tetraethylene glycol methacrylate (TEGMA) with different hydrophilic comonomers as diethylene glycol methacrylate (DEGMA), octaethylene glycol methacrylate (OEGMA), AAm, 4-vinylpyridene (4-VP), and MBAA as crosslinking agent and tested for their release properties.

Polyherbicide derivatives based on PMMA resins were prepared by the reactions of crosslinked PMMA (2 % DVB) with hydrazine, ethylene- and hexamethylene diamine followed by modification with the acid chlorides of 2,4-D and CMPA (Scheme 3.8). The effect of the polymer structure and pH of the aqueous environment on hydrolysis rates were investigated [133].

3.4.1.2 Polymeric Herbicide-Fertilizer Combinations

To eliminate the disadvantage of using excessive amounts of inert polymers as carriers, in addition to the drawbacks of using soluble nitrogen fertilizers, the principle of dual application of a controlled-release herbicide-fertilizer combination has been



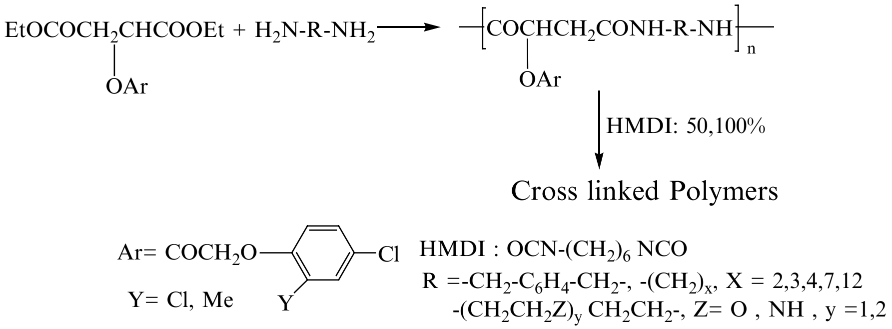
Scheme 3.9 Polyherbicides of 2,4-D derivatized tartrate [134]

introduced [17]. This principle is based on the use of appropriate condensation polymers as carriers for herbicide moieties, in which the residual products from the cleavage of the polymeric backbone act as a fertilizer. Herbicides chemically bound to various condensation polymers such as polyamides, polyureas, poly(Schiff base) s, and polyesters were reported. The herbicide release rates and the polymer backbone degradation have been investigated under various conditions. A series of polymeric herbicides were prepared by condensation of various diamines with diethyl tartrate derivatized with a conventional herbicide (Scheme 3.9) [134]. The effects of hydrophilicity of the main chain, the pH, and temperature of the aqueous environment on the rate of release of herbicides were studied.

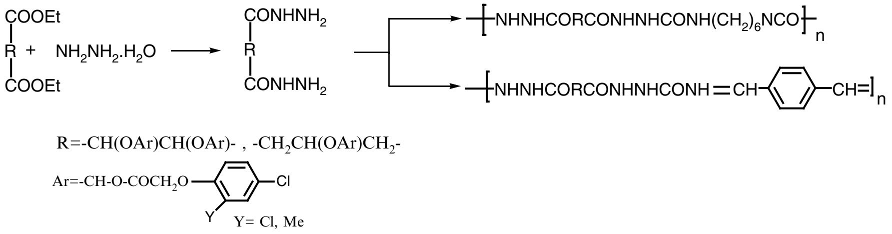
Polyamides containing herbicides were also prepared from diamines and diethyl-2-hydroxy-glutarate derivatized with 2,4-D. The effects of polymer microstructure, and the environmental conditions on the rate of release were studied (Scheme 3.10) [135].

Monomeric dihydrazides were prepared by the reaction of 2,4-D and CMPA derivatized tartrate and glutarate with hydrazine hydrate, and polymerized by reactions with HMDI to form polyureas. These monomeric derivatives were also polymerized with terephthaldehyde to form poly(Schiff base)s containing herbicide moieties (Scheme 3.11) [136]. The effect of structure and of the aqueous environment on the hydrolysis rates of 2,4-D from the polymers were investigated under various conditions.

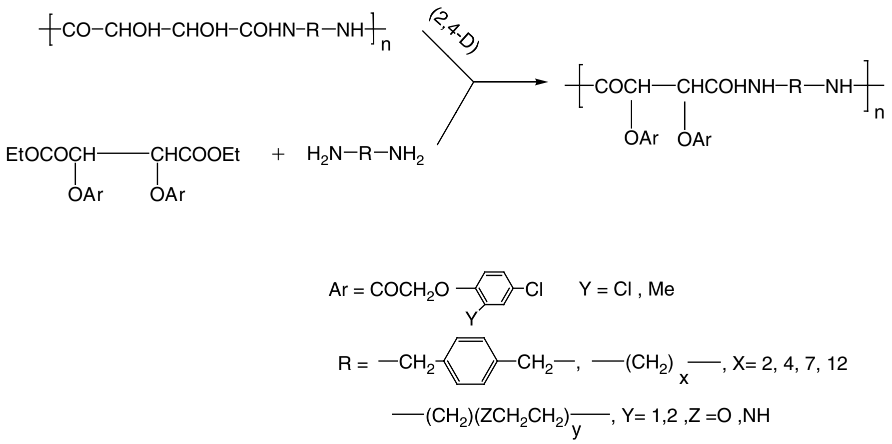
A group of polyamides containing free hydroxyl groups were prepared by polycondensations of diethyl tartrate with various diamines under mild conditions of room temperature, without using a solvent and catalyst (Scheme 3.12) [137]. Loading of these polyamides with 2,4-D was carried out by chemical modification in the presence of dicyclohexylcarbodiimide (DCC). The effects of polymer



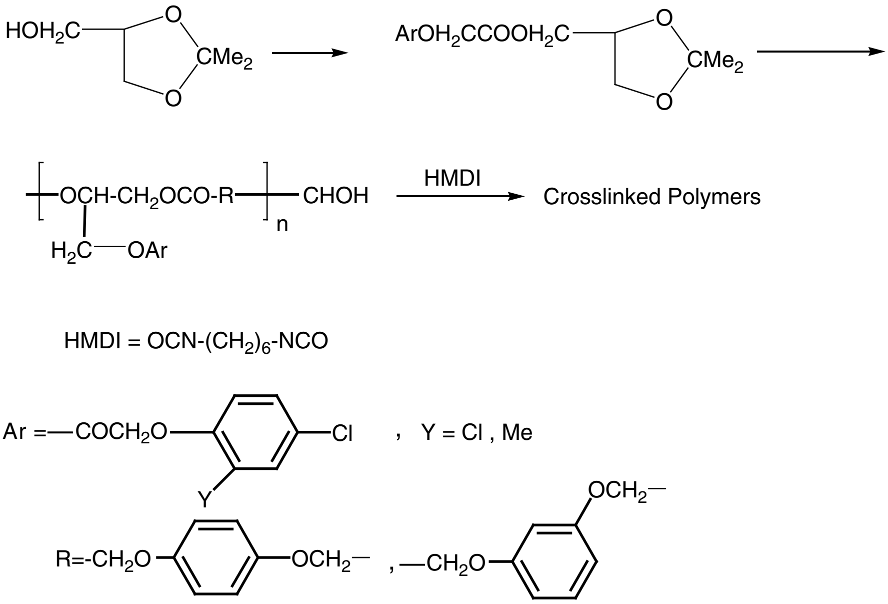
Scheme 3.10 Polyamides of 2,4-D derivatized glutarates [135]



Scheme 3.11 Polyureas and poly(Schiff base)s of 2,4-D derivatized tartrate and glutarate monomers [136]



Scheme 3.12 Polyamides of 2,4-D derivatized tartrate (Diester) [137]

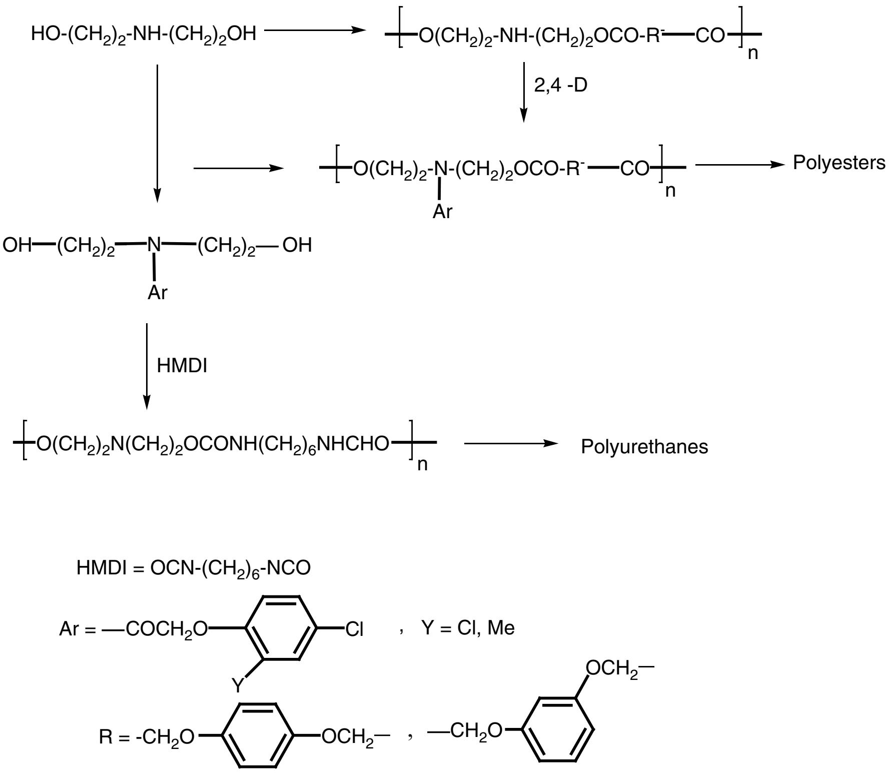


Scheme 3.13 Preparation of monomeric and polymeric Solketal herbicide derivatives [138, 139]

hydrophilicity, the medium temperature, and pH on the hydrolysis rates of 2,4-D were also investigated, although there is some uncertainly about the precise value of initial molecular weights of the polymer.

Monomeric Solketal derivatives containing 2,4-D and CMPA were prepared and polymerized by reaction with dicarboxylic acids of resorcinol and hydroquinol diacetic acids, and adipic acid to give the corresponding linear polyesters (Scheme 3.13) [138]. Crosslinked polymers were also prepared by reacting the linear polyesters with different ratios of HMDI (5, 10 wt%). The hydrolysis rates of the polymers obtained was measured as a function of pH and temperature.

Monomeric herbicides of diethanolamine derivatives were also prepared, followed by melt polycondensations with dicarboxylic acids to give the corresponding herbicide polyesters (Scheme 3.14) [139]. Solution polycondensation was used in the synthesis of the herbicide-polyurethane derivatives by the reaction of diethanolamine derivatives with HMDI. The linear polymers were crosslinked by reaction with HMDI (5, 10 %) to afford swellable polymeric materials. The preformed amine-containing polyester was also modified with 2,4-D. The hydrolysis rate of 2,4-D from the polymers was measured under different simulated conditions.



Scheme 3.14 Monomeric and polymeric diethanolamine derivatives [139, 140]

3.4.2 *Polymeric Plant Growth Regulators*

Plant growth regulators are those chemicals which beneficially affect the physiological process of plant growth and lead to an economic or agronomic benefit by protecting crops from the effects of environmental stress. They display certain advantages in agronomic improvement of plant growth such as: (a) increasing of floral initiation, flower and fruit retention, square and boll retention, root growth, tolerance, germination rate, tolerance to low and high temperatures, green pigmentation (darker), and crop yield; (b) decreasing internode length, wilting, and senescence. They include different classes: auxins (indol-3-ylacetic, 1-naphthylacetic, 4-(indol-3-yl) butyric acids), gibberellins, cytokinins [kinetin, zeatin], inhibitors [abscisic acid], and ethephon [$Cl(CH_2)_2PO(OH)_2$] (Fig. 3.3). They are used to modify the crop by changing the rate of its response to the internal and external factors that govern all stages of crop development, from germination through vegetative growth, reproductive development, maturity, and senescence or aging, as well as postharvest preservation. They are applied directly to the plant to alter its life processes or structure in some beneficial way so as to enhance yield, improve quality, or facilitate harvesting.

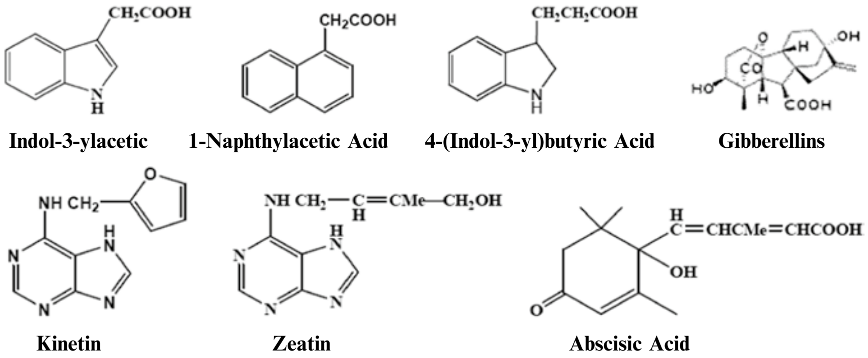
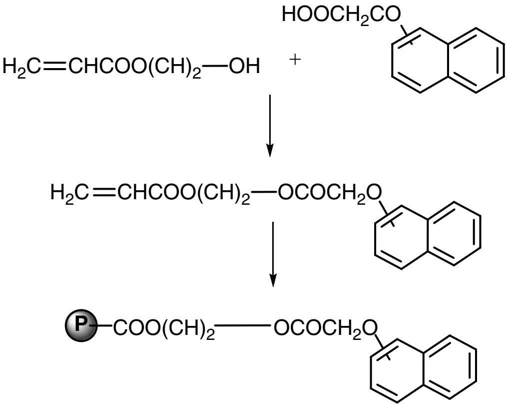


Fig. 3.3 Some plant growth regulators

The principles of controlled release have been applied to several agrochemical formulations; however, an area which has received little attention is plant growth regulators [140–146]. Polymeric plant growth regulators are characterized by the ability to release the active groups from the attached to the polymeric chain by hydrolyzing the binding chemical bond under certain conditions. The release of the plant growth regulators can be controlled by (a) external factors, such as pH, temperature, solution concentration, (b) the inherent properties of the polymer chemical structure, such as the type of the hydrolysable bond between the active group and the polymeric main chain, (c) the structure of the polymer chain, such as molecular weight, level of hydrophilicity, and content of hydrophobic groups. The polymeric controlled slow release of plant growth regulators displays certain advantages over conventional plant growth regulators due to their prolonged action, improved efficiency (wide range of effective concentrations), greater safety to nontarget organisms and the applicators. In addition, the ability of altering the solubility level and modifying the application form is of considerable interest. The biological activity efficiency of polymeric plant growth regulators is considered to solve certain problems in agriculture [147].

The microencapsulation of chlormequat stimulated and retarded the growth of tomatoes, petunias, snapdragons, and marigolds [123]. A granular slow release formulation of ancymidol impregnated with clay has been applied to potted poinsettias [142]. Chemical linkages of plant growth regulators to active polymers have also been described for the slow controlled release of the active agents [117]. Chemical combinations of cytokinins to starch and cellulose have been prepared to release the free active agent at a very low concentration over an extended period of time [140]. Maleic hydrazide derivative in combination with P(MMA-AA) has been used as slow-release plant growth inhibitor on turf [141]. Poly(L-lactic acid) and poly(L-lactoyllactic acid) are shown to promote plant growth [148]. Dry weight of duckweed and corn was more than doubled when plants were grown in media containing these polymers. However, monomeric lactic acid and poly(D-lactic acid) showed no biological activity. Increased plant biomass was accompanied by



Scheme 3.15 Plant growth regulator poly[2-(1-naphthylacetyl)ethyl acrylate] [149150]

increased chlorophyll accumulation and root growth. Promotion of chlorophyll accumulation and biomass may be due to increased ability to assimilate nutrients as plants treated with L-lactoyllactic acid showed no decrease in biomass when grown in medium that was growth limiting for control plants.

The monomeric 2-(1-naphthylacetyl)ethyl acrylate was synthesized by esterification of 1-naphthylacetic acid (NAA) and 2-hydroxyethyl acrylate and then polymerized to obtain the polymer which is potentially useful as a plant growth regulator through hydrolytic release of NAA. Copolymers with hydrophilic comonomers were also prepared by solution polymerization and the influence of their microstructure on the behavior of controlled release was investigated (Scheme 3.15) [149].

3.4.3 Polymeric Fertilizers

Fertilizers are one of the most important products of the agrochemical industry. They are added to the soil to supply nutrients to plants and promote their abundant and fruitful growth. In addition, they are important in adjusting the pH of the soil. The essential nutrients used in fertilization of soils for supporting plant growth are classified into micro- and macronutrients: (1) Micronutrients are elements that are essential to plants only at very low levels and generally function as components of essential enzymes, or may be involved in photosynthesis; these include B, Cl_2, Cu, Fe, Mn, Ni, Co, Mo, Na, V, and Zn. Some of these elements are found in primary minerals that occur naturally in soil and others occur as specific minerals or may be coprecipitated with secondary minerals that are involved in soil formation. (2) Macronutrients are those elements that occur in substantial levels in plant materials or in fluids of the plant. Thus, they are a set of biogenic elements that correspond to the physiological demands of a plant from the soil. The elements generally recognized as essential macronutrients for plants are C, H, O, N, P, K, Ca, Mg, and S. Some are obtained from the atmosphere while the other must be obtained from the soil, and commonly added to soil as fertilizer. Liming, a process used to treat acid soils, provides a more than adequate Ca^{2+} supply for plants. However, Ca^{2+} uptake by plants and leaching may produce Ca^{2+} deficiency in soil. Most of Mg^{2+} is strongly bound in minerals. Exchangeable Mg^{2+} is considered available to plants and is held by ion-exchanging organic matter or clays. The availability of Mg^{2+} to plants depends upon the Ca^{2+}/Mg^{2+} ratio. If this ratio is too high, Mg^{2+} deficiency results and may not be available to plants. Excessive levels of K^+ or Na^+ may cause Mg^{2+} deficiency. Sulfur is assimilated by plants as sulfate anions, SO_4^{2-}, and may be absorbed as sulfur dioxide by plant leaves. Soils deficient in sulfur do not support plant growth well, largely because sulfur is a component of some essential amino acids. Sulfate ion is generally present in the soil as immobilized insoluble sulfate minerals or as soluble salts, which are readily leached from the soil and lost as soil water runoff. Little sulfate is adsorbed to the soil (bound by ion exchange binding) where it is resistant to leaching while still available for assimilation by plant roots.

The three major fertilizers for crop productivity are based on nitrogen, phosphorus, and potassium which are commonly added to the soil. (a) *Phosphorus* must be present in a simple inorganic form before it can be taken up by plants. The most available phosphorus to plants is in the form of orthophosphate ion [HPO_4^{2-}]. In acidic soils, orthophosphate ions are precipitated or sorbed by species of Al and Fe. In alkaline soils, orthophosphate ions may react with $CaCO_3$ to form insoluble hydroxyapatite [$Ca_5(PO_4)_3(OH)$]. Because of these reactions little phosphorus applied as fertilizer leaches from the soil. Controlled release systems are of no benefit for phosphorus fertilizer because soluble phosphorus nutrient is immobile, not subject to volatilization losses, and the percentage of phosphorus in plant material is relatively low. Repeated applications are unnecessary since most crops require a high concentration of available phosphorus early in their growth cycle and absorb it soon after the application. (b) *Potassium*: relatively high levels of potassium are utilized by growing plants to activate certain enzymes. It also plays a role in the water balance in plants and is essential for some carbohydrate transformations. Crop yields are generally greatly reduced in potassium-deficient soils. When N_2 fertilizers are added to soils, removal of potassium is enhanced. Therefore, potassium may become a limiting nutrient in soils heavily fertilized with N_2 nutrients. (c) *Nitrogen*: the organic N_2 content in most soils is primarily the product of the applied N_2 fertilizer or the biodegradation of dead plants and animals. The applied nitrogen to soils in the ammonium ion (NH_4^+) can be oxidized to nitrate anion (NO_3^-) by the action of nitrifying bacteria in the soil. Nitrogen bound to soil humus is especially important in maintaining soil fertility. Soil humus serves as a reservoir of nitrogen required by plants. Its rate of decay and hence its rate of nitrogen release to plants, roughly parallels plant growth during the growing season. Nitrogen as one of the macronutrients is an essential component of proteins and is mostly available to plants as NO_3^- for cultivation.

Plants may absorb high amounts of nitrate from soil, particularly in heavily fertilized soils under drought conditions. N_2 fixation is the process by which atmospheric N_2 is converted to N_2 compounds available to plants by nitorogen-fixing bacteria which form so-called root nodules on the roots of leguminous plants.

$$\text{N}_2\text{-Fertilizer } (\text{NH}_4^+) \longrightarrow \text{NH}_3$$

$$\text{NH}_3 \text{ ——(Nitrosomonas bacteria)}\longrightarrow \text{NO}_2^-$$

$$\text{NO}_2^- \text{ ——(Nitrobacter, Nitrifying bacteria)}\longrightarrow \text{NO}_3^-$$

Scheme 3.16 Nitrification conversion of nitrogenous fertilizer to nitrate anion [152]

This microbially fixed N_2 is essential for plant growth in the absence of synthetic fertilizer. Such plants may add significant quantities of nitrogen to the soil, which is comparable to the amounts commonly added as synthetic fertilizer. Soil fertility in respect to nitrogen can be maintained by these N_2-fixing bacteria.

The most important and commercially available nitrogen fertilizer is urea because of its high nitrogen content (45–46 %) and relatively low cost of production, and as it effects rapid plant growth [150, 151]. Other common nitrogenous fertilizers are calcium nitrate, ammonium phosphates and sulfate, usually containing nitrogen as ammonium ions which are converted in the soil to nitrate ions. Nitrification is the conversion process of N(III) to N(V) in soil which is important because nitrogen is absorbed by plants primarily as NO_3^-. The nitrification conversion of ammoniacal nitrogen to nitrate ion takes place if extensive aeration is allowed to occur in the activated sludge sewage treatment process. Ammonia derived from nitrogen fertilizers applied in moist soil is converted by nitrification catalyzed by two groups of bacteria: (a) *Nitrosomonas* bacteria oxidize ammonia to nitrite, (b) *Nitrobacter* (nitrifying bacteria) oxidize nitrite to nitrate (Scheme 3.16) [152].

Nitrogen fertilizers, unlike others, are easily lost from soil, depending on the method of application, the soil, the climate, and nature of the crop. Nitrate ions are most readily absorbed by the crop through plant roots but they are not retained in the soil, same as ammoniacal nitrogen. Soluble nitrogen fertilizers are readily absorbed and may often result in a high concentration of nitrogen in the plant tissue to levels far greater than the actual crop requirement soon after fertilizer application. This large consumption of fertilizer results in less available nutrients for crop growth at a later stage. Larger doses of fertilizer sometimes cause damage to the crop. Thus, split fertilizer application is used for achieving better utilization of fertilizers, but it results in increased costs of fertilizer material and extra cost for its application, besides causing water and air pollution. In addition, soluble nitrogen fertilizers have many disadvantages: (1) they are highly mobile in sandy soil, especially in high rainfall conditions or under intensive irrigation, and hence their loss to drainage water by leaching without a growing crop on the land may be large [153]. (2) They may be lost from dry soil by denitrification which transforms the ionic species into gaseous N_2 and nitrogen compounds with the help of denitrifying bacteria in the soil. (3) The unused nitrogen fertilizer enters canals, lakes, or groundwater in the form of nitrate creating an environmental pollution problem [154, 155]. (4) Single heavy applications of nitrogen fertilizer may result in maximum losses of ammoniacal nitrogen to the atmosphere where release of NH_3 exceeds the capacity of the crop or soil to absorb it. (5) Toxicity of soluble nitrogen fertilizers to many crops may be produced by high ionic concentrations resulting from rapid dissolution of soluble fertilizers or from evolution of NH_3 by hydrolysis of certain salts, particularly urea.

Recently, controlled-release fertilizers have been receiving much attention because of their economic and environmental concerns. Whilst controlled-release fertilizers are economically attractive for general farm use, particularly for long-term tropical crops, their use is still limited to non-farm markets because of their higher cost to seasonal crops. However, synthetic controlled-release fertilizers are being developed for increasing the efficiency of fertilizers by controlling the appropriate dose of nutrients at the rate needed by growing plants, mainly with nitrogen sources [156–169]. A variety of investigations have been reported on the controlled release of nutrients and fertilizers, especially urea as a significant nitrogen source. The goal is to alleviate the pollution of water supplies, and to increase the efficiency of fertilizer by regulating the correct dosage of nutrient to the plant at the right time in the right place [170]. In general, controlled-release fertilizers demonstrate several advantages over the traditional type, which include: (1) reduction in the number of applications to supply nutrients in accordance with normal crop requirement, particularly for long-term tropical crops as sugar cane and orchard trees, (2) reduction of the application costs, (3) increase in nutrient uptake by crops increases crop yields, (4) reduction in nutrient loss by leaching to drainage water under heavy rainfall conditions or by irrigation water, chemical decomposition, denitrification, volatilization, large consumption, or soil fixation, (5) a reduction in environmental hazard from large applications or volatilization of soluble fertilizers, (6) decreased toxicity [171–173]. There are two common routes developed to achieve the objective of slow release characteristics of fertilizers.

3.4.3.1 Physically Controlled Release of Fertilizers

Coated fertilizers consist of nitrogen fertilizers surrounded by a barrier that prevents the fertilizer from rapid release into the environment. Urea granules coated with a rate-controlling membrane made of sulfur have been developed for field use [174, 175]. However, these coatings may crack during shipment [176]. Accordingly, fertilizer granular coated with insoluble synthetic resins, which comprise a core consisting of water-soluble fertilizer and a layer enveloping the core, have been produced. These fertilizer reservoirs give a slow release rate of nutrient to the crop by diffusion through the pores or by erosion and degradation of the coatings [157, 158]. Although the release and dissolution of water-soluble fertilizer material depend on the properties of the coating materials, the rate of release can be controlled within the desired range by the proper selection of total coating weight and multiple application for these incremental coatings. In addition to hydrogels [177] and laminated structures [178, 179], microcapsules of water-soluble fertilizers such as urea, potassium chloride, ammoniated superphosphoric acid, ammonium nitrate or sulfate, or nitrophosphate have been coated with natural and synthetic polymers. Microcapsules have been formed by the application and curing of film-forming solutions to fertilizer granules of natural rubbers [180, 181], PE, P(VC-AEs), and copolymers of dicyclopentadiene and a glyceryl ester of an unsaturated fatty acids such as linseed oil, soybean oil, tung oil, or fish oil [182]. They provide a water-insoluble coating around the fertilizer and perform a mattering function which delays and affects the slow and gradual release of water-soluble components contained in the fertilizer. Fertilizer granules have been coated with prepolymer of phenol- or urea-formaldehyde followed by curing with additional formaldehyde [183, 184].

Also granules of a soluble fertilizer are sprayed with a solution of urea and formaldehyde and then dried to form thin, insoluble film, which is claimed to give some resistance to leaching by water [185]. PU coating compositions [186] have been produced by the reaction of toluene diisocyanate with PEG followed by curing. Epoxy resins produced by the reaction of epichlorohydrin with bisphenol-A and cured with primary amines are coated onto granules [186]. Also a mixture of epoxidized soybean oil and polyester as curing agent [186] and poly (butadiene-b-methylstyrene)s [187] have been used as coatings. Of particular interest is the inclusion in the polymerization reactant medium, in addition to the base water-soluble plant nutrient material, of small amounts of a proteinaceous material consisting of casein, albumin, zein, and gelatin. These materials provide a gel-like property thereby providing protection to the water-soluble base against attack and dissolution by the water or acid present in the reaction system. Superabsorbents based on crosslinked hydrophilic PAA network are capable of holding large amount of water in the swollen state and can be useful for the release of nitrogen fertilizers through the coated barrier [188]. Their water absorbency and retention capacity depend on varying conditions like temperature, soil pH etc., or composition [189–191]. The rate of nutrient release from the coated fertilizers is determined by the composition, thickness, and crosslinking density of coating [192–194].

3.4.3.2 Chemically Controlled Release of Fertilizers

Uncoated fertilizers depend on the physical characteristics of fertilizers as low solubility, that determine their slow release. Thus, fertilizer solubility is the parameter that determines the performance of a slow-release fertilizer [195]. In this type, polyurea was prepared by covalently immobilizing urea on a poly(acryloyl chloride) matrix and used for a slow-release nitrogen fertilizer. The uncoated fertilizers have some advantages over the coated fertilizers: the homogeneous distribution of nitrogen fertilizers is, and nitrogen release rate is not dependent of the coating. However, the performance of these uncoated fertilizers, as polyurea, showed some other advantages: (1) decreased solubility, (2) not producing any toxic effect on the growth of plants as evident from the increased growth rate of plants measured in terms of average plant height and number of leaves, (3) greatly improved the release behavior and plant uptake of nitrogen, (4) minimized the loss of nitrogen through surface runoff, vaporization, and leaching, improved yield in terms of average plant size over the cultivation period [196]. The nitrogen uptake from polyurea-treated soil by the plant during the cropping season as determined by measuring the average nitrogen content in plant parts (leaves, stem, root) at different time intervals during plant growth indicates that the use of polyurea maximizes the uptake of nitrogen continuously at such a rate from polyurea that it causes accumulation of nitrogen [197, 198]. Thus polyurea increases the rate of nitrogen uptake that increases the average height and the growth of plants.

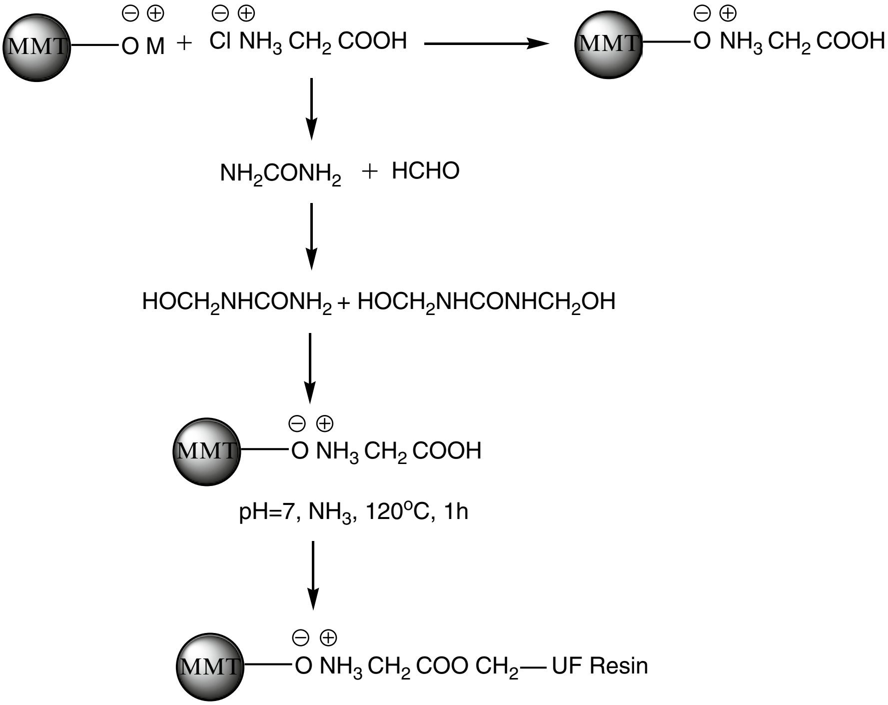
A variety of urea-formaldehyde condensates and isobutylidene diurea have been produced by reacting formaldehyde with urea [199]. Such polymers yield the available nitrogen at low rates upon biodegradation, dissolution, or hydrolysis when applied to the soil [200–203]. Urea-formaldehyde condensate contains 38–42 % nitrogen, is less hygroscopic than urea, does not have a caking tendency, and is used as slow-release nutrients for horticultural crops [204]. The idea of using ion-exchanger mixtures saturated with ions of biogenic elements as a nutrient medium for plant growing originates directly from comparison of their properties with those of natural soils [205]. Ion-exchange resins can fulfill ion-exchange functions of colloids present in soils. Selected compositions of ion-exchanger mixtures, which are analogs of natural ion exchangers present in soils, are required in order to be valuable nutrient mixtures and completely satisfy the demands of plants for nutrient elements without additional feeding during their growth.

Plants receive nutrient elements from the medium in dissolved form. For the solution to be continuously renewed, either a deliberate correction of its composition, or desorption of a new portion of biogenic elements from the solid substrate instead of those absorbed by plants, is required. Besides, it is necessary that metabolites should be removed from the solution, which can occur at the expense of their sorption with a solid substrate. The main metabolites of plant root systems are ionizing compounds H^+ and HCO_3^- that exchange with the ions of biogenic elements absorbed on ion exchangers. Ion-exchange resins can serve as a perfect buffer, retaining the composition of an intragranular solution practically constant and providing an efficient exchange of ion metabolites for ions of biogenic elements. Artificial nutrient media for plants from mixtures of cation anion exchangers saturated with K^+,Ca^{2+}, and Mg^{2+} for the cation and NO_3^-, $H_2PO_4^-$, and SO_2^{2-} for the anion exchanger phases represent composition regions corresponding to the physiological demands of plants.

In an attempt to eliminate the drawbacks of using soluble nitrogen fertilizers in addition to increasing the water retention by sandy soil as soil conditioner, clay-UF systems have been prepared by attaching UF resin as source for CRF of nitrogen fertilizer to MMT for water conservation. These materials, which are characterized by high water uptake, were investigated in greenhouse and open-field experiments (Scheme 3.17) [206].

3.4.4 Polymers in Stored Food Protection

Protection of stored food products from deterioration is made difficult by many interacting physical, chemical, and biological variables. With stored grains, the quality of the products are affected by temperature, moisture, oxygen, local climate,



Scheme 3.17 Preparation of clay-UF resins [206]

granary structure, and physical, chemical, and biological properties of grain bulks, as well as attack by microorganisms, insects, mites, rodents, and birds [207]. The presence of any of these variables can significantly diminish the food supply. Controlling pests can reduce the deterioration of stored products, because grain injury and organic litter due to insect feeding will be minimal and much of the growth of fungi and bacteria can be eliminated.

Fumigants and a few residual insecticides have been used widely to control general insect infestations [208]. Insecticides are used against such stored product insects as the confused flour beetle, the rusty grain beetle, and larvae of the black carpet beetle. The rapid degradation or volatilization of pesticides under actual use conditions greatly curtails their effective lifespan. Since stored products require protection from harvest through storage, transport, and processing to consumption, repeated insecticidal treatments are needed, though they are often difficult or impractical. In addition, some of these chemicals are encountering regulatory difficulties and may have to be withdrawn from use because they are potentially hazardous. Other problems also exist such as off-flavors, pesticide residues, and development of insecticide resistance among stored-product insects. These problems have spurred the search for improved or new pest-control methods.

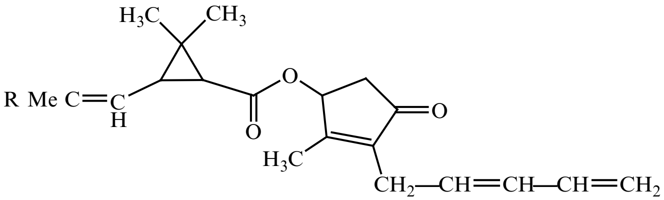


Fig. 3.4 Pyrethrin, R = CH_3, $COOCH_3$

Multilayered laminated dispensers have been used for the protection of stored food products. Such protection can help increase the food supply, which is urgently needed as the exploding population of the world is rapidly outpacing agricultural production. Insecticides incorporated into fabrics and protected by polymer multilayered structures have been used as toxicants repellents or as attractants against stored-product insects [209]. Such polymeric repellents or attractants are potentially useful in packaging containers or insect-resistant barriers for stored food products. A polymeric film containing pyrethrins and piperonyl butoxide is now being used successfully to protect packaged dried fruits [210]. Repellent chemicals, which are undesirable for use in insect control, have also been incorporated into polymeric multilayered fabrics which are potentially useful agents in preventing insect attack [211]. Pyrethrins (Fig. 3.4) are currently used to treat multilayered paper bags for holding flour and cereal products that are used for protection against insect infestations [212]. Polymer packages consists of two layers, the virgin polymer layer being in contact with the food is the active package that is able to deliver an antimicrobial agent in the food. The process of release of the polymer additives into the packaged food has been investigated. The transfer is controlled either by transient diffusion through the thickness of the package or by convection at the package–food interface and through the food as well [213, 214].

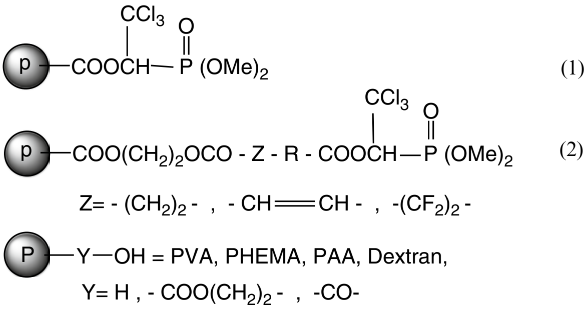
3.4.5 Polymeric Insecticides

Insects are highly destructive pests of fruits and vegetables and of many flowers. Agricultural destructive damage is caused by the feeding of the insects on seedlings, germinating seeds, and flowers. Fruits and vegetables can be protected from insect damage by spraying the insecticides several times on the fruits or vegetables during the growing season. Such spraying procedures have the disadvantage of exposing both the environment and the applicator to active compounds which do not reach the targeted fruit or vegetable crop. Polymeric insecticidal compositions with improved insecticidal properties have been used to overcome the disadvantages of using conventional insecticides for protecting fruit and vegetable crops from insect damage under the principle of CR formulations. CR technology by polymeric insecticides for crop protection must meet the goal that the toxicant must be environmentally acceptable and display delayed toxicity over a high concentration range – and offers definite economic *advantages*: (1) eliminating multiple spraying operations i.e., eliminate reapplications which may be impractical because of crop growth or adverse weather conditions, (2) better insect control than traditional spraying operations, (3) reducing the toxic hazard to both the environment and the applicator, (4) reducing the levels of insecticide present on the fruit or vegetable, (5) prolonging the effectiveness of insecticides, and (6) reducing the amount of insecticide and the cost of overspraying [215].

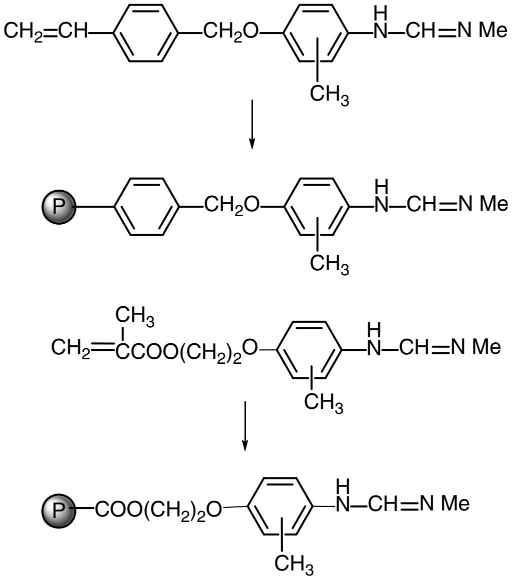
CRF of insecticides have been used in various physical forms as polymeric granules, bags, sheets, films, flowables, laminate strips, tapes, and other forms. In soil-insect control of corn, potatoes, and other crops, granular formulations are widely used as banded or broadcast applications [216]. Protecting the active ingredient of a formulation under field conditions is necessary when the local environment adversely affects the stability of the toxicant. Type and method of application of an insecticide also affects toxicity. Banded treatments of insecticide granules were shown to be more effective than broadcast treatments [217]. However, granular insecticide formulations are not just limited to soil applications [218]. Multilayered granular formulations, which are ground-up laminated materials, have been used against soil insects and for other agricultural and turf applications. Laminated polymeric membrane systems with release through the permeation process have been used to produce slow-release insecticide formulations [219]. *Pheromone* release strips for insect control and housefly and cockroach strips for release of insecticides are in commercial use. Encapsulating insecticides through CR polymeric systems has also been investigated especially for formulations of short-lived insecticides, because these display high mammalian and acute toxicity. Microencapsulated *Mirex-oil* baits have been used for CR to yield toxicants with delayed action to extend the field life of the toxicant and limit its dissipation into the environment [220, 221]. The microcapsules were not designed to be ingested by the insects but rather to be carried to their nests and broken open there. Microcapsules prepared with plastic wall materials did achieve the desired effect [222, 223]. Erodible matrix containing *Mirex* was used for treating soils for controlling termites [224]. Microencapsulation has also been used to encapsulate *methylparathion* that is released at a zero-order rate.

Another approach is to attempt to chemically modify the toxicants to yield non-toxic products which are returned to their active state by digestive or metabolic processes. The pesticide *trichlorfon*, which is toxic to fire ants, is not effective as an agent for control of the species due to its rapid action. Polymeric insecticides of the ester of trichlorfon with PAA have been prepared with hydrolytically unstable covalent linkages [225]. The preparation of polymeric esters of trichlorfon with spacer groups between the insecticide and the polymer backbone **2** have been prepared to eliminate the limited toxicity of the polymeric insecticide **1**, which is a reflection of the limited loading and slow hydrolysis of the insecticide due to the steric hindrance of the polymer backbone (Scheme 3.18).

Polymeric insecticides containing benzoin- or ethyleneglycol carbamate via hydrolysable or light-sensitive spacer groups, or containing chlordimeform bound as a salt



Scheme 3.18 Preparation of polymeric trichlorfon derivatives [225]



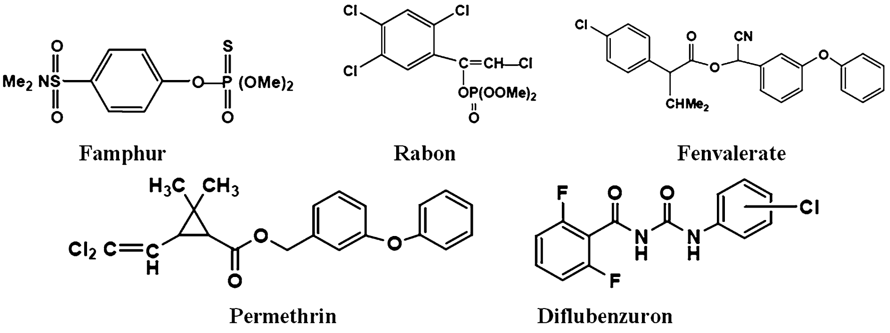
Scheme 3.19 Preparation of polymeric chlordimeform derivatives [227]

to sulfonic acid groups in the resin provide evidence for the benefits of the site-specific release principle with respect to improved efficiency and safety of insecticides in practical use [226]. Polymeric CR insecticide systems of *chlordimeform* and *N-demethyl-chlordimeform* have been used for foliar applications in cotton with tailored site-specific release characteristics. Polymeric insecticides of polymerizable *N*-(4-chloro-2-methylphenyl)-*N*-methyl(*N*,*N*-dimethyl)-formamidine derivatives were prepared, bearing either vinylbenzyloxy- or methacryloyloxyethoxy groups and used to release the insecticide chlordimeform and *N*-demethyl-chlordimeform under the particular environmental conditions on cotton leaves by hydrolytic cleavage (Scheme 3.19) [227]. Homo- and copolymers containing covalently bound pendant moieties of chlordimeform showed advantageous physiochemical properties with improved efficiency and reduced environmental and handling risks in conventional foliar applications. The release rates of the active agent from the polymers vary significantly, depending on the hydrophilicity of the comonomers and the type of formulation used.

Polymeric insecticide compositions containing tetrahydro-2-(nitromethylene) 2*H*-1,3-thiazine facilitate their application to the plant, seed, soil, or other object to be treated, storage, transport, or handling [228]. The effective dosage of active ingredients depends on many factors, including the carrier employed, and the method and conditions of application. Solid polymeric carriers may be inorganic as clays and silicates, or synthetic or natural organic resins such as PVC, PS, and polychlorophenols, coumarone resins, bitumen, waxes, periodate-oxidized polysaccharide with free carboxyl moiety as celluloses, hemicelluloses, starches (amylose, amylopectin), dextrans, dextrins, inulins, algins, and gums.

Attractants as fruit fly lures have been developed that can be used for detection, surveying, and control of the insects. Only actively fermenting lures are effective for attracting females. Plastic traps treated with *trimedlure* and *phantolid* [1-(2,3-dihydro-1,1,2,3,3,6-hexamethyl-1*H*-inden-5-yl)ethanone] as attractant to male fruit flies, have been used to enhance the duration of effectiveness against these insects [229]. Plastic traps treated with trimedlure-phantolid [methyl-(*E*)-6-nonenoate] formulations have also been used as attractants to male fruit insects [230]. Polymeric insecticides prepared from LDPE or P(PE-MA/or AA) blended with phosphorothioate derivatives have been used for the potential use of CRFs of *chloropyrifos* [*O*,*O*-*diethyl*-*O*-(3,5,6-trichloro-2-pyridyl)phosphorothioate] and *acephate* [*O*,*S*-*dimethylacetylpho-sphoramidothioate*] for insect crop protection which provide effective wireworm control in potato and sweet corn insect control. The insecticidal polymeric compositions are produced for controlling insects over a longer period of time through the moving or diffusing of the insecticides to the surface of the polymer films [215].

Polymeric insecticide compositions containing *O*,*O*-diethyl-*O*-(2-isopropyl-6-methyl-5-pyrimidinyl)phosphorothiate, *diazinon* [*O*,*O*-diethyl-*O*-2-(2-isopropyl-4-methyl-6-pyrimidinyl)phosphorothioate], or 2-(1-methylethoxy)phenolmethylcarbamate, dispersed throughout the polymer matrix as in a monolithic manner have been used in insecticidal strips for cluster fly control and for cockroach control. Through the appropriate polymeric matrix as PEP or PEVAc and attractant-porosigen agents as soy oil or lecithin, the insecticide attractant slowly migrates to the polymer surface whereby various insects that damage fruit trees and other agricultural plants are generally destroyed through contact with the insecticide [231]. Granular formulations were obtained by grinding impregnated laminated polymeric sheets containing the active ingredient into particles. Starch-encapsulated insecticide systems were also utilized for diazinon where the soluble starch is crosslinked by xanthate [232]. Such CR granules of diazinon were used to protect corn plants from injury by soil insects by preventing rootworm feeding [233]. The treated plants showed the least root damage and highest yields. Slow release formulations of *disulfoton* and *aldicarb* were effective against cotton aphids compared to the fast-release standard [234]. *Temephos* [*O*-tetramethyl-*O*,*O*-thiodi-*p*-*phenylenephosphorothioate*] was incorporated in elastomeric matrices and a diffusion-dissolution type release mechanism was established [235]. Long-term toxicant release from a plastic matrix could be achieved through a leaching process keyed to the use of a water-soluble additive whose emission led to the development of the necessary porosity in the matrix [235].



Famphur **Rabon** **Fenvalerate**

Permethrin **Diflubenzuron**

Fig. 3.5 Active insecticides encapsulated into polymers

3.4.5.1 CR of Insect Growth Regulators to Livestock

The CR technology was applied to the control of arthropod pests of livestock. An active ingredient can be delivered at a controlled rate into the circulatory system of a host animal via implanted pellets or microcapsules to affect feeding parasitic insects or ticks. A preparation of injectable microcapsules of the systemic pesticide *famphur* [*O*-(*p*-(dimethylsulfamoyl)phenyl)-*O*,*O*-dimethyl-phosphorothioate] has designed from biodegradable polymers. Systemic insect growth regulators are analogs of natural insect hormones and are active at very low levels. They are usually specific to a target insect parasite pest with essentially no activity or toxicity to the host or other nontarget organisms.

The common cattle grub is among the most destructive pests that attack cattle (Fig. 3.5). The grubs are commonly found in cysts on the back of cattle. The grubs cause irritations, causing secondary bacterial infections, and create holes in the hides. Losses at slaughter include damaged hides and reduced value of the carcasses due to trimming of the grub infested area. Bot flies, in attempting to lay their eggs on the hairs of the cattle, cause the animals to run widely (gadding). As a result, cattle do not graze properly, are difficult to handle, and occasionally injure themselves. CR technology applied to the unique problem of livestock pest control provides the potential for solving many of the problems associated with pest control agents to livestock insects [236]. A variety of CR systems have been used in livestock insect control. The sustained release of pesticides from ear tags [237] and a plastic matrix provides control of adult horn flies on cattle [238, 239]. The application of the insecticide *rabon* [2-chloro-1-(2,4,5-trichlorophenyl)vinyldimethylphosphate] in impregnated ear tags that release insecticides from a plastic matrix provided control to the more widespread problem of horn fly control.

Cattle can be protected from horn flies with ear tags containing *fenvalerate* [cyano(3-phen-oxyphenyl)methyl-4-chloro-α-(1-methylethyl)benzene acetate [240]. The use of insecticide-impregnated leg bands is equal in effectiveness to ear tags when used against horn flies [241]. An external device such as ear tags or leg bands appears to be the technique of choice for control of adult horn flies on cattle.

Such devices have been shown to be capable of delivery of systemically active compounds as in the use of *dichlorvos* [$Cl_2C{=}CHOPO(OMe)_2$, 2,2-dichlorovinyldi methylphosphate] against the cattle grub [242]. Internal implant devices appear to be a better system than tags for delivering a systemic pesticide. The bolus form, although capable of delivering a systemic insecticide, would be more appropriate for delivering a larvicide [243]. A sustained-release formulation that could be sprayed onto cattle would have advantages over both the ear-tag and leg-band systems. A sustained release spray-on formulation, from solvent-incorporated *permethrin* [3-phenoxyphenylmethyl-3-(2,2-dichloroethyenyl)-2,2-dimethylcyclopropane carboxylate] in a plastic-rubber blend is used as insect growth regulators to cattle for controlling of horn and face flies [236]. Boluses containing *diflubenzuron* [*N*-((4-chlorophenyl)aminocarbonyl)-2,6-difluorobenzamide], a chitin inhibitor, were shown to be effective in preventing the development of horn and face flies in cattle. *Methoprene* [isopropyl-(*E*,*E*)-methyloxy-3,7,11-trimethyl-2,4-dodecadienoate], an insect juvenile hormone mimic, is a nonpersistent insect growth regulator of minimal mammalian toxicity. It is effective at very low levels against the horn fly [244] and the common cattle grub [245] in drinking water [246–248] or in boluses permitting CR. 1-(8-Methyloxy-4,8-dimethylnonyl)-4-(1-methylethyl)benzene is a systemic insect growth regulator that acts on the larval stage of insects to prevent development of the adult [249]. Methoprene formulated as implantable CR pellets was successful in preventing the development of adult cattle grubs. Both types of devices of implantable CR pellets made of vicryl, a rapidly biodegradable suture material, and reservoir devices made of a slowly biodegradable polycaprolactone material provided control by methoprene of arthropod pests of livestock in cattle grubs [250].

3.4.6 Polymeric Molluscicides

Bilharzia is one of the most widespread endemic diseases in tropical countries where the spreading of cultivated areas increases. The establishment of large areas with perennial irrigation has increased the infection rate since such environments are suitable habitats to the snails which are the intermediate vectors of the parasite [251]. The fight against bilhariza is an international effort for health and economic development. Since the chemotherapy of schistosomiasis has always met with toxicity problems, the application of molluscicides for eradicating the snails has opened up new concepts in disease control by interrupting the cycle of transmission of snail-borne trematode parasites [252, 253].

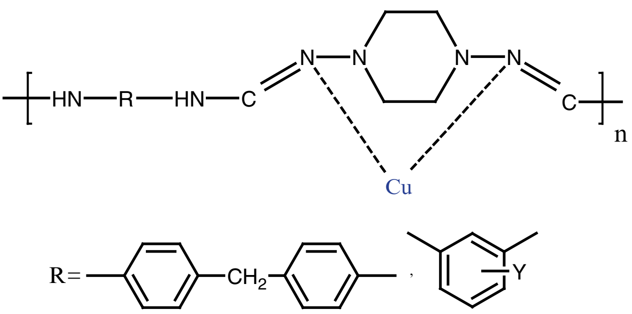
Freshwater snails and land slugs do not harm mammals directly but are alternative hosts for the *Schistosoma* parasites, the causal agent of the debilitating human disease bilharzia. Since molluscicides kill various molluscs and offer rapid means for extermination of the causative organism, a great increase in the quantities of these costly and toxic chemicals will be necessary for any substantial improvement in controlling and eradicating *Schistosoma* snails. However, the main problem with the use of conventional molluscicides for producing the desired biological response is the relatively massive dosage needed. This overkill is essential in that a lethal quantity of the toxicant must reach each target snail prior to natural detoxification processes which reduce the active concentration. However, it is not practical in most situations to maintain a continuous toxicant concentration in the treated water. In addition, such chemicals result in a major contamination of the surrounding environment and make it toxic for aquatic plants, birds, fish, and mammals, which is a serious handicap to their practical value. Furthermore, it is also difficult to achieve effective distribution of chemical molluscicides in moving water and hence multiple applications are often used. Thus more effective elimination of snails with a smaller amount of molluscicides that have little or no detrimental effect on the surrounding environment but a high biological activity is necessary for combating the bilharzia disease.

During the last years, the combination of molluscicides with polymeric materials has emerged as a new approach for enhancement and increasing the efficiency of molluscicides by allowing a continuous release of a lethal quantity of toxicant for controlling snail vectors of schistosomiasis [254]. The technique, in addition to increasing the persistence of conventional molluscicides activity, eliminates the environmental and toxicological problems associated with their use. Furthermore, it allows the possibility to incorporate an attractant and toxicant into the same polymeric matrix, so that snails are attracted by a species-specific attractant and ingest the polymers containing the toxicant.

Trialkyltins were incorporated in elastomers and showed considerable merit as molluscicides [255]. The release of the agent from elastomers for long-term snail control is based upon a diffusion-dissolution mechanism. In thermoplastics, the incorporation of a water-soluble porosity enhancing agent (porosigen) proved useful. As the porosigen leached slowly from the system, water penetration of the developing pores allowed contact, solvation, and egress of the organotin agent [256].

The physical incorporation of nonmatrix soluble molluscicides such as copper sulfate pentahydrate into PEPD elastomers [257] has been used to overcome the detoxification processes due to the combination of the copper ion with negative ions forming insoluble materials. However, the incompatibility of the copper salt with the elastomers and the high temperature of vulcanization necessary to initiate cross-linking that leads, in the presence of this salt, to degradation of the rubber are probably the major disadvantages of this physical blending. An attempt to increase the efficiency of copper(II) for the eradication of snails has been described, using ion-exchange resin as a substrate to hold copper(II) so that natural water-soluble salts would exchange away the copper(II) while the regenerable ion exchange was in a fixed accessible site (Scheme 3.20) [258].

As an active molluscicide, ethanolamine salt niclosamide (5,2-dichloro-4-nitrosalicylanilide) has been introduced by Bayer Co. under the trademark Bayluscide or Bayer-73 and used extensively in Egypt for combating bilharzia. However, the use of great amounts of this compound has led to some economic and environmental toxicity problems. Baylucide has been incorporated in elastomers such as natural rubber, polychloroprene, poly(styrene-butadiene), PEPD, and PANs,



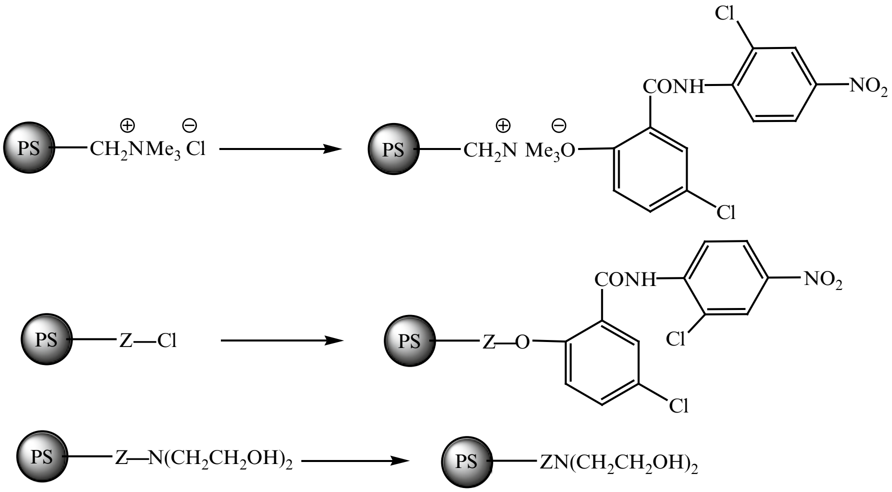
Y= 4- Me, 4- t-Bu , 5-COOEt , 5-$COOC_{16}H_{33}$

Scheme 3.20 Polymeric molluscicide of ion-exchange resins containing copper [258]

in which a diffusion-dissolution mechanism was operated for continuous release rates from pellets cut from cured sheet stock [255, 259].

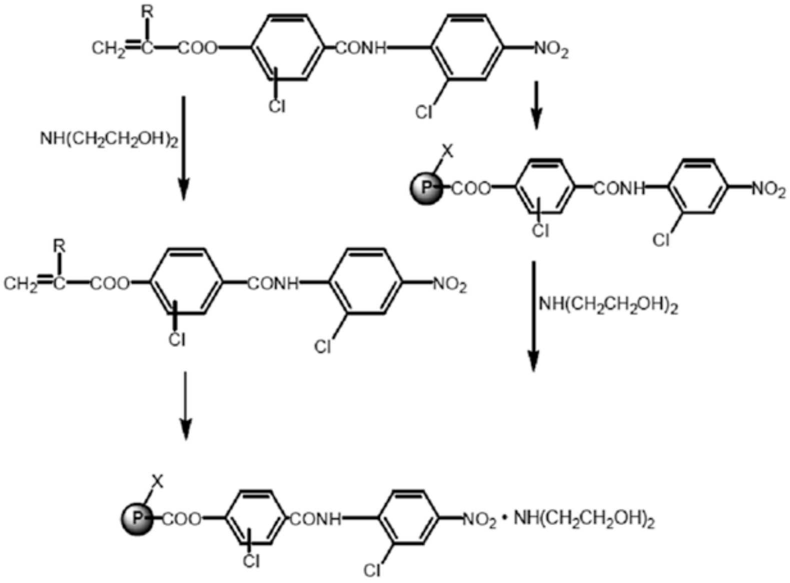
Chemical combination of molluscicides with functionalized polymers has been used in an attempt to facilitate the eradication of the snails and eliminate the side effects associated with the use of a relatively massive niclosamide dosage. Accordingly, the polymeric molluscicides containing a niclosamide moiety either via physical interaction with the diethanolamine groups of the modified polymers or through covalent and ionic bonds were prepared by the chemical reactions of the commercial polymers with Bayluscide (Scheme 3.21) [105, 106, 124]. The amounts of niclosamide released from the polymers were determined periodically under different conditions to demonstrate the relative effects of polymer structures and compositions, such as hydrophilicity, the linkage between the polymer and the niclosamide moiety, the spacer groups, and the neighboring groups, as well as the pH and temperature of the medium and the time; on the hydrolysis rates.

The hydrolytic release of niclosamide from the polymers indicated the following: (1) The hydrolysis of polymeric molluscicide containing niclosamide via ester bonds is slower than that of polymeric molluscicide containing the active moiety as a counterion associated with the ammonium salt group. This can be attributed to (a) the nature of the covalent ester groups which are more stable towards hydrolysis than the ionic ammonium salt groups and (b) the intramolecular interactions of the neighboring hydrophilic ammonium salt groups which are not modified or generated during the hydrolysis. (2) The increase in the degree of crosslinking results in decrease in the rate of exchange. However, the main drawback with the polymeric molluscicides, prepared by the chemical modification technique is their low loading with active moieties. In an attempt to obtain niclosamide polymers having higher loadings, the synthesis of the niclosamide monomers and their salts with diethanolamine followed by their homo- and copolymerizations with styrene and oligooxyethylene monomers in different ratios were carried out by a free radical technique (Scheme 3.22) [260].



Z= CO , SO_2 , CH_2 ,

Scheme 3.21 Niclosamide polymers by modifications [105, 106, 124]



R= H , Me

CH_2 ═CH—X , X = H , — Ph (1:1) , —$CO(OCH_2CH_2)_n$ OH , n = 2 , (1:1) , 4 , (3:1) , 8 (5:1)

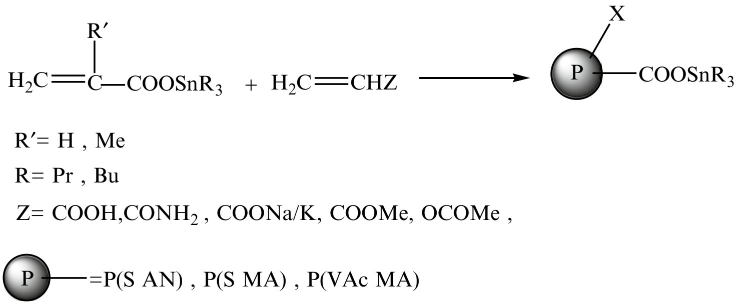
Scheme 3.22 Synthesis of niclosamide monomers and polymers [260]

3.4.7 Polymeric Antifouling Paints

Fouling is the growth of marine fouling organisms on submerged surfaces such as the bottoms of ships, submarines, buoys, sonic transmission equipment, etc. These organisms destroy the smooth regularity of the hull's surface, thereby producing surface roughness which increases the frictional resistance to the boat's passage through the water, leading to reduced speed and increased fuel consumption. They also destroy the anticorrosion coating, thus leading to corrosion damage to the surface of marine equipment and causing an increase in the weight of submerged structures. In general, antifouling toxicants are applied to surfaces in continual contact with water as protective coatings. They are designed to prevent the attachment and growth of all fouling marine organisms by continuously releasing a biocide compound at the surface of the paint.

Various principles of formulation of antifouling paints have been described that give a continuous toxic release from the paint to kill the settled organisms. These methods include the physical incorporation of the antifouling agent into the polymers or by the chemical attachment the antifouling agent to the polymer backbone via chemical bonds. However, the physical properties of the polymeric film, as chemical resistance, solubility, toughness, adhesion, and flexibility, may be varied by selection of appropriate combinations. Since the biocides are simply dispersed into the paint which is a thin film and has a large surface area, the rate of water leaching, evaporation, or migration is in excess of the amounts required to control fouling. Hence large amounts of biocide are wasted and the coating is left empty of toxin in a short period of time. Thus, the biocide concentration drops below the critical level and the coating is free to interfere with the life processes of all organisms and hence is susceptible to fouling. Furthermore, whereas the antifouling action is needed mainly when the ship is in port, because the fouling organisms are at the sea shore, a very high percentage of biocide material is released when the ship is moving, owing to the turbulent conditions around it. In recent years, the development and application of organometallic polymers with controlled-release properties as antifouling paints have received considerable interest because fouling is one of the most serious problems in the marine environment. Polymeric antifouling paint may be applied by spray-painting onto a steel plate previously coated with a protective anticorrosive paint based on an aluminum-pigmented, bituminous resin. The adhesion of the film was excellent and the antifouling action is highly effective against visible macrofouling organisms.

Elastomeric antifouling formulations have been prepared by the physical combination of an elastomer such as natural rubber or poly(styrene–butadiene) with organotin compounds and used to overcome the drawbacks of the conventional antifouling paints [261]. These antifouling rubbers are used as a solid sheet formulation attached through an adhesive system to the object to be protected and operate through a diffusion-dissociation mechanism. They have eliminated the major disadvantages of the antifouling paint films such as (a) the easy damage of films due to their low physical strength, (b) the requirement of a subcoating barrier to prevent



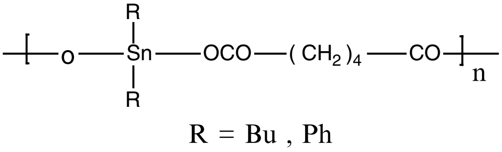
Scheme 3.23 Synthesis of polymeric antifouling biocide [262]

electrolytic attack on metal substrates, by using ionically active agents. However, their use is associated with various problems regarding adhesion and sealing. In addition, conventional toxicant salts of mercury and lead impart no effective antifouling property when used in this system because they do not release upon immersion.

Film-forming biocidal polymers useful in marine antifouling compositions selected from trialkyltin groups chemically bound to homo- and copolymeric chains of "organotin acrylate" were prepared by various methods such as (1) the polymerization of trialkyltin acrylate or methacrylate monomers, (2) chemical modification of functionalized polymer as P(S-MA) with bis(tributyltin) oxide, (3) grafting or blending of the polymers, e.g., PVC, with trialkyltin acrylate (Scheme 3.23) [262].

A more recent important development in this field to decrease the rate of antifouling decay is the synthesis and use of polymeric materials containing organometallic toxicants chemically bound to the polymer backbone to provide a relatively low dose level of biocides and hence to extend the effective lifetime of antifouling protection [263–273].

Polymeric antifouling paints have considerable potential advantages in applications as biocidal marine coatings, such as: (i) allowing the use of highly water-soluble antifouling agents; (ii) incorporating more than one biocide group in order to be highly toxic to a wide range of marine organisms; (iii) decreasing wasted biocide amount and not toxic to human when handled with normal care either in the solid form or in solution; this is due to the fact that the toxic groups are chemically bound to the polymer and normally are not released until the polymer is immersed in seawater; (iv) degrading to nontoxic compounds, i.e., not dangerous as pollutants of the marine environment because the toxic trialkyltin compounds released from the polymers are readily degraded to harmless tin salts in the seawater; (v) no discoloration in water polluted by sulfide; (vi) noncorrosive to steel and hence these polymers can be used for protective coatings without the need for extensive barriers or anticorrosive coatings on steel; (vii) preventing surface roughness which leads to reduced speed and hence decrease fuel consumption; (viii) increasing period of effective action, i.e., more effective in preventing the attachment of fouling organisms to immersed surfaces because the toxic release rate (i.e., the rate of release of



Scheme 3.24 Tin antifouling polymers [286]

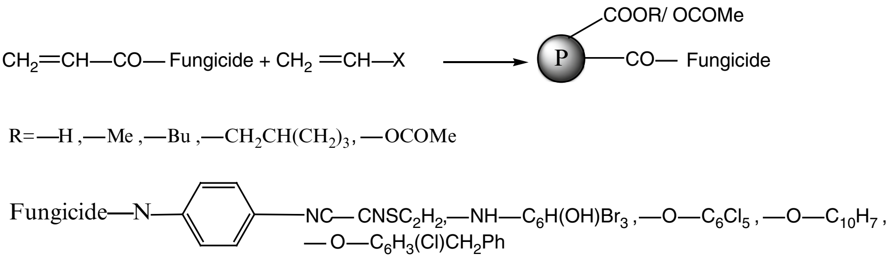
the toxic organotin groups) can be controlled to a minimum level, the toxic concentration of active groups in the trialkyltin polymer can be adjusted to be quite high, and the toxic release is not affected by allowing the paint surface to dry out, as in docking procedures. These properties have considerable importance for shipping since the interval between dry-dockings can be extended for periods of up to 3 years and since repainting is not essential during intermediate dockings.

The duration of the effective action of polymeric antifouling agents is influenced by factors such as the structure and the properties of the polymer backbone and the bond linking the polymer to the active agent. The most reported antifouling polymers are organotin-PUs [274] and organotin-polymers or copolymers which contain the trialkyltin carboxylate groups either as pendant substituents or as a part of a polymer backbone [275–283]. For example, a crosslinked antifouling polymer with a variable density of the crosslinker has been prepared by the reaction of the carboxy groups of the partial tin-esterified polymer with epoxy monomers [284, 285], as shown in Scheme 3.24. Poly(carboxystannyloxcarboalkylenes) have also been prepared by the interfacial polycondensation technique [286].

These polymers have an antifouling action due to slow hydrolysis of the organometallic carboxyl groups. However, the polymers with arsenic and mercury are very effective antifouling agents, but they are not used to any extent as toxic agents in marine antifouling coatings because of their effect on the environment.

3.4.8 *Polymeric Fungicides in Wood Preservation*

Fungi can infect plants and cause serious damage in agriculture, resulting in critical losses of yield, quality, and profit. Fungicides are chemical compounds or biological organisms used to kill or inhibit fungi. They are used to fight fungal infections in agriculture and animals by either contact, translaminar or systemic [287]: (a) *Contact fungicides* are not taken up into the plant tissue, and only protect the plant where the spray is deposited; (b) *translaminar fungicides* redistribute the fungicide from the upper, sprayed leaf surface to the lower, unsprayed surface; (c) *systemic fungicides* are taken up and redistributed through the xylem vessels to the upper parts of the plant. Most fungicides can be either in a liquid form or in powdered form. Sulfur is a very common active ingredient for more potent fungicides. Fungicide residues have been found on food for human consumption, mostly from postharvest treatments [288]. Some fungicides are dangerous to human health, such as vinclozolin – its use has been disbandoned [289]. However, some plants and other organisms



Scheme 3.25 Monomeric and polymeric fungicide [294, 295]

have chemical defenses that give them an advantage against microorganisms such as fungi. These active ingredients can be used as *natural fungicides* which include: tea tree oil, cinnamaldehyde, cinnamon essential oil [290], jojoba oil [291], neem oil, rosemary oil, milk [292], *Ampelomyces quisqualis* AQ10, CNCM I-807

Films of poly(pentachlorophenyl acrylate/methacrylate) have been allowed to undergo exchange reactions with amino- or hydroxyl-triphenyltin benzoates and the release of tin compound was assessed when the films were immersed in aqueous media [293]. Organotin polymeric films prepared contained pendant triphenyltin moieties provide an array of fungicidal and antifouling effects useful for a number of applications including water sterilization. Organotin polymers must have good film properties and release of tin compounds [293]. Polymeric fungicides of acrylates and chain-extended (2-fungicidalethyl) acrylates of 1*H*-2-(4′-thiazolyl)benzimidazole [294], pentachloro-phenol, 3,4,5-tribromosalicylanilide, 8-hydroxyquinoline, and 2-benzyl-4-chlorophenol were prepared by homo- and copolymerization with acrylic monomers (MMA, *n*-butyl acrylate, vinyl acetate, 2-ethylhexyl acrylate). In addition, terpolymers of pentachlorophenyl acrylate, 3,4,5-tribromosalicylanilide acrylate, and 2-pentachlorophenylethyl acrylate were also prepared. These polymeric fungicide coatings containing chemically bonded fungicide showed fungicidal activities (Scheme 3.25) [295].

Wood, as one of the most important natural resources, supplies structural material for many objects necessary to everyday life. Wood, hard or soft, can be successfully used in manufacturing windows and doors, furniture, and wood floors. The hard woods have generally higher density and modulus than soft woods resulting in a heavier and stiffer product. It is important to modify wood to improve wood properties as strength, appearance, resistance to penetration by water and chemicals, and resistance to decay.

3.4.8.1 Wood–Polymeric Antifouling Formulations

Wood can be modified by treating with organic biocides which have low solubility in water and their organic solution can be dispersed in water using surfactants to stabilize a mostly aqueous liquid-in-organic liquid emulsion. Controlled release formulations of antifouling moieties have been used for the protection of wood against biodegradation [296–298]. They are designed to permeate the entire body, thereby protecting the exterior as well as the interior, and hence to minimize environmental hazards and improve other mechanical properties of the wood at the same time. The long-term protection of wood against microbiological decay can be achieved by impregnating with a solution of a mixture of vinyl biocide monomer as tributyltin-methacrylate, comonomer as glycidylmethacrylate, and initiators and then heating it to initiate a copolymerization reaction within the impregnated wood. As a result, the accessible voids of the wood are impregnated with polymer and hence the amount of water that can be absorbed by the wood is decreased, thereby preventing the growth of marine organisms which cause rotting. It minimizes the alternate swelling and shrinking of wood and thus increases its mechanical and the dimensional stability in water. The treatment of wood with biocide chemically bound to the polymer chain also decreases the leach rate of the toxic moiety and hence increases its service life while ensuring minimal impact on the environment. In addition to in-situ polymerization, grafting of the polymeric biocide to wood by the reaction between the hydroxyl groups of wood and the functional groups in the polymer has also been described [297]. Polymeric alkylpyridinium salts acting as antifouling and anticholinesterase agents show hemolytic and cytotoxic activities against susceptible marine algae, and inhibitory effects on the proliferation of wood decay fungi. Their hemolytic activity is due to their detergent-like structure and behavior in aqueous solutions [299].

Fungicide-containing polymeric nanoparticles were introduced as a new way to introduce organic wood preservatives into wood products [300]. Polymeric nanoparticles from PVPy, PVPy-10 % or 30 %-St, containing fungicides such as tebuconazole and chlorothalonil were used to protect the treated wood against fungal attack by a common brown rot and white rot wood decay fungus, at low concentrations [300, 301]. The advantages of using polymeric nanoparticles as carrier include: (1) It permits biocides with low solubility to be introduced into wood with water. (2) It serves as a “protected reservoir.” (3) It gives protection to the biocide against potential microbial or other degradation processes prior to release. (4) It serves as a diffusion-controlled release device. It extends the range of biocides introduced into wood using aqueous methods, wood treated requiring lower amounts of organic biocide, and greater longevity for treated wood. (5) Hydrophobic carriers have slower release rates, i.e., deliver less efficiently into wood than faster-releasing hydrophilic polymeric nanoparticles [300].

3.4.8.2 Wood–Polymeric Insect Repellent Treatments

Wood is susceptible to many forms of degradation, especially when it is exposed to fungi and insect species as termites, powder post beetles, and carpenter ants which are wood-destroying organisms. This was the original idea behind the development of wood preservatives by destroying wood-insects, and various chemicals have been used for wood treatment. The chemicals used extensively for wood protection and as insect repellents for wood preservatives include: pentachlorophenol, arsenic solutions, and "*creosote*" which is coal tar and has a high level of effectiveness as a wood preservative and exhibits a high resistance to insects. The composition of a typical creosote is: phenols, *o*-, *m*-, *p*-cresols, *o*-ethylphenol, guaiacol, 1,3,4- and 1,3,5-xylenol, creosol and homologs. Arsenic solutions for resisting rot and decay are prepared by the addition of ammonia, copper, and chromium resulting in chromated copper arsenate, ammoniacal copper arsenate and acid copper arsenate. The effectiveness of wood treatment against wood-destroying organisms is dependent on the characteristic of treatment i.e., the ability of the chemical to penetrate to the heartwood of the timber. The problem of pests is attributed to the use of untreated wood materials that increases insect populations, such as those of the pine shoot and the long-horned beetle, against which insect repellents such as methyl bromide have been used as fumigant. Potential health hazards in using wood treatment as an insect repellent have to be taken into consideration. The use of acid copper chromate solution as an insect repellent in wood preservatives for residential purposes is restricted being a human carcinogen.

3.4.8.3 Wood–Polymer Composites

As an attractive group of structural materials wood–polymer composites are generating increased interest in many applications. As organic-organic composites they contain wood as natural material associated with a wide range of synthetic polymers in various proportions to produce molded objects with the structural integrity and workability of wood. Woods itself is a cellulose fiber-reinforced composite that consists of cellulose fibers dispersed in lignin matrix. The hydrogen bonds and other linkages in cellulose provide the necessary strength and stiffness to the fiber, while lignin is responsible for most of the physical and chemical properties. The natural agrofibers used as reinforcing phases include cotton, flax, hemp, jute, kenaf, ramie, sisal, coir, and wood fibers which are obtained by the chemical treatment of saw mill chips, sawdust, wood flour or powder, pulp and wood residues (Kraft process) that removes the lignin and low-molecular-weight waxes. The most common sources of wood feed stocks suitable for wood–polymer composite production are: (a) primary wood wastes from saw mills, (b) secondary wood wastes generated from wood products, as furniture, cabinets, doors, and (c) postconsumer wood wastes from construction and demolition debris of packages, crates, and pallets [302]. However, binder matrices for these fibers use both thermosetting as phenolic, epoxy, polyester resins and thermoplastics as PE, PP, PVC, and PS. Thermoplastics are less expensive in processing than thermosetting composites manufactured into complex shapes. Wood flour-thermoset (Bakelite) composites, in which waste wood is mainly used, are considered environmentally friendly and low-cost alternatives for inorganic-organic composites. Thus, wood makes excellent functional filler, but within limits of the heat used to melt and process polymers, and with great care since wood has an absorbance tendency for moisture.

Wood–polymer composites are claimed to be superior to natural wood and have several advantageous features: (1) natural abundant, cheap and renewable agrofibers,

(2) light weight, nonabrasive, biodegradable products, (3) products with high energy recovery, (4) good acoustic and thermal insulating properties, (5) resistance to rot and insects, (6) longer product life and less maintenance requirement, (7) increased product rigidity and stiffness but with reduced impact strength, (8) easy workup by current tools and fastening techniques, (9) easily pigmented products during processing for long-lasting color, or painted after installation, (10) production from completely recycled postconsumer polymeric waste and wood fiber scrap as from furniture or window producers, (11) biodegradability, flammability, moisture sensitivity, UV-light degradability [302].

3.4.8.4 Properties of Wood–Polymer Composites

In wood–polymer composite, individual wood fibers are encapsulated in a continuous plastic matrix which serves to protect the wood from the environment. The plastic stabilizes the wood fibers against UV light and other environmental factors, and prevents their absorption of moisture that would lead to swelling, de-lamination, and fungal decay [303]. These composite products are not changed with humidity variation, and are characterized by low linear thermal expansion. Consequently, these composite products exhibit significantly less mold shrinkage than plastics. Wood-filled PVC is gaining popularity because of its balance of thermal stability, moisture resistance, and stiffness [304, 305]. Several industries include coextruding wood–polymer composites with PVC that can be painted on the outside layer for increasing durability [306], and with a foamed interior for easy nailing and screwing [305].

Wood–polymer composites increase the stiffness of objects sufficiently for certain building applications. However, they have moduli of elasticity less than that of wood, but with increasing content of wood in the composite product, the tensile strength decreases, flexural strength increases, melt index decreases, and notched impact energy increases [303]. Wood particle size has an effect on the property performance of wood–polymer composite products. With increasing wood particle size in composite products, melt index, tensile elongation, and notched impact energy increases but unnotched impact energy decreases, while flexural modulus and strength increase for smaller particles.

3.4.8.5 Applications of Wood–Polymer Composite Products

The wood–polymer composite industry has the greatest growth potential in building products that have limited structural requirements and the materials selected depend very much on the intended end product and cost, availability, market value, and product performance requirements. The main composite product is decking or splintering [304]. Other areas of activity are outdoor furniture such as picnic tables, park benches, naturetrails/walkways, fencing piers, boardwalks, window and door profiles, automobile components, and pallets [307]. Commercial use of wood–polymer composite includes wood flour-filled PVC for flooring tiles and wood flour-filled PP extruded in thin sheets. The use of natural fiber-reinforced thermoplastics in interior decorative, structural, and furniture applications offers technology for production of profiles suitable as decorative moldings and trimmings. Wood–polymer composite sleepers are presently being assessed to replace wooden sleepers for railroad cross-ties [302]. They are used as planks for front porches, siding [308], and roof shingles with a class fire rating made from natural fibers and PE. They replace treated timber currently used to support piers and absorb the shock of docking ships. Other products include flowerpots, shims (thin washer or strip), cosmetic pencils, grading stakes, tool handles, hot-tub siding, and office accessories [304].

3.4.9 Polymeric Antimicrobials

Antimicrobial agents are those materials capable of killing pathogenic microorganisms, and have gained great interest due to their potential to provide quality and safety benefits to many materials. They are used for the sterilization of water, as food preservatives, and for soil sterilization. However, they can have the limitation of residual toxicity even when suitable amounts of the agents are added [309]. Antimicrobial polymers, as a class of polymeric biocides, have the ability to inhibit the growth of microorganisms such as bacteria, fungi, or protozoans. They can enhance the efficacy of some existing antimicrobial agents and minimize the environmental problems accompanying conventional antimicrobial agents by reducing the residual toxicity of the agents, increasing their efficiency and selectivity, and prolonging the lifetime of their activities. Antimicrobial polymers are made by bonding active moieties to the polymeric material on the molecular level, and can be specified for rapid bacterial control or be made suitable for less-demanding applications. They kill bacteria via different means: by direct binding through adsorption of the cationic antimicrobial polymer onto the negatively charged bacterial cell wall, leading to the disruption of the cell wall and cell death, or by depleting the bacterial source of food preventing bacterial reproduction [310, 311].

Polymeric antimicrobials are produced by attaching or inserting conventional antimicrobial agents onto a polymer backbone via chemical linkers by different techniques: (1) Polymerization of antimicrobial monomers involves covalently linking antimicrobial agents that contain functional groups such as hydroxyl, carboxyl, or amino groups to a variety of polymerizable monomeric derivatives. The functionalized polymer may be prepared by the polymerization of functionalized monomers as vinylbenzylchloride, MMA, 2-chloroethylvinylether, acrylic acid, and maleic anhydride to form the homo- or copolymers. The antimicrobial activity of the active agent attached to the polymer depends on how the agent kills bacteria, either by depleting the bacterial food supply or through bacterial membrane disruption and the kind of monomer used. Antimicrobial homo- and copolymers prepared

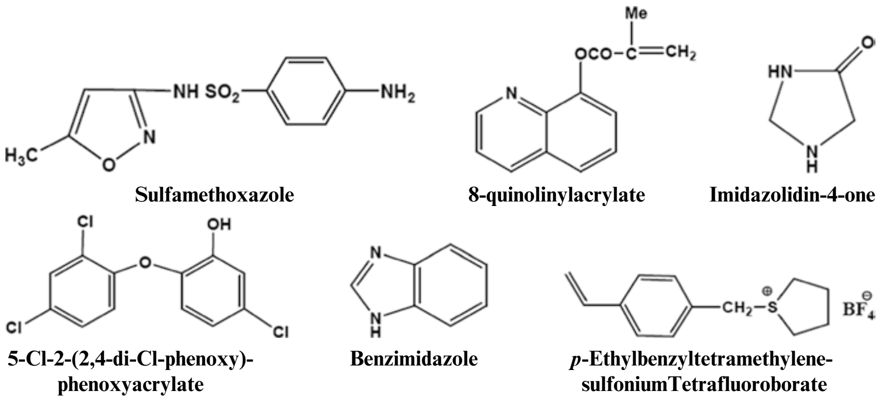


Fig. 3.6 Some antimicrobial monomers

by the polymerization of antimicrobial monomers include: sulfamethoxazole (4-amino-*N*-(5-methyl-3-isoxazoly)benzenesulfonamide) [312–314], *p-ethylbenzyltetramethylene* sulfonium tetrafluoroborate [315], benzimidazole and phenol derivatives [316, 317], 8-quinolinyl acrylate/methacrylate [318], 5-chloro-2-(2,4-dichlorophenoxy)phenoxyacrylate derivatives [319], and methacrylate copolymers containing ammonium iodide [320] (Fig. 3.6). Immobilization of chlorine, as *N*-halamine polymeric biocides containing imidazolidin-4-one derivatives, leads to the liberation of very low amounts of corrosive free chlorine into water that enables rapid killing antimicrobial properties [321, 322]. Another series of homopolymers and copolymers of 2,4-D, *N*-cyclohexylacrylamide ($c\text{-}C_6H_{11}HNCOCH{=}CH_2$) and 8-quinolinylacrylate/methacrylate were also prepared by polymerization and showed antimicrobial activities against various fungi at different concentrations [323–328]. (2) Chemical modification of preformed polymers with antimicrobial agents has been used for polymer functionalization with anitimicriobially active agents, such as phosphonium salts [312], *m-2-benzimidazolecarbamoyl* moiety [329], quaternary ammonium salts [330], and phenolic groups [331]. This technique also involves the incorporation of antimicrobial agents into the polymeric backbones of polyamides, polyesters, PU, and a series of polyketones using chemical reactions [332]. (3) Modification of naturally occurring biopolymers such as chitosan, which is obtained by deacetylation of chitin, has antimicrobial activity against fungi and bacteria without toxicity to humans. However, chemical modification of the amino groups of chitosan with antimicrobially active moieties is a convenient way to obtain antimicrobial chitosan materials with unique chemical and physical properties. The quaternization of the amine groups to make quaternized *N*-alkyl-chitosan derivatives and modification with phenolic moieties has increased its antimicrobial activity [333]. In addition, the antimicrobial activity of chitosan has been increased by the modification with vanillin, *p*-hydroxybenzaldehyde, *p*-chlorobenzaldehyde, anisaldehyde, methyl 4-hydroxy-benzoate, methyl 2,4-dihydroxybenzoate, propyl 3,4,5-trihydroxybenzoate, 2-hydroxy-methylbenzoate.

The main advantages of antimicrobial polymers may include the increased efficiency and activity persistence of conventional antimicrobial agents, while decreasing the associated environmental hazards due to the controlled release of the active moieties over long periods of time. However, the activities of the antimicrobial polymers are affected by various factors. (a) *Molecular weight*: the polymer molecular weight plays an important role in determining the activity of the antimicrobial polymer, since the macromolecular structure of the polymer chains will prevent its diffusion through the bacterial cell wall and cytoplasm [334]. (b) *Ionic strength*: most bacterial cell walls are negatively charged, therefore most antimicrobial polymers must be positively charged to facilitate the adsorption process. The structure of the counteranions, or the cation associated with the polymer, affects the antimicrobial activity. Counteranions that form a strong ion-pair with the polymer impede the antimicrobial activity because the counterion will prevent the polymer from interacting with the bacteria. However, ions that form a loose ion-pair or readily dissociate from the polymer, exhibit a positive influence on the activity because it allows the polymer to interact freely with the bacteria [335, 336]. (c) *Spacer groups*: increasing the length of the spacer groups between the main chain and the antimicrobial groups increases the activity of the antimicrobial polymer due to the available active sites for adsorption with the bacterial cell wall and cytoplasmic membrane, and better chain aggregates that provide a better means for adsorption [335, 336].

However, several basic requirements must be fulfilled for the industrial commercial production of antimicrobial polymers: (a) The antimicrobial polymer should be easy produced by ideal techniques that are relatively inexpensive. (b) It should be stable over long periods of time at the storage temperature for which it is intended. (c) It should be insoluble in water, by introducing hydrophobic groups, to prevent toxicity in the use for the disinfection of water. (d) It should not decompose during use or emit toxic residues. (e) It should not be toxic or irritating during handling.(f) It should be able to regenerate its antimicrobial activity upon its loss. (g) It should possess biocidal activity to a broad range of pathogenic microorganisms in brief times of contact.

The contamination by microorganisms is of great concern in several areas such as water purification systems, food packaging, health care products, hospital and dental equipment, textiles and wound dressing, coating of catheter tubes, and necessarily sterile surfaces. One possible way to avoid such microbial contamination is by developing a number of antimicrobial polymers which provide significant improvement in fighting infection in many fields. The use of chlorine or water-soluble disinfectants in water treatment is associated with problems regarding residual toxicity, even if minimal amounts of the substance are used. Toxic residues can become concentrated in food, water, and in the environment. In addition, because free chlorine ions and other related chemicals can react with organic substances in water to yield trihalomethane analogs that are suspected of being carcinogenic, their use should be avoided. These drawbacks can be solved by the removal of microorganisms from water with insoluble polymeric disinfectants [337, 338]. Polymeric disinfectants are ideal for applications in hand-held water filters, surface coatings, and fibrous disinfectants, because they can be made insoluble in water. The design of insoluble contact disinfectants that can inactivate or kill microorganisms without releasing any reactive agents to the bulk phase being disinfected is desirable. Irrigation sprinkler systems often use reclaimed water in which bacteria can thrive. This polymer can help to prevent the clogging and blockage of parts that this growth can cause. In humid areas, an antimicrobial surface can render stains and odors caused by bacterial growth a problem of the past. Antimicrobial polymeric materials are also well suited to a range of domestic bathroom, pool, and spa products.

Antimicrobial polymers are suitable for applications in food processing, serving, and storage. They are incorporated into packaging materials to control microbial contamination by reducing the growth rate and the maximum growth population. This is done by inactivating the microorganisms or by reducing the rate of growth of microorganisms when the package is in contact with the surfaces of solid foods [339]. These applications are used to extend the shelf life and promote safety of food. Antimicrobial packaging polymeric materials also greatly reduce the potential for recontamination of processed products and simplify the treatment of materials to eliminate product contamination, e.g., self-sterilizing packaging eliminates the need for chemical treatment in aseptic packaging. They can also be used to cover surfaces of food processing equipment as self-sanitizer, e.g., filter gaskets, conveyors, gloves, garments, and other personal hygiene equipment. Some polymers are inherently antimicrobial and have been used in films and coatings. Cationic polymers such as chitosan promote cell adhesion [340]. This is because charged amines interact with negative charges on the cell membrane, and can cause leakage of intracellular constituents. Chitosan has been used as a coating and appears to protect fresh vegetables and fruits from fungal degradation. Although the antimicrobial effect is attributed to antifungal properties of chitosan, it may be possible that chitosan acts as a barrier between the nutrients contained in the produce and microorganisms. Antimicrobial polymers are effective and suitable for use in areas of the food industry to prevent bacterial contamination in the systems of food handling, food processing plants, and food serving, and storage. They are also suitable in giving the benefit of partial antimicrobial protection in potable water applications for water purification to inhibit the growth of microorganisms in drinking water.

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Part II
Applications of Polymers in Food

In general, agriculture is the process of producing food, feed, and fiber products by the cultivation of certain selected plants and the raising of domesticated animals (livestock). Natural and synthetic polymers are not absorbed by the human body due to the size of macromolecules that prevents their diffusion across the membranes of the gastrointestinal tract. However, the gastrointestinal tract contains digestive enzymes which break down certain types of degradable polymers to monomeric units that can be absorbed systemically. Thus, nonpurified polymers may be of toxicological concern regarding the contained unreacted monomeric low-molecular-weight fractions, catalysts, and manufacturing aids which might be absorbed by the gastrointestinal tract and have toxic effects. Thus, the choice of particular polymers, especially reactive polymers, in food materials of synthetic or natural (plant or animal) origin is determined by their ability to accomplish certain technical effects, improve safety, and lead to advantages regarding market considerations such as price and consumer acceptance. There is a promising potential in utilizing polymers in the food processing industry for continuous industrial processes in large-scale applications [1–5]. Polymeric ingredients accepted for use in the food industry are classified into three categories: (i) food processing and fabrication, (ii) food additives, (iii) food protection and packaging.

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Chapter 4
Polymers in Food Processing Industries

Various polymeric materials are used in food processing that do not become substantial components of the foods. These serve purposes especially for purification, recovery, and utilization of by-products, are not considered as food additives, i.e., as preserving agents. In general, they are intentionally used in food manufacture to improve food characteristics, to aid in food processing, to keep food unspoiled for longer periods of time under the conditions of storage, or to make foods more attractive. The food industry is a complex network that links farmers and consumers i.e., that links farming, industrial food production, packaging, distribution, and retail via supermarkets to consumers. The links include also farm equipment and chemicals as well as agribusiness services (transportation and financial), food marketing industries, and food service establishments. The food service industry by contrast offers prepared food, either as final products, or as partially prepared components for final "assembly." The most prominent driving factor behind the increasing needs within the food industries is the increasing populations around the world.

The food industry requires polymers that: (1) simplify food production processes and reduce food production costs, (2) do not deteriorate foods from a hygienic and health standpoint, and (3) do not alter the foods basic equilibria. Consequently, suitable polymers are needed to meet these specific requirements for the food industry. In addition, they must not contaminate the processed foods and not lead to undesirable food alternation. In general, the fundamental principles are based on health protection, and preservation of food quality. In respect to the required health protection the composition of the employed polymers must be known in detail, and be designed so as to avoid any harmful effects. Thus, the quantity of matter transferred from polymers to foods, must be limited and precisely controllable.

The food processing industries use a set of methods and techniques to transform raw agricultural or animal ingredients into food or to transform food into other forms for human consumptions. Food processing uses clean, harvested crops or butchered animal products to produce attractive, marketable, and often long-lasting food products. The employed procedures include. (1) *One-off production method*. This is the procedure used customers place an order for a product to be customized

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to their own specifications. The production time of one-off products depends on the design and the complexity of the procedure for preparing the food product. (2) *Batch production method*. In this case the size of the food product market is not clear, and there is a range within a product line. This method involves estimating the number of customers that may want to purchase the particular product. (3) *Just-in-time method*. This is the scheme of sandwich bars. All the components of the product are held ready, the customers choose what they want in their product and the customer witnesses its preparation directly on the spot. (4) *Mass-food production* method. This is the mass market procedure for a large number of identical food products, such as canned foods and ready meals. The food product passes in the production stages along a production line. Various techniques may be used for mass-food processing including slaughtering, fermenting, drying (as sun-, spray- or freeze-drying), salting, various types of cooking (as roasting, smoking, steaming, and oven baking), canning, vacuum bottling, tinning, pasteurizing, concentrating (e.g., juices), curdling, pickling. The mass-food production industries must consider and are involved in: (a) rules and regulations for food production and sale, including food quality and safety, and industrial activities, (b) food technology, (c) manufacturing of agrochemicals, seed, farm machinery, and supplies, (d) raising of crops, livestock, seafood, (e) preparation of fresh products for market, food processing of prepared food products, (f) marketing, packaging, distribution, and transportation. A transportation network is required by the food preparation industries in order to connect their numerous parts: from suppliers, fulfilling additional necessary food requirements, via food processing manufacturers, to warehousing, retailers, and to the end consumers.

Food products resulting from mass-food processing have obvious advantages: toxin removal, preservation, easing marketing and distribution tasks, and uniform food consistency. In addition, it increases seasonal food availability, enables transportation of delicate perishable foods across long distances, and makes many kinds of foods safe to eat by inactivating spoilage and pathogenic microorganisms; additionally processed foods are usually less susceptible to early spoilage than fresh foods and can be made with reduced fat content in the final product. Processed foods help to alleviate food shortages and can improve the overall nutrition of populations in making many new foods available to the masses. Processing can also reduce the incidence of food-borne disease, since fresh food materials are more likely to harbor pathogenic microorganisms capable of causing serious illnesses. Transportation of more exotic foods, as well as the elimination of much hard labor gives the modern eater easy access to a wide variety of food unimaginable to their ancestors. The act of processing can often improve the taste of foods significantly. Mass production of food is much cheaper overall than individual production of meals from raw ingredients. Therefore, a large profit potential exists for the manufacturers and suppliers of processed food products. Individuals may see a benefit in convenience, but rarely see any direct financial cost benefit in using processed foods as compared to home preparation. Processed food reduces the large amount of time involved in preparing and cooking “natural” unprocessed foods and therefore there is little time for the preparation of food based on fresh ingredients. Food processing improves the quality of life for people with allergies, diabetes, and for individuals who cannot consume certain common foods; it can also add extra nutrients such as vitamins.

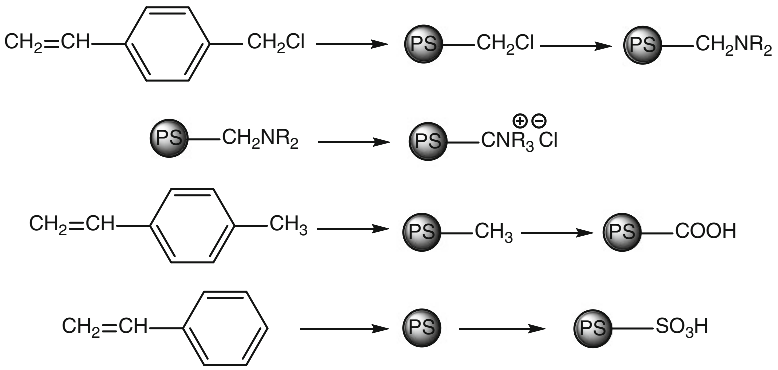
Consumer pressure has led to a reduction in the use of industrially produced ingredients in processed food. The potential for increased profits apparently has barred widespread acceptance by the industry of recognizing possible health problems associated with excessive consumption of processed foods. Processed food products such as canned fruits may have some disadvantages over fresh foods (naturally occurring products processed by washing and simple kitchen preparation). Processed food products may contain: (1) a lower content of naturally occurring vitamins, due to their destruction by heat, (2) lower content of nutrients that are removed to improve longevity, appearance, or taste, (3) higher calories relative to nutrients, (4) some introduced hazards that my cause health problems (certain food additives, as flavorings, preservatives, and texture-enhancing agents may cause health complications such as high blood pressure, weight gain, diabetes, etc.).

4.1 Polymers in Food Production

The food processing and fabrication industries have been applying various reactive functional polymers in the process of preparing many kinds of foods. The employed reactive functional polymers are usually in the form of (1) ion-exchange resins, (2) immobilized enzymes, (3) membranes, and (4) smart polymers and nanomaterials.

4.1.1 Ion-Exchange Resin Catalysts in the Food Industry

Ion-exchange resins are insoluble crosslinked polymeric matrices normally in the form of macroporous or microporous beads prepared by suspension polymerization. The macromolecules of the polymer chains are composed of repeating structural units typically having ionic groups connected by covalent bonds. They have pores in the network structure that can easily trap and release ions. The process of ions trapping takes place with simultaneous releasing of other ions, referred to as ion exchange. In many cases ion-exchange resins were introduced in such processes as a more flexible alternative to the use of natural or artificial supports as zeolite or PS. Zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents. PS is an aromatic polymer made from styrene monomer, which is commercially manufactured from petroleum by the petrochemical industry, and crosslinked by divinylbenzene, which is a mixture of ethyl- and *m*/*p*-divinylbenzene isomers. The ionically active groups can be introduced into the repeating structural units of the polymer chains either by using substituted monomers or after polymerization of unsubstituted monomers by chemical modification. The resins are made



Scheme 4.1 Preparation of weak and strong anion- and cation-exchange resins [1]

as beads or as membranes. Particle size of the beads influences the resin parameters; smaller particles have larger outer surface. The ion-exchange membranes used in electrodialysis are made of highly crosslinked resins that allow passage of ions from one solution through membranes to another solution under the influence of an applied electric potential difference. There are four main types of ion-exchange resin which can be prepared, depending on the physical and chemical nature of their functional groups as well as the requirements of the different applications, i.e., strong and weak cation-exchange resins such as poly(styrene sulfonic acid), poly(acrylic acid), strong and weak anion-exchange resins such as poly(ammonium salts), polyamine (1ry, 2ry, or 3ry amine) or poly(ethylene amine) from of aziridine, and chelating resins as poly(iminodiacetic acid) ligand to form a metal complex with chelate rings (Scheme 4.1) [1]. Acidic resins can be stored in the proton or alkali metal ion forms, but strongly basic resins are most conveniently stored in the chloride ion form since their hydroxide forms tend to absorb CO from the atmosphere and lose their activity.

Ion-exchange resins are widely used for a specific purpose in different separation, purification, and decontamination processes. They are most commonly used in the technology of demineralization, i.e., in water softening in which their action is to reduce the dissolved Ca, Mg, and to some degree Fe^{2+} ion concentrations in hard water. The purification treatment of potable water intends to remove undesirable chemicals, materials, and biological contaminants from raw water. Thus, the goal of using ion-exchange resins is to produce water fit for food processing, or for using in the production of a number of products utilized in the food industry making it possible to simplify production processes [2, 3]. Ion-exchange resins have also the ability to remove different components present in foods. The ion-exchange resins technology is currently used in the food industry for the treatment of milk and dairy products (whey demineralization, lactose hydrolysis) and in wine production (tartrate stabilization, wine treatment). They are also used in fruit juices manufacturing for stabilization of apple juice haze, reducing the color of apple and pear juices, de-bittering of citrus products. They are used in the orange juice industry to remove bitter tasting components and so to improve the flavor. This allows poorer tasting fruit sources to be used for juice production. They are also used in sugar manufacturing, referring to edible crystalline carbohydrates, mainly sucrose, lactose, and fructose characterized by a sweet flavor. In food, sugar almost exclusively refers to sucrose, which primarily comes from various sources as sugar cane and sugar beet. In addition, they are used in the sugar industry to help in the decolorization and purification of sugar syrups, separation of glucose and fructose from liquors, demineralization of sugar, and conversion of one type of sugar into another type of sugar, e.g., by isomerization of glucose and fructose.

The use of ion-exchange resins as acidic and basic catalysts in the food industry incorporates several advantages over the existing traditional techniques such as: (a) elimination of the huge amount of waste material that is linked with large-size production in industrial processes, (b) simplification of the work-up processes because of the lack of extensive separation steps, (c) elimination of corrosion problems, (d) high-quality products and improved yields, (e) reduction in the amount of chemicals used in the production processes, and (f) transformation of a batch process into a continuous one, i.e., automatic process, and (g) providing an easy process for isolating and purifying the product. However, there are also a number of drawbacks in using ion-exchange resins in the food industry, including: (a) high cost of the resins which may be lessened by the recycling and reuse of the resins, and (b) the lower thermal stability of the basic resins (<60 °C) that may limit their commercial application on some industrial scales, whilst acidic resins can be employed without loss of activity up to 125 °C.

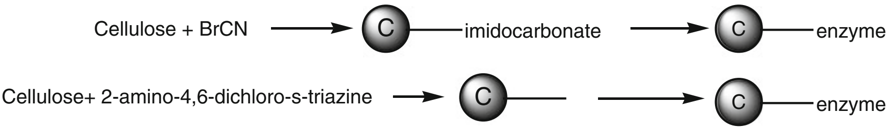
4.1.2 Immobilized Enzymes in the Food Industry

Enzymes are natural polymeric catalysts of many different kinds produced by living cells and are present in most fresh food materials. They efficiently catalyze biochemical transformations, usually with high activity, Their specific binding to the active site of the substrate results in high specificity. They exert high reaction velocities and bring about various reactions at ambient temperature and pressure and in neutral aqueous solution. They may also contribute to the desirable characteristics of foods and be an important factor in the deterioration or spoilage of the food. Industrial products that are very difficult to be prepared by purely chemical methods may be obtained quite readily and economically by employing enzymes under mild conditions. However, enzymes are not always ideal catalysts for industrial application and have some disadvantages, such as their instability and limited use at elevated temperatures and their extraction and purification are often complex and expensive. Furthermore, enzymes are invariably lost after each batch operation and lose their catalytic activity which makes their reuse very difficult. Accordingly, a number of major problems are encountered in using soluble enzymes as food industrial catalysts. One of the approaches to prepare superior enzyme catalysts for food application purposes is the use of polymeric enzymes, which increase their stability, recovery, reuse and use in column processes, i.e., continuous applications.

Enzyme immobilization is when the enzyme is bound to or restricted in solid support materials such as polymers, glass, inorganic salts, metal oxides, or silica gel materials. Immobilized enzymes on semisynthetic polymeric supports have been made by the combination of natural enzymes with modified natural polymeric carriers. They were among the first functionalized polymers used as catalysts to attain the specificity and the activity of enzymes. The possibility of using immobilized enzymes as stable reusable catalysts has an interesting potential for continuous flow-through industrial processes. A considerable number of immobilized enzyme systems are described in the literature to catalyze biochemical reactions [4–13].

Enzyme immobilization can be achieved by various physical processes such as adsorption or embedding, and by chemical covalent bonding processes. The *adsorption* of the enzyme onto a polymer matrix offers the advantage of simplicity in that the enzyme can usually be attached to the support materials under mild conditions without covalent bonding, using physical interaction (physical adsorption) and ion interaction (ion adsorption) bonding [14]. The *entrapment* of an enzyme within the support can be achieved by its inclusion within the pores of the support which forms a network matrix around the enzyme [15, 16]. The unmodified enzyme in the microcapsules is not actually attached and the micropores cannot allow the enzyme's escape, e.g., PAAm gels have mostly been used for entrapping enzymes [17, 18]. The *embedding* of enzymes in a variety of supports such as PAAm gel, silicate gel, alginate, or carrageenan can be achieved during polymerization, precipitation, or gelation. Physical immobilization of enzymes on polymeric supports (physical adsorption or entrapped) offers the advantage of relatively mild reaction conditions which do not significantly alter the enzyme structure, and the enzyme is not modified chemically during the attachment phase and hence has a broad applicability to most enzymes. However, the reversible nature of the bonding of the enzyme to the polymeric support may lead to the main drawbacks of desorption, dissociation, or leaching of the enzymes into the surrounding substrate solution. This undesirable property limits the commercial use of this technique of enzyme immobilization for column or cyclic reuse applications.

Immobilization of enzymes by *chemical bonding* (covalent or ionic bond) between the reactive polymeric supports and the enzymes through functional groups other than their active sites is the most used type to reduce the loss of the enzyme from the support during subsequent use. In addition, these chemical immobilization systems have many advantages: (a) recovery and reuse of recyclable enzyme, (b) continuous production processes, (c) greater environmental stability toward changes in pH or temperature and improved storage properties, (d) enhanced activity towards a substrate, (e) ease of controlling or stopping the reactions at any desired stage by simple filtration, (f) ease of separation and purification of the products from immobilized enzyme, (g) increasing enzyme stability and optimum temperature, (h) ease of control of reaction conditions leading to increased product yield and quality, (k) low cost and efficient technique for automatic continuous industrial production [19]. However, immobilized enzymes have also certain



Scheme 4.2 Polysaccharide immobilized enzymes [23]

disadvantages that include: (a) loss of enzyme activity in the immobilization process, (b) restricted enzyme conformational mobility [20], (c) possibility of chemically altering the enzyme that reduces its reactivity, (d) chemical attachment may involve the participation of reactive groups on the enzyme that leads to its inactivation, (e) severe reaction conditions used in the attachment reaction may lead to damage of the enzyme's active site, (f) production costs [14, 21].

The activity of the chemically immobilized enzyme depends on the structure and composition of the support, the size of the support particles, and the degree of hydration of the polymer matrix. Several factors must be considered in order to retain the optimum activity of the immobilized enzyme: (a) the enzyme must be attached in such a conformation as to allow its interaction with the support [20], (b) the active site of the enzyme must be accessible to the surrounding medium and not buried in a pore or blocked by some other component, (c) the loss of enzyme activity should be minimized either by selecting a suitable way of enzyme attachment, or by protecting the enzyme during the attachment, (d) appropriate selection of the conditions of pH and ionic strength may minimize the bonding of enzyme active sites. In addition, a polymeric support should have the following properties: (1) chemical stability and complete insolubility in solvents and reagents under the environmental conditions employed, (2) capable of undergoing functionalization reactions, (3) a good mechanical strength and not be susceptible to bacterial attack or degradation, (4) no interaction with the substrates both before and after coupling of the specific ligand, (5) a loose porous network structure that permits the easy passage of reactants and retaining a good flow rate.

Polymeric supports of a wide variety of physical and chemical properties are used for the attachment of enzymes including synthetic polymers, inorganic supports, and polysaccharides such as cellulose, starch, Sephadex, Sepharose (agarose gel) derivatives. However, polysaccharides can be modified with enzymes after activation with cyanogen bromide (BrCN) which reacts to form a cyclic reactive imidocarbonate [22], or with cyanuric chloride as 2-amino-4,6-dichloro-s-triazine which are susceptible to nucleophilic attack by amino groups present in enzymes (Scheme 4.2) [23]. Polysaccharide derivatives containing carboxyl groups have also been used for linking enzymes after activation with carbodiimide or through azide formation which make it susceptible to nucleophilic attack [24, 25]. Dialdehyde starch, produced by oxidation with periodic acid, can react directly or after derivatization with the amine groups present in the enzyme [26]. Inorganic supports such as porous glass have been extensively used for enzyme attachment at the surface through the use of derivatized silane-coupling reagents [27]. However, a variety of water-insoluble polymeric supports that can swell in water and whose reactive groups can react with the functional groups of the enzyme under mild reaction conditions without interfering with the biologically active center of the enzymes have been used as enzyme carriers, e.g., PAAm, PEMA [28], phenolic resins in which the enzyme is coupled through glutaraldehyde or by an oxidative formylation system [29]. The incompatibility of PS with polar biomaterials and water is the most important limitation of such supports [30].

Immobilized enzymes have been widely used in chemical biology, in biological engineering within the life sciences, and in the food processing industry, because they save energy and resources, reduce pollution and adverse ecological effects, and are consistent with sustained development strategic requirements [31]. Use of single or multiple (multienzyme) immobilized enzyme systems such as immobilized glucose isomerase, amino acid acylase, glucoamylase, lactase, or protease, in the food industry has been demonstrated to bear many attractive advantages in some techno-economically feasible industrial food enzymology systems. The use of immobilized-enzyme technology in the food industry has received particular attention in several important food processing areas [32–37].

4.1.2.1 Dairy Industry

Immobilization technology is applied in various ways in the dairy industry, such as (a) for the continuous coagulation of milk in the production of cheese [38], (b) to remove lactose from cheese whey, and (c) stabilization of milk to extend shelf life without change in flavor [39, 40]. Sodium alginate-chitosan-immobilized lactic acid bacteria are used in fermented whey drink [41], and show reusable and sustainable energy [42]. Immobilized lactase, also known as galactosidase, has been used in a wide range of industrial applications, especially in dairy processing. Yeast lactase fixed with glutaraldehyde-crosslinked porous silica shows intermittent handling of pre-superpasteurized milk. The enzyme activity and mechanical strength of PAAm gel-entrapped lactase is promising [43]; immobilized enzyme expands the range of thermal stability, while the substrate in the gel diffusion of lactose does not affect the enzyme's reaction rate constant. The use of immobilized-enzyme in the treatment of skim milk can maintain the original flavor and also appears to prevent development of other undesirable flavors and destabilization of milk proteins.

4.1.2.2 Sugar Industry

Immobilized enzymes are used in the sugar industry for (a) producing glucose syrups from corn starch by hydrolysis with fixed glucoamylase, and (b) producing fructose from glucose syrups by isomerization with immobilized glucose isomerase, [44]. In the preparation of fructooligosaccharides, sugar syrup can be obtained with high fructose and sucrose equivalent sweetness, an economic impetus. Fructosyltransferase adsorbed onto porous silica or fixed on DEAE-cellulose retains a higher column activity [45, 46]. By immobilization of fructosyltransferase by fixation on styrene-derived porous ion exchanger, some of the initial activity of the immobilized enzyme is lost, while the covalent bonding of fructosyltransferase to poly(methyl acrylamide) particles can retain 100 % of the enzyme's activity [47]. Immobilized glucose isomerase can also be used to catalyze the production of high fructose corn syrup sweetness from starch, which is achieved in three steps: (a) amylase liquefied starch, (b) the translation of amylase into glucoamylase glucose, that is glycosylated, and (c) heterogeneous glucose with glucose isomerase to fructose [44].

4.1.2.3 Clarification of Fruit Juices

Bitter orange is produced from overprocessed citrus juice, in which the bitter substance is composed mainly of two substances: terpene lactones and flavonoid glycosides. Naringin is the main bitter flavonoid in grapefruit and bitter orange and other citrus fruits and is connected to rhamnose and glucose on the molecular conformation [48]. Juice bitterness can be reduced by using hollow glass beds, DEAE-Sephadex, tanninaminoethylcellulose fiber, and cellulose-acetate fiber membrane as a carrier for fixing the different enzymes that act on limonin and naringin [49]. In fruit juice processing, pectinases are used to break down pectic substances and serve to clarify the juice; pectinase is a term referring to a variety of enzymes used in juice clarification. Nylon membrane after activation of *O*-alkyl and pectinase covalent coupling, and then placed in a microfiltration reactor is used for degradation of pectin molecules by membrane flow, and liquid viscosity is decreased, thereby reducing the colloidal state [50]. The immobilized pectinase obtained from sheets of nylon after activation with 3-dimethylaminopropylamine and covalent coupling with glutaraldehyde pectinase, is used in a wide range of pH values to maintain normal activity where the temperature stability has improved greatly [51]. Chitin as a carrier with glutaraldehyde as a coupling agent is commonly used for fixing pectinase and endocellulase [52].

4.1.2.4 Clarification of Beer

Beer contains certain proteins which combine with tannins forming an insoluble precipitated cloudiness that affects the quality of beer. By adsorption crosslinking, trypsin has been adsorbed on the surface of magnetic colloidal particles with glutaraldehyde crosslinking bifunctional reagent to form an "enzyme net" which prevents cloudinesss [53]. Glutaraldehyde crosslinking has improved the thermal stability of the immobilized enzyme in respect to pH value and storage stability in dairy products [54]. Lactase is being more widely used in dairy processing as many people are afflicted with lactose intolerance; the enzyme degrades lactose into glucose and galactose which reduces the symptoms.

4.1.2.5 Resolution of DL-Amino Acids

The chemical synthesis of amino acids leads to a racemic mixture. Only the L-form is usable for medicines and foodstuffs. Immobilized enzymes have been used for the industrial separation of enantiomers of various amino acids, e.g., amino acid acylase immobilized onto DEAE-Sephadex. Processing efficiency in the fermentation of amino acids has been greatly facilitated through the use of immobilized amino acid acylases such as L-glutamate aminoacylase.

4.1.3 Membranes in the Food Industry

The food processing industries are making extensive use of membrane technology involving reverse osmosis, nanofiltration, ultra- and microfiltration, as well as ion-exchange membranes and membrane gas separations. The use and development of new membrane materials requires an understanding of membrane transport phenomena, morphology, mechanical and thermal properties of polymer, and polymer interaction in solute-solvent-membrane systems [55–58]. Thus, membranes are chosen according to their solute retention, permeability to solvent, chemical inertness to solution components, and durability in a given solvent. Their retention limit depends on the nature of the solute, solvent, and temperature as well as on the history of the membrane. In swollen membranes with relatively wide pores, the transport of solution components can be considered to consist of a combination of diffusion and viscous flow.

Cellulosic membranes are widely used in applications requiring a membrane permeable to relatively polar hydrophilic materials [59]. Since pure cellulose does not dissolve because of its high crystallinity, modification of its hydroxyl groups decreases the crystallinity by reducing the regularity of the main chains and decreases the interchain hydrogen bonding, and making it more hydrophobic and suitable for membrane uses [60, 61]. Cellulose acetate membranes have been applied in a large number of food applications in which their permeability can be increased by adding hydrophilic plasticizers as PEG to increase the water diffusion coefficient or by adding hydrophilic flux enhancers to increase the water sorption of the membrane. However, the use of these membranes lacks universal applicability as a membrane material due to: the susceptibility to creep-induced compaction [62], biological attack [63], acid hydrolysis, alkaline degradability [64], and thermal instability [65]. Porous cellulose membranes have been applied in the dairy industry for separation of whey proteins in a short time at high flow rates and low back-pressures [66].

Silicone rubber polymers have been used as membrane materials because of their high permeability due to the high flexibility of the silicone rubber backbone [67–71]. However, PE is a rigid, crystalline polymer with relatively low permeability, but on addition of small amounts of VAc it becomes rubbery and permeable. Thus, the change of the polymer morphology by the comonomer ratios has an effect on the membrane flux which is proportional to the product of the sorption and diffusion coefficients. The permeability of PEVAc changes substantially with the ration of the VAc content, and thus it is possible to tailor the permeability to the desired value by small changes in the membrane composition. These changes in the permeability are related to changes in the crystallinity and T_g of the polymer, i.e., the addition of VAc into PE reduces the polymer crystallinity by destroying the regularity of the polymer chain [72]. However, as the amount of VAc increases, the T_g of the polymer also increases [73, 74]. Flexible PU elastomers make useful membranes for hydrophilic polar compounds having low permeability through hydrophobic polymers such as silicone rubber or PEVAc [75]. The membranes of PAN-natural rubber blends find application in the dairy industry, where good mechanical properties and swelling resistance are required. The blend ratio and penetrant size have effects on the sorption and the transport properties that depend on the diffusion and permeation parameters, i.e., equilibrium solvent uptake by blends decreases with an increase in PAN-rubber concentration [76]. Microporous membranes of hydrophobic polysulfone made from polyethersulfone or other polymers as poly(vinyl pyrrolidone)s, PEGs, or PEOs, have found many important applications in the food processing industry [77].

In addition to the well-known ion-exchange membranes, enzymes can be encapsulated within a membrane system, in which the membrane creates an intracellular environment for the enzymes preventing them from leaking out or coming into direct contact with the external environment. Substrates that are permeable can equilibrate rapidly across the membrane to be acted on by the enzymes inside and the product can diffuse out, e.g., the immobilization of β-galactosidase by covalent bonding to PP hollow fiber membranes using hexamethylenediamine [78]. Membrane surface morphology and structure have a great effect on the surface and internal fouling within the used membranes for milk filtration performance in industry. The internal fouling, during filtration of skim milk, proceeds by protein-polymer interactions [79].

The main applications of membrane operations are in: (a) the dairy industry for milk protein standardization, whey protein concentration for recovering the fat substances, and the use of cross-flow microfiltration for the production of drinking milk and cheese milk, and to achieve the separation of skim milk micellar casein and soluble proteins. Both streams are given high added value in cheese making (retentate) and through fractionation and isolation of soluble proteins (lactoglobuline, lactalbumine) [80]; (b) in the alcoholic beverages industry: enzymatic hydrolysis combined with selective ultrafiltration can produce beverages from vegetable proteins. In the wine industry the cascade cross-flow microfiltration-electrodialysis allows limpidity and microbiological and tartaric stability to be ensured in concentrated grape juice for wine must. In the beer industry, recovery of maturation and fermentation tank bottoms is already applied at industrial scale, and microfiltration membranes are used in rough beer clarification [80]. Final beer and flavored malt beverages derived from malt-based fermentation require no less than 51 % of alcoholic content. Traditionally, a majority of the alcoholic content in flavored malt beverages was derived from the addition of flavorings that contain distilled spirits.

Since the malt base is the larger component of the final beverage, existing production systems must be expanded in order to accommodate the increase in malt base usage. Additionally, it is important to produce an alcohol stream that is free of unwanted colors and flavors. Several methods can be used to produce a clear malt base: membrane filtration can separate alcohol in the malt base from unwanted materials such as sugar, salts, and large color and flavor components. This essentially clarifies the ethanol and water in the stream. Separation of yeast and other suspended material by cross-flow membrane filtration. Membrane filtration for processing malt base in which alcohol and water permeate through the membrane while undesirable components, such as sugar, salts, color, flavor compounds, are retained by the membrane. (c) The insertion of membrane operations in food processing has been reported in other foods as: fruit and vegetable juices and soft drink clarification and concentration, tomato juice concentration, meat, poultry, and fish products, sugar and starch, vegetable oils, wastewater treatment and water reuse, and other animal products [80–82]. Separations in food processing represent one of the numerous applications of membrane operations on an industrial scale. Clarification of fruit, vegetable, and sugar juices by micro- or ultrafiltration allows the flow sheets to be simplified or the processes made cleaner and the final product quality improved. For the reverse osmosis concentration of fresh fruit juice, ultrafiltration membranes have been used to permeate sugars and salts completely.

4.2 Polymers in the Dairy Industry

Polymers in the food processing industry have an interesting potential for continuous industrial processes in large-scale applications. In the dairy industry they are used in milk and related products to simplify production, especially for obtaining high-quality and improved yields of food products produced from milk by-products. The uses of reactive polymers in the area of dairy industry can be classified into three major categories: (a) *milk treatment* for the continuous coagulation of milk in the production of cheese [33, 38], stabilization of milk to extend shelf life without change in flavor [39, 40], demineralization, casein production, and cooked flavor removal from milk, (b) *whey treatment* to recover lactose and protein from cheese whey, concentration of whey, and sweet syrup from whey, and (c) *other dairy applications* as polymeric coatings of cheese to extend shelf life.

4.2.1 Milk Treatment

Milk contains a large number of natural enzymes, some of which, such as lipase and phosphatase, are destroyed by pasteurization. The presence of phosphatase in milk is used in quality control to determine whether the milk has been adequately pasteurized. Milk lipases may lead to undesirable rancidity if freshly drawn milk is cooled too rapidly, or if raw milk is homogenized and agitated, or if foaming or great temperature fluctuations occur. Polymers in the modification of milk and dairy products derived from milk such as cheese, ice cream, and butter, serve in stabilization to extend shelf life without change in flavor, demineralization for the removal of the calcium, production of pure lactose, and other manufacturing processes based upon milk such as the continuous coagulation of milk in the production of cheese, casein production, and cooked flavor removal from milk [38–40].

4.2.1.1 Continuous Coagulation of Milk

Cheese is produced from milk proteins which must be converted into an insoluble form by coagulation. There are two types of milk coagulation for cheese production: (a) enzyme-induced coagulation from which sweet whey is derived, and (b) acid-induced coagulation from which sour whey is derived. Then the coagulated protein is separated from the components of the remaining milk that include water, salts, lactose, and the whey proteins. Traditionally, cheese production uses rennet enzyme to coagulate the milk, but the increase in cheese production has brought about a world shortage of rennet [83]. In the production of cheese, immobilized-rennin and pepsin were used [84] to catalyze the milk coagulation continuously in a fluidized bed reactor [85]. Immobilized papain and rennin were also used for the hydrolysis of skim milk in the manufacture of cheese [38]. Cheese production by membrane filtration involves the concentration of the proteins by ultrafiltration in the soluble form, i.e., before enzyme treatment. The concentration is controlled in such a way that the composition of the concentrate regarding fats, protein, salts, and water is equivalent to the composition of the final cheese. The enzyme is added, causing the cheese to set in the form into which it has been poured. The whey proteins, which previously had been wasted during the traditional process, remain in the final cheese, resulting in increased production and therefore higher profits. The product composition, i.e., the proportion between protein and lactose in the final product, may be controlled to produce protein powder with compositions varying from 35 % to 85 % protein of total solids.

4.2.1.2 Demineralization

Calcium removal: one of the disadvantages of cow's milk as a food is its tendency to cause stomach problems, which develop by casein in the presence of calcium. The tendency to curding can be reduced by removing the calcium in the milk. The other benefits produced from lowering the calcium content can make milk more stable during the manufacturing of evaporated milk. Dried creams are manufactured from low-calcium milk because its presence tends to break or separation of milk fat. The treatment prevents curd formation and stabilizes the viscosity during heating for sterilization. Removal of excess calcium improves casein stability so that it does not coagulate during sterilization and does not form undesirable tough curds during digestion. Modification of the calcium content of milk has been carried out with a cation-exchange resin. Another factor aside from the ion-exchange equilibrium is the effect of pH: at high pH a stable complex is formed which decreases calcium removal, while lower pH enhances calcium ionization and increases its removal.

The adjustment of the salt content of the milk also seems to have an effect on the crystallization of lactose from milk solids used in ice cream. If milk having a content of nonfat solids higher than 10 % is used in ice cream, there is a tendency for lactose to crystallize out, causing sandiness. This formation is accentuated if the ice cream is allowed to warm up and refreeze during storage. The adjustment of the calcium content by the addition of milk treated with a sodium cation exchange resin can prevent this undesirable drawback. Lowering the calcium content of the milk retards lactose crystallization and improves the stability and delay. However, drying calcium-reduced milk was not successful, since drying appeared to reduce casein stability, thus cancelling the effect of the calcium reduction.

Sodium removal: polymers are used for modifying other inorganic ions than calcium in milk to prepare the adjusted low sodium-content milk. Milk foods of low sodium content are useful for treating edema caused by sodium retention in tissues as in some types of heart failure, which in such cases limits daily sodium intake. The milk is treated by ion exchangers and can be prepared by several different processes to prevent changes in flavor, taste, and appearance of the milk, i.e., to maintain the original content while exchanging out the sodium. The demineralizing technique has been used to remove all ions, inclusing sodium, from whole or skim milk. Low-sodium milk can be fortified to higher protein content by adding coagulated casein from milk. The low-Na/Ca dairy food products produced by demineralization are thus heat-stabilized so that they can be spray-dried or sterilized by heating. Thus, by treating with a weak base anion-exchanger in the OH form, the shelf life of the milk can be improved without a loss of flavor [86]. A demineralization technique by ion exchangers has also been used for removing radioactive fallout from milk products [87] and ions from aqueous solutions simulating such materials as whey. In addition, they have been used for the removal of organic acids from milk, e.g., the improvement of milk by reducing lactic acid.

4.2.1.3 Casein Production

Casein as a milk product has a number of uses, both nutritionally and industrially. The usual method of its preparation from milk is the addition of cation-exchange resins to reduce the pH to the isoelectric point to substitute hydrogen ions from other cations in the milk and so acidifying it. Normally the casein is put back into solution by the addition of an alkali metal hydroxide to form soluble caseinate. This treatment tends to degrade the casein. However, the degradation of caseinate can be avoided by redissolving the casein with a cation exchanger. The purity of the caseinate produced makes it quite suitable for industrial use, as in glue or fiber manufacture. The stability and bland flavor give it an advantage when it is used to stabilize ice cream or mayonnaise, or to prepare dairy food, such as low-sodium products.

Cation-exchanger resins can be used as acid catalysts to hydrolyze casein, the resulting amino acid mixture serving as a good bacterial nutrient medium.

4.2.1.4 Cooked Flavor Removal from Milk

Processes for producing ultrahigh-temperature sterilized milk result in prolonged shelf life without the necessity of refrigeration. The resulting cooked flavor is a chalky flat or insipid taste attendant in the fluid milk, which may be unpleasant both to taste and smell. The developed undesirable cooked flavor of heated milk is due to the liberation of sulfhydryl groups in the milk. Immobilized sulfhydryloxidase [88] catalyzes the oxidation of sulfhydryl groups to disulfides in heat-treated fluid milk and eliminates the cooked flavor [89]. The use of immobilized sulfhydryloxidase has the advantage that the enzyme is obtained from whole raw milk and is thus a natural constituent and hence there is no additive to the milk being treated. Treating with immobilized enzyme may be more far reaching than simply removing the cooked flavor, as such treatment also appears to prevent development of other undesirable flavors and destabilization of milk proteins.

4.2.1.5 Stabilization of Milk

Milk stabilization by treatment with immobilized enzymes is a very attractive application of functional polymers. Immobilized trypsin extends milk shelf life without change and prevents loss of flavor [40]. Food gelling agents of water or milk are used either at a neutral pH or after acidification by adding a fruit juice. In the case of milk, this acidification may be obtained by microbic action leading to a yogurt product. Yogurt has a certain gellified texture obtained by adding to milk certain fermenting agents which acidify the milk through a coagulation of the casein. If yogurt is preserved at an ambient temperature, the fermenting agents continue their action and hence the acidity continues to develop. Thus, the product loses its quality and thereby limits its preservation. The composition blend for stabilizing yogurt consists of propylene glycol alginate, sodium alginate, guar gum, carrageenan, and an emulsifier [90]. Gums and blends have been found to react with the milk protein during the processing, resulting in yogurts which are coarse-bodied, grainy, and which exhibit whey-off, i.e., the separation of fluid from solid material.

A stabilization problem with conventional ice cream is that at deep-freeze temperatures they cannot be served or eaten as readily as when they are at normal eating temperature. Reformulation to ensure such properties, e.g., spoonability at deep-freeze temperatures, as approximately those expected at normal eating temperatures is comparatively simple. The difficulty is that such reformulation leads to products that do not have acceptable properties at normal eating temperatures. The properties of ice creams, that have the serving and eating properties conventionally expected at normal eating temperatures and that are sufficiently stable, are improved by incorporating stabilizer mixtures comprising (a) locust bean gum or tara gum, and (b) κ-carrageenan or xanthan gum or agar-agar [91].

4.2.2 Whey Treatment

Whey is the watery part of milk separating from the curd during cheese and casein production and is waste by-product of the dairy industry, obtained in large quantities. It is a highly environmentally polluting waste material and is disposed off by using it as animal feed or fertilizer, or by dumping it in sewers and watercourses. With increasing environmental controls, there is now more interest in whey utilization. There are two types of whey, classified according to source: (a) sweet whey at a minimum of pH 5.6 is obtained from the manufacture of products in which rennet enzymes are used to coagulate milk, and (b) sour whey, with a maximum of pH 5.1, is derived from acid-induced coagulation. Whey contains proteins and large quantities of lactose as well as mineral substances (Ca, P), and nonproteins such as citric acid and water [92].

The modified polymers used in the dairy field can be used in the production of products that are derived from milk, such as the recovery of lactose from cheese whey. After treatment with membrane techniques and deionization by means of ion exchangers, whey may be dried, thus originating a high lactose content powder containing proteins that may be used as an ingredient in various foods, as, e.g., powdered milk. By means of acid or enzymatic hydrolysis, lactose may be transformed into glucose and galactose, and used as sweetener. By mixing demineralized whey with butter fat or cream, food products providing a wide range of nutritional elements can be prepared. These food products can be made to simulate human milk and can be employed in low-sodium diets.

4.2.2.1 Concentration of Whey

Whey concentration may be achieved by direct evaporation or alternatively by hyperfiltration. Membrane processes are among the most important separation technologies in the food industry. Although reverse osmosis is mainly used for water desalination, it has been applied to numerous pollution-control and concentration problems, including industrial and municipal wastewaters [93, 94], pulp and paper waste streams [95], food processing liquids [96], and dairy wastes [97]. The major area for ultrafiltration and reverse osmosis in food applications is whey purification and the dairy industry in general. Reverse osmosis was first proposed as a method for the concentration of liquid foods [98]. The development of commercial ultrafiltration equipment has made recovery of the whey proteins and the remaining lactose economically feasible in an attempt to achieve complete utilization of the whey solutes. Concentration of the whey or whey ultrafiltration is necessary at some stage prior to a central processing facility transport, or prior to evaporation, or to produce a concentrate which can be used directly. Reverse osmosis is less costly than the evaporation technique. Whey concentration by reverse osmosis takes advantage of the fact that it operates at ambient temperatures, so that the functional properties of the whey proteins are less affected and the energy consumption is lower than for alternative processes, i.e., it saves the high energy otherwise necessary by evaporation [99]. In the ultrafiltration and reverse osmosis of whey the important factor determining the process economics is the decline in flux rate through the membrane that occurs during operation and is caused by a build-up of whey components and the accumulation of fouling layers at the membrane surface.

Reduction of membrane fouling of whey: in the reverse osmosis of cheese whey only part of the fouling layer at the membrane surface has been able to be removed with fluid shear, the major whey components that remained at the membrane being casein [100]. This was ascribed to the lower diffusion coefficient of casein relative to the other solutes of whey components. Fouling of the membrane surface would retard diffusion of the microsolutes and so increase the microsolute concentration polarization. Fouling thus reduced flux rates by contributing an added hydraulic resistance, and by reducing the effective driving force for water permeation through the membrane.

Fouling has been minimized by dispersing the whey proteins, and so preventing their deposition on the membrane [101]. Some of the protein components causing fouling are affected by factors such as pH, ionic strength, and composition, particularly calcium concentration, and the interactions between the various solutes [102, 103]. The possibility of pretreating the whey before membrane processing to reduce fouling is commercially attractive, provided that the product properties, such as the functionality of the proteins are not detrimentally affected. In whey ultrafiltration pretreatment, removal of the lipid fraction involves flocculation and gravity settling [104]. pH variation in the ultrafiltration of cheese and HCl casein whey can improve flux rates. Demineralization can also give higher flux rates. The rate of flux decline decreases by whey demineralization and increases by NaCl addition [105–107]. Membrane fouling conditions in reverse osmosis of whey is somewhat different than in ultrafiltration, because of the range of solutes present (proteins, lactose, and salts) and their interactions with each other. Altering the state of aggregation of the fouling material by pretreatment of the whey causes little change in the reverse osmosis flux rates. This result, together with the effects of demineralization or salt addition, indicates that the flux-determining process in reverse osmosis of whey is the concentration polarization which is increased by the presence of the fouling layer. The aggregates formed by the pretreatment procedure, whilst forming a more water-permeable fouling layer, do not lead to a significantly greater back-diffusion rate of solute from the membrane surface.

4.2.2.2 Protein Recovery from Whey

The whey proteins, lactalbumin and lactoglobulin, constitute up to 20 % of the total protein content in milk, which are wasted during the industrial processes and may be industrially separated and fractioned by means of special functional polymers and used in food products. This involves acidification to the isoelectric point of the protein in the whey, coagulation by heat, and then filtration. However, the introduction of membrane filtration in connection with dairy production has resulted in a wide range of new protein-enriched products from the whey proteins. Recovery of whey proteins essentially has been achieved by means of ultrafiltration. If a higher purity is desired than obtained by normal ultrafiltration, water may be added during the diafiltration process, so that more impurities pass through the membranes.

4.2.2.3 Lactose Removal from Whey

The recovery of lactose from whey is a large industrial operation because of its important utilization as a special food product and also in antibiotics synthesis. Lactose is present in both sweet and sour whey and can be extracted by conventional chemical means. After removing the coagulated protein by filtration, the resultant clear whey is deionized to remove inorganic constituents as well as lactate, citrate, and phosphate, purified and concentrated to crystallize the lactose which is then washed and sometimes recrystallized. Whey typical contains 4–5 % lactose, of which 50 % are generally recovered. The yields and purity of crystallized lactose can be improved by applying ion-exchange techniques. The crude solution may be passed through an exchanger in order to increase the efficiency of the cation removal, where lactose is readily crystallized from the purified solution. Either the deproteinized whey by heating at the isoelectric point can be purified by ion exchange before the crystallization or by removing all ions by demineralizing the whey. Beside the actual economical value of lactose, there is the added incentive of reducing the problem of disposing of the whey. Whey can present a severe waste disposal problem due to its high biochemical oxygen demand.

4.2.2.4 Sweet Syrup from Whey

Lactose intolerance is the inability to utilize milk sugar causing serious gastrointestinal symptoms. The conversion of whey lactose to glucose and galactose by hydrolysis is being explored as a means of making this milk waste solution useful as a food sweetener [108]. Consequently, the enzymatic hydrolysis of whey lactose by immobilized lactase (β-galactosidase) has evoked considerable interest to be converted it into sweet syrups. This enzymatic hydrolysis breaks down the milk lactose into its monosaccharides glucose and galactose, which taste sweeter and crystallize out less readily than lactose. A large number of immobilized β-galactosidases have been investigated on various supports, such as phenol-formaldehyde resin [109, 110], a porous silica support [111], and ceramic by covalent bonding through glutaraldehyde [112]. A fiber-entrapped lactase [113] has also been used in this conversion. Another approach used to convert lactose to sweet syrup includes immobilization of whole cells in membranes or thin films. Clearly, a vast potential exists for immobilized β-galactosidase in the dairy industry for large-scale treatment of sour whey. Immobilized-enzyme technology allows continuous processing of dairy products at temperatures sufficiently high to minimize microbial contamination.

Although immobilized enzymes on various support materials have been used in pilot plant operations for the hydrolysis of lactose in whey, this procedure is limited on commercial industrial scale due to a number of main drawbacks: immobilized β-galactosidases are inhibited to an appreciable degree by their reaction product galactose, and have a poor half-life in deproteinized whey and with increasing temperature. To increase the sweetener value of the sweet syrup products, combining immobilized lactase with immobilized glucose isomerase has been used [114]. The process involves treating whey with immobilized lactase to hydrolyze lactose to glucose and galactose, removing calcium ions from the whey, adjusting the pH of the whey to “sweet,” followed by treating the whey sugar with immobilized glucose isomerase to isomerize glucose to fructose [115]. Immobilized glucose isomerase has also been used to increase the sweetness of β-galactosidase hydrolyzed whey lactose syrups. Sweetness near to that of sucrose could be obtained by isomerizing whey lactose hydrolysate after increasing its glucose level.

4.2.2.5 Exopolysaccharides from Whey

Poly(β-hydroxyalkanoate), being a biodegradable polymer, is composed of glucose and galactose, and is produced by biosynthesis from largely available lactose via microorganisms (such as lactic acid bacteria used in the dairy industry for flavor enhancement) for the conversion of lactose from agroindustrial wastes and from whey produced as by-product in the dairy industry [cheese whey or whey permeate (deproteinized whey)] [116]. This fermentation process by microorganisms uses lactose and glucose in dairy whey as the main energy (carbon) source [117–119]. These microbial biopolyesters can also be prepared by the economic fermentation with lactic acid bacteria from cider, beer, and wine [120, 121], and from vegetable oils and animal fats, molasses, and meat-and-bone meal as substrates in microbial synthesis [122]. The produced polymers play a key role in the rheological behavior and the texture of fermented milk [123].

Polylactide, also a biodegradable biopolymer, can also be produced from sweet cheese whey in the course of fermentation by lactic acid bacteria and is used in dairy industry for flavor enhancement and resistance to bacteriophages [124]. However, enhancement of quantities and reduction of cost in lactic acid production by fermentation are required in the dairy industry [124]. Polylactide is used in packaging bottles for noncarbonated beverages, salad bar containers, water, dairy products, and juices [125]. Gellan gum is a polysaccharide with a high acyl content, and varying acetate and glycerate levels and is produced from sweet cheese whey by biosynthesis (*Sphingomonas paucimobilis*) in growth media containing lactose as a carbon source [126, 127]. Whey permeate (deproteinized whey) from the cheese industry as an industrial waste presents serious economic and environmental problems. Part of the phenol and formaldehyde in PF resins has been replaced by lactose and lactose derivatives [128]. In addition, dilactosylurea and *N*-hydroxymethyl-*N*-*lactosylurea* (up to 50 % wt) has been incorporated in UF resin formulations without substantially affecting the wet shear strength of plywood bonded with these whey-modified resins [129].

4.2.3 Other Dairy Applications

Cheese-coating polymers: polymeric antimicrobial coatings are used to protect dairy products. Natural polymeric antimicrobial waxes are used as cheese coatings to inhibit microbial growth. Polymeric antimicrobial solutions based on silver-ion zeolite polymer have been used for coating of cheese products, continuously inhibiting the growth of bacteria and fungi. Polymeric food coatings based on aqueous dispersions of PVCVdC and butyl rubber possess physicochemical properties that still ensure the biochemical processes in the maturing of the cheese [130]. Antimicrobial technology is used in consumer, industrial, and healthcare industries, as, for instance, in: cell phones, shoes, keyboards, pens, water filters and faucet handles, air conditioning and heating units, medical catheters, ice machines, and milking machine inflations in the dairy industry [131].

4.3 Polymers in the Sugar Industry

Reactive polymers are being used in the different segments of the sugar industry such as (1) sucrose sugar manufacture (can sugar, beet sugar), (2) liquid sugar manufacture (glucose syrups, glucose and fructose syrups), (3) isomerization of glucose to fructose, (4) purification of raw sugars (de-ashing, decolorization, demineralization), (5) by-product recovery.

4.3.1 Sucrose Manufacturing

Sucrose, the common table sugar, is manufactured in large quantities as a sweetening agent for both direct and indirect consumption. It is obtained by extraction and purification through refining of raw sugar juice manufactured from both cane and beets. Through these processes high purity crystalline and liquid sugar are obtained. Processes increasing the pure sucrose sugar content but decreasing the molasses content in production are highly desirable. Reactive polymers have been used in the various stages of sucrose production with major qualitative, technical, and economic advantages.

4.3.1.1 Cane Sugar

After crushing the cane, the juice is screened to remove the floating impurities and treated with lime to coagulate a part of the colloidal matter, to precipitate some of the impurities, and to change the pH. Filtration and evaporation to a thick pale yellow juice result in a mixture of crystals and syrup of sugar. Centrifugation of this mixture removes the syrup, which is retreated to obtain more crystals (raw sugar) and black strap molasses as a final liquid. Refining of raw cane sugar includes the sequences of affination process and either mechanical or chemical clarification process by treatment of the melted raw sugar dissolved in hot water. A polymeric anionic flocculant is added prior to the clarification of sugar cane juice and results in fast settling of the sediment in the clarifier. Its addition to the clarifier promotes drier cakes and increased filter clarity of the turbid juice going to the filter from the clarifier.

Decolorization of the clarified effluent liquor is carried out by bone char or activated carbon to remove a large amount of dissolved impurities. After certain amount of use, the char loses its decolorizing ability and must be revitalized. Activated carbon may be used on a single-use and does not have the ability to absorb inorganic materials. In the cane sugar industry, polymers are used for recovery of sugar from both black strap and refiner molasses by ion exchange. The production of bland syrups, which can replace solid sugars, by demineralizing diluted molasses and decolorizing the resultant syrups were not successful because of the blocking of resin beds by the precipitated solids. The high ash and color content made necessary large resin and short operating cycles, and the process proved to be economically unattractive.

4.3.1.2 Beet Sugar

Sucrose can also be obtained from many sources other than sugar cane, such as sugar beet, maple syrup, and sugar palms. The manufacture of sucrose from sugar beets is an important branch of the sugar industry. The conventional beet sugar process involves countercurrent diffusion of sugar, with removal of impurities from sliced beets as a first step. The resulting juice is defecated by limiting to pH 9 and carbonating. This treatment effects a considerable purification and it may be repeated, and also SO_2 treatment may be used in order to bleach the juice and provide a white sugar. The thin juice which results is finally concentrated with or without additional clarification, and crystallized. A variety of recrystallization or remelt cycles have been developed to maximize the extraction of sugar from the juice. In order to avoid precipitation in the beds and consequent loss of resin capacity, treatment of at least first carbonation juice is to be preferred. Zeolitic clays were used in treatment of sugar beet juice in order to increase sugar yields. These processes had the disadvantage of increasing the calcium content of the solutions and consequently inhibiting evaporation and encouraging evaporator scaling. This scale prevents effective heat transfer in the evaporator stages, leading to increased energy costs and production losses due to shutdowns of the evaporators for cleaning and scale removal. ***Polymeric antiscalants*** are stable to hydrolysis at the evaporation temperatures and inhibit scale formation in evaporators caused due to the presence of hardness components in the sugar juice.

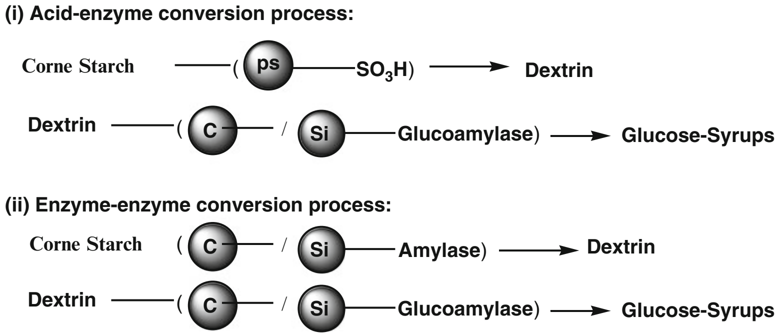
Hydrolysis of raffinose: Depending on climate, beet sugar contains varying small amounts of raffinose that becomes concentrated in the mother liquor during sucrose sugar crystallization. At higher concentrations raffinose begins to interfere with sucrose crystallization and has an inhibiting effect on this process. The raffinose resulting in the beet sugar industry can be broken down into sucrose and galactose by β-galactosidase (melibiase) that increases the yield of beet sugar. However, the β-galactosidase must be entirely free of invertase activity since this would break down the desired end product of sugar manufacture, sucrose, into fructose and glucose. Consequently, the immobilized β-galactosidase which is used for hydrolysis of β-galactosides in soybean milk has been utilized for the biocatalytic hydrolysis of raffinose to sucrose and galactose.

4.3.2 Liquid Sugar Manufacture

The increasing requirement for glucose syrups as a substrate for the production of high-fructose syrups and the rapid growth of the use of this liquid sugar by the food industry has led to the use of different materials for the industrial production of glucose syrups. It does not seem logical to carry the refining process through the crystallization stage only to redissolve the crystalline sucrose sugar in water in order to offer it to the manufacturing consumer as sugar syrup. The use of the liquid sugar has many advantages compared with dry sugar such as labor savings in shipping, storage space, and handling costs, greater cleanliness, lower process losses, elimination of process steps such as the dissolving of dry sugars, increased uniformity, and plant capacity. However, its use has some disadvantages such as additional equipment for storage and handling, a decreased stability in storage, and higher distribution costs.

4.3.2.1 Glucose Syrups

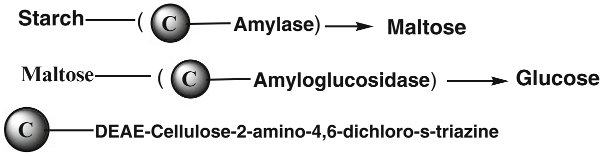
The use of starch for the preparation of glucose syrups has led to a commercial success in the industrial production of this material [132]. However, starch is chemically converted to dextrin or dextrose syrups. Crystalline dextrose (glucose) is the major product of the starch conversion industry from corn, milo-maize, grain sorghum, and other vegetable starches with acid under pressure and at high temperature [133]. Starch hydrolysis is an equilibrium reaction and depending upon the



Scheme 4.3 Starch hydrolysis to glucose syrups [132]

concentration of starch, the hydrolyzate can contain 85–90 % dextrose. Because many side reactions take place in the acid environment, the glucose syrup produced is often of poor quality. This major problem is due to the absence of the crystallization process.

In general, two processes are used for hydrolyzing starch to dextrose (Scheme 4.3) [132], which are grouped into: (i) Acid-enzyme conversion process: in which starch is first liquefied by partial hydrolysis to low-molecular-weight dextrins (dextrose 25 %, reducing sugar 42 %) using an acid such as HCl. The suspension is then enzymatically treated with a glucoamylase to convert the partially hydrolyzed starch (dextrins) to dextrose. Glucoamylase catalyzes the sequential hydrolysis of glucose moieties from the nonreducing ends of starch or amylodextrin molecules. (ii) Enzyme-enzyme conversion process: in which a starch slurry is partially hydrolyzed by heating with starch-liquefying bacteria with β-amylase which is capable of promoting random cleavage of β-1,4-glucosidic bonds within the starch molecule. The partially hydrolyzed starch is then treated with glucoamylase. While HCl is conventionally used as a catalyst, continuous hydrolysis by ion-exchange techniques has successfully been applied. This success is due to the flexibility which ion-exchange treatment gives to the refiner in varying the degree of ash removal. Direct dual enzymatic saccharification system for the industrial production of glucose syrups by the conversion of raw grain material is carried out in a continuous process by initially liquefying starch containing an immobilized amylolytic enzyme and thereafter saccharifying the liquefied starch to the desired sugar yield by immobilized saccharifying enzymes such as immobilized amyloglucosidase. Despite such emergence of a two-enzyme system, there are continuing drawbacks, e.g., the inability to separate in liquified form a good yield of filtrate from the converted liquor. During the production of fermentable sugars such as maltose by enzyme systems or to dextrose by the use of amyloglucosidase, it appears to introduce processing time, costs of both enzyme utilization and equipment used during or subsequent to saccharification. The use of immobilized amyloglucosidase to enzymatically catalyze the breakdown of corn starch for the industrial production of glucose syrups has largely eliminated the problem of side reactions. The immobilization of



Scheme 4.4 Conversion of starch to glucose and fructose by immobilized enzymes [145]

glucoamylase on cellulose [134], DEAE-cellulose by ionic or covalent bond [134, 135] and other organic supports has been applied for hydrolysis conversion of corn starch and dextrin to glucose [136–138]. Immobilization of glucoamylase by covalently bonding to a variety of inorganic supports [115], such as controlled pore glass [139] and glass [115], has been used for conversion of corn starch to glucose. Immobilized glucoamylase fixed to porous silica by covalent bonds with glutaraldehyde [136] has also been used to convert dextrin to glucose.

Immobilized enzymes have also been investigated to convert large quantities of cellulose in biomass to glucose [140, 141]. Glucose syrup could be produced in very large quantities from this source for use in fermentation to food and food products. Cellulose was immobilized with collagen on glass beads and used in a fluidized bed to produce glucose [142]. Mixed immobilized β-amylase and glucoamylase have also been used to provide a substantially complete conversion of starch to dextrose [143]. Very high dextrose hydrolysates were produced by using a multistep hydrolysis process [144], which comprises four steps of: (i) reacting starch with hydrolytic enzymes or acid to produce a low-dextrin starch hydrolysate, (ii) treating the low-dextrin starch hydrolysate with soluble glucoamylase to produces a high-dextrin starch hydrolysate, (iii) reacting the starch hydrolysate with an effective amount of immobilized glucoamylase, and (iv) recovering a dextrose product

4.3.2.2 Glucose and Fructose Syrups

A process of obtaining high yields of glucose and fructose from liquefied starch by using an enzyme system comprising immobilized glucoamylase, immobilized glucose isomerase, and immobilized debranching enzyme has been described (Scheme 4.4) [145]. There are a number of advantages associated with the use of this process involving a multicomponent enzyme system for converting liquefied starch to a mixture of glucose and fructose. Starch can be hydrolyzed in high concentrations to a lower degree of hydrolysis starch to produce a hydrolyzate containing dextrose (25 %) and reducing sugars (42 %). β-Amylase covalently bonded to cellulose beads was used for conversion of starch to maltose [146], whereas amyloglucosidase immobilized on DEAE-cellulose by covalent bonds through 2-amino-4,6-dichloro-s-triazine was used for conversion of maltose to glucose [147].

Immobilized whole-cell invertase appears to be remarkably stable. Yeast provides an inexpensive source for the enzyme, making immobilized whole-cell invertase attractive to invert sugar production. Continuous bio-catalysis would eliminate

Scheme 4.5 Conversion of glucose to fructose by immobilized enzymes [150, 151]

the need to regenerate the resin, and the formation of by-products typical of hydrogen ion catalysis could be avoided. Furthermore, processing of such substrates as beet or cane molasses would be possible. Invertase covalently bonded to glass or cellulose has been used for conversion of sucrose to glucose [148]. Inversion of sugar is the conversion of sucrose to glucose and fructose. Cation-exchange resin technology using sulfonated polystyrene cation exchangers regenerated with sulfuric acid behave as solid acid catalysts in place of mineral acids for the inversion of sucrose.

4.3.3 Isomerization of Glucose to Fructose

Corn glucose syrup is not sufficiently sweet to compete with sucrose in many applications. However, the sweetening properties of fructose are considerably greater than those of glucose. Fructose is a ketose monosaccharide occurs naturally in a large number of fruits, and sweeter than sucrose, hence it finds a large market in the preparation of processed foods and drinks. A number of microorganisms are capable of transforming glucose into its isomer fructose by means of glucose isomerase. This isomerization property is of potential commercial significance as the enzyme can in principle be used to produce a mixture of glucose and fructose using corn-based glucose syrup as a raw material. The isomerization of glucose to fructose is catalyzed by glucose isomerase until a state of equilibrium is attained. This mixture, referred to as high-fructose corn syrup is an important competitor for sucrose as a sweetener. The industrial production of high-fructose corn syrup by immobilized enzymes is employed in continuously operated packed and fluidized reactors. In addition to high-fructose syrup production, immobilized whole-cell glucose isomerase can be applied to glucose conversion for recirculation in the fructose separation process, either for the second generation high-fructose syrup or for pure fructose manufacture. Two different grades of high-fructose syrup are presently available at 42 and 55 % fructose content in the glucose-fructose mixture [149]. High-fructose syrup (90 % fructose) is prepared in a two-step process from the glucose-fructose mixture (55 % fructose) using immobilized glucose isomerase (Scheme 4.5) [150, 151]. Because of the high sweetening power, i.e., high fructose content, of sugar syrups, they are increasingly used instead of sucrose in beverages and in the food industry in general.

The majority of current industrial-scale applications of immobilized microbial cells in continuous biotechnical processes are based on single-enzyme-catalyzed transformations. Potential applications involve carbohydrate conversions, of which the biggest single success story of immobilized biocatalyst technology is the development of high-fructose corn syrup production. Immobilized microbial cell-catalyzed carbohydrate transformations involve: glucose isomerase, invertase, and α/β-galactosidase. The immobilized enzyme activity could be retained within cells during repeated or prolonged processing by preventing cell lysis at operating temperatures, making possible the reuse of the whole-cell biocatalyst, as well as continuous processing in a column reactor. A whole cell immobilization technique is used for the production of an immobilized glucose isomerase system. The potential for using immobilized glucose isomerase in the food industry for the commercial production of high-fructose syrups by isomerizing sugar glucose, obtained from corn starch or from any available starch as potatoes, is one of the most successful processes in the food insustry [108, 152].

Entrapment of whole microbial cells in polymer matrix is a simple technique for large-scale biocatalyst preparation. Some activity loss is likely during immobilization as a result of the cytotoxicity of the polymerizing catalyst and the denaturing of enzyme caused by the monomer. The adsorption immobilization of glucose isomerase within a porous alumina carrier [153], porous ceramics [154], or anion exchange cellulose or synthetic resin [155] has also been used to convert glucose to fructose. Immobilized glucose isomerase adsorbed onto DEAE-cellulose was used commercially for production of fructose syrup [156]. Glucose isomerases chemically immobilized on porous glass beads by covalent bonds through azo-linkages, and on chitin by crosslinking with glutaraldehyde were also used to convert glucose to fructose [157, 158].

4.3.4 Purification of Raw Sugars

Raw sugar is conventionally refined by the lowest cost means for separating the nonelectrolytes (sugars) from nonsugar constituents such as ash, electrolytes (organic acids), and colorants which are present naturally or which result from processing steps. Refining of raw cane sugar includes the following steps: affination, wherein the film of adhering molasses is removed from the raw sugar crystals. The dissolved crystals in hot water are then treated by either mechanical or chemical clarification (defecation). The affination process consists in hot mingling the raw sugar with partial affination syrup from a later step of the process, then centrifugation of the obtained viscous mass. The affined raw sugar is melted or dissolved in a minimum of water, clarified with lime and a filter aid, and the solution is filtered. The resulting syrup normally containing solids (60–65 %) is run over bone char filters and the resulting partially de-ashed and decolorized liquor is pumped to vacuum crystallizers where successive batches or strikes of crystals are removed until the sugar content is depleted to a range where it is no longer economical to crystallize any further.

In the production of solid sucrose sugars, most of the noncarbohydrate materials, which are inorganic or organic ionizable or nonionizable materials, interfere with the process of crystallization by decreasing the crystallization rate or by increasing the residual solubility of the particular sugar, hence they cut the yield and increase the cost. In the manufacture of sugar syrups, the noncarbohydrate constituents contribute to unpalatability and to color and detract from the price of the product. Thus, in the refining process of sugar, it is desirable to remove soluble ash, color constituents, and other electrolytes that reduce the overall yield of crystalline sugar. The main aim of polymer treatment of sugar solutions is to improve the quality of the sugar for marketing purposes by the removal of the impurities from the solution before crystallization, to decrease molasses formation, and to increase sucrose yields. However, resin life is an important factor in the economics of using polymers such as ion exchangers in sugar processing.

Membrane filtration can be used to clarify the raw juice in the sugar industry, thereby eliminating many environmental problems and improving the quality and yield of the juice. The ability to produce very specific separations and purifications at ambient temperatures makes membrane filtration a much more cost-effective technology than more conventional methods. Membrane clarification systems have been used to replace the traditional separation methods, such as filter presses and rotary vacuum filters, in a number of process steps such as clarification, concentration, depyrogenation, fractionation, employed in the sugar-syrup industry from starch. The primary benefits are elimination of using kieselguhr and increasing product yields in the following areas: clarification of corn syrups (dextrose and fructose), concentration of starch wash water, dextrose enrichment, depyrogenation of dextrose syrup, fractionation and concentration of steep water. Both the cane and beet sugar industries have used liming and flocculation to clarify the raw juice and remove impurities such as waxes, dextrans, and gums before the refining step for evaporation and crystallization of the juice.

4.3.4.1 De-ashing

Ash and small amounts of organic matters which are present in the raw sugar are ordinarily eliminated by the crystallization process. Pure crystalline sugar can be produced directly by the multiple crystallization technique of sugar cane juice. However, traditional recrystallization methods are unable, from an economic point of view, to minimize this loss. Bone char and clays are the most widely used agents for the refining of sucrose. These adsorbents cannot be regenerated chemically. A portion of the ash which is absorbed by these materials remains behind and results in a gradual buildup in ash content of the char until it reaches a point where its effectiveness is exhausted and it must be discarded. To improve the ash removal properties of these refining agents, dehydration by sawdust, lignite, and coal with H_2SO_4-$ZnCl_2$ have been employed.

The major entry of ion-exchange technology into sugar manufacturing has come through its utilization in the sugar refining industry primarily as a substitute for the crystallization process. Ion-exchange processes have been used for de-ashing the sugar to eliminate the large amount of molasses ordinarily produced in raw sugar refining. The application of ion-exchange resins to sugar purification has successfully increased the sugar yield and quality and eliminated for the most part other sources such as beet molasses.

Certain deficiencies in the ion-exchange processes have resulted from the requirements of specific sugar refining processes and from an inability to adapt conventional techniques of ion-exchange refining to these specific requirements. For example, it is desirable in most sugar refining processes to operate at high sugar concentrations in order to minimize evaporation costs. Furthermore, to minimize viscosity effects and to speed up the flow rates, it is necessary to operate at relatively high temperatures and thus often beyond the stability range of the most efficient resins. The development of sugar refining with ion exchangers today as a supplement or even replacement of conventional processes is concentrated on reducing the regeneration costs and the problem of cooling the sugar juices to decrease inversion. Ion-exchange resins have also been used in the sugar industry to combine de-ashing and decolorizing functions in one refining agent.

The application of ion exchangers extends to the treatment of sugar syrups for the production of pure sugar syrup. Generally, the production of sugar syrup rules out crystallization and thus eliminates a very important purification step so that ion-exchange processes are highly appropriate here for a reduction of the ash content and elimination of small quantities of organic matter. For this purpose, a mixed bed consisting of a strong base anion exchanger and a weak acid cation exchanger, results in the desired syrup qualities. The process of refining starch conversion sugars by ion-exchange treatment produces sugar syrups for marketing that are lower in ash and better in flavor, and show greater stability. These sugar syrups are generally preferred for manufacturing candies, ice creams, and other food products. However, one of the minor drawbacks to wider use of ion-exchange resins in this industry has been the failure of the anion-exchange resins to withstand operation at high temperatures. This makes it necessary to cool the liquor, which may lead to fermentation if the dilute solution is allowed to stand for an extensive period.

4.3.4.2 Decolorization

The coloring in sugar solutions arises from a variety of sources. Depending on the cane sugar source, the colored molecules themselves vary to some extent. They may consist of plant pigments extracted or expressed from the sugar source. Further variation is caused by degradation products from processing treatments.They may be formed as in the case of sucrose solutions by the alkaline processing and result from sugar/amino acid interaction or from sugar fragments or as in the case of dextrose manufacture they may be due to polymerization of intermediate dehydration products formed during acid processing. The hydrolysis of starch also results in the formation of small amounts of color substances which are themselves weak acids including such organics as levulinic and formic acids.

In the refining process of sugar, it is desired not only to remove soluble ash but also to remove other colored constituents that reduce the overall yield of crystalline sugar. The decolorization processes of refined sugars produce sugars that have less color-forming substances and are better in flavor, and show greater stability. A certain part of the colorants is separated either by general adsorption or by ion exchangers. Decolorization of the clarified effluent liquor is carried out by bone char or activated carbon to remove a large amount of the dissolved impurities. After a certain amount of use, the char loses its decolorizing ability and must be replaced. Activated carbon may be employed on a single-use basis and does not have the ability to absorb inorganics. Ion-exchange resins which are increasingly being used remove the inorganics and coloring materials. In cane sugar refining, an ion-exchange process is advantageously used after carbon treatment for final refining to remove the last colored components from the partially decolorized cane sugar so that the last coloring components can be removed with strong base macroreticulars or gel anion exchangers.

In the course of removing the ionic constituents from the sugar solutions, considerable decolorization frequently takes place. Depending upon the nature of the coloring constituents, the ion-exchange materials used may retain their color-removing properties almost indefinitely. Although the demineralization process often results in considerable decolorization of the sugar solution being treated, the use of this type of treatment is not recommended as the solitary means of decolorization because of the high cost and because of losses in ion-exchange capacity and color-removing capacity of the resins. Certain resins have been developed for color removal which have little or no ion-exchange properties. They are effective as color adsorption substances because they are highly porous, contain certain polar groups, and show a high capacity and excellent adsorption properties. After exhaustion, they are regenerated with alkali treatment and neutralization.

Polystyrene and polyacrylic resins have been employed by the cane industry for quite some time, essentially for decolorizing the weakly acidic organic coloring complexes. A major problem has been acceptability of resin-treated liquors for liquid sugar products, which are uncrystallized. The resins, if overheated or abused, release ammoniacal fishy odors which are most objectionable. Chlorine liberated in resin operations or treatments may react with naturally occurring phenols in the sugar liquors to give chlorophenols, with their characteristic medicinal flavors. The heightened awareness of carcinogens, such as nitrosamines, in food or the environment was also a factor in the stringently regulated approval of acrylic resins.

Since the use of ion exchange depends on ionic potential, i.e., the number of suitable, available charges on molecules, it would appear reasonable to assume that the larger, darker, more ionized complexes lend themselves more to attachment to these resins than do the lighter (less highly charged), smaller, less ionized colored complexes. The resins used are strongly anionic and the compatibility of the resin with the processes on either side is a major factor. Continuous operation procedures have been developed. Resin decolorization should yield a cheaper process. The use of macroporous anion exchangers permits decolorizing of sugar juices and syrups on the largest industrial scale [159]. A number of commercial ion exchangers can be used as decolorizing resins, as Amberlite IRA-900 (strongly basic, *macroreticular*

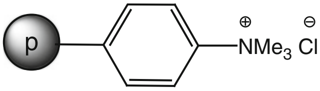


Fig. 4.1 Amberlite IRA-900

resin), Amberlite XE-258 (macroporous or macroreticular polystyrene beads), and Amberlite IRA-401S (strongly basic *gel-type* resin) (Fig. 4.1).

A cationic colored polymeric precipitant removes colloidal/dissolved color from sugar cane juice prior to the separation of mud. It is added to the limed and sulfited juice emerging from the juice sulfitor. After its addition, the limed and sulfited juice goes through the juice heater and the flocculant is added at this stage at the entry to the clarifier. The clear juice emerging as supernatant of the clarifier has reduced color to the extent of 30–60 % depending on the nature of color-causing substances which finally translates into a minimum reduction in color of sugar produced from this juice. A cationic polymer is effective as a decolorization agent for syrup clarification in the phosflotation process of sugar solids. It is effective in removing most of the color and also high-molecular-weight impurities such as starch and dextran which results in good decolorization as well as good filterability of the clarified liquor. The color of the syrup is reduced by as much as 30–60 %. The unsulfured syrup is treated with the color precipitant while it is being pumped to a buffer tank which also acts as a feed tank for the clarifier. The treated syrup is passed through a heat exchanger to raise its temperature which is then mixed with phosphoric acid and lime superheated in a specially designed flash reactor to create primary flocs.

The particulate fouling of resin beds is a major problem and is taken care of by backwashing. Organic fouling is the main cause of resin life reduction, and is reflected in the resin performance. Resins will show this quite dramatically by changing color from the new amber or white to dark brown and black, within five or ten cycles.

4.3.4.3 Demineralization

The ionizable substances that are present in the sugar liquors mostly consist of inorganic cations (Na, K, Fe, Ca) together with organic acids (amino, aconitic, and malic acids), and inorganic anions (Cl^-, SO_4^{2-}). The presence of these ionizable substances is undesirable because they may precipitate in later use of the sugar product, interfere with crystallization, or combine with other impurities to produce off-colors. Improved sugar liquor quality is obtained by the removal of both inorganic and organic impurities from the solution before evaporation and crystallization that lead to the presence of less impurities to coat the sucrose crystals.

Inorganic impurities are removed to a small degree by adsorption on activated carbon or bone char. In the corn industry, sodium zeolite has been used in a conventional softening cycle for removing calcium ions from corn syrup and thus avoiding the occurrence of gypsum haze. Organic impurities are more completely removed by decolorizing agents, but considerable amounts of the color and organic containing amino and acidic groups are removed from sugar solutions by demineralization. Ion-exchange resins are ideal for the complete removal of such an undesirable contaminant where adsorption technique cannot be practiced because of the low pH required for treatment. The cationic components of cane sugar juices are demineralized by cation-exchange resins, whereas the anionic components are removed by strong base anion-exchange resins. In conventional treatment of clarified juice, the conditions may be changed to about pH 2 and as a consequence inversion may occur rapidly. The introduction of the sugar solution into the anion- and then into the cation columns reduces the time the solution is in contact with free acid and tends to minimize inversion of sucrose solutions. Continuous ion exchange, which involves the continuous countercurrent flow of resin and solution through a contacting medium, and electrodialysis through semipermeable membranes made from ion-exchange resins play an important role in the sugar industry. In the use of ion-exchange resin membranes, solutions to be deionized are passed through alternate cells.

Deionized juice consists primarily of sucrose, glucose, fructose, and any other sugars which are present as well as the nonionic organic constituents which include small amounts of gums. The purity is improved due to ion-exchange treatment which makes possible an increase in the recovery of sugar and a consequent reduction in the quantity or even elimination of molasses. Resin has allowed the application of demineralization to cane juice in an effort to minimize inversion. A large application of ion-exchange resins to cane sugar production has been made for the production of liquid sugars for direct consumption. The useful and successful application of ion-exchange resins in the demineralization of starch conversion liquors, of both glucose and dextrose syrups greatly decrease the color and ash content. However, commercial demineralization of cane sugar solutions was not successful because of the high concentrations of ash and organic impurities present which permit only a small amount of molasses to be treated per unit volume of resin. Thus, the chemical costs for regeneration are high per pound of sugar produced. In addition, the large amounts of organic matter present in molasses rapidly poison the resins, and the physical and chemical fouling of the ion exchanger causes decreased capacity, impaired quality of the treated solutions, and excessive rinse water requirements after regeneration.

Ion-exchange resins as used by the sugar beet industry have some drawbacks including: (i) the value of the sugar contained in beet molasses is not sufficiently lower than the price of marketed sugar due to the cost of demineralization and recovery, and (ii) the resins sometimes become poisoned and replacement and chemical treatment add to the cost of demineralization. One of the drawbacks of using sulfonated cation-exchange resins in the demineralization of sucrose solutions is the catalytic hydrolysis of sucrose to invert sugar. Even at low temperatures, a considerable amount of the sucrose becomes hydrolyzed in this way and does not crystallize. Promising results in decreased inversion are being obtained in the use of carboxylic acid of exchange resins in place of the sulfonic acid exchange resins. Since incomplete demineralization results from the use of carboxylic acid resins followed by anion-exchange resins, the demineralizing process is reversed, i.e., the first step is salt splitting by a highly basic anion-exchange resin, followed by carboxylic acid hydrogen-exchange treatment to remove the metal cations.

Maize juice produced from corn starch, which has received considerable attention as a sucrose source, has been successfully deionized by conventional treatment with the result that improved sugar recoveries are possible. In the manufacture of dextrose, the organic acids and colored substances produced as degradation products during starch hydrolysis were eliminated economically by the use of the ion-exchange process to produce a high-quality sugar.

4.3.5 By-products Recovery

In addition to the use of reactive polymers in the various segments of the sugar industry, they have been used for by-product recovery from sugar. Sugar juices as they are extracted from plants are normally associated with a variety of organic acids which are also natural plant constituents or are artifacts resulting from processing steps. In addition to the removal of ash and color compounds, the ion-exchange resins involve effective separation of other functions as organic acid. Aconitic acid as a tribasic acid occurs naturally in cane juice and is concentrated in the molasses during the production of raw sugar. The commercial utility of aconitic acid has led to a good deal of efforts to recover this acid from molasses by reactive polymers. Citric acid from pineapple mill juice and the malic acid in apple juice were concentrated and recovered on ion exchangers. The recovery of tartaric acid from still slops and grape pomace extracts has been achieved by using ion exchange resins. Ion exchange technology has also been successfully applied for by-product recovery in the beet sugar field, in which economic demand comes from the sale of molasses for cattle feed and from the recovery of glutamic acid from beet molasses.

Reactive polymers have also been used in extraction and purification processes of many other products from the food industry, such as: (i) amino acids from sugar juices, (ii) lactic acids and sodium glutamate, (iii) natural sweeteners and sweetening derivatives such as xylitol, sorbitol, mannite, (iv) anthocyanines from vegetables to be used as natural dyes, and (v) conversion of glucose to gluconic acid has been achieved by using glucose oxidase immobilized on polyacrylamide by entrapment [160]. Reactive polymers are also used in other areas of food technology for the treatment of fruit juices and the recovery of sugar values from pineapple wastes and from sulfite waste liquors, which are a potential sugar source but need extensive purification and fractionation [2].

4.4 Polymers in the Juice and Beverage Industry

In addition to the use of reactive functional polymers, either as membranes or solid materials in various physical forms, in the other areas of food technology, they have been employed successfully in the treatment of fruit juices and alcoholic beverages and in wine production. They have also been used in different segments of the fruit juice and beverage industry such as for: (1) fruit juice production and purification, (2) dry beverage mix composition, (3) wine and beer production, e.g., wine and other alcoholic beverages, treatment of cider, beer production and stabilization.

4.4.1 Fruit Juice Production and Purification

Reactive polymers are extensively being used for the treatment of fruit juices [2]. They have pronounced decolorizing effect for clarification and demineralization [32]. Maple syrup has been improved by ion-exchange treatment to remove lead (Pb) introduced during the processing without affecting the flavor of the syrup. The extraction of organic acids from juices by ion exchangers has generally been considered in many industries. They have been employed for deacidification of friut juices from organic acids (citric, malic, ascorbic acids) and for taste improvement of the juice. The extraction of tartaric acid from grape juice intended for consumption, or of aconitic acid as a by-product from sorghum juice when sugar recovery from the seed is carried out has also been proposed. Anion exchangers have been employed for deacidification of orange juice to render it suitable for direct consumption.

In the fruit industry, wastes which formerly constituted a disposal problem are now pressed for their juice content which is then deionized to provide both a valuable by-product syrup and a solution to the disposal problem, i.e., elimination of fruit wastes. Reactive polymers have been used to improve sugars of many types derived from fruit sources. One of the credits to the employment of ion exchangers to treat fruit sugars for recovery of the sugar is the alleviation of the waste disposal problem. Reactive polymers such as ion-exchange resins have been used on a commercial scale for treating fruit juices, such as pineapple mill press juice, citrus peal juice, and apple juice, to produce high-quality fruit sugar syrups. Numerous other fruit juices have been de-mineralized including artichoke syrup, grape juice, and cherry juice.

In the pineapple industry, the fruit hulls are pressed for their juice content and the residue dried for use as a feed supplement. The clarified pineapple mill juice, obtained from pineapple hulls and other waste portions of the fruit, is decolorized after liming and filtration to recover calcium citrate. The demineralized syrup produces a sugar solution which when concentrated may be used as a syrup for sweetening sliced pineapple or as sugar syrup for use in fruit canning operations. Apple juice expressed from peels, cores, and hulls has been deionized to produce bland apple syrup. Ion exchange produced a stable apple syrup from which was removed not only a major portion of the fruit ash but also some of the introduced insecticides. Apple juice, on demineralization and subsequent concentration by evaporation, yields heavy syrup which has fine humectant properties. In apple juice demineralization, the malic acid in the juice was concentrated on an anion-exchange resin [160].

Demineralization of citrus peel juice produced by liming orange skins remaining after squeezing out the orange juice, removes all of the inorganic constituents and half of the organic impurities. Evaporation of the demineralized juice gives syrup which can be substituted for sucrose for sweetening of grapefruit. Citric acid recovery from pineapple mill juice, and exchange of organic acids in sugar beets have been described, as well as the recovery of tartaric acid by means of ion-exchange resins from still slops and grape pomace extracts.

4.4.2 Dry Milk Beverage Mix Composition

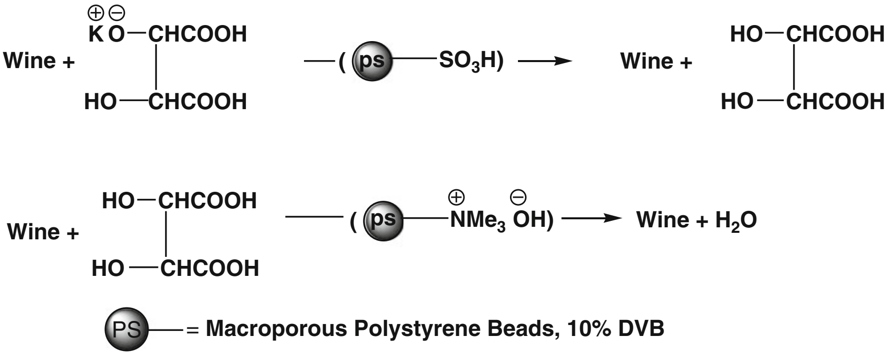
A milk beverage is prepared by reconstituting with milk or a milk substitute a dry mix composition containing a pregelatinized starch, an edible acid, and a hydrocolloid gum, which is a mixture of guar gum and xanthan gum[161]. An acidified dry milk beverage mix, when combined with milk, is ready to serve as a tangy instant yoghurt-like beverage. Although liquid yogurt analogs may be made by direct acidification, dry mix products require either low levels of acid or gluconolactone. A major problem with making yogurt-like products by direct addition of acid to milk is that the larger quantities of acid required to give a yogurt tartness results in the precipitation of the milk protein, due to curding of milk when its pH sinks below the isoelectric point of milk protein, and thus the use of weaks acids in a milk-based desserts is restricted. A number of modified starches function in beverage mix systems and a hydrocolloid gum is added to aid in increasing the viscosity when the mix is first reconstituted with milk and to provide body and aethetically appealing mouthfeel to the final beverage. Guar gum is employed, which is preferably used in conjunction with xanthan gum for additional viscosity control. Carrageenan can also be employed as a viscosity control agent as well as sodium carboxymethylcellulose.

4.4.3 Wine and Beer Production

4.4.3.1 Wine

Wine production (red, white, rosé) starts with grape harvest, crushing and pressing, primary and secondary fermentations, and ending with the bottling of the wine. (1) *Grape harvest* is the first step in wine production by picking of the grapes either mechanically which has the disadvantage of indiscriminate inclusion of foreign non-grape materials in the product that may increase grape juice oxidation, or by hand picking of grape clusters that prevents inferior quality fruit and contamination. The selection of the grapes and grape harvest is determined by the level of sugar, acid, and pH of the grapes, phenological ripeness, flavor, tannin development (seed color and taste). (2) *Grape crushing* is the process of breaking the skins to start to liberate the contents of the berries by the mechanical crusher, where grape clusters are crushed, juice, skins, seeds, and some debris exit out the bottom. *White wines* are processed from white grapes without destemming (removing the stem holding the grapes) or crushing and are transferred from picking bins directly to the press. The presence of stems with the berries facilitates pressing by allowing juice to flow past flattened skins and a short period of skin contact serves to extract flavor and tannin from the skins as well as potassium bitartrate precipitation, resulting in an increase in the pH of the juice. White wine is also produced from red grapes by the fast pressing of uncrushed fruit to minimize contact between grape juice and skins. *Red wines* are processed by removing the stems of the grapes before fermentation since the stems have relatively high tannin content and can give the wine a vegetal aroma due to extraction of 2-methoxy-3-isopropylpyrazine which has an aroma reminiscent of green bell peppers. Red wines derive their color from grape skins, and therefore contact between the juice and skins is essential for color extraction. They are produced by destemming and crushing the grapes into a tank and leaving the skins in contact with the juice throughout the fermentation. *Rosé wines* are produced by crushing the grapes, and the dark skins may be left in contact with the juice for a shorter period to give the desired color, and the must is then pressed and fermentation continues. (3) *Grape pressing* is the act of applying pressure on grapes to separate juice from grapes and grape skins. Pressing is not always necessary if grapes are crushed and a considerable amount of juice is immediately liberated. Red wine is made by pressing crushed red or black grapes that undergo fermentation together with the grape skins. White wine is made by pressing crushed grapes to extract the juice that is separated from the must before fermentation to remove the grape skins, or made from red grapes by extracting their juice with minimal contact with the grapes' skins. Rose wine is made by pressing crushed red grapes where the juice is allowed to stay in contact with the dark skins long enough to pick up a pinkish color or by blending red wine to white wine. Increasing the pressure of the pressing increases the amount of tannin extracted from the skins into the juice. (4) *Primary fermentation* of the crushed grapes can begin by the addition of cultured yeast to the must in addition to the natural yeast already present on the grapes. During the fermentation, the yeast cells feed on the sugars in the must and convert most of the sugars into ethanol and carbon dioxide. The temperature affects both the taste of the end product, and the speed of the fermentation for white and red wines. Once fermentation begins, the grape skins are forced to the surface by carbon dioxide released in the fermentation process. This layer of skins and other solids needs to be mixed through the liquid each day. Malolactic fermentation can also take place by specific bacteria which convert malic acid into the lactic acid during or after the alcoholic fermentation. After the primary fermentation of red grapes, the free wine is pumped off into tanks and the skins and other solid matter are pressed to extract the remaining juice and wine. The free wine is kept warm and the remaining sugars are converted into ethanol and carbon dioxide. After the contact period of the skins with the wine, the wine is separated from the dead yeast and any solids that remained, and transferred to a new container. (5) Stabilization: *Cold stabilization* is the process used after fermentation to separate potassium bitartrate crystals ("wine crystals") by sedimentation in the wine. During this process, the temperature of the wine is dropped to freezing that causes the crystals to separate from the wine and stick to the sides of the holding vessel, and the wine separation from the tartrates. *Heat* *stabilization* is the process used to remove unstable proteins by adsorption onto bentonite, preventing them from precipitating in the bottled wine. (6) *Secondary fermentation* is the bacterial fermentation of red wine which converts malic acid to lactic acid. This process decreases the acid in the wine and softens the taste of the wine. The wine must be settled or clarified and adjustments made prior to filtration and bottling. This process is kept under an airlock to protect the wine from oxidation. The degraded proteins, the remaining yeast cells, and potassium bitartrate are allowed to precipitate and settle by cold stabilization to prevent the appearance of harmless tartrate crystals and the cloudy wine after bottling. Sweet wines are made by retaining some residual sugar after fermentation is completed by freezing the grapes to concentrate the sugar, or by killing the remaining yeast before fermentation is complete or by the addition of sweet grape juice to the wine after the fermentation. Red wine has high levels of malic acid which causes an unpleasant harsh and bitter taste sensation and to improve the taste of wine the malic acid is fermented by the bacteria to produce less sour lactic acid and carbon dioxide. The most common preservative used is SO_2, applied in the form of sodium metabisulfite, which acts as antimicrobial agent and as antioxidant. Its addition after the complete alcoholic fermentation of white wine has the effect of stopping malolactic fermentation and should be maintained until bottling. Filtration in wine is used to achieve two objectives: (a) clarification by removing large particles that affect the visual appearance of the wine, and (b) microbial stabilization by removing organisms that affect the wine's stability, therefore reducing refermentation or spoilage. Fining agents, as gelatin, potassium casseinate, bone char, PVPP, bentonite clay, cellulose pads, polymeric membrane films having uniformly sized holes, are used to clarify the wine by removing the tannins and particles that form sediment or cloud by filtration prior to bottling. (7) *Bottling* of wine is traditionally used for storing bottles to preserve them from bacterial spoilage and fungal growth and to avoid unwanted fermentation. The bottled wine must contain SO_2 to inhibit the growth of bacteria.

Wine is the juice from fermented grapes and, like all fermentation products used for human consumption, it must have the qualities of palatability, stability in long-term storage, ability to resist changes in its microbial content (sterility), remain clear, and maintain a perfect odor. Wine defects can include: (i) residues from anti-fungicidal treatment of the grapes, (ii) microorganisms originating from the grape surface which disappear only partially during fermentation, (iii) potassium bitartrate supersaturation after grape fermentation due to the high solubility of the salts of tartaric acid which is higher in grape juice than in wine that contains ethanol formed gradually from the sugar fermentation. After bottling the wine, the tartrate crystallizes out with time, and with the change of the acidity of the wine. This leads also to the separation of organic matter, especially the colored components which are highly sensitive to pH changes. Wine treatment for eliminating possible defects consists of combating the microorganisms by the use of sulfur compounds and eliminating organic impurities by artificial precipitation, consisting in tanning after coagulation and frequently by air oxidation. It is required to overcome the continuous deposits of tartrate by clarification and filtration. A cold stabilization technique where the wine is chilled just above its freezing point is generally used to avoid



Scheme 4.6 Separation of potassium bitartrate from wine with ion-exchange resins [162]

sedimentation of the excess potassium bitartrate after the wine is bottled. Protective colloids, which prevent the crystallization of the excess potassium bitartrate, make a wine resistant to cold stabilization even during prolonged refrigeration. Electrodialysis has also been suggested to render the entire lot of wine potassium bitartrate stable.

The reactive polymers have been employed successfully in the treatment of alcoholic beverages and in the wine production. Ion-exchange resins have been used in the wine industry to replace other techniques for the stabilization and clarification of wines [162]. They have advantages for improving wines through partial or total removal of faults, and make the possibility to obtain high quality products. The elimination of excess potassium, in order to avoid precipitation of potassium bitartrate after storage for several months, has been achieved by filtration of wine through a hydrogen cation-exchange resin. The exchange of potassium ions for hydrogen ions results in the formation of tartaric acid which is soluble in alcoholic solutions. This can eliminate not only the acidic faults but also the intrinsic fault of wine due to the tartrate deposits. The exchange of potassium for hydrogen appreciably increases the acidity of wines and can render them less palatable. Thus, it is then necessary to lower the acidity resulting from this cation exchange by passing the treated wine through an anion-exchange resin, which results in the removal of the tartaric acid and the adjustment of the acid content required after the stabilization. The acid removed by the anion-exchange resin does not exceed the acid formed by the passage of the wine through the cation-exchange resin. However, intense deacidification can lead to a reduction of the dry matter or dry extract of the wine due to the elimination of substances not usually removed in the crystallization of potassium bitartrate. To adjust the proper degree of potassium elimination, it is necessary to use a cation exchange resin of special selectivity to remove only a part of the potassium and all the multivalent cations (heavy and alkaline earth metals). Macroporous beads of a sulfonated PS cation-exchange resin (10 % DVB) have a selectivity which is influenced by the swelling character of the resin and this in turn is a direct function of the degree of crosslinking (Scheme 4.6).

In general, the uses of functional polymers such as ion-exchange resins for the treatment of wines have major advantages including: (1) uniform qualities of the obtained wine, (2) control of potassium content to the desired value to prevent potassium bitartrate precipitation, thus avoiding long and costly wine refrigeration, (3) removing of the nitrogen compounds to prevent turbidity, (4) control of Fe and Cu content to prevent wine clouding, (5) control of must and wine acidity that eliminates the addition of organic acids or inorganic bases and salts that may give wine an unpleasant taste, (6) production of concentrated deionized musts with high sugar and low mineral salt content, as needed for the preparation of special wines, (7) suppression of the Fe and Cu turbidity caused by reactions of these heavy metals with insoluble colloids, (8) suppression of the tartrate deposits avoids the immobilization of wines during the long months before bottling, (9) elimination microbial activity by removing the ions of earth metal and organic constituents that are necessary for microbial growth, (10) resistance to contamination, reducing the need for adding sulfurous acid derivatives otherwise required for sweet wines, (11) elimination of aldehydes resulting from fermentation products that give a harsh taste and odor to wine.

Membrane processes in must and wine treatment: separation techniques involved in wine technology include membrane processes. Pressure-driven membranes (ultrafiltration, reverse osmosis) play an important role in must and wine treatment and have solved some of the problems in traditional wine making technology. Various polymeric membranes of different configurations have been used in must stabilization.

Certain enzymes present in grapes are responsible for wine defects such as clouding, darkening, or an oxidized taste. To prevent these problems, must and wines are treated with SO_2 that is antimicrobial and antioxidative and prevents browning and taste defects. Polyphenol oxidase has detrimental effects on wine quality and is responsible for the formation of certain desirable esters. The undesirable effects are reduced by thermal treatment of must with bentonite.

Depending on the type of grapes, the length of fermentation, and the type of wine produced, the fresh wine after racking and rough filtration may still be cloudy because of suspended colloidal particles of grape or yeast components. This cloudiness may remain for a long time. It is unusual when a good wine becomes brilliantly clear by natural settling. This cloudiness caused by yeast proteins, peptides, pectins, gums, dextrans, grape pigments, and tannins may be removed from wine by the use of fining agents as bentonite, which adsorb or physically combine with the colloidal particles causing the agglomeration and precipitation of the colloidal particles. Such treatment followed by subsequent filtration clarifies the wine. Activated carbon, gelatin, casein, and poly(vinyl pyrrolidone) may also be used for the removal of tannins and other pigments. Bacteria can be removed from the wine by membrane filtration containing SO_2 groups to stabilize the wine against malolactic fermentation.

4.4.3.2 Cider

Cider is less rich in alcohol and contains more sugar and nitrogeneous compounds than wine, and hence it needs to be more carefully preserved than wine for improving palatability. Cider juice produced from certain varieties of apples is intensively aerated, followed by microbial fermentation, and enzymatic action on the tannins and pectins. The fermentation brings about the degradation of malic acid into lactic acid and the simultaneous production of CO_2 by the decomposition of sugars present in the juice, which can cause the cider to develop an excess of acid. To preserve their sweet taste, fermentation of certain ciders is completely interrupted by sterilization. The development of high acidity in cider may necessitate the employment of ion-exchange resins for the elimination of a part of its total acidity.

The demineralization of cider by ion-exchanger resins is accompanied by a reduction in fermentability and mineral constituents which is necessary for the metabolism of the fermenting organisms because calcium and magnesium retard the fermentation. Cation-exchange resins reduce the ash and nitrogen of the original and arrested fermentation. The stabilization of cider by ion-exchange resin treatment removes the flavor of cider, hence flavor must be added after the treatment. The decrease of the flavor, due to some hydrolysis of the esters by the anion-exchange resin, may be avoided by passing the cider through the anion-exchange resin under CO_2 which lowers the basicity of the exchange resin. Certain contact periods between the cider and the anion-exchange resin may cause the formation of acids, which are retained on the resins, and a decrease of the corresponding sugars. The sugars present in cider are fructose (75 %), sucrose (15 %), and glucose (10 %). The anion-exchange resin does not affect the sucrose, but decomposes the glucose and fructose into alcohols and acids as quinic, citric, malic, glycolic, acetic, and succinic acids. This appears to be the cause of the decrease of the sugars and the increase of acids observed when cider is treated by anion-exchange resins.

4.4.3.3 Beer

In beer production clear malt base is obtained by: (1) *Fermentation* of malt and other brewing ingredients. (2) *Membrane separation* for beer clarification from yeast and any other suspended materials in the beer by cross-flow membrane filtration. Membrane filtration can separate alcohol in the malt base while unwanted materials such as sugar, salts, color, flavor components, are retained by the membrane. (3) *Secondary separation* for processing by ion-exchange resins to further purify the alcohol and water. (4) *Beverage formulation* by the addition of flavorings to produce the desired flavor. (5) *Bottling* of the final malt beverage.

Beer, after being poured, should form a voluminous, creamy textured, and long-lasting foam. This can be enhanced by adding starch acid esters of substituted dicarboxylic acids to the beer [163]. While many types of additives, such as gum arabic and algin, which enhance the quantity and quality of foam, are utilized in the brewing industry, all of them suffer to a certain degree from one or more shortcomings or defects. Certain additives used to enhance foam volume and foam stability produce undesirable effects on taste, clarity, and other properties of the beer.

A type of dextrin derived from modified starch can be added to enhance foam properties, good taste, and clarity. This dextrin is usually mixed in during early or later stages of the brewing process. The starch acid esters are prepared by the reaction of an ungelatinized starch, in an alkaline medium, with a substituted cyclic dicarboxylic acid anhydride such as substituted succinic acid and glutaric acid anhydrides.

The continuous process for producing beer under sterile conditions uses the replacement of fresh hops with a hop extract that can be sterilized plus the use of supported enzymes in two stages: the fermentation tower and the treatment tower [164]. The fermentation tower is a fermenter of the homogenous or heterogeneous type where yeast is in liquid medium or immobilized on a support which is inert with respect to the fermentation. This support may be formed of PVC in granules mixed with yeast or other feed plastics and yeast.

A large part of the volatile substances present in beer stems from the metabolic degradation of amino acids utilized by yeast cells. If there were not this multiplication of cells, the final product emerging from the fermentation tower would be different. The treatment tower is provided with a support of natural or synthetic organic polymers, brick, silica, glass, previously activated clay materials mixed with a protease and the beer passes into this treatment tower on which proteases are fixed. The liquid flows through the treatment tower and the proteases are retained by physical and chemical bonding. The treatment tower is for the purpose of reducing the amount of diacetyl, decreasing the quantity of sulfur compounds, and improving the organoleptic quality of the product.

Polymers are employed as clarifying agents for the treatment of beer to improve its stability during storage. In this process the beer is contacted with modified finely divided silica obtained by precipitating silica from an aqueous alkali metal silicate solution with an acid in the presence of water-soluble poly(vinyl pyrrolidone), poly(vinyl-3-methyl-pyrrolidone), or poly(vinyl pyrrolidone-acetate) [165]. The stabilizing effect of the finely divided silica on beer can be explained essentially in that it selectively adsorbs the high-molecular-weight proteins which are responsible for clouding. Poly(vinyl pyrrolidone) can also be used for beer stabilization, its activity being caused by its adsorption of polyphenolic components. The modified silica with water-soluble poly(vinyl pyrrolidone) is characterized by the incorporation of the poly(vinyl pyrrolidone) produced in the silica particles that cannot be washed out with water, acid, or organic solvents.

A new field is the removal of alcohol in beer by means of hyperfiltration membranes. The advantage of hyperfiltration is that the alcohol percentage may be adjusted according to the marketing requirement without having to change the brewing process. Immobilized enzymes have also been used in the treatment of beer to prevent the formation of haze [166]. Reactive polymers such as ion exchangers have been used to stabilize argol, by carefully controlling the final sodium content, since its high percentage leads to an unpleasant soapy flavor in champagne bases [167].

4.5 Polymers in Tomato Sauce Production

Tomatoes are eaten fresh in salads and processed for a wide variety of foods. Their nutritional value is in its energy content, carbohydrates (sugars, dietary fiber), fat, proteins, water, and vitamin C. Tomatoes are acidic, making them especially easy to preserve in canning as sauce or paste. Tomatoes contain natural antioxidants that are considered to prevent prostate cancer, improve the skin's ability to protect against harmful UV radiation, and being strongly protective against neurodegenerative diseases. Plum or paste tomatoes are bred with a higher solid content for use in tomato sauce and paste and are usually oblong. The tomato is processed into tomato soup, to make salsa, or pickled. Tomato juice is sold as a drink, and is used in cocktails.

By using a combination of microfiltration and reverse osmosis as membrane filtration systems, valuable by-products can be obtained from tomato sauce. Membrane filtration technology has been applied for tomato juice concentration for storage of the juice till the next harvest. Reverse osmosis for concentrating fresh tomato juice has two disadvantages: (i) the high osmotic pressure of tomato juice prevents concentrating the juice to the required concentration. The required sugar content of concentrated tomato juice is about 20 %, which is exceptionally low in respect to the reverse osmosis process. (ii) The loss in the membrane process of the flavor typical of the conventional evaporation process which provides improved product quality especially regarding taste and color. The major problem has been to develop a system which produces high-quality condensed juice without adding to the cost over that of the conventional process.

Factors effecting membrane performance and system efficiency are the osmotic pressure and the viscosity of the tomato juice as a function of juice concentration, feed velocity, and operating pressure. The rise in temperature increases water flux and the osmotic pressure of tomato juice increases with concentration. Tomato juice forms a gel layer which controls the water flux. In order to eliminate the influence of osmotic pressure which exponentially rises with juice concentration, UF membranes have been used which permeate sugars and salts completely.

Thermally processed and concentrated tomato paste is typically storable over longer periods of time and diluted for production of sauces, salsas, and other products. Thermal processing and concentration into tomato paste occurs either by: (a) *Hot-break process*: the tomatoes are disintegrated and rapidly heated to thermally inactivate the pectin-degrading enzymes (pectin methylesterase and polygalacturonase) resulting in a high pectin content and high consistency product. This juice is then passed through screens to remove seeds and skin fragments and then moves through a series of evaporators to remove the water from the juice at high temperatures and reduced pressure [168–171]. The greatest loss of consistency occurs in the early stages of concentration [172, 173]. The final concentrated paste contains soluble solids that are stable for storage [174]. The quality depends on factors such as the cultivar of tomatoes used, the finisher screen size, and the break temperature which is the initial heating temperature [175], [176]. (b) *Cold-break process*: unheated tomatoes result in a better color and flavor in the product but this is associated with a decrease of consistency as of the action of pectin methylesterase and polygalacturonase which results in a product with substantially lower pectin [177–179].

The rheological properties of fluid tomato sauce products are important quality parameters. The flow properties of the juice, i.e., viscosity and consistency, are determined primarily by the insoluble components [180–186]. The viscosity of the serum, the soluble fraction of the tomato juice after removal of insoluble material, is mainly determined by the polymeric substances, mostly pectin, i.e., the flow properties of the whole juice depend primarily on the presence of insoluble materials [180–182, 187, 188].

Tomato paste must be suitable to produce the desired consistency in the final product. The tomato paste manufacture accurately reflects the consistency of the paste at the time of use which is the critical point between the end users and paste producers. The loss of consistency occurring during juice concentration to paste production shows difference from the possible changes in consistency occurring during subsequent tomato paste storage [168]. Changes in pectin quantity, solubility, and size properties during the concentration of juice to paste are due to the transfer of pectin from the water-insoluble to the water-soluble fraction and loss of pectin during the process. The total pectin content of the alcohol-insoluble solids from the concentrated paste was less than that obtained from the original unconcentrated juice, due to the heat effect during concentration that led to thermal hydrolysis and solubilization of pectin [170, 173, 189]. The loss of consistency [168–171] is attributed to the loss of pectin [190] during the concentration of juice at commercial processing plants, which occurs by: (a) hot-break process: by nonenzymatic thermal breakdown of pectin via chemical (acid) hydrolysis of pectins at the heating of the juice under reduced pressure to evaporate the water [191, 192], irreversible polymer dehydration (elimination) by the high solute concentrations in the paste [168, 173], and mechanical shear of the juice particles by the pumping through the system [193]. (b) cold-break process: the reduction of consistency by enzymatic breakdown that lead to pectin degradation. Heating tomato serum for extended periods of time causes a loss in viscosity which is attributed to a loss of pectin [187]. Thus, reducing heat inputs would reduce the thermal breakdown pectin and change in tomato consistency, and improve tomato paste quality [193]. The loss of consistency is also attributed to the irreversible crosslinking between biopolymers within the juice particles, which cannot fully reexpand upon dilution and the original consistency is not recovered [168, 173]. Both hot and cold break processes for concentrating the tomato juices induce the changes in consistency and pectin content that occur during the production of tomato paste at a commercial processing plant [189].

4.6 Polymers in Potable Water

High amounts of water are used in the food industry, e.g., for soft drinks, or for washing meats, fruits, vegetables, or containers. Degree of hardness, alkalinity, and salinity are essential in the manufacturing process of foods. Hard water is disadvantageous as Ca and Mg ions in the presence of carbonate, oxalate, and sulfate ions encourage the formation of evaporator scaling and corrosion. This scale prevents effective heat transfer in the evaporator stages, leading to increased energy costs in addition to production losses due to shutdowns of the evaporators for cleaning and scale removal. ***Polymeric antiscalants*** are stable to hydrolysis at the evaporation temperatures and inhibit scale formation. Water softening is important in food processing, specifically in: (a) boiling and steam cooking of foodstuffs, especially vegetables, to be processed and canned, (b) diluting syrups for soft drinks, (c) beer brewing, (d) distillation/alcoholic liquors processing, (e) dairy farming and cheese industry; (f) improving taste and flavor of cooked foods such as vegetables and legumes, and (g) in washing bottles and drink containers.

4.6.1 Water Sources

Water used in the food industry is obtained from different sources. (1) *Groundwater* is obtained from deep layers in the ground and is naturally filtered by the soil to a high degree before reaching the water treatment plant. The majority of water must be pumped from its source and directed into pipes or holding tanks. This physical infrastructure must be made from appropriate materials and constructed to avoid adding contaminants to the water, so that accidental contamination does not occur. Groundwater generally is free of pathogenic bacteria or protozoa, rich in dissolved calcium and magnesium carbonate, sulfates and iron, manganese chlorides and bicarbonates. Thus, it is adequate for drinking, cooking, and industrial uses. (2) *Land surface waters* (rivers, canals, upland lakes, reservoirs): Natural lakes are usually located in the headwaters of river systems; most upland reservoirs are positioned above human settlements and may be surrounded by a protective zones to restrict possible contamination. Pathogenic microorganisms, protozoa, and algae are usually present. Where uplands are forested or peaty, humic acids can color the water and many upland water sources have low pH that requires adjustment. Lowland surface waters have a significant bacterial load and may also contain algae, suspended solids, and a variety of dissolved constituents. *Storage reservoirs* of river water are often located close to river banks; this water can be stored for longer periods of time and needs to be further adequately purified after treatment by slow sand filters. Storage reservoirs also provide a buffer against short periods of drought or to allow water supply to be maintained during transitory pollution incidents in the source river. (3) *Atmospheric water* is generated by extraction from the air by condensation and can provide high-quality drinking water. (4) *Rain water* can be collected and used especially in areas with significant dry seasons. (5) *Sea water* can be desalinated by distillation or membrane reverse osmosis.

4.6.2 Water Treatment

The treatment methods of municipal wastewater is to produce an effluent that can be discharged without causing detrimental environmental impact and to produce water which can be reused internally in a closed loop within the facility or water which can be discharged either to a municipal wastewater treatment plant or to the environment. The major contaminants found in municipal wastewater include suspended solids, biochemical oxygen demand, phosphorus, nitrogen, heavy metals, toxic organics, fats, oils, grease, and pathogens. Physical, chemical, and biological treatment processes may all be employed, depending on the contaminants to be removed. Water treatment that plays an important role in maintaining human health. Water purification intends to remove undesirable chemicals, biological and other contaminants from contaminated water to produce water meeting the requirements for drinking water, and also for a variety of other purposes in the food industry. Thus, the objective of water treatment is to produce drinking water that is safe for human consumption and which is aesthetically pleasing in terms of odor, appearance, and taste. Water purification processes reduce the concentration of particulate matter including a wide range of dissolved solids and particulate materials derived from surfaces that contact the water, such as suspended particles, parasites, bacteria, algae, viruses and fungi. The standards for drinking water quality are typically set at minimum and maximum concentrations of contaminants for the particular use that of the water. Water utilities using surface water as their source for drinking water will need to carefully monitor contaminants in the drinking water to protect the users from microbial contaminants. The processes used in water purification depend on the scale of the plant and quality of the water. The methods include the use of techniques to remove fine solids, microorganisms, and dissolved inorganic and organic materials. Critical parameters are the cost of the treatment process and the quality standards expected of the processed water. The necessary information for deciding on the appropriate method of purification is obtained from chemical analyses.

4.6.2.1 Physical Processes

Sedimentation and filtration: *Screening* is the first step in purifying surface water to remove undissolved large particles which may interfere with subsequent purification steps. Deep groundwater does not need screening before other purification steps, because it has already been subject to natural slow sand filtration. The use of physical processes as activated carbon filters is not sufficient for treating all the possible contaminants that may be present in water from an unknown source. (A) *Sedimentation* basin (clarifier or settling basin) is a large tank with slow flow, allowing floc to settle to the bottom. The amount of floc that settles out of the water is dependent on basin retention time and on basin depth. As particles settle to the bottom of the basin, a layer of sludge is formed on the floor of the tank. The cost of treating and disposing of the sludge can be a significant part of the operating cost of a water treatment plant. The tank may be equipped with mechanical cleaning devices that continually clean the bottom of the tank or the tank can be taken out of service when the bottom needs to be cleaned. (B) *Filtration*: After separating most floc, the water is filtered as the final step to remove remaining suspended particles and unsettled floc. (i) *Rapid sand filters* are the most common type of rapid filter; often they consist of a layer of activated carbon above the sand for removing organic compounds that affect water taste and odor. Most particles pass through surface layers but are trapped in pore spaces or adhere to sand particles. Effective filtration extends into the depth of the filter. To clean the filter, water is passed quickly upward through the filter, opposite the normal direction (backflushing or backwashing) to remove embedded particles. Prior to this, compressed air may be blown up through the bottom of the filter to break up the compacted filter media to aid the backwashing process (air scouring). This contaminated water can be disposed of, along with the sludge from the sedimentation basin, or it can be recycled by mixing with the raw water entering the plant although this is often considered poor practice since it reintroduces an elevated concentration of bacteria into the raw water. (ii) *Slow sand filters* may be used where there is sufficient space for slow "artificial" filtration (bank filtration) of groundwater. The water passes very slowly through the filters, which are constructed using graded layers of sand with the coarsest sand, along with some gravel, at the bottom and finest sand at the top. Drains at the base convey treated water away for disinfection. An effective slow sand filter may remain in service for many weeks if the pretreatment is well designed and produces water with a very low nutrient level which physical methods of treatment rarely achieve. Very low nutrient levels allow water to be safely sent through distribution systems with very low disinfectant levels thereby reducing consumer irritation by offensive levels of chlorine and chlorine by-products. Slow sand filters are not backwashed; they are maintained by having the top layer of sand scraped off when flow is eventually obstructed by biological growth.

A specific "large-scale" form of slow sand filter is the process of bank filtration, in which natural sediments in a riverbank are used to provide a first stage of contaminant filtration. While typically not clean enough to be used directly for drinking water, the water gained from the associated extraction wells is much less problematic than river water taken directly from the major streams where bank filtration is often used. (iii) *Membrane filters* are widely used for filtering both drinking water and sewage by removing virtually all particles larger than 0.2 μm. Membrane filters are an effective form of tertiary treatment when it is desired to reuse the water for industry, for limited domestic purposes, or before discharging the water into a river that is used by towns further downstream. They are widely used in industry, particularly for beverage preparation (bottled water). However, filtration cannot remove substances that are actually dissolved in the water such as phosphates, nitrates, and heavy metal ions.

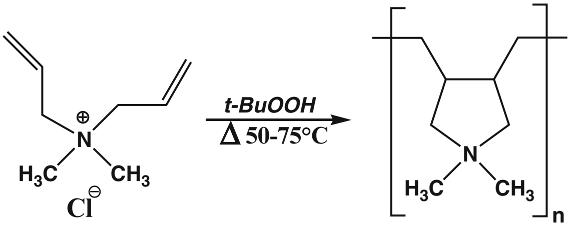
4.6.2.2 Biological and Chemical Processes

Water is chlorinated to minimize the growth of fouling organisms on the internal surfaces of pipe-work and tanks. Water treatment chemicals are utilized to improve the quality of raw drinking water, to reduce pollutants in industrial wastewater, and to remove contaminants from municipal sanitary sewers. The principal contaminants which may be found in water include: particulate matter, coloring, hardness, iron and magnesium, toxic organics, and water-borne pathogens. A combination of chemical and physical processes is typically used to purify potable water, typically consisting of coagulation-flocculation followed by settling, filtration, or flotation. Coagulation and flocculation involve chemicals to remove particles during water treatment by altering suspended and colloidal particles so they adhere to each other.

An alternate and improved means to achieve enhanced coagulation in treating drinking water, a composition for removing turbidity, particles, and color from drinking water, includes: (a) primary polymeric coagulant refers to a cationic polymer (a natural, cationic polymer as chitosan or a cationic starch) which enhances the adherence of the particles causing turbidity and color to form a flocs, and (b) flocculants aid refers to a anionic or nonionic polymer, added to enhance the aggregation of the floc. (clay mineral as bentonite) which becomes attached to polymeric coagulants via electrostatic forces or ion exchange, then followed by bridging between particles, that assists in increasing the rate and efficiency of coagulation. The coagulated floc containing particles that cause turbidity and color is then separated from the drinking water. In preferred methods, the step of separating comprises separating suspended matter from drinking water by a method selected from the group consisting of gravity settling, filtration and flotation.

(A) **Primary coagulant** is used to initiate the coagulation process, i.e., to make a turbid (cloudy) water begin to form floc particles that are subsequently removed later in the treatment processes. Turbidity of water is caused primarily by inorganic and organic colloidal particles that typically have an anionic charge and these particles tend to repel each other because they have the same charge, thus they remain in suspension. Hence water treatment requires the use of coagulation chemicals in order to increase the removal of these suspended matters. Coagulation causes the alteration of suspended and colloidal particles so they adhere to each other. It is the process that causes the neutralization of charges or a reduction of the repulsion forces between particles. The negative electrical charge associated with suspended and colloidal particles is usually neutralized by the addition of positively charged coagulants. The use of a cationic polymer performs two functions: (1) neutralizes the negative charge associated with the colloidal particles allowing the occurrence of interparticles agglomeration, and (2) destabilizes colloidal particles by entrapping in the molecular chains. These two actions initialize the starting of the coagulation process. The most frequently used chemical coagulants in water treatment are of different types, each has its advantages and disadvantages when it comes to applicability and pollutant removal efficiency. (a) *Inorganic mineral coagulants* as alum [$Al_2(SO_4)_3{\cdot}18\ H_2O$], ferric hydroxide, lime ($CaCO_3$), activated silica, clays (as bentonite). However, higher doses of aluminum sulfate coagulant will depress pH, reduce alkalinity and generate large quantities of sludge, thereby requiring additional doses of pH adjustment chemicals. (b) *Organic polymeric coagulants* nonionic polymers as PAAms, polyamines, poly(ethylene imine)s, polyamides-amines, PEO, polyDADMAC, anionic polymers as poly(acrylamide-acrylic acid), cationic polymers as poly(acrylamide-cationic monomer), are used in drinking water treatment to control potential problems with impurities. PolyDADMAC is a cationic linear polymer used extensively for water purification. It is synthesized by the free radical initiated addition polymerization of diallyldimethylammonium chloride, according to Scheme 4.7, [194]. (c) *Natural polymeric coagulants* are water soluble anionic, cationic or nonionic polymers as: (a) positive charge chitosan salt with acids: acetic acid, formic, adipic, malic, propionic or succinic acids, or (b) natural starches (potato, waxy maize, corn, wheat and rice starch), anionic oxidized starches or amine treated cationic starches, guar-gums and alginates. They are used for treating drinking water to provide an alternate and improved means to

Scheme 4.7 Synthesis of PolyDADMAC by free radical polymerization of DADMAC [194]



achieve enhanced coagulation for removing organic matter and color from drinking water, and the problems arising from the uses of other coagulants. Chitosan, as a naturally occurring biodegradable-biopolymer made from chitin that derived from recycled crustacean shells, insect exoskeletons or fungi, shows superior performance in water treatment applications [195]. Chitosan-clay compositions have been employed for removal of greases, fats, oils, proteins, and minerals from animal and/or food processing industrial wastewater streams from industrial wastewater [196, 197]. The principal factors affecting coagulation include the type of coagulant, dosage of coagulant, mixing time and speed, order of coagulant addition, pH and alkalinity, temperature, properties of the natural organic matter in the raw drinking water.

(B) **Flocculants aid.** Once the initial step of coagulation has begun, the flocculants aids which are typically higher in molecular weight than primary coagulants are used to increase the size and density of a flock particles that allow faster settling rate in the sedimentation process. There are two additional steps in a conventional treatment process (sedimentation and filtration) where the aggregated particles can be more easily removed. The floc particles not removed in the sedimentation process will be more easily removed in the filtration process, due to its increased size and density. Initially the small particles stick together to form bigger particles that precipitate by gently stirring the water. Many of the small particles that were originally present in the raw water adsorb onto the surface of these small precipitate particles and so get incorporated into the larger particles that coagulation produces. The aggregated precipitate takes most of the suspended matter out of the water and is then filtered off, generally by passing the mixture through a coarse sand filter or through a mixture of sand and coagulants/flocculating agents which may include: Flocculating agent is used to describe the action of polymeric materials which form bridges between individual particles of a suspension form aggregates. Bridging occurs when segments of a polymer chain adsorb on different particles and help particles aggregate. Flocculants carry active groups with a charge which will counter balance the charge of the particles. Flocculants adsorb on particles and cause destabilization either by bridging or charge neutralization. They are used to increase the efficiency of settling, clarification, and filtration operations. An anionic flocculants will usually react against a positively charged suspension, e.g., salts, metallic hydroxides and clays which are electronegative. A cationic flocculants will react against a negatively charged suspension, e.g., silica or organic substances.

4.6.2.3 Disinfection

Aside from chemical disinfectants, irradiation by UV light, solar or electromagnetic radiation are optionally used for disinfection and may be applied in the last step of purifying drinking water to kill any remaining pathogens (viruses, bacteria, protozoa) which may have passed through the filters. Public water suppliers are required to maintain a residual disinfecting agent throughout the distribution system to the consumer. Disinfection is the primary goal; aesthetic considerations such as taste, odor, appearance, and trace chemical contamination do not affect the short-term safety of drinking water. The most common disinfection methods are: (a) *Chlorination.* Chlorine, as an oxidant, is released from sodium hypochlorite (Na^+OCl) which is the most common disinfectant used that rapidly kills many harmful microorganisms. Although chlorine is effective in killing bacteria, it has limited effectiveness against protozoa. Chlorine has the drawback of being toxic and it reacts with natural organic compounds in the water to form potentially harmful chemical by-products, which may be minimized by effectively removing as many organics from the water as possible prior to chlorination; *chlorine dioxide* (ClO_2) is a faster-acting disinfectant than chlorine, but it is relatively rarely used because it may create chlorite as a by-product; *chloramine* (NH_2Cl) is commonly used as a disinfectant because it provides a long-lasting effect and can be obtained by adding ammonia to the water after addition of chlorine. (b) *Ozone* (O_3) is a broad-spectrum disinfectant that provides a powerful oxidizing effect and is toxic to most waterborne organisms. It is an effective method to inactivate harmful protozoa that form cysts and works against all other pathogens. The advantages of ozone include the production of fewer dangerous by-products and the lack of taste and odor produced by ozonization and it is applied as an antimicrobial agent for the treatment, storage, and processing of foods. (c) *UV light* is used in disinfection but its disinfection effectiveness decreases as turbidity increases as a result of the absorption and scattering caused by the suspended solids. It is sometimes used after primary disinfection by chloramines. Solar disinfection is a low-cost method for disinfecting water that can often be implemented with locally available materials. (d) *Hydrogen peroxide* is used in disinfection in the presence of activators (acetic acid) to increase the efficacy of disinfection. Disadvantages are that it is slow-working, phytotoxic in high dosage, and decreases the pH of the water.

4.6.2.4 Dissolved Substances

Water-soluble materials can readily be removed. If the resulting wastewater containing the dissolved substances is discarded to the outside, environmental pollution issues may result, so that clarification treatment may be required. Water color may indicate the presence of organic material. It may be necessary to isolate and eliminate the water-soluble materials in wastewater by means other than boiling, which may not sufficiently remove dissolved contaminants (inorganic, organic). Procedures employed include: (a) *Ultrafiltration membranes* are made of polymers with microscopic pores that can be used to filter out dissolved substances under pressure avoiding the use of coagulants. (b) *Electrodeionization (EDI)* where the water is passed between positive and negative electrodes. Ion-exchange membranes allow only positive ions to migrate from the treated water toward the negative electrode and only negative ions toward the positive electrode. High-purity deionized water is produced with a lower degree of purification in comparison with ion-exchange treatment. Complete removal of ions from water can be achieved by electrodialysis. The water is often pretreated with a reverse osmosis unit to remove nonionic organic contaminants. (c) *Ion-exchange resins* are used for water softening by removing unwanted Ca^{+2} and Mg^{+2} ions. They are also used for water purification to remove toxic ions (as nitrate, nitrite, lead, mercury), and poisonous substances that can cause disturbances to organisms, or organic contaminants from water [198–200]. Hardness salts are usually removed in several steps with "mixed bed ion-exchange columns" at the end of the treatment chain. Water of highest purity, i.e., with no metal ions (for electronics as superconductors, nuclear industry) is produced using ion exchange or combinations of membrane and ion exchange. Isolation and elimination of a water-soluble materials present in wastewater can be attained by coagulating the material in the presence of acid, alkali, or by salting out. However, the obtained coagulated product is highly adhesive so that its isolation and elimination can be effected only with difficulty and blockage of the circulation system for washing water results. As the acidic and alkaline agent, one can employ ion-exchange resins which are most preferable because they can form salts by neutralization which remain attached to the resins and the active resins can be regenerated for reuse again by washing with acidic or alkaline solution. Water with excessively high nitrate content is subjected to reduction of nitrates to nitrites in order to be suitable for use in the food industry. Nitrites may pose the risk of converting blood hemoglobin into *m*-hemoglobin which cannot transfer oxygen to the tissues. Moreover, nitrites may react with many amines contained in foods, forming nitrosamines which are cancerogenic. Hence for these reasons, there are strict limits of admitted concentrations of nitrates in potable water. Ion-exchange resins have been used to effectively remove nitrates from water. (d) *Other water purification techniques* include: *i*) *Boiling* the water long enough to inactivate or kill microorganisms, also decomposing bicarbonate ions in hard water, precipitating as $CaCO_3$. Boiling does not leave a residual disinfectant in the water, but storing for longer periods of time may acquire new pathogens. (ii) *Activated carbon filters* are used in water purification for adsorbing toxins and tasting or odorous organic contaminants. (iii) *Distillation* involves boiling the water to produce water vapor. This does not necessarily completely purify the water because certain contaminants with similar boiling points and droplets of unvaporized liquids are also carried with the steam. (iv) *Reverse osmosis* under applied pressure to force water through a semipermeable membrane is used for water purification on a large scale. However, algae and other lifeforms can cause fouling of the membranes. (v) In-situ *chemical oxidation* processes are used for groundwater remediation to destroy or reduce the concentrations of chemical environmental contaminants that are resistant to natural degradation, by using chemical oxidizers directly into the contaminated groundwater.

4.6.2.5 Additional Water Treatment

(a) *Water fluoridation* is usually the addition of fluoride to water after the disinfection process with the goal of preventing tooth decay. However, excessive levels of fluoride in water can be toxic or cause undesirable cosmetic effects such as staining of teeth and can be reduced through treatment with activated alumina and bone char filter media. (b) *Water conditioning* reduces the effects of hard water. Hardness salts are deposited in water systems subject to heating because the decomposition of bicarbonate ions creates carbonate ions that crystallize out of the saturated solution of calcium or magnesium carbonate. Water with high concentrations of hardness salts can be treated with soda ash (Na_2CO_3) which precipitates out the excess salts through the common-ion effect, producing $CaCO_3$ of very high purity. (c) *Plumbosolvency reduction* may be necessary in areas with naturally acidic waters of low conductivity (i.e., surface rainfall in upland mountains of igneous rocks) where the water may be capable of dissolving lead (Pb) from lead pipes that it is carried in. The addition of small quantities of phosphate ion and slightly increasing the pH both assist in greatly reducing plumbosolvency by creating insoluble lead salts on the inner surfaces of the pipes. (d) *Radium removal* can become a requirement if the groundwater source contains radium; it can be removed by ion exchange or by water conditioning.

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Chapter 5
Polymeric Food Additives

Foods for commercial human use are regulated by particular specifications of each item of concern by commerce and law. Food standards are set with respect to quantity, weight, value or quality to guarantee, to a certain extent, honesty and fair dealing in the interest of consumers [1]. With the increasing use of processed foods of both natural and artificial origin, there has been a great increase in the use of *food additives* to enhance food quality as to preserve or enhance food flavor, taste, and appearance without affecting the food's nutritional value. However, food additives are substances or purposeful chemicals, other than basic foodstuffs, which are either present in food as a result of any aspect of production, processing, storage, or packaging, or used to provide some benefit to health and vitality. They are added to keep nutritional supplies ahead of the population explosion by replacement of nutrients lost in processing, and to result, directly or indirectly, in affecting the characteristics of food. The great majority of additives exhibit their functions prior to consumption of the food products, either acting as aids in the manufacture, preservation, coloration, and stabilization of food products, or to improve the biological value of certain foods. Nonnutritive sweeteners are added solely to make an initial contact with the taste buds, after which they do not serve any further function.

However, there can be significant harms associated with the benefits of food additives. Certain artificial food additives are carcinogenic or cause digestive problems, neurological conditions, heart disease, or obesity, although natural additives may also be harmful and may cause allergic reactions in certain individuals. Thus, mostly food additives of known safety are used in foods. Food additives generally should not alter or interfere with metabolism or other biological functions of the body. Artificial polymeric additives make it possible for these substances to pass virtually unmodified through the body and consequently they do not participate in body chemistry, relieving concern over possible adverse long-term health effects. Increasing demands for food additive safety have led to the application of functionalized polymers in the food industry to rid food problems associated with certain artificial additives while maintaining product appearance, texture, flavor, and cost [2–5]. Functionalized polymers attaching desirable food reactive groups by

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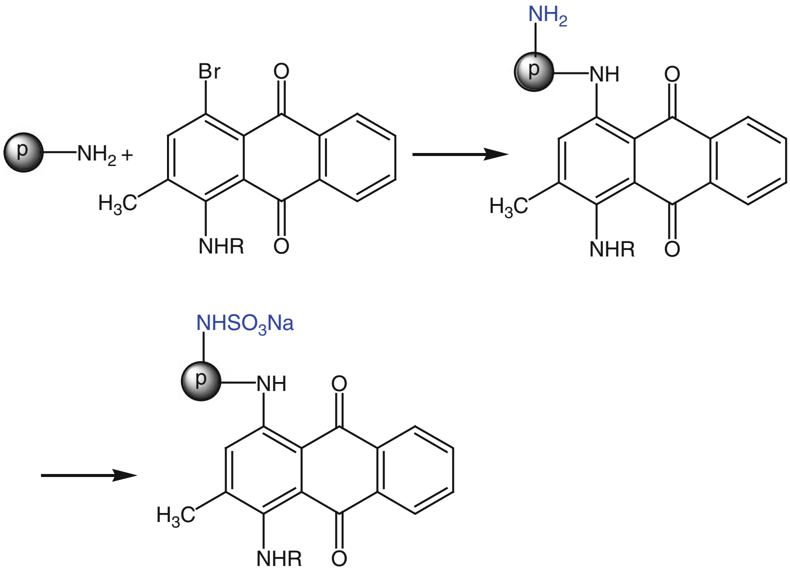
chemical bonding possess a combination of the physicomechanical properties of a high polymer and the chemical properties of the attached group and hence lead to a polymer that combines the advantages of a conventional reactive moiety and of a polymer. In addition to the typical applications of immobilized enzymes on polymeric supports in the food industry [6, 7], e.g., cheese making [8, 9], stabilization of milk in dairy industry [10, 11] and clarifying fruit juices and wines [12], another important and successful application is the development of safe polymeric food additives employed for a specific purpose other than nutritional purposes.

Functionalized polymers as food additives are designed to attach certain functional groups of food additives to an appropriate functionalized macromolecule to produce a complex of large molecular size which cannot be absorbed through the intestinal wall, i.e., they cannot migrate across the intestinal membranes and therefore cannot pass into the blood stream or be metabolized. Consequently, the large resulting molecule would not contact the usual organs, such as kidneys or liver, but would be excreted in the feces without any metabolization. This can eliminate possible side effects which may result from the absorption of soluble additives. The charged or modified activity of polymeric food additives is affected by the nature of the functional groups and the polymeric macromolecule matrix these determine any possible toxicity. Hence the following factors are important and must be taken into consideration during the design of polymeric food additives so that they are nonabsorbable: (i) *Stability*: the chemical linkage attaching the food additive to the polymer and also the polymeric backbone must be resistant to breakdown by the chemical or biological environment, under food processing, shipping, or storage conditions, including light and heat exposure, and under the enzymatic and microbiological conditions of the gastrointestinal tract. This stability is required in order to eliminate the formation of any low-molecular-weight species, by depolymerization, degradation, digestion, or hydrolysis, which will give rise to absorbable fragments. In addition, chemical stability is also important to preserve functionality. A simple hydrocarbon backbone is especially stable under product processing conditions or under the conditions of metabolism and does not interfere with the additive properties. (ii) *Solubility*: the choice of the chemical nature of the polymer backbone often depends on the degree of water or oil solubility of the final polymeric food product. In some cases, e.g., in polymeric food dyes, it is desirable to incorporate water-solubilizing groups either into the backbone or into the food functional groups to obtain the clear solutions necessary for food processing. Water solubility is achieved by incorporating hydrophilic polar group up to 10 % or more. Conversely, in some cases it is desirable to increase the oil and fat solubility of the polymeric food additives, as in the case of antioxidants used for the stabilization of oils and fats. This property can be achieved by the incorporation of nonpolar oleophilic groups such as hydrocarbon chains into the polymeric food additive. (iii) *Molecular weight*: to achieve the desired nonabsorption through the intestinal wall and hence to eliminate any risk of systemic toxicity, the chemical backbone of the polymeric food additives must have a sufficiently large molecular weight and size. This is generally achieved when the polymer has a high molecular weight. (iv) *Type of bonding*: in addition to the resistance of the chemical linkage to rupture, it must be tasteless and odorless, give no color, interact only mildly with food components, and not interfere with the properties of the food activity. (v) *Compatibility and blendability*: the polymeric food additives must be compatible and blendable with the other food components. In some food applications, encapsulation of food ingredients is used to control its diffusion through the walls of the polymer membrane.

Functionalized polymers have been employed as convenient supports for various food additives. A variety of nonconventional polymeric functional food additives have been developed and are utilized in the formulated food processing industry. The different types include: (1) *colorants* to improve the appearance and appeal of processed food products, (2) *antioxidants* to act as preservatives by inhibiting the effects of oxygen on food, (3) *sweeteners* for flavoring, or to keep the food energy low, or for their beneficial effects in respect to tooth decay, (4) *preservatives* to prevent or inhibit spoilage of foods due to microorganisms (enzymes, fungi, bacteria), (5) *acidity regulators* to control the acidity and alkalinity of foods, (6) *anticakings* to keep powders from sticking, (7) *antifoamings* to reduce or prevent foaming in foods, (8) *flavors* and *flavor enhancers* to give the food a particular taste or smell or to enhance a food's existing flavors, (9) *glazings* to provide a shiny appearance or protective coatings of foods, (10) *thickeners* to act as stabilizers or gelling and to increase the viscosity without substantially modifying the other properties of the food, (11) *emulsifiers* to homogenize the mixing of water and oils.

5.1 Polymeric Food Colorants

Colored materials ("*colorants*") are widely used in the food industry to change the food color or to enhance and improve the appearance and appeal of processed food products, but their presence can be hazardous to health [13]. In addition, food colorants are added to food to replace colors lost during preparation, or to make food look more attractive. Other chemical materials may be used to preserve the food's existing color which is called "*color retention*" or "*color enhancer*" agent. However, the presence of food colorings can be hazardous to health, and one of the solutions to this problem is the use of a polymeric backbone chemically attached to conventional food chromophores. The molecular weight of the polymer support is sufficiently large to permit the colorant to pass through the walls of the gastrointestinal tract without absorption into the body [3, 14–17]. Under these conditions, conventional chromophores, which are not suitable for food coloring because of their water insolubility or toxicity, can be used in a polymeric form since they will achieve improved solubility and nonabsorbability and hence will be nontoxic. The preferred polymeric supports for nonabsorption of the chromophoric groups are those formed by addition polymerization, i.e., polymers composed of hydrocarbon backbones, because they do not undergo degradation under the conditions of use. In addition, polymeric food dyes must have good water solubility with color purity in aqueous media, which can be achieved by introducing ionic solubilizing groups. Solubilizing groups, such as sulfonate or alkyl sulfonate groups, increase the polymer's

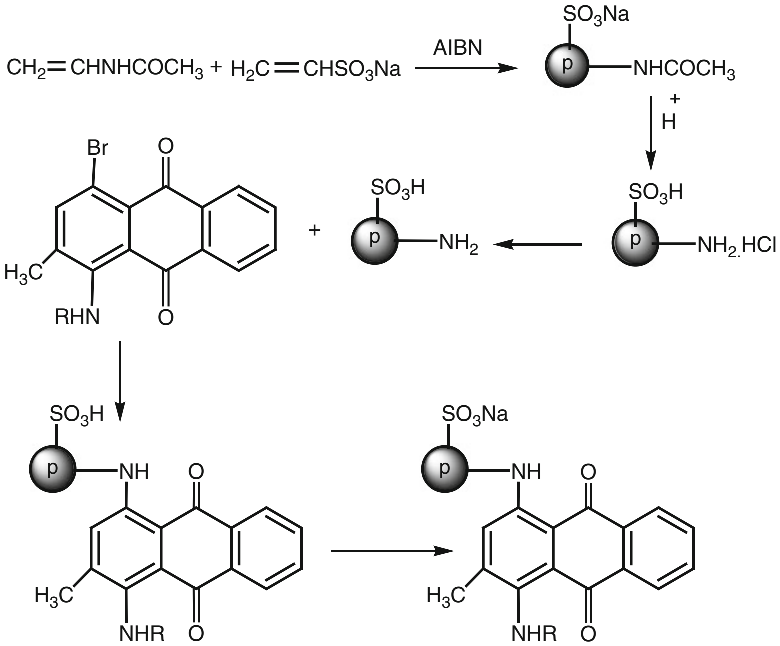


Scheme 5.1 Preparation of polymeric anthraquinone colorants [18, 19]

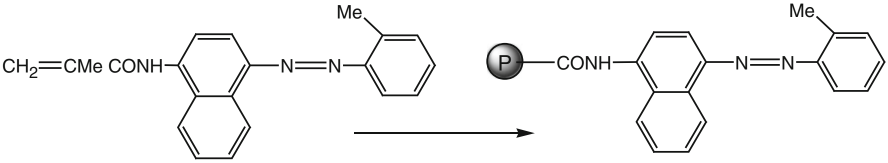
hydrophilicity and hence impart the desired water solubility and compatibility with other food product ingredients. For example, water-soluble polymers with water-insoluble anthraquinone chromophores were prepared by treating poly(vinyl amine) or poly(vinylamine-*co*-vinylsulfonate) with 1-amino-4-bromo-2-methylanthraquinone and converting the unreacted amines into water-solubilizing sulfamate groups by treatment with complex of trimethylamine sulfur trioxide (Me_3NSO_3) (Scheme 5.1) [18, 19]:

Polymeric colorants composed of chromophoric groups bound to or into water-soluble polymers were prepared by attaching water-solubilizing groups and chromophoric groups directly and separately to the polymer backbone. The water-soluble polymeric food colorants with anthrapyridine chromophores were prepared by treating poly(vinyl amine) or poly(vinyl amine-*co*-vinyl sulfonate) with bromoanthrapyridine (Scheme 5.2) [20]. The backbones are generally prepared separately prior to chromophore and solubilizer attachment by free radically copolymerizing olefinically unsaturated amine and sulfonate monomers. The amine groups serve to covalently attach the chromophoric groups to the backbone and the chromophoric group exhibits a visual color to the human eye on the attachment to the polymeric backbone via amine linkages.

Polymeric food colorants have been prepared either by polymerization of monomeric chromophores or by chemical modification of preformed polymers through a suitable functional dye group. For example, the methacrylamide naphthyl derivative was polymerized to give a polymeric food colorant (Scheme 5.3) [21, 22]:



Scheme 5.2 Preparation of polymeric anthrapyridine chromophores [20]



Scheme 5.3 Polymeric food colorant of methacrylamide derivative [21, 22]

Because azo dyes, as amaranth, are the most widely used food colorants and are water soluble, they were bonded to selected polymers via a sulfonamide linkage. However, the azo linkages in the dyes themselves were unstable to intestinal microbial action and do not meet the requirements of biological stability because they are cleaved in the gut to yield absorbable aromatic amines. Hence a variety range of chromophore classes have been reported to be incorporated into polymers. For the anthraquinone class of chromophores, the basic water insolubility was changed by converting a portion of the backbone to sulfonic acids that impart anionic solubilizing functions. However, this meant that fewer chromophores could be attached and less intense colors would result.

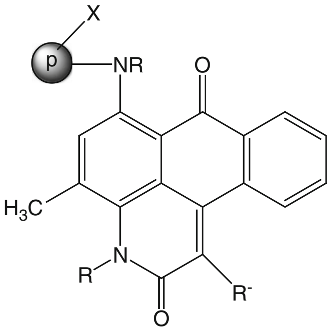
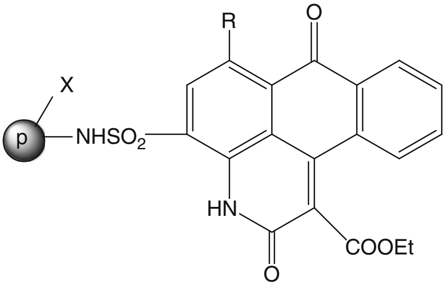
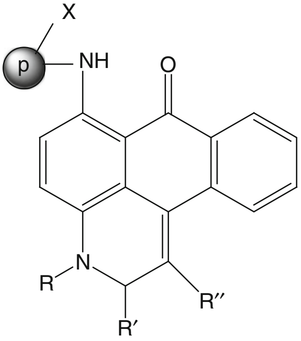
Solid polymeric colorants may also be prepared by using solid absorbent materials such as metal oxides, metal salts of aluminosilicate, clays, diatomites, hydrotalcite, silica, zeolite, hollow glass spheres, organic–inorganic mesoporous hybrid materials, cellulose, PS, crosslinked porous polymers, crosslinked modified starch, crosslinked acrylate polymers, urea-formaldehyde resins, epoxy resins, and polyalkyleneoxy chains [23, 24]. For example, the polymerization of formaldehyde, urea, polyamine, and a dye [25], or the polymerization of benzguanamine, melamine, formaldehyde, and curing catalyst [26] may lead to the formation of solid polymeric colorants. A growing number of synthetic food colorants are being commercially produced including the chromophore groups of azo, anthraquinones, xanthenes, indigoids, anthrapyridones, anthrapyridines, benzanthrones, nitroanilines, and triphenylmethanes that have been incorporated into polymers, as shown in Table 5.1.

5.2 Polymeric Food Antioxidants

Many naturally occurring and synthetic foods are subject to deterioration by naturally occurring and induced environmental conditions that either render them unsuitable for consumption or severely decrease the nutritional value of the food. Deterioration of food materials by oxidation, not only can destroy the desirable nutritional value of the food, but also can make their consumption unacceptable. The nutritional value of foods arises from carbohydrates, fats, proteins, vitamins, and other useful nutrients and deterioration and spoilage can occur either simultaneously for all the ingredients or for a single one. The carbohydrate portion of many food products can lose its nutritive value by oxidation as evidenced by discoloration and undesirable flavors. The discoloration often is due to autoxidation of valuable natural pigments as carotenes or to a chemical browning reaction that can occur between carbohydrates and essential amino acids present in foods. Foodstuffs containing fats and oils often become unacceptable for use by undergoing oxidative deterioration. This deterioration is due to their tendency to react with oxygen, which results usually in rancidity, i.e., undesirable odor, taste, and color, from the products formed during the oxidation. The oxidation products generally include peroxides, aldehydes, ketones, and acids that impart an undesirable rancidity to the foodstuff thereby making their use unacceptable. Oxygen can convert proteins to a different form, as in the discoloration in meats. Also, livestock and poultry feeds mixed with vitamins and subjected to oxygen can considerably lose their nutritive value due to these oxidizing influences.

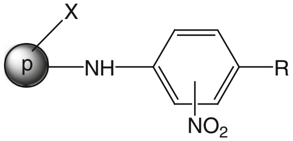
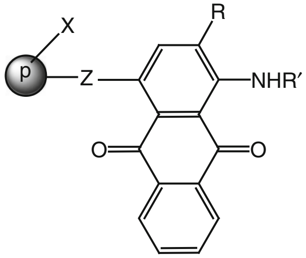
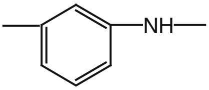
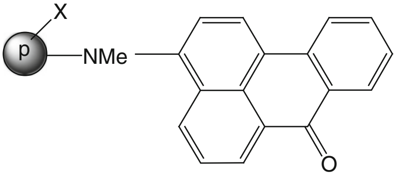
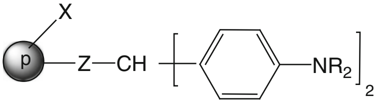
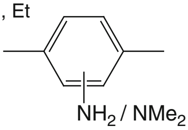
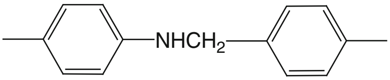
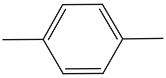
The prevention of oxidation is important to preserve the quality and shelf life of a wide range of food components. Many attempts have been made to stabilize foodstuffs by adding antioxidants. Antioxidants increase the stability of foodstuffs in storage as well as increasing the retention of nutritional and flavor values by delaying rancidity, thus they are particularly employed in food products containing oils and fats. In general, antioxidants either prevent reactive oxygen species (ROS) from being formed, or remove these reactive species before they can deteriorate the food components. They usually function either by hydride (H^-) or electron donation, or by forming a complex with the foodstuff. Although several antioxidants of different chemical structures as phenolic amines and hydroquinolic compounds have been

Table 5.1 Polymeric food colorants

Polymeric structure	Color	References
 R = H, —CH_3 R^{-}= H, —Ph,—COMe,—COOEt	Red	[14, 18, 19, 27, 28]
 R=—NH—C_6H_4—Me	Yellow, orange	[18, 28]
 R=H , Me R′=—Me,—OC_nH_{2n+1} R″=H ,—COOEt n=1-4		[18, 20, 28]

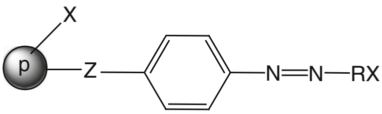
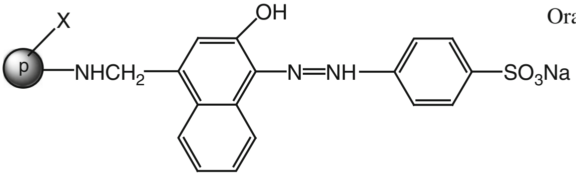
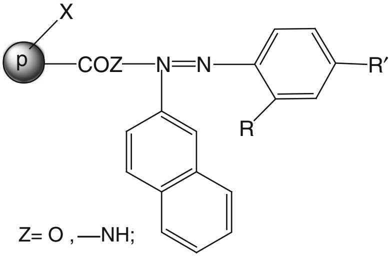
(continued)

Table 5.1 (continued)

Polymeric structure	Color	References
 R= —NO_2 , —SO_3H	Yellow	[14]
 a) Z = —NH— ; R= H , —SO_3Na , R = H, Me b) Z= —$NH(CH_2)_2$ SO_2  R = —SO_3Na ; R′ = H	Blue	[14, 18, 28, 29]
	Purple	[28]
 R= Me , Et a) Z =  b) Z =  C) Z = 	Blue, violet, green, blue	[30]

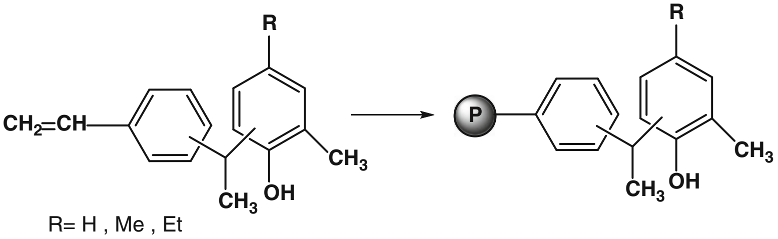
(continued)

Table 5.1 (continued)

Polymeric structure	Color	References
 a) $Z= —NHSO_2—, X=X^2$ b) $Z= —NHSO_2—, X=X^4$ c) $Z= —SO_2—, X=X^3$	Orange, yellow, burgundy, red, black, amaranth burgundy	[14, 21, 24, 27, 31–34]
	Orange	[28]
 Z= O, —NH; R=R′ = H, —Me, $—SO_3Na$	Red,, orange	[21, 22]

used to stabilize the food, their addition presents certain disadvantages to the user and they are not satisfactory due to the toxicity of many phenolic derivatives and because they lose their inhibitory action by evaporation during food processing. In addition, they have no food value and often are of questionable safety due to their absorption by the gastrointestinal tract [35]. Antioxidants are of two broad classes: hydrophilic and lipophilic antioxidants. The protection provided by the antioxidant depends on its concentration, interaction, and reactivity towards the particular ROS.

Certain disadvantages associated with traditional antioxidants have become pressing issues. Thus there is a need for useful alternative antioxidants that are essentially free from the unwanted effects associated with antioxidants and yet satisfy the inherent needs of both animals and humans. Such alternative antioxidant additives have been developed. Polymeric antioxidants have recently been designed and employed. These can be used without any appreciable absorption or metabolization, i.e., they are nonnutritive and noncaloric food stabilizers [36]. Various natural and synthetic polymeric materials have been used to support the antioxidant moieties such as cellulose, hydroxyalkylcelluloses, alkylcelluloses, carboxymethyl cellulose, agar, agarose, algin, alginates, gums, dextran, as well as synthetic polymeric materials as poly(acrylic acid), PVA, PEG, PPG, PEO, poly(vinyl pyrrolidone), polysorbate, polyaziridine, phenolic formaldehyde resins, phenolic styrene polymers,



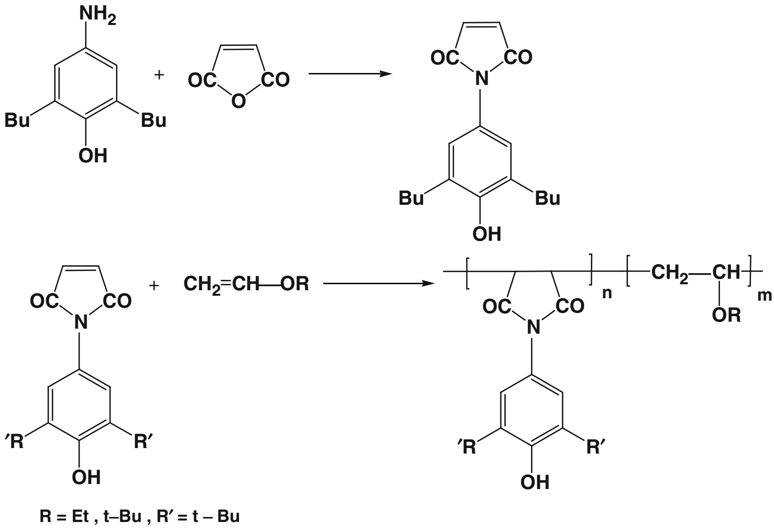
Scheme 5.4 Polymeric food antioxidant of phenol derivative [37–41]

PAAm, modified PAAms, and P(AAm-AA). For example, poly(styryl phenol) derivatives (Scheme 5.4) were prepared by polymerizing the vinyl monomer of α-(2-hydroxy-3,5-dialkylphenyl)ethylvinylbenzene either cationically or by free radical polymerization after blocking the hydroxyl group [37–41]. They exhibit substantial activity as antioxidants for fats, oils, and other foodstuffs. Similarly, polymers containing hydroquinone were prepared by the reaction of *p-vinylbenzylchloride* with substituted hydroquinone in the presence of a cationic catalyst such as $ZnCl_2$ and used as food antioxidants [42]. Other polymeric antioxidants containing various active moieties have been described such as polymethacrolein–(2,4-di-Me-phenol), poly(methyl vinyl ether-maleic anhydride)–(3,5-di-*t*-Bu-4-hydroxybenzylamine), PVA-(*t*-Bu-benzoquinone), polyepichlorohydrin–(2,6-di-*t*-Bu-hydroquinone), poly (chloromethylstyrene)–(*N*- -*naphthyl*-*p*-phenylenediamine), polybenzthiazole [39].

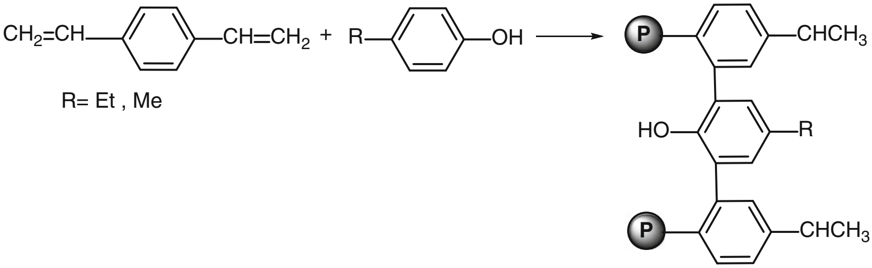
High-molecular-weight *N*-substituted maleimides have been prepared and used as polymeric food antioxidants which can achieve the desired gastrointestinal nonabsorption. *N*-(3,5-Di-*t*-Bu-4-hydroxyphenyl)maleimide was prepared in two steps: (a) formation of 2,6-di-*t*-Bu-4-aminophenol either from 2,6-di-*t*-Bu-phenol by nitration followed by reduction, or from 4-aminophenol by alkylation, (b) amidation of maleic anhydride with the 2,6-di-*t*-Bu-4-aminophenol followed by dehydration. The nonabsorbable poly(*N*-(3,5-di-*t*-Bu-4-hydroxyphenyl)maleimide)s were prepared from the monomeric maleimides by free radical homo- and copolymerization with comonomers of alkyl vinyl ethers (Scheme 5.5) [43].

Because of the high molecular weight of the polymers they are nonvolatile and hence keep their inhibitory action in the final food products to the desired degree without the need of additional antioxidants. Also, they prevent the absorption of the antioxidant group through the intestinal wall, thereby eliminating any risk of toxicity. Since antioxidants are used in food products containing oils and fats and also in high-temperature operations where oil solubility properties and thermal stability are particularly important. Based on the good thermal stability of condensation polymers, nonabsorbable antioxidants have been prepared recently by condensation polymerization of active monomers with desired functionalities and that consist of hydrocarbon backbones. Phenolic divinylbenzene polymers were prepared by the *o*-alkylation of phenols such as *p*-cresol or *p*-ethylphenol with divinylbenzene in the presence of acidic catalyst (Scheme 5.6) [44].

Other polymeric antioxidants have been prepared by condensation of divinylbenzene with various phenols and hydroquinones such as hydroxyanisole, *t-butylphenol*,



Scheme 5.5 Preparation of monomeric and polymeric maleimide antioxidants [43]

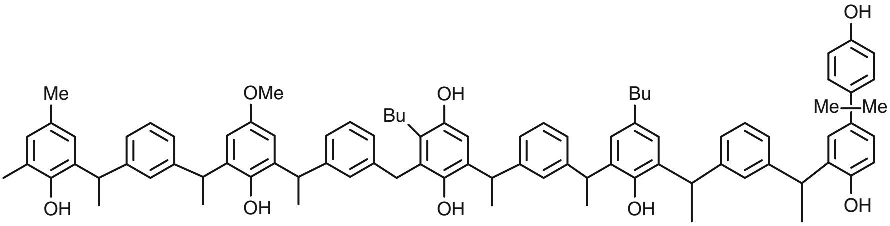


Scheme 5.6 Preparation of polymeric phenol antioxidants [44]

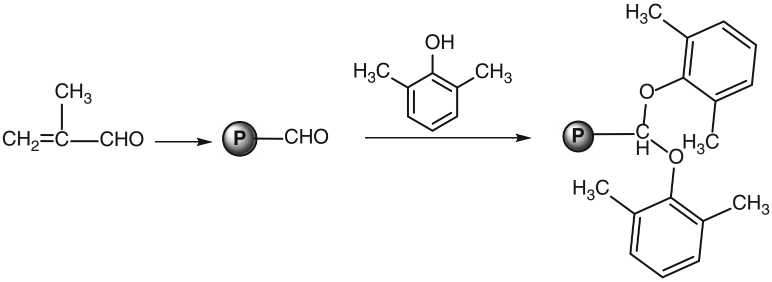
p-cresol, bisphenol A, and *t*-butylhydroquinone in the presence of an aluminum chloride catalyst (Scheme 5.7) [45–52]. This phenolic polymer is also an effective antioxidant for edible fats and oils.

Polymeric antioxidants have also been prepared by the chemical modification of preformed polymeric materials with antioxidant groups. For example, the polymeric antioxidant (Scheme 5.8) is prepared by the condensation of 2,4-dimethylphenol with polymethacrolein in the presence of a strong base or acid as a catalyst [38].

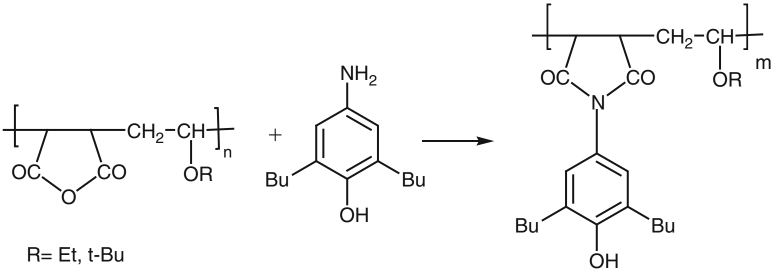
The covalent bonding of antioxidant to a preformed polymer can also be prepared by chemical modification reactions such as the reaction of 3,5-di-*t*-butyl-4-hydroxybenzylamine with poly(methyl vinyl ether-maleic anhydride) under a basic condition to give the polymeric phenol-maleic acid derivative which on treatment with acetic anhydride gave the corresponding polymeric phenol-maleimide derivative (Scheme 5.9) [39, 53].



Scheme 5.7 Polymeric antioxidants of phenol derivatives [45]

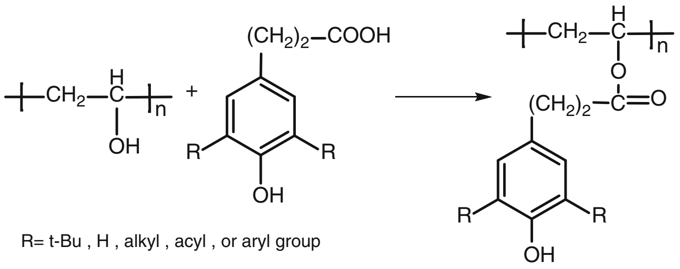


Scheme 5.8 Polymeric antioxidants of phenol derivatives [38]



Scheme 5.9 Polymeric antioxidants of maleimide derivatives [39, 53]

Phenolic compounds as butylated hydroxytoluene and butylated hydroxyanisole have found wide use as antioxidants in foodstuffs. The major problem has been raised concerning the possible toxicity of these compounds. Antioxidant polymers of PVA modified with phenol derivatives are nontoxic to animals and have been used as food antioxidants (Scheme 5.10) [54, 55].

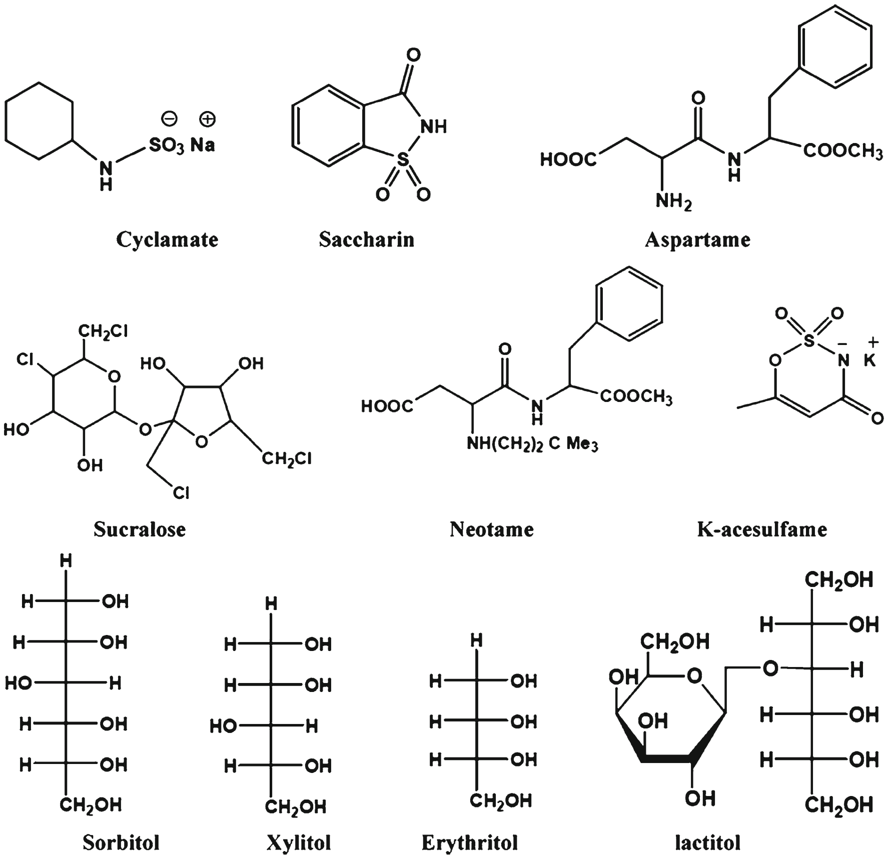


Scheme 5.10 Polymeric antioxidants of PVA-phenol derivatives [54, 55]

5.3 Polymeric Nonnutritive Sweeteners

Sweetness is one of the primary tastes and cravings of humans. The use of naturally occurring sweeteners to satisfy this natural craving has been met with its accompanying physiological disadvantages, e.g., the use of carbohydrate compounds that have an inherent food value, has a nutritional imbalance and promotes dental decay. The disadvantages associated with naturally occurring sweeteners present the need for useful sweeteners that are essentially free from the unwanted effects and yet satisfy the inherent needs of humans.

Artificial sweeteners can serve as sugar substitutes which increase the effect of sugar in taste with negligible food energy and may overcome the unwanted disadvantages of the naturally occurring sweeteners. They are food additives for flavoring and keep the food energy low, or because they have beneficial effects for tooth decay, generally need three prerequisites that must be fulfilled to obtain an approval for use according to food laws and regulations: (a) safety for the consumer under normal use conditions to exclude risks originating from consumption of these products, (b) technologically whether synthetic or semisynthetic, fulfill the requirements of a sweet taste, (c) have no food value, do not cause tooth decay, and free of caloric input to the consumer. They can be grouped on the basis of different characteristics into: fully or partly metabolized, completely absorbed, and fully metabolized into carbon dioxide and water. Sweeteners are less rapidly absorbed than sucrose and, therefore, their contribution to the caloric content of the diet is below that of the sucrose level and offer limited possibilities for energy reduction only. *High-intensity sweeteners* are known as an important class of sugar substitutes, with sweetness higher than that of sucrose, and a sweetness sensation different from sucrose. The majority of intensely sweet sugar substitutes approved as food additives are artificially synthesized, such as aspartame, sucralose, neotame, K-acesulfame, saccharin, and cyclamate (Fig. 5.1). However, some natural sugar substitutes are known, such as sorbitol and xylitol, which are found in fruit and vegetables, and are produced by catalytic hydrogenation of reducing sugars, e.g., the conversion of xylose to xylitol, lactose to lactitol, and glucose to sorbitol. Many artificial sweeteners in a range of sweetness as sucrose have been reported to replace sugar or corn syrup in the food industry, in an attempt to remove the unwanted physiological disadvantages of naturally occurring carbohydrates such as obesity and tooth decay [55–60].



Cyclamate Saccharin Aspartame

Sucralose Neotame K-acesulfame

Sorbitol Xylitol Erythritol lactitol

Fig. 5.1 Artificial sweeteners

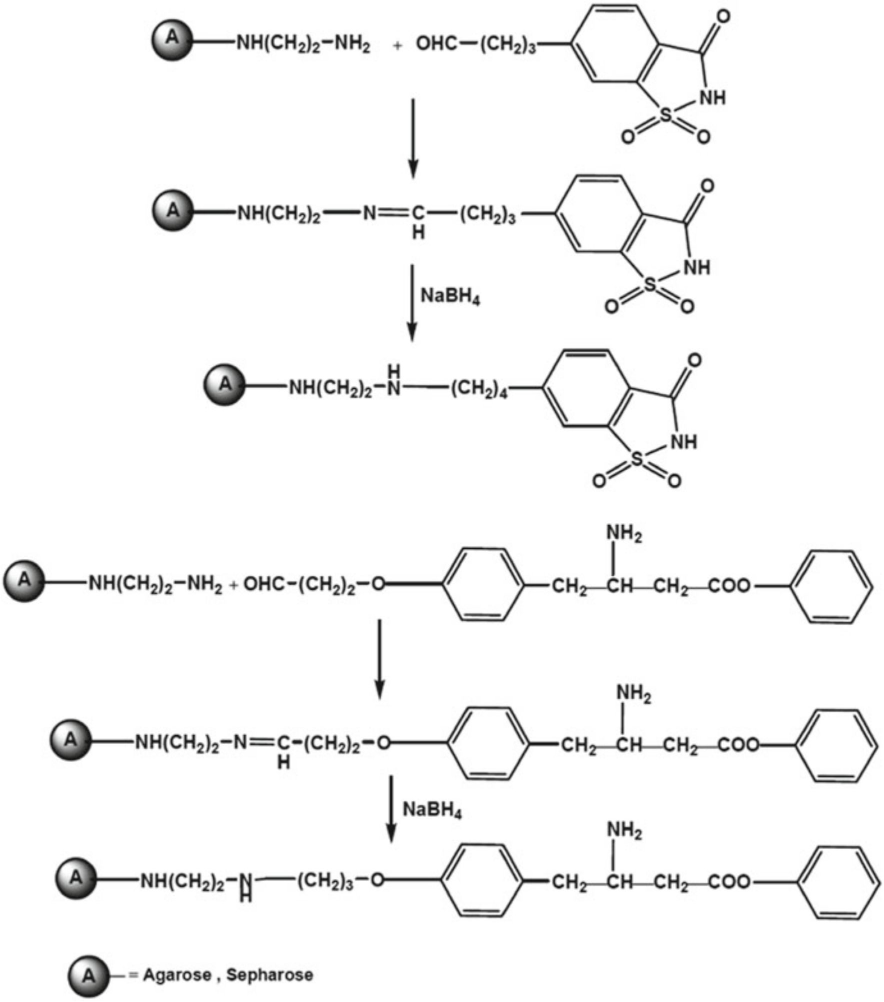
These sugar substitutes as alternative sweeteners are added to many food products today due to a number of reasons, including: (1) *Weight loss*: personal choice to limit food energy intake by replacing high-energy sugar or corn syrup with artificial sweeteners being noncaloric. This allows to eat the same foods with weight loss avoiding the problems associated with excessive caloric intake. (2) *Dental care*: artificial sweeteners prevent dental decay, i.e., are tooth friendly because they are not fermented by the microflora of the dental plaque. The carbohydrates and sugars consumed usually adhere to the tooth enamel and the bacteria can feed upon this food source allowing them to quickly multiply. As the bacteria feed upon the sugar, they convert the sugar to acid waste that in turn decays the tooth structure. A sweetener that can benefit dental health is xylitol that prevents bacteria from adhering to the tooth surface; the bacteria cannot ferment the xylitol thus preventing plaque formation and decay. (3) *Hypoglycemia*: persons with reactive hypoglycemia produce an excess of insulin after quickly absorbing glucose into the bloodstream that causes blood glucose levels to fall below the amount needed for proper body and brain functioning. As a result, hypoglycemics must avoid intake of high-sugar foods, and often use artificial sweeteners as an alternative because they do not greatly affect the blood sugar levels and aid in maintaining low insulin in the body and normal blood sugar levels. (4) *Diabetes*: persons with diabetes have difficulty in regulating their blood sugar levels. By limiting their sugar intake with artificial sweeteners, they can control their sugar intake. Also, some artificial sweeteners do release energy, but are metabolized more slowly, allowing blood sugar levels to remain more stable over time. (5) *Cost*: many artificial sweeteners are cheaper than sugar and often low cost is due to their long shelf life.

Many polymeric nonnutritive sweeteners do not match the taste profiles of sucrose or maize syrup. Derivatives of dihydrochalcones, formed from flavanones found in grapefruit and other citrus peel, retain some unwanted taste sensations, commencing slowly, and lingering longer than sucrose.

Since water-insoluble materials have no taste, polymeric sweeteners must have good water solubility. In addition, they should not be hygroscopic since this would impede manufacturing, packaging, distribution, and use. Their water-soluble compositions comprising the active sweetening agents are covalently bonded to the polymer support via a position on the molecule of the active sweetening agent that is nonessential for its sweetening activity. The covalent bond that resists disruption in the environment of the digestive system is capable of maintaining physical and chemical integrity of the active sweetening agent under the conditions of the host. It is also capable of producing a nonmetabolizable support macromolecule which has a high molecular weight to be absorbed through the mucosa of the gastrointestinal tract and which thereby maintains the active sweetening agent within the gastrointestinal tract by substantially restricting the agent's passage from the mucosal to the serosal side of the gastrointestinal tract as the sweetener composition passes through the gastrointestinal tract.

The polymeric materials may be linear or crosslinked structures of high-molecular-weight macromolecules having varying degrees of solubility in various media as: hydroxyalkylcellulose, agar, agarose, alginates, gums, dextran, PAA, PVA, PEG, PPG, PEO, poly(vinyl pyrrolidone), PAAm, PAAmAA, and polysorbate. The active sweetening moiety is the chemical group capable of stimulating a sense receptor to arouse a sweet response, and can be covalently bonded directly or a via spacer group to a polymeric support, and must be able to resist cleavage or rupture in the biological environment of use. The sweetening group can be of natural (saccharose group) or synthetic origin as: 4-methoxy-2-aminobenzonitrile, guiacol (2-MeO-C_6H_4-OH), *p*-alkoxy-phenylurea, 2-nitro-3-hydroxyphenol, 4-nitro-2-aminophenyl-alkylethers, 5-nitro-2-haloanilines, *p*-aminosaccharine, (alk = Me, Et, Pr, Bu).

Polymeric sweeteners prepared by chemical bonding of a natural or synthetic, active sweetening group to a polymer backbone, have recently been used to produce a sweetening effect with nonnutritive value and without any appreciable absorption, hence eliminating all the problems associated with naturally occurring and artificial sweeteners. For example, nonnutritive sweetener composed of saccharin covalently bonded to agarose has been prepared by the reaction of agarose-amine derivative with *o*-sulfobenzimide derivative (Scheme 5.11) [61]. In a similar way, agarose-containing

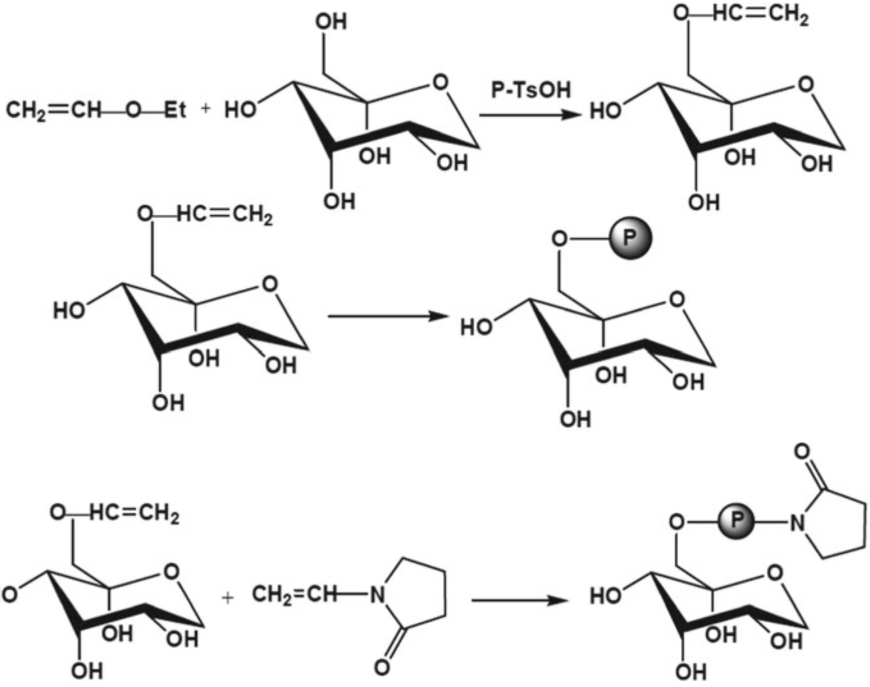


Scheme 5.11 Preparation of agarose-bound sweetener moieties [61]

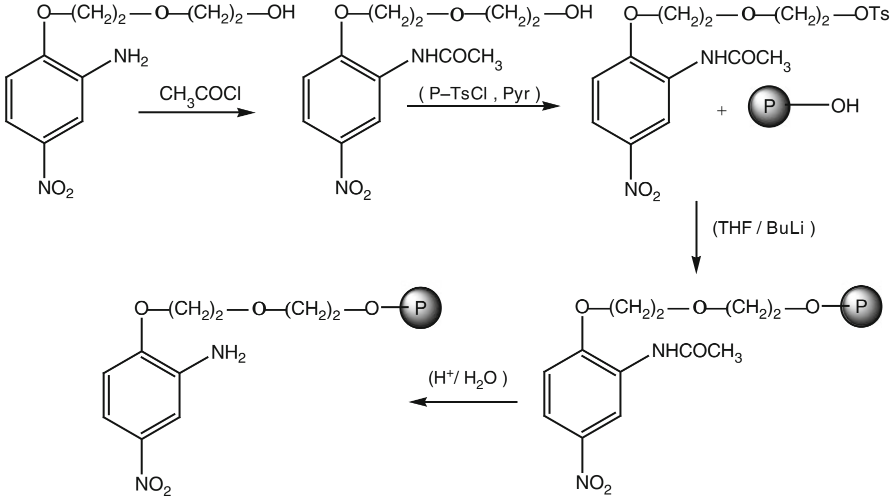
dipeptide of the benzylester hydrochloride of aspartic acid and methylester of tyrosine has also been prepared by the modification of agarose amine derivative.

The monomeric α-D-fructose vinyl ether has been prepared by esterification between α-D-fructose and ethyl vinyl ether in the presence of traces of *p*-TsOH, which is free-radical homopolymerized. Its copolymers with vinyl ether *N*-vinylpyrrolidone have also been prepared (Scheme 5.12) [61].

The reaction of PVA with the tosylate ester of 2[2′-(2-hydroxyethoxy)-ethoxy]-5-nitroacetanilide in the presence of pyridine gave the desired polymeric sweetener after hydrolysis of the amide function to the free amine (Scheme 5.13) [61]



Scheme 5.12 Polymerization of monomeric **α**-D-fructose vinyl ether [61]



Scheme 5.13 Preparation of polymeric sweetener of nitroaniline derivative [61]

Polydextrose, prepared by condensation melt polymerization of a mixture of (16)-α-D-glucose with sorbitol and citric acid as crosslinker, followed by neutralization, possesses all the necessary properties for use in conjunction with artificial sweeteners in reduced-calorie foods [62]. It provides no sweetness but contributes all the other properties of sucrose, i.e., bulk, humectancy, water solubility, and texture without any significant increase in caloric content. It can also be used to replace some of the butterfat of reduced-calorie ice cream-type products.

5.4 Polymeric Nonnutritive Hydrocolloids

Hydrophilic colloids (*gums*), which are usually polysaccharides, make up the majority of nonnutritive polymers added directly in the fabrication of food products to function as an integral part of the food, but do not become substantial components of the food. Gums are hydrocolloidal polymers that can be dissolved or dispersed in water to form highly viscous dispersions or swelling gels at low, dry substance content in an appropriate solvent [63–68], i.e., give a thickening or a gelling effect. Gums can be classified into: (a) *Natural gums*: gum arabic, larch gum (tree extracts) [69, 70], carob gum, guar gum (seed, root) [71], agar, algin, carrageenan (seaweed extract), pectin [72], gelatin, starch [73]. (b) *Modified gums*: cellulose derivatives as carboxymethyl-, hydroxyethyl-, methyl-, or propyl cellulose [74], starch derivatives as carboxymethyl-, hydroxyethyl-, or propyl starch, dextran, methoxyl pectin, carboxymethyl-carob gum or -guar gum. (c) *Synthetic gums*: PVA, poly(vinyl pyrrolidone), PAA, partially hydrolyzed PAAm, PEO, poly(ethylene imine), PE and PS sulfonates, hydrophobic gums as butadiene-acrylonitrile elastomers.

Gums have several advantageous physical properties: (1) *Dispersibility*: in fine particulate size they are often difficult to disperse in water so that hydration takes place quickly, i.e., the gum will take up water to form lumps or gel-like masses which are wet on the outside, but dry or gel-like in the center, and are very difficult to break up and dissolve. Several techniques are commonly used to facilitate dispersion and avoid lumping, which include: (a) adding the gum slowly while vigorously agitating the water, (b) mixing the gum thoroughly with other dry ingredients in the formula before adding to the water, (c) wetting the gums, which are soluble only in hot water, firstly with cold water to facilitate their dispersion, (d) dispersion of the gum in a retardant such as alcohols, acetone, liquid sugar, glycerol before adding to water. (2) *Solubility*: gums do not form true solutions and are termed hydrocolloid because of their high molecular weights and intermolecular interactions. The gums commonly used as food additives have very limited solubility in alcohol and other organic solvents but soluble in water, the degree of solubility depends on the solution temperature. Most of the gums are used at 1–2 % concentration, while above 5 % concentration it is difficult to form solutions. The stability of gum solutions greatly depends on pH and the presence of electrolytes. Some gums such as gum arabic and carboxymethylcellulose are soluble in cold water, while others such as agar are insoluble in cold water but dissolve in boiling water. (3) *Viscosity*: gums are tasteless, odorless, colorless, nontoxic, and noncaloric. They can be subjected to bacterial attack and degraded by acid- or enzyme-catalyzed hydrolysis of the acetal linkages joining the saccharide units. The use of preservatives is necessary if long-term stability is desired.

The rheology of gum solutions is a function of particle size, shape, flexibility, solvation, and ease of deformation, and the presence and magnitude of charges. Variables that affect the rheology of gum solutions include: (i) polymer composition which varies with the type and amount of substitution and the distribution regularity of substituent groups along the polymer chain, (ii) macromolecule size, i.e., molecular weight, (iii) concentration affects both the apparent viscosity and the rheology, (iv) shear rate: the apparent viscosity is dependent upon the shear-stress/shear-rate ratio, (v) temperature increase decreases the apparent viscosity, (vi) pH does not affect the viscosity of neutral gum solutions, but acidity increases the viscosity of solutions of anionic gums bearing carboxylate groups followed by precipitation or gelation.

In general, the viscosity of a gum solution depends on the type of gum, along with temperature, concentration, and degree of polymerization of the gum. Gum dissolution occurs by particle swelling until the particles disappear. Factors that affect dispersion and dissolution are the solvent, gum type, particle size, surface treatment of particles, shear rate, and dispersion method (mixing efficiency). Because all gums modify and control the flow of aqueous solutions, dispersions, and suspensions, the choice of gum for a particular application often depends upon its physical characteristics. The importance of gums in food products is based on their hydrophilic properties which affect the food structure, texture, and related functional properties. Gum constituents are indispensable to foods as additives that provide gelation, thickening, stabilization of emulsions and suspensions, texture modification, surface tension control, encapsulation of flavor oils, and film-forming properties. Accordingly, gums are used in a wide range of applications [66, 67]. In addition to their special application in chewing gum base such as poly(butadiene-*co*-styrene) rubber, poly(isobutylene-*co*-isoprene), PE, PVAc, polyisobutylene, and certain terpene resins, they are also used to perform other functions as (1) inhibitiors of crystallization in ice cream and sugar syrups, (2) clarifying agents in beer and wine, (3) cloud agents in fruit juice, (4) flocculating agents in wine, (5) mold-release agents in jelly candies, (6) stabilizers in beer, (7) thickening agents in sauces, (8) swelling agent in processed meats, (9) syneresis inhibitors in cheeses, (10) suspending agents in chocolate milk, (11) emulsifiers in salad dressings.

Thickeners, gelling agents, and stabilizers are extracted from a variety of natural raw materials and incorporated into foods to give provide structure, flow, stability, and eating qualities desired by consumers. These additives include traditional materials such as starch, a thickener obtained from many plants; gelatin as an animal by-product giving characteristic melt-in-the-mouth gels; and cellulose as the most abundant structuring polymer in plants. Seed gums and other materials derived from aquatic plants extend the range of polymers. Recently approved additives include the microbial polysaccharides of xanthan, gellan, and pullulan (Fig. 5.2). Polymers in food technology are helping to stabilize, thicken, and gel foods, resulting in consistent, high-quality products [75].

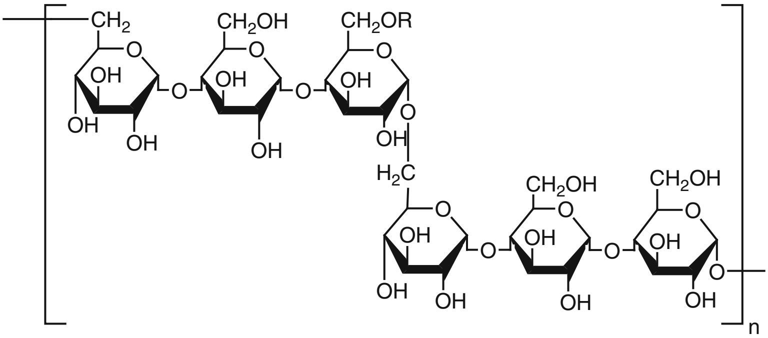


Fig. 5.2 Pullulan chemical structure

5.4.1 Polymeric Thickening Agents

Food thickening agents (thickeners) are water-soluble polymers of high molecular weights that are capable of increasing the viscosity of food aqueous solutions. They are natural or synthetic polyelectrolytes based on either polysaccharides (starch, vegetable gums, pectin, agar, carrageenan), or proteins (collagen, gelatin: the latter made by hydrolysis of animal collagen), which are suitable for modifying the viscosity properties of aqueous dispersions or solutions without substantially modifying other food properties, as taste [76, 77]. Thickeners provide body, increase stability, and improve suspension of added ingredients. Thickening agents are often used as gelling agents, forming gel materials that are used to thicken and stabilize liquid solutions, emulsions, and suspensions. They dissolve in the liquid phase as a colloid mixture that forms a weakly cohesive internal structure. The suitability of different thickeners in a given application depends on their characteristics of taste, clarity, and their responses to chemical and physical conditions.

The main problem with the use of starches as thickening agents is that they break down at high temperatures resulting in separation of absorbed water from a previously homogeneous mixture, particularly after freezing and thawing the food contents. The deficiencies inherent in the use of these thickening agents have been overcome by the chemical modification of starches by crosslinking, etherification, esterification, or phosphorylation [78]. Water-swelling crosslinked starches, crosslinked with trimetaphosphate, are used as foodstuff thickening agents, which are characterized by superior viscosity properties with no degradation or breakdown even after exposure to high temperatures for long periods of time [79]. Many natural and synthetic polymeric ingredients are used as thickeners, usually in the final stages of preparation of specific foods, and are very convenient and effective, and hence are widely used in the preparation of sauces and as soup thickeners.

Xanthan gum (Fig. 5.3) exhibits high viscosity at low concentrations and is used as a thickener and suspending agent in food relishes, where acid stability and high

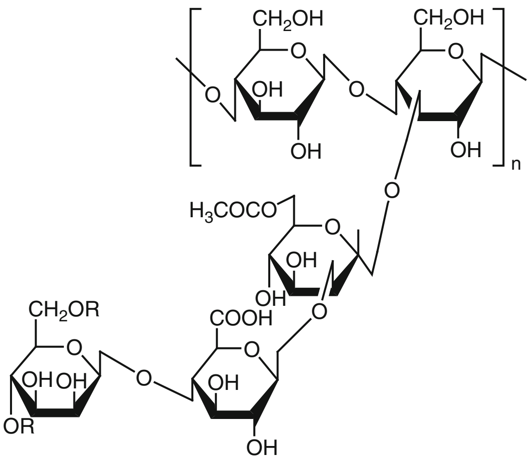


Fig. 5.3 Xanthan gum

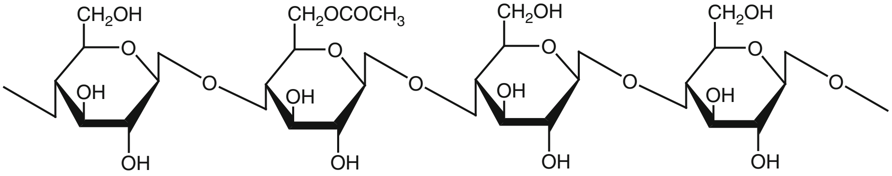


Fig. 5.4 Guar gum

salt compatibility are required. It is also employed in formulating flavored milks, citrus and fruit-flavored beverages, sweet sauces, and gravies [80]. At high concentrations, gum arabic functions as a thickener in candy. It is also employed to emulsify fat and flavor oils.

Guar gum, which is galactomannan polysaccharide consisting of β-D-mannose branched with α-D-galactose, forms gels in an aqueous medium and hence is used as thickening agents, e.g., for ice cream to thicken the mix. A specific advantage deriving from the replacement of agar with guar gum is the considerably lower cost (Fig. 5.4) [81]. Compositions of a mixture of a guar gum and a copolymer of an unsaturated dicarboxylic acid anhydride, e.g., poly(maleic anhydride-*co*-isobutylene), contribute high viscosity to an aqueous solution due to the interaction of the polygalactomannan and copolymer components and hence are utilized as thickening agents in food manufacturing processes [82]. Guar gum is also used often in combination with xanthan gum as a thickener in the manufacture of processed cheeses.

Carrageenan forms high viscosity solutions and is useful as a thickener; its thickening effect in milk is greater than in water. This property is applied in the preparation of chocolate milk, ice cream, evaporated milk, infant formulas, and freeze-thaw-stable whipped cream. The mixture of the two gums of carrageenan and carob gum produces a much more elastic gel with greater gel strength. Such

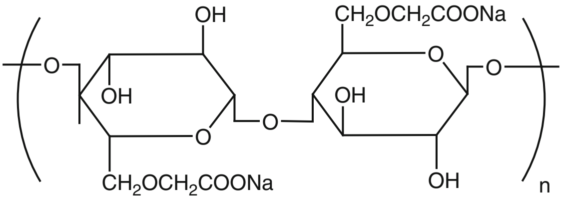


Fig. 5.5 Carboxymethylcellulose

gels are used in canned pet foods and also to provide body and fruit suspension in yogurt. Carrageenan can be used in water-dessert gels (where refrigeration is unavailable), whipped toppings, and cooked flans.

Carboxymethylcellulose (Fig. 5.5), as a cellulose-modified derivative, is most widely used in the food industry for noncaloric thickening and as a bodying agent in dietetic foods, and as a bulking agent with nutritional value. Propylene glycol alginate is used as a thickener for low-pH syrups.

5.4.2 Polymeric Gelling Agents

Gelling agents are food additives used to provide the foods with texture through formation of a gel, and to thicken (thickening agents) and stabilize (stabilizing agents) various foods, as jellies, desserts, and candies. Some stabilizers and thickening agents are used as gelling agents. An aqueous medium thickened with a gelling agent is applicable as a vehicle for many food products such as making jams, jellies, and marmalades from fruit juices or whole fruits. The hydrocolloids used as gelling materials in foods are based on polysaccharides, proteins, or synthetic polymers including: PAAm, poly(vinyl pyrrolidone), hydroxypropylcellulose acetate [83], modified starch, carboxymethylcellulose, natural gums, pectin, alginates, carrageenan, furcellaran, agar, guar, and gelatin [84–89]. Gelatin is a hot-water-soluble, thermally reversible, clear, elastic gel and has low nutrient value because of its low content of essential amino acids. Applications requiring gel formation may use percentages of gelatin that affect the physical properties or modify consistency because of its colloidal protective capabilities. Pectin is hot-water-soluble with high solid gels in the presence of sugar and acids, whereas starch forms hot-water-soluble and cloudy gels. Alginates are irreversible gels in hot or cold water and not elastic, but agar, carrageenan, and furcellaran are thermally reversible gels.

The gelling agents normally used to gel milk are polysaccharides such as carrageenans, furcellarans, and agars at pH 6. However, the use of acidified milk (pH 4) brings about a flocculation of the casein which deteriorates the aspect and quality of the product and makes it unappealing to be eaten. This phenomenon is increased by the presence of sulfated polysaccharides which chemically precipitate with the casein in these pH conditions. The addition of a gelling composition of a mixture of two gelling agents consisting of a galactomannan such as carob gum and agar or xanthan avoid the precipitation of the casein by protecting the colloid effect and improving the texture [90]. This food gelling composition mixture is used in water or milk either at a pH 7 or after acidification by adding a fruit juice. In the case of milk, this acidification may be obtained by microbic action leading to a food product (yogurt).

Mixtures of hydrocolloidal gelling agents in an aqueous medium have also been employed as water-soluble or water-dispersible additives to provide gels having solids-suspending properties. Such mixtures include a mixture of hydroxypropylcellulose and poly(1-alkene-maleic anhydride) as poly(isobutylene-*co*-maleic anhydride), and a blend of hydroxypropylcellulose and poly(alkyl vinyl ether-*co*-maleic anhydride) as poly(methyl vinyl ether-*co*-maleic anhydride) [91].

Gelatin is used as a gelling agent in prepared meat products, where it maintains moistness and improves consistency. Carob gum is used in combination with xanthan gum and starch to make chewy fruit confections, and also used as blend with carrageenan in pet food. Alginate gels have been widely used for many years in food products. Sodium alginate is used as a coating for frozen fish to prevent moisture loss and freezer burn, in fountain syrups, in tomato paste to hold water, and in meringues to prevent syneresis, but calcium alginate-alginic acid gels are applied in structured foods, e.g., fruit pieces, onion rings, pimiento paste for green olives, and shrimp pieces; and in jelly-type bakery fillings [92]. Alginic acid is also employed in soft, thixotropic, nonmelting gels, such as dessert gels, tomato aspic, and pie fillings. Furcellaran is used in milk puddings, eggless custards, and cake-covering jellies, e.g., flan jelly, Tortenguss, apricoture, and nappage.

5.4.3 Polymeric Stabilizers

Stabilizers inhibit the chemical reaction between two or more other chemicals, and inhibit the separation of suspensions, emulsions, or foams. Stabilizers include: (1) antioxidants that prevent unwanted oxidation of food materials. (2) UV stabilizers that protect food materials from harmful effects of UV radiation, being: (a) UV absorbers which absorb UV radiation and prevent it from penetrating the materials, as sunscreens, (b) Quenchers which dissipate the radiation energy as heat instead of letting it break chemical bonds, (c) Scavengers that eliminate the free radicals formed by UV radiation, as hindered-amine light stabilizers. (3) Sequestrants that inactivate traces of metal ions that would otherwise act as catalysts by forming chelate complexes. (4) Emulsifiers and surfactants that stabilize emulsions.

Yogurt is a product having a certain gellified texture obtained by adding to milk certain fermenting agents which acidify the milk through a coagulation of the casein. If yogurt is preserved at an ambient temperature, the fermenting agents continue their action, the acidity continues to develop, the product loses its qualities, and its preservation is thereby limited. Gums and their blends have been used to stabilize yogurts during processing. However, they were found to react with the milk protein, resulting in yogurts which are coarse-bodied, grainy, and which exhibit whey-off, i.e., the separation of fluid from solid material. Accordingly, a composition blend consisting of a combination of propylene glycol-alginate, alginic acid (Fig. 5.6), guar, carrageenan, and an emulsifier has been used for stabilizing soft-serve and hard-frozen yogurt [93, 94].

Fig. 5.6 Alginic acid

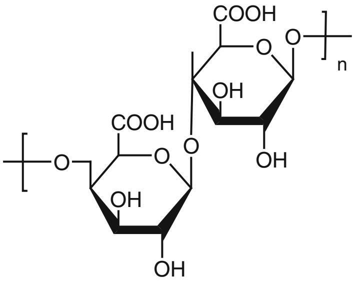
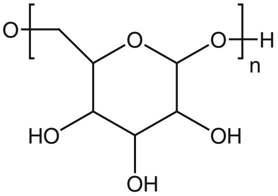


Fig. 5.7 Polydextrose



A problem with conventional ice creams is that at deep-freeze temperatures they cannot be served or eaten as readily as when they are at normal eating temperature. Reformulation to ensure such properties of eating at deep-freeze temperatures as those expected at normal eating temperatures is comparatively simple. The difficulty is that such reformulation leads to products that do not have acceptable properties at normal eating temperatures. Thus attempts have been made at obtaining an ice cream that has the serving and eating properties conventionally expected at normal eating temperatures and that is sufficiently stable. The properties of ice creams at deep-freeze temperatures have been improved by incorporating stabilizer mixtures comprising: (a) carob gum or tara gum, and (b) carrageenan, xanthan gum, or agar agar [95].

Carrageenan is commonly used as a *secondary stabilizer* in ice cream to prevent whey-off. The negatively charged carrageenan complexes form ion–ion interactions with proteins by direct association with positively charged regions of the proteins. In the presence of calcium, casein forms weaker complexes with carrageenan by an indirect association between the polyanionic carrageenan chains and proteins based on the divalent Ca^{2+} bridges. Both types of interactions are probably responsible for the usefulness of carrageenan as a stabilizer, e.g., its ability to stabilize cocoa in chocolate milk and form gels with milk, e.g., custards. Guar gum is used in foods as a *primary stabilizer* for ice creams to thicken the mix by preventing ice-crystal formation. It is also used as a stabilizer in pet foods and in ice pops and sherbets, but it is often used in combination with xanthan gum in the manufacture of processed cheeses. Carrageenan is used as an emulsion stabilizer in such products as whipped cream, instant breakfast drinks, milk shakes, and imitation coffee cream. Polydextrose (poly-D-glucose) (Fig. 5.7) can also be used to replace some of the butterfat of reduced-calorie ice cream-type products.

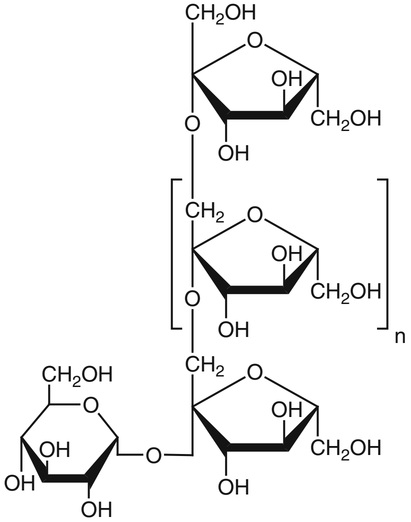


Fig. 5.8 Inulin chemical formula

Propylene glycol-alginate is used as a stabilizer in beer foam, in cottage cheese, in buttered pancake syrups, in tartar sauce, sandwich spreads, and in relishes to hold water. Gum arabic is also used as a foam stabilizer in beer and as an adhesive in sugar syrup glazes in bakery products. Edible gelatin is used as a flocculating agent in beer and wine fining to aid in clarification. Gum arabic protects flavor oil from oxidation and prevents volatilization. This action is probably due to adsorption as well as the physical barrier provided by the gum. Gum arabic and gelatin also are employed in a complex coacervation microencapsulation process. Cellulose is also used as a stabilizer when blended with carboxymethylcellulose.

5.4.4 Polymeric Crystallization Inhibitors

Carboxymethylcellulose is widely used in the food industry especially to bind the water in ice cream, thus inhibiting ice-crystal formation and growth. In addition it retards phase separation in frozen products, slows sugar-crystal growth, and is a physiologically inert and noncaloric thickening and bodying agent in dietetic foods. Arabic and guar gums are also used to prevent ice-crystal formation, sugar crystallization, and to emulsify fat and flavor oils. Dairy and confectionary products may contain gelatin to limit crystallization of ice and sugar, prevent water separation, and to reduce dissolution.

Specifically, the influence of biodegradable, environmentally friendly carboxylated polysaccharide additives, such as carboxymethyl inulin (CMI), has been used to delineate the crystallization kinetics of calcium oxalate. The retardation in crystal growth is controlled by the carboxylation degree of CMI and its concentration [96]. CMI is produced by chemical reaction of the biopolymer inulin [97]. Inulin (Fig. 5.8) is extracted from the roots of the chicory plant and is a polysaccharide consisting mainly of β-(2→1)-fructosylfructose units with one glucopyranose unit at the reducing end [98]. Inulin is used as dietary fiber, fat substitute, and sweetener (fructose syrups). Calcite crystal growth rate is inhibited by poly(carboxyclic acid)s which appear to involve blockage of crystal growth sites on the mineral surface by several carboxylate groups [99]. The effects of the kinetic inhibitors on calcite growth depend on their interactions with specific growth sites on the calcite surfaces.

5.4.5 Fibrous Simulated Food Product with Gel Structure

Simulated solid-consistency cohesive food products are provided by incorporating flavoring, coloring, and texturizing agents with a low-calorie oleaginous-fibrous food base composition. The base composition may also comprise a mixture of edible oil, water, and particulate fibrous cellulose combined with a cohesive gelling agent to provide a product having a cohesive gel structure as gelatin, alginate, agar, carrageenan, furcelleran, methoxylated pectin, modified starch, and gum [100]. Because of the desirability of increasing the fiber content of foodstuffs, both to decrease caloric content and to obtain the beneficial properties of fiber, attempts have been made to add refined fibrous cellulose to food compositions. Soluble cellulose derivatives such as cellulose ether and gums and cellulose crystallite aggregates have been added to food products and are widely used as stabilizers and texture enhancers for natural food materials. However, the use of these cellulose derivatives has been limited to only very small percentages in relation to the weight of the overall food product.

A product of fish meat paste simulating shrimp or lobster is prepared by mixing fish meat paste, fibers or edible fibrous material having a three-dimensional reticulate structure as texturing agents, starch, and other selected additives. The edible fibrous material or fibers incorporated into the fish meat paste impart to the product a texture which gives a particular oral sensation as if real shrimp or lobster were being eaten [101].

5.4.6 Polymeric Flavors

Food flavor is the sensory impression of a food and is determined mainly by the chemical senses of taste and smell given by the food. The senses, which detect chemical irritants in the mouth as well as temperature and texture, are very important to the flavor perception. The existing flavor of the food can be enhanced with natural or artificial flavorants, which affect these senses, i.e., making the food products taste more savory, so-called *flavor enhancers*. The primary function of the flavor in food is the flavoring rather than nutritional. *Flavorant* is the chemical substance or extract that gives or enhances the flavors of natural food product or creates flavor characteristics for food products. Thus, it denotes the combined chemical sensations of taste and smell, or alters the flavor of food and food products through the sense of smell. Of the three chemical senses, smell is potentially limitless and the determinant of the food flavor, while the taste of food is limited to sweet, sour, bitter, and salty. A food flavor can be easily altered by changing its smell while keeping its taste similar. Artificial flavoring is made of bases with a similar taste, having dramatically different flavors due to the use of different scents or fragrances [102].

Most types of flavorings are focused on scent and taste. There are three principal types of flavorings used in foods: (1) *natural food flavoring* substances are obtained from materials of vegetable or animal origin as oil, extractive distillate, protein hydrolysate, by enzymatic, microbiological, fermentative, or by physical means. They can be used either in their natural state as raw or have been subject to a process normally used in preparing food for human consumption, but cannot contain any artificial flavoring substances. Due to the high cost or unavailability of natural flavor extracts which are obtained from natural sources, most commercial artificial flavorants are nature-identical flavorings, chemically synthesized rather than being extracted from a natural source. (2) *Artificial food flavorings* that give specific flavors are obtained by synthesis or isolated through chemical processes, which are chemically identical to natural flavoring substances present in products intended for human consumption. Artificial flavors are often mixtures of naturally occurring flavor compounds to enhance a natural flavor. The compounds used to produce artificial flavors are almost identical to those of natural origin. (3) *Semiartificial food flavorings* are typically produced by fractional distillation of natural-source flavoring chemicals or from crude oil or coal tar, followed by subjecting to additional chemical modifications. Because the extracted flavoring substances are sensually not identified as natural flavoring products and not intended for human consumption, they are prepared by semisynthesis. While salt and sugar can be technically considered flavorants that enhance salty and sweet tastes, usually only compounds that enhance flavors are considered and referred to as *taste flavorants*. Glutamic acid salts are the most commonly used flavor enhancers in food processing. Glycine salts are also used as flavor enhancers.

Flavor encapsulation enables the creation of a dry, free-flowing powdered flavor. The encapsulation protects the flavoring from interaction with the food, inhibits oxidation, and can enable controlled flavor release. A variety of commercial processes are used for flavor encapsulation within the film, as spray drying and extrusion, in which the encapsulated flavor properties depend upon processing and the composition. Hydrocolloids are used in flavor-encapsulation systems for foods by: (a) *Spray-drying encapsulation*: has been widely used for flavoring of drying, heat-sensitive foods, due to the rapid evaporation of the solvent from the droplets. Spray drying can also be used as an encapsulation method when it entraps active material within a protective matrix, which is essentially inert to the material being encapsulated. Compared to the other conventional microencapsulation techniques, it offers the attractive advantage of producing microcapsules in a relatively simple, continuous processing operation. Spray drying generally involves producing an emulsion of the flavoring in an encapsulation matrix and homogenization is used to prepare the emulsion with a small particle size. The successful drying of the small flavoring particles is achieved through hot air streams. The matrix materials need to be water soluble, because many flavoring materials are designed to be released by contact with water, making hydrocolloids a good choice. In addition, the encapsulation matrix should not become sticky at high temperatures, i.e., the manufactured product should not be hygroscopic. Furthermore, the two main prerequisites in the material for processing are low viscosity and a high concentration of solids, and the emulsion should be stable. These requirements limit the use of matrix materials, e.g., maltodextrins, modified starches, and acacia gum are a suitable matrix for encapsulation. A mixture of two volatile products, citral (lemon-like odor, bittersweet taste) and linalyl acetate (bergamot-lavender odor, sweet, acrid taste), was formulated with blends of maltodextrin and gum arabic. (b) *Extrusion encapsulation* for food ingredients is a relatively low-temperature entrapping process and involves dispersion of the core flavor material in the molten coating material which forms the encapsulating matrix, and hardens. Encapsulated food ingredients that have undergone emulsification include orange peel oil in molten dextrose mass, fruit essences, and orange juice solids. Orange peel oil containing antioxidant and dispersing agent was added to an aqueous melt of corn syrup solids and glycerol. Agitation of the syrup mixture forms an emulsion which is forced through a die into mineral oil, followed by cooling, extrusion, and solidification. A combination of sucrose and maltodextrin is used as encapsulating matrix, and starches are used as emulsifying agents to increase the loading capacity of flavoring. (c) *Film encapsulation* for food flavor ingredients requires many characteristics for the selection of an appropriate coating material to form film from natural or synthetic polymers. Encapsulation allows separation of reactive ingredients from their environment until their desired release. Encapsulated food flavors must not diffuse during processing, but only release slowly during consumption. The coating protects the core material from oxygen, light, other food ingredients, and moisture. However, the controlled release depends on the capsule's geometry, type, wall material, solvent effects, coating degradation, as well as on fracture and diffusion. The flavor retention of volatiles during convective drying is a function of selective diffusion [103].

Cyclodextrins (α-, β-, γ-) are widely used in the food industry as food additives, for stabilization of flavors, for elimination of undesired tastes or other undesired compounds such as cholesterol, and to avoid microbiological contamination and browning reactions. The characteristics of the cyclodextrins at the industrial level and their main properties from a technological point of view, such as solubility and their capability to form inclusion complexes, are important in the use of these compounds in the food industry [104].

5.4.7 Polymeric Defoamers

In food industrial processes, the mechanical system may generate surface foam and entrapped air that may cause problems with liquid levels and give overflow which may reduce the process speed and the availability of process equipment. Problems associated are: (a) reduction of pump efficiency and capacity and storage tanks, (b) bacterial growth, (c) dirt flotation or deposit formation, (d) reduced effectiveness of the fluid solution(s), (e) eventual downtime to clean tanks, (f) drainage problems in sieves and filters, (g) cost of replenishing the liquid, and cost of entire material rejection due to imperfections.

Defoamers are antifoaming chemical additives that reduce and hinder the formation of surface foam and entrapped air, and thus are often used to increase speed and reduce other problems in food industrial processes. Defoamer are usually insoluble in the foaming media and have surface-active properties. Their effect is to lower the viscosity and spread rapidly on foamy surfaces. They concentrate on the air-liquid surface where they destabilize the foam lamellas causing rupture of air bubbles and breakdown of surface foam. Entrapped air bubbles are agglomerated to larger bubbles that rise to the surface of the bulk liquid more quickly. Antifoaming agents are used in a variety of food processes. *EO-PO-based defoamers* contain PEG, PPG, PEGPG, PEOPO, or PEGPO and have good dispersing properties for use as oil- and water-based defoamers. Alkyl polyacrylates are suitable for use as defoamers in nonaqueous systems where air release is more important than the breakdown of surface foam. These defoamers are used in a solvent carrier like petroleum distillates [105].

5.4.8 Polymeric Preservatives

Preservatives are food additives used to prevent or inhibit spoilage of food due to bacteria, fungi, or other microorganisms. They are naturally occurring or synthetic substances that when added to food products prevent biological decomposition by microbial growth or by undesirable chemical changes. They can be used alone or in conjunction with other food additives. They are either (a) *antimicrobial preservatives*, which inhibit the growth of bacteria or fungi, (b) antioxidants such as oxygen absorbers, which inhibit the oxidation of food constituents. Natural substances as salt, sugar, vinegar, and alcohol, are used as traditional preservatives. Certain processes such as freezing, pickling, smoking, and salting can also be used to preserve food. Another group of preservatives including citric and ascorbic acids from lemon or other citrus fruits can inhibit the action of enzymes (phenolase) in fruits and vegetables that continue to metabolize after they are cut and cause browning on surfaces of cut apples and potatoes [106].

Anticaking agents are powdered or granulated materials used to prevent the formation of stickiness during packaging, transport, and consumption. Some anticaking agents are soluble in water and others are soluble in alcohols or other organic solvents. They function either by adsorbing excess moisture, or by coating particles and making them water-repellent.

Acidity regulators are pH-control agents added to foods to control the acidity and alkalinity. They are usually organic polymeric acids or bases.

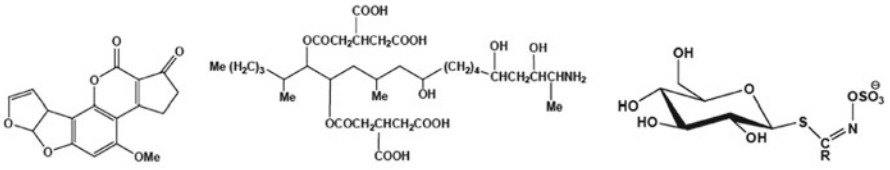
5.5 Animal Polymeric Feed Additives

Regular feed usually is a mixture of various plant raw materials ranging from grain to orange rinds to beet pulp that provides the required nutrients with an adequate ratio of proteins and energy. Feed supplements may need to be provided to the diet aside from regular feed, in order for animals to grow properly. The nutritional content of animal feed is influenced also by feed presentation, digestibility, effects on intestinal health, and the cost of quality feed [107]. Most farm animals receive a diets consisting of corn, soy, or corn-soy mixtures; for poultry feed, binder may be incorporated. The manufacture of animal feed formulations is typically dictated by the availability and low cost of the agricultural ingredients. Often these are dusty, unpalatable, of low density, and have inadequate nutrient profiles.

To correct the shortcomings of an inadequate nutrient profile of animal regular feed, ***feed additives*** are provided as a mixture of various raw materials and additives according to the specific requirements of the target animal. Such may be formulated as complete meals providing all the required nutrients. The supplements may include additional essential micronutrients as: vitamins, minerals, fats/oils, chemical preservatives, antibiotics, fermentation products, and other nutritional and energy sources that meet the nutrient requirements of the animals. These mixtures are then manufactured via extrusion or compaction techniques in the form pellets, blocks, or briquettes in order to prevent ingredient segregation, increase bulk density, reduce dust, mask unpalatable ingredients, and reduce wastage [108]. Animal feed additives are of different types: (a) *sensory additives* stimulate the appetite and improve the voluntary intake of a diet, (b) *nutritional additives* provide specific nutrients as vitamins, (c) *zoo-technical additives* improve the nutritional value of a diet but do not provide nutrients directly, (d) *medicated additives* for improved health and to cambat diseases.

The medicated animal feeds may contain drugs that must be approved by regulatory statutes. It is more practical and efficient to add therapeutics to the drinking water. Depending on the disease to be treated, the absorption of these substances through drinking water may be beneficial, especially in cases of fever, since the animals usually stop eating and drink larger quantities of water than they normally do. The adsorption of these substances through drinking water is more practical when raising cattle since there is no cause for discomfort to the animals because they do not have to be caught for individual treatments. Furthermore, the application of these ingredients through water is given to the whole lot at once. There is an actual saving of time and labor, since the incorporation of a solid substance through the cattle feed necessarily includes a mixing process by which it is not always possible to obtain a homogeneous proportion of the active substances. Individual treatments of the animals no doubt increase the amount of work proportionally to the number of heads [109].

Animal feeds provide a practical outlet for plant and animal by-products not suitable for human consumption. Any substance added to or expected to become a



Aflatoxin **Fumonisin** **Glucosinolates**

Fig. 5.9 Some mycotoxin derivatives

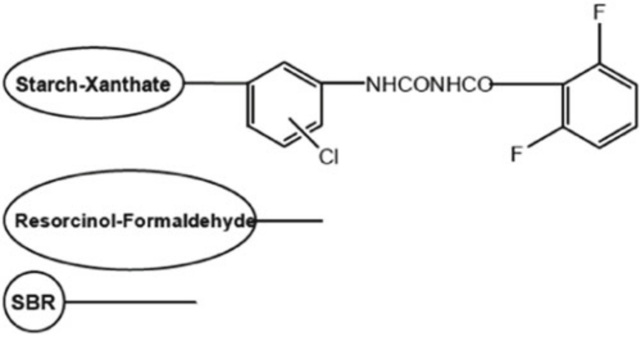
component of animal food, either directly or indirectly, must be used in accordance with current food additive regulations and generally recognized as safe for that use. Thus, the ingredients of the feed additives must meet the criteria for public health and be recognized by the extent of the presence of the contaminants in the ingredients used as sources of nutrients, aroma, or taste, and approved to provide the apparent safety concerns. The potentially hazardous feed contaminants to humans and animal health are of two types: (1) the toxic or hazardous chemical results from environmental and industrial contamination or is produced by fungi from agricultural crops, e.g., mycotoxins as aflatoxin and fumonisin B-1, glucosinolates, heavy metals like lead and cadmium (Fig. 5.9). (2) The industrial substances are not naturally occurring and are increased to harmful levels in the animal feed through mishandling or other actions, e.g., pesticides.

The ingredients of feed formulations have poor binding qualities and may even be antagonistic to binding. In such feed formulations, a binder is often included to insure that a durable pellet, block, or briquette is produced. Typically, lignosulfonate (usually including both lignosulfonate and sulfonated lignin) is a naturally occurring polymer generated via sulfite digestion of wood in the manufacture of pulp and paper, and is added (25–50 %) as binder to feed pellets, blocks, or briquettes. Lignosulfonate contains no protein and little metabolizable energy and is therefore unpopular in nutritionally dense formulations, e.g., poultry feeds, although it reduces the diluting effect of the binder on the feed. “Low-inclusion” binders have been introduced to the animal feeds industry, particularly to an improved animal feed composition and method of compounding animal feed. In addition, animal feed binders such as lignosulfonate-starch blends, protein-colloid, cellulose gum, carboxymethyl cellulose, a urea-formaldehyde, carboxylic polymers as PAA, poly(methacrylic acid) or poly(maleic acid), or lignosulfonate-acrylic acid blends, may be incorporated with the animal feed formulations to a small extent (<4 %). Each of these products provides some improvement in pellet, block, or briquette quality. Lignosulfonates are biopolymer salts of sulfite lignin formed as by-products in the manufacturing of wood pulp by the sulphite process. They are of varied composition and the different extent of the lignin degradation and sulfonic groups depend on the wood type. Lignin is a polymer with varied composition with structural units of “hydroxyphenyl propane”. The distribution of nonpolar and polar groups, including hydroxyl, phenolic, methoxy, and sulfonic acid groups formed in degradation determines the properties of the lignosulfonate. Sulfonated lignin as sulfate lignin (3-(2-hydroxy-3-methoxy-phenyl)-2-[2-methoxy-4-(3-sulfopropyl) phenoxy]propane-1-sulfonic acid) is lignin containing sulfonic acid groups introduced by the sulfate process for pulping.

Because of the importance of meat as a food product for human consumption it is desirable to increase the nutritional efficiency of feed supplied to domesticated animals such as poultry, cattle, and sheep generally raised as sources of meat [110, 111]. An improved animal feed is effective when the rate of growth of the animal and the amount of growth per unit weight of feed devoured by the animal are improved. For example, poly(vinyl pyrrolidone) incorporated as additive in the feed of domesticated animals at relatively low concentrations has produced the desirable stimulation in growth and improvement of feed efficiency [110]. In addition it has promoted the rate of growth and was also capable of counteracting some of the undesirable effects of toxic agents, as 3-nitro-4-hydroxyphenyl-arsenic acid, incorporated into feeds for various medicinal purposes.

The feed granules composed of mineral salts, vitamins, amino acids, antibiotics, hormones, and other therapeutic substances may be emulsified in the water provided to the animals by means of emulsifying agents as poly(vinyl pyrrolidone), alginates, or PEG to produce combined-feed substances for poultry and livestock [112]. An improved fermentation control containing laminate for retarding of the spoilage of silage and like materials on storage has also been described [113]. This laminate comprises a poly(vinylidene chloride) layer and a layer of a Kraft paper impregnated with sodium sulfate and a malt diastase. Erodible matrices containing sulfamethazine or sulfathiazole were applied for delivery of veterinary medicines in ruminant animals [114]. Water-soluble erodible matrices containing a sustained urea release compositions were used as ruminant feed supplement [115]. Fabric wick containing insecticides and repellents were also used for repelling face flies from cows and other animals [116].

Larvicides have been considered for use as feed additives as a way of controlling flies that breed in the droppings of hens housed in caged-layer poultry operations. Although many compounds (mainly organophosphorous insecticides) are active in the use to achieve such purposes, none have been applied primarily because residues of the insecticides were found in the eggs when the compounds were fed at the levels needed for fly control [117]. Several formulations containing the larvicide *diflubenzuron* [1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl)urea] were reported using starch-xanthate as the encapsulating agent and resorcinol-formaldehyde or SBR as additive. Residues of the larvicide in eggs using starch or cellulose xanthate formulations were lower than without (Scheme 5.14) [118, 119].



Scheme 5.14 Encapsulated larvicide diflubenzuron [118, 119]

5.6 Polymeric Indicators and Biosensors in Food

Simple, quick, and effective devices for determining the quality of food products are required to determine microbial by-products and to indicate quality and safety for human consumption. Microbial growth in contaminated food generates harmful chemicals that alter the pH, which can be determined by color change of pH indicators. Polymeric indicators provide for visual monitoring, detecting, or determining of the presence of metabolic by-products from harmful microorganisms. They detect whether the food is spoiled or contaminated with microbes, and correlating the presence or absence of a colorimetric change to whether the food is edible or not. Polymeric biosensors comprise organisms that respond to toxic substances at lower concentrations. These devices can also be used in environmental monitoring and detection of trace toxic substances in water treatment [120].

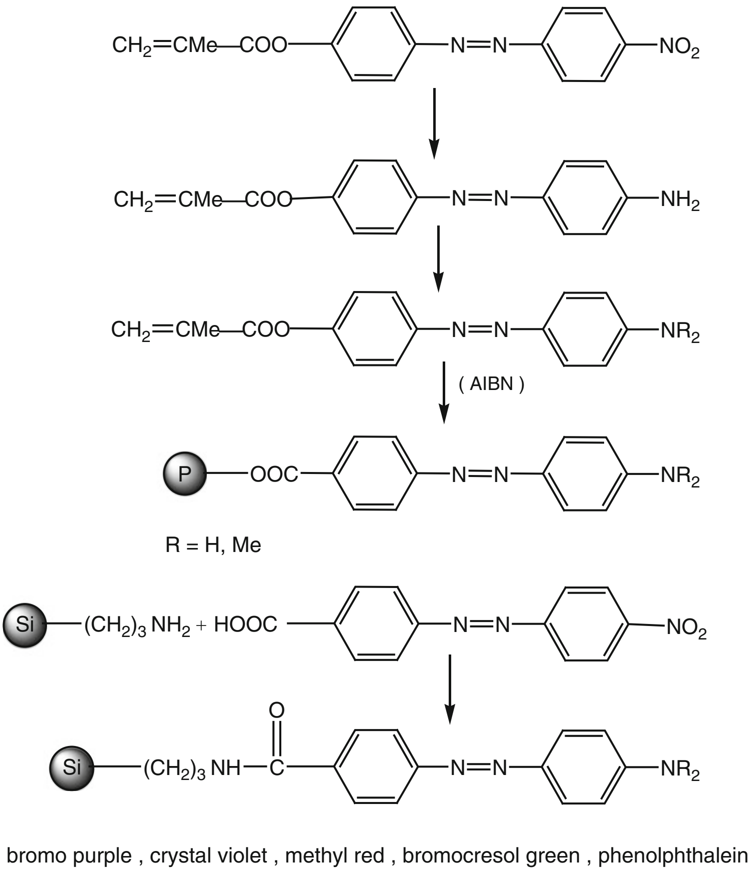
5.6.1 Polymeric pH Indicators in Food

The concentration of hydrogen ions is quantified in terms of pH by the negative logarithm of hydrogen ion activity: $\mathrm{pH} = -\log a\mathrm{H}^+$, and is widely used in determining chemical and biological water quality and in food monitoring [121]. The earliest method of pH measurement was by means of litmus paper indicators that change their color in accordance to a solution's pH, i.e., change from blue (basic) to red (acidic) in solution. The most common systems for pH measurements are based upon pH indicators which are either amperometric or potentiometric sensing devices. The potentiometric approach utilizes a glass electrode because of its high selectivity for hydrogen ions in solution, reliability and straight forward operation. Ion-selective membranes, ion-selective field effect transistors, two different terminal microsensors, fiber optic and fluorescent sensors, metal oxides, and conductometric pH-sensing devices have also been developed [122, 123]. Developments have focused on the application of functionalized polymers in various sensor devices [124] and more specifically pH devices [125, 126].

The by-products from microbes in foods include gaseous CO_2, H_2S, and SO_2 that mix with moisture resulting in the formation of acids which react with the indicator to produce a color change. Polymeric pH indicators also detect food spoilage by the pH change resulting from metabolic by-products of contaminating microbes in the food product. Polymeric pH indicator devices consist of a polymeric indicator layer coated onto the substrate, made from materials capable of supporting the indicator layer, such as paper, plastic (e.g., polyester, PE, PVC), cotton, flax, resin, glass, fiber glass, or fabric. The second polymeric matrix covers the first polymeric matrix with the exception of its edges and is impermeable to volatile bases generated by decomposing food, and the indicator compound is deposited within the first polymeric matrix and is colorimetrically responsive to the volatile bases generated by food decomposition. The first polymeric matrix is formed by an acid-catalyzed polymerization of a monomer material composed of tetraalkoxysilane, an alkyl trialkoxysilane, or a mixture. The distance of the colorimetric response of the indicator compound deposited within the first polymeric matrix increases with increased exposure to the volatile bases, and the food quality can be determined by measuring the distance of colorimetric response over a predetermined time period at a particular temperature.

Conducting polymers with ion-exchange properties are ideally suited for sensor applications, especially for potentiometric sensors [127, 128] because they exhibit high conductivity and electroactivity and can also be used as a general matrix for further modification with other compounds in order to change selectivity [129]. Nonconductive polymers have a high selective response and high impedance, which is important for eliminating interference by other electroactive species [130]. Polymeric pH indicators have several advantages over soluble indicators: (a) they can be used for a long time with quantitative recovery of the indicator, (b) they are not susceptible to microbial attack, (c) they are insoluble and hence do not contaminate the tested systems, and (d) they are superior in the determination of the pH values of weakly buffered or nonbuffered solutions. However, these types of devices can often suffer from instability or drift and, therefore, require constant recalibration.

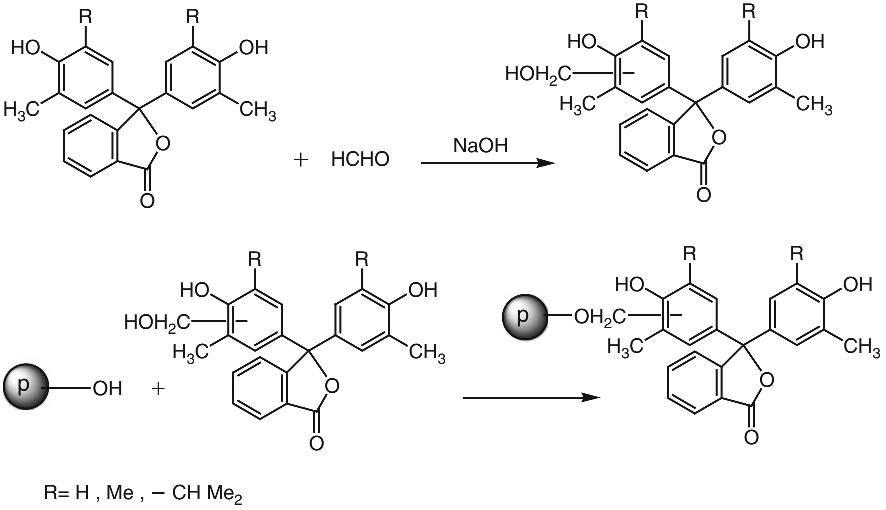
Conventional electrochemical sensors provide precise measurements within the common pH range, but do not work in extreme pH conditions [131, 132]. Other methods as titration, flow injection analysis, measurement of reaction index and density, and near-IR spectroscopy also have their limitations [133–135]. Optical pH indicators are adequate for high basicity (high pH values). For determining very strong bases, various optical pH sensors have been described as a renewable reagent-based fiber optical sensor [136], immobilized pH indicators on cellulose thin films over a polyester support [137], a thiazole yellow-immobilized cellulose membrane sensor and another detector containing pH indicator based on the length of the stain produced by OH^- [138, 139], a durable optical sensor system, and a dual-transducer approach to decompose the optical signals to give base and alcohol concentrations in concentrated $NaOH/H_2O/ROH$ (R = Me, Et, i-Pr) solution [140]. These optical base sensors consist of sol–gel SiO_2/ZrO_2–organic polymer composite doped with high pK_a indicators, thiazole yellow, alizarin yellow, etc., which are chemically



Scheme 5.15 Preparation of polymeric pH indicators [142, 143]

stable under severe conditions. Another luminescence sensor and a related ligand have been used which operate on the basis of a quenching effect [141].

A variety of polymeric pH indicators for food spoilage operating over various pH ranges have been prepared and used either alone or in combination to detect the pH change caused by the presence of microbic by-products involving the indicators: xanthene dyes (phloxine B, rose bengal, erythrosine), azo dyes (congo red, metanil yellow), and hydroxy-functional triphenylmethane dyes (bromophenol blue, bromocresol green, phenol red) containing acidic functional groups: –COOH, $-SO_3H$. The according polymeric matrix of the indicator layers are made of: PP, PE, PS, and ABS, SBR, silica sol-gels, poly(dimethyl silicone)s, Teflon (PTFE), PVC, or butylated cellulose. The pH indicators have been covalently bound to polymers by free radical polymerization of the monomers 4-(*p*-aminophenylazo)phenyl methacrylate and 4-(*p*-dimethylaminophenylazo)phenyl methacrylate (Scheme 5.15). The prepared monomers and polymers have been used as stable acid–base indicators [142, 143].

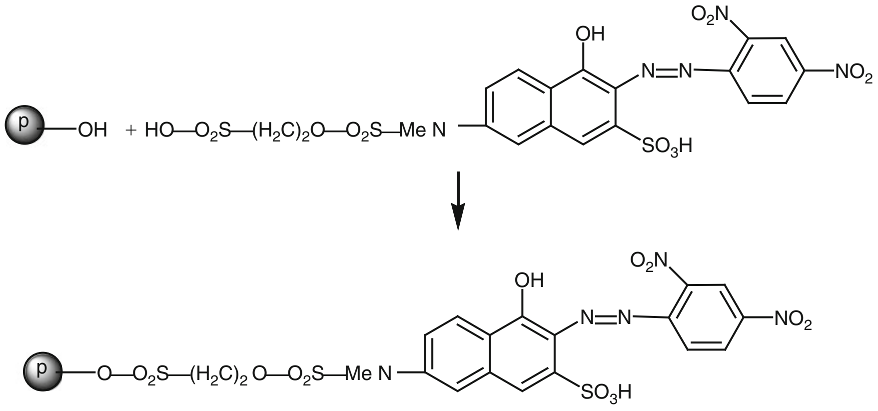


Scheme 5.16 Polymeric pH indicators of PVA-phenolphthalein derivative [149]

Polymeric membranes containing pH-sensitive dyes have been prepared to indicate conditions of food preparations [144, 145], e.g., polymeric membrane containing oxalic acid and phenolphthalein [146]. Diffusion through liquid-impregnated paper carriers containing diazo and anthraquinone dyes [147], and filter paper wick containing methylene blue [148] were also used as indicators for foods. Polymeric pH indicators of PVA derivatives were prepared by the reaction of phenolphthalein, *o*-cresolphthalein, or phenol red with formaldehyde under alkaline conditions. The resulting intermediate mixture containing hydroxylmethyl groups at various positions of the aromatic rings were immobilized by covalently bound to crosslinked PVA membranes wherein the pH-indicating moieties undergoe a detectable, colorimetric change in response to a pH change brought on by the presence of metabolic by-products from microorganisms (Scheme 5.16) [149].

Switchable, organic microporous networks were synthesized by coupling of tetrabromophenolphthalein with 1,4-diethynylenebenzene, having microporous structure with specific surface areas exceeding 800 m^2/g and pore polarity sensitive to the pH value. The switching between the open and closed form of the lactone ring is reversible [150]. Another polymeric pH indicator has been designed which binds DNSA ([2-(2,4-dinitrophenylazo)-6-(*N*-methyl-*N*-(2-hydroxysulfonyloxyethylsulfonyl)-amido]-1-naphthol-3-sulfonic acid) to the matrix of PVA via a sulfonoxy bond by the chemical modification of the polymeric support (Scheme 5.17) [151].

Direct chemical binding of the pH indicator moieties to a polymeric matrix requires several factors including: (a) the presence of a suitable functionality on the pH indicator that can bind to the polymeric matrix without loss of its pH-indicating properties, (b) the stability of the resulting bond during storage and under aqueous acidic or basic environments, and (c) the level of indicator bound to the polymer and avoiding trace organic solvent moieties to prevent the contact with foods.



DNSA : { 2-(2,4- dinitrophenylazo)-6- (N- methyl-N - (2-hydroxysulphonyloxyethylsulphonyl)amido}-1-naphthol-3- sulfonic acid

Scheme 5.17 Polymeric pH indicators of PVA-DNSA [151]

An anionic pH indicator for monitoring pH in aqueous solutions has been designed based on lipophilic ion pairs consisting of bromocresol green and a quaternary ammonium cation as cetyltrimethyl ammonium, which are homogeneously distributed inside the plasticized PVC membrane. A change of pH in an aqueous solution causes the change of optical property of the immobilized indicator membrane [152]. 6-Fluoropyridoxal–polymer conjugates have also been synthesized and characterized as potential pH indicators for magnetic resonance spectroscopy and imaging applications. The pH indicator–polymer conjugates have been prepared from 2-fluoro-5-hydroxy-3-(hydroxymethyl)-6-methyl-4-pyridine-carboxaldehyde conjugated to polyamino-dextran carriers by reductive alkylation [153]. As an alternative to the glass pH electrode, an entirely solid-state pH sensor (pH sensing and reference electrodes) has been developed based on Nafion-coated iridium oxide pH-indicator electrode and a polymer-modified silver-silver chloride reference electrode. Nafion coated onto an iridium oxide surface becomes permselective to cations [154]. The membrane thus transports protons, but attenuates the effects of anionic oxidizing or reducing (redox) species that interfere with the response of an uncoated electrode. The reference electrode involves coating a silver-silver chloride surface with a chloride-ion-containing polymer (e.g., triethylamine quaternized polychloromethylstyrene). The chloride ion is trapped within this polymer layer by encapsulating it with a Nafion outer layer. The Nafion membrane effectively blocks chloride ion diffusion to the test solution and maintains a constant chloride ion activity on the silver chloride surface; thus a constant electrode potential is maintained. Several sensor designs based on coated wires, cements, and alumina ceramics have been evaluated for pH response and stability. Distinctive features of the solid-state technology include glass-free construction, chemical resistance, and high impact strength.

5.6.2 Polymeric Biosensors

Biosensors are analytical indicator devices of proteins or cells contained within a polymeric matrix as immobilized enzymes deposited on the substrate, for the accurate detection and determination of the changes in the concentration of chemical or biochemical of biological species by converting the biological response into an electrical signal. Their biological response is determined by the biocatalytic membrane which accomplishes the conversion of reactant to product and has a number of advantages: (a) reusability over a long period with the same catalytic activity, (b) enzyme stabilization by the immobilization process, (c) use of an excess of the enzyme as indicator within the immobilized sensor system to ensure an increase in the apparent stabilization of the immobilized enzyme. However, the reaction occurring at the immobilized enzyme membrane of a biosensor is limited by the rate of external diffusion. These biosensor devices for the detection of biological species with a physicochemical detector component consist of three parts: (1) *sensitive immobilized enzyme membrane*, and the sensing microzone where the chemical reaction takes place, and connected with a transducer, (2) *transducer* using the physicochemical change (thermal, electrical, optical, mass, or electron) accompanying the reaction to transform the signal resulting from the interaction of the analyte with the biological element into another signal for more easy detection and measurement, (3) *electronic* or *signal processor* responsible for the display of the results [155]. The important part in the biosensor is the attachment of the biological agents to the surface of the sensor (metal, polymer, or glass). The functionalization of the surface with nitrocellulose or epoxy silane in order to coat it with the biological agents by layer deposition of alternatively charged polymer coatings [156]. Alternatively, three-dimensional hydrogels or xerogels can be used for chemical bonding or physical entrapping of the biological agents. The used hydrogel is a sol–gel, glassy silica generated by polymerization of organosilicate monomers as coupling agents in the presence of the biological elements along with other stabilizing polymers, as PEG in the case of physical entrapment [157]. Acrylate hydrogels as PAAm gel, which set under conditions suitable for cells or proteins, are commonly used for protein electrophoresis [158]; alternatively light can be used in combination with a photoinitiator, as 2,2-dimethoxy-2-phenylacetophenone [159]. The biosensor must possess: (1) stable and highly specific biocatalyst, (2) reactions independent of physical parameters, (3) accurate and reproducible response over the useful analytical range, (4) biocompatibility with no toxic or antigenic effects, (5) cheap, small, and easily used.

Biosensors are of various types: (a) **Optical biosensors** (photometric) in which the transducer works by using an *optical* change accompanying light output or absorbance during the reaction. These are based on the use of a thin layer of gold on a high-refractive-index glass surface that can absorb laser light, producing electron waves, at a specific angle and wavelength of incident light and are highly dependent on the gold surface that produces a measurable signal. Sensors operate using a sensor chip consisting of a plastic supporting a glass plate, one side of which is coated with a layer of gold. This side contacts the optical detection of the instrument. The opposite side contacting the flow system creates channels across which reagents can be passed in solution. This side of the glass sensor chip can be modified by coating with carboxymethyl dextran to allow easy attachment of indicator compound. Light is reflected off the gold side of the chip. This induces the evanescent wave to penetrate through the glass plate and some distance into the liquid flowing over the surface. The refractive index at the flow side of the chip surface has a direct influence on the behavior of the light reflected off the gold side. Optical biosensors are function on the basis of changes in absorbance or fluorescence of indicator compound. The device detects changes in absorption of a gold layer [160]. (b) **Biological biosensors** incorporate a genetically modified form of protein or enzyme. The protein is configured to detect a specific analyte and the ensuing signal is read by a detection instrument such as a fluorometer or luminometer commonly used in pharmaceutical applications and in biotechnology [161]. (c) **Electrochemical biosensors** function by enzymatic catalysis of a reaction that produces or consumes electrons (redox enzymes). The sensor substrate contains different electrodes: a reference electrode, a working electrode, a sink electrode, and a counterelectrode as an ion source. The target analyte is involved in the reaction that takes place on the active electrode surface, and the ions produced create a potential which is subtracted from that of the reference electrode to give a signal. The current (rate of flow of electrons is proportional to the analyte concentration) can be measured at a fixed potential or the potential can be measured at zero current. Potential of the working or active electrode is space charge sensitive. Further, label-free and direct electrical detection is possible by their intrinsic charges using biofunctionalized ion-sensitive field-effect transistors [162]. (d) **Potentiometric biosensors**, in which the transducer works by using the changes in the distribution of charges accompanying the reaction causing the electrical potential produced. They are conducting polymer coatings based on conjugated polymer immunoenzymes, and consist of two extremely sensitive electrodes. The signal produced by electrochemical and physical changes in the conducting polymer layer due to changes occurring at the surface of the sensor, may be attributed to ionic strength, pH, hydration, and redox reactions due to the enzymatic turnover of a substrate. (e) **Ion-channel switch biosensor** in which the transducer has the ion channels imbedded in supported or bilayer membranes attached to a gold electrode, allowing highly sensitive detection of biological molecules. The binding of the biological molecule to the ion channel controls the ion flow through the channel and results in a measurable change in the electrical conduction which is proportional to the concentration of the target molecule. The magnitude of the change in electrical signal is greatly increased by separating the membrane from the metal surface using a hydrophilic spacer [163]. The target biological molecules, including proteins, bacteria, drugs and toxins, using different membrane and capture configurations have been used for quantitative detection [164, 165]. (f) **Piezoelectric biosensors** in which the transducer is designed to use the mass change accompanying the reaction between the reactants and products. They utilize crystals which undergo an elastic deformation on the application of electrical potential. An alternating potential produces a standing wave in the crystal at a characteristic frequency. This frequency depends on the elastic properties of the crystal, such that if a crystal is coated with a biological recognition element, the binding of a target analyte to a receptor will produce a change in the resonance frequency, which gives a binding signal. (g) **Thermometric biosensors** (calorimetric), in which the transducer operates on the basis of the thermal change accompanying the reaction, i.e., the heat output or absorbed by the reaction, for transforming the signal resulting from the interaction of the analyte with the biological element into another signal that can be more easily measured and quantified. (h) **Amperometric biosensors** in which the transducer works by using the electron change accompanying the movement of electrons produced in a redox reaction.

Biosensors can detect specific chemicals at analytical levels and have been applied in various analytical fields. These devices are used for (a) food product quality: these are simple, quick, and effective for determining the quality of food products by analysis and estimation of food spoilage and for indicating the suitability or safety of the food. Biosensors are applied in various fields of food analysis, especially in detecting pathogenic viruses or bacteria [166], and toxins from chemical contaminantion of food products and drinking water [167, 168]. (b) Environmental monitoring, for detection of pesticides and river water contaminants, and sensing of airborne bacteria activities. (c) Healthcare: glucose biosensors are based on glucose oxidase that oxidizes glucose and breaks down blood glucose. Two electrons reduce the enzyme, which in turn is oxidized by accepting two electrons from the electrode. The resulting current is a measure of the concentration of glucose. The electrode is the transducer and the enzyme the biologically active component. They are used to determine glucose in analytical and clinical laboratories, to monitor glucose levels in fermentation reactors, estimate glucose in the food industry, and in pharmaceutical processes. The performance and usefulness of these types of biosensors are often dictated by the immobilization methods and the type of matrixes employed for the deposition of the enzyme layer. The sensor lifetime, its dynamic range, sensitivity, selectivity, response time, stability, and susceptibility to interferents are some of the parameters affected by the enzyme immobilization procedure and the type of support materials used for the biosensor fabrication [169].

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Chapter 6
Polymers in Food Packaging and Protection

Most food products are complex blends of various components that may deteriorate by exposure to excessive levels of oxygen, moisture, and heat. Food deterioration can result from the biological activity within the food or from external agents acting on the food. The extent of deterioration needs to be known throughout the shelf life of foods. The degree of product spoilage is reflected by off-tastes, flavors, or odors, and changes in appearance. Grains are stored in rigidly sealed containers to prevent intrusion of moisture or attack by vermin. Storage in grain sacks as jute sacks is not effective, because mold and pests can destroy the cloth material from which the grain sacks are made, even if they are stored in a dry area. Grain for domestic use is stored in other containers and might have to be dried before it can be milled. Food stored under unsuitable conditions may risk spoilage. Dry aging techniques and semidried processing with salt, smoke, sugar, acid, or others are sometimes used for readily spoiling foods. Food storage in both traditional domestic and industrial scales intends to preserve foods for preparation at times of scarcity or famine, taking advantage of short-term surplus of foods as at harvest, enabling a better balanced diet throughout the year [1–3].

Food packages are used to provide protection for food products against physical, chemical, biological, and environmental factors and to extend shelf life by modifying the atmosphere in food packages, and keeping the food contents clean, fresh, and safe. Food packages are labeled to show required information on the nutritional content of the food and to communicate to the consumer how to use, transport, recycle, or dispose of the package. Consumer labeling should also involve the nature of the potential deterioration of the product and any subsequent health problems if the food is consumed beyond the expiry date. Traditionally, food packages are designed to retard or delay the undesirable effects of environmental conditions on food quality. Their primary role in food safety is preservation and protection from external contamination, maintenance of food quality, and increased shelf life. They protect foods from the influence of environmental effects such as light, heat, oxygen, moisture, enzymes, microorganisms, insects, dust, gaseous emission, pressure, which can lead to the deterioration of food products. Shelf life of foods is enhanced

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by decreasing microbial, biochemical, and enzymatic reactions through moisture and temperature control, removal of oxygen, or addition of chemical additives or preservatives. In order to avoid recontamination, proper integration of the product, process, package, and distribution are important. Perfect packages should not allow molecular transfer to or from packaging materials, and should be inert and resistant to hazards. Food packages provide primary important functions including (a) portion control by dividing the food into a more suitable size for individual household supply and for cost savings, (b) food protection from physical and chemical damage, and (c) convenience during supply, processing, handling, distribution, storage, marketing, and sale. They have also several other functions such as food protection from microbial and other environmental contaminants, offer the consumer information as nutritional value, source, ingredients, cooking instructions, product weight, brand identification, and pricing. Package labeling serves in communication between the consumers and the food processor. Packages are designed to tolerate the environmental conditions of storage and the packaging design is adapted to the type of food contained, the susceptibility of the food to heat and oxygen, the physical protection needed, and the product visibility and heat desired.

Recently, many different food packaging systems have been developed in response to increased trends in consumer preferences towards fresh, mildly preserved, tasty, and convenient food products with a prolonged shelf life. Depending on the working of the packages used with the food products, the food packaging systems are classified as: traditional [4–8] and advanced, active [9–13], intelligent [14–16], or smart packages [17]. The food package is an essential component in the complex distribution system which transports food products from the agricultural production site to the point of consumption. Packages recently have become specialized and more complex, such as the active, intelligent, and smart packages that monitor freshness of fresh food products by the use of time-temperature indicators which show color change, and also display information on quality, improved safety, and improved convenience of microwave-safe containers.

Food can serve as a growth medium for microorganisms that can cause food spoilage, poisoning, and transmittance of diseases. To avoid potential health hazards, food safety should be followed in the preparation, handling, and storage of foods in ways that prevent microbial growth and microbiological processes. Agricultural production and the manufacture of packaged food products, containers, and chemical additives, should follow food regulation requirements to solve food safety problems and to obtain pollution-free “green food”. The packaging materials should be able to tolerate heat so that the food product can be sterilized in the containers. Many food products are hot-filled into packages at low temperatures, which are not able to tolerate heating. Glass and tin cans were the original processed food packages because they could tolerate sterilization temperatures. Because food flavors are able to change during heating, the packaging materials must be sterilized before they are used for food product storage. Various sterilization techniques have been designed to kill or remove microbes from food products using little or no heat processing for sterilization, such as the use of steam or chemicals as hydrogen peroxide, or by irradiation (UV light or γ-ray).

The hygiene requirements in the food packaging industry have significantly increased in the production of ready meals, which are thought to be heated by the final customer without undergoing any antiseptic treatment like boiling or grilling. A great number of factors are essential in order to protect the hygiene and the quality of the food products. By continuously following all the necessary hygiene requirements, a quality product can be offered for most fresh foods. The materials used for the packaging of these products must meet high hygiene standards in order not to cause the quality of the packed food products to deteriorate. The production of packaging films must comply with the highest hygienic standards assuring safety for the final customer, these standards are part of the quality and environment management systems and include several aspects: handling of raw food materials, protection against insects and rodents, automatic food packaging, and infection control of all workers involved in production.

Environmental protection measures include collecting and reusing recycled food packages, but improper and unsuitable reuse of the food packages has led to increased pollution and decreasing natural resources and landfill space for disposition for the used packages that can threaten health. Generally, it is safe to reuse glass that has been used for food packages after sterilization, but it is not safe to reuse recycled polymeric or paper packages from food storage. Understanding the uses, specialized functions, and limitations of packaging materials used for food protection can help for making safe decisions regarding the reuse of recycled packaging materials. With the exceptions of glass containers, most packaging materials are designed for single use to then be discarded or recycled to other industrial products. Recycled packaging materials from products other than food products should not be reused as food containers, because they may contain non-food residues and not satisfy the safety requirements of food systems. The food packaging materials that qualify to be recycled are reused only as food containers, after sterilization, with foodstuffs similar in acidity, sugar, fat, or alcohol content to the food originally stored in the packages. Foods with strong odors or flavors ought not to be stored in reused food packages, because the packaging materials absorb the chemicals that produce the odor or flavor and release them into a subsequently stored product, and some packaging materials allow certain chemicals to pass through them, transferring odors or flavors to other foods stored in the same area. In general, the reuse of recycled food packages often saves packaging costs.

6.1 Polymeric Traditional Food Packages

The main functions of a food package are to contain the food products and protect them against hazards which affect their quality during handling, distribution, and storage. The food package also plays an important role in marketing and selling the food product. The protective role of the food package by means of the designed containers is to isolate the contents from outside influences. The product should be contained in a suitable environment within the package to completely isolate the contents from the external environment. The food products are supplied to the markets in packaged, bagged, or boxed forms at the stage of their distribution. A wide range of packaging materials is used for food packaging including: papers, paperboards, fiberboards, cellulose, and polymeric films, semi-rigid and rigid containers made from polymeric materials, metals, glass, textiles, wood, or combinations of these materials. Packages should also be convenient to use, i.e., easy to open and resealable, and readily dispense the contents from the container. The reuse and recycling of packaging materials have positive influences on the environment, because the disposal of nonbiodegradable waste packaging materials is undesirable and causes environmental problems [18–22].

6.1.1 Types of Food Packages

The majority of food packages are designed in laminated form of different layers in which the inner layer holds the processed food, the mid-layer that combines the inner layer with the outer layer, and the outer layer that combines all in the package. Food packages are designed into various forms as trays, bags, boxes, and are of different types such as paperboard, plastic, glass, or metal. Recycled materials can be designed for the use in the outer layer of new food packagings that do not come in contact with the food products, or as containers for non-food items. Porous packaging materials such as paper, paperboard, and expanded foam packages are not reused, because they have air spaces that will entrap food materials and microorganisms and release them later. Also, flexible film bags for food storage printed on the outside are not reused in food packages since the printing inks may contain toxic substances and may migrate into the food on direct contact. Many polymeric materials pick up small amounts of the substances stored in them and release them later.

The materials used in the processing of containers or packages for food products include the following types:

6.1.1.1 Cellulose Derivatives

Cellulose is a natural polymer obtained from plants and used in different forms to store food products. (**A**) **Paper packages** may be manufactured from wood pulp or repulped waste paper. Since paper processing uses a variety of chemicals and the raw materials can contain residues which would be unacceptable in foods, thus paper products used for contact with the food products must be manufactured by processes which minimize residues in the final products. Ground wood pulp containing cellulose, lignin, carbohydrates, resins, and gums is produced by digesting the mechanically ground wood chips in an alkaline (sulfate pulp) or acid (sulfite pulp) solution. The washed wood pulp is pure cellulose free from the other ingredients which are dissolved during the digestion and removed by washing. The chemical pulp suspension in water is subjected to controlled mechanical treatment in order to split the fibers longitudinally and produce a mass of thin fibrils that hold them together and to increase the strength of the paper. The structure and density of the final paper is mainly determined by the extent of this mechanical treatment and by the additives, such as mineral fillers and sizing agents. The paper pulp is subjected to a series of refining operations before being converted into paper. Types of paper used for packaging foods include: (a) Kraft paper made form sulfate pulp and used for bags and multiwall sacks, (b) sulfite paper made from pulp acid digestion and used for sachets and bags, (c) grease-proof paper made from sulfite pulp, close-textured paper with grease-proof properties, (d) glassine paper made by polishing the surface of grease-proof paper and resistance to moisture penetration, (e) vegetable parchment, decreased porosity, grease-proof characteristics, (f) tissue paper, open structure, protect fruit surfaces, (g) wet-strength papers, crosslinked, not used in direct food contact but for outside packaging, (h) wax-coated papers, resistant to water and vapor transfer, (i) coated papers with polymers with improved functionality, increased strength, improved barrier properties. (1) *Paperboards* are made from the same raw materials as papers and consist of two or more layers of different quality pulps, used in the form of cartons. The types of paperboard used in food packaging include: (a) chipboard made from a mixture of repulped waste with chemical and mechanical pulps and used as outer cartons for food products, (b) duplex board made from a mixture of chemical and mechanical pulp and used for frozen foods, (c) solid white board made from fully bleached chemical pulp and used for frozen foods, (d) paperboards coated with wax or polymer as PE, PVdC, and PAm and used for packaging wet or fatty foods. (2) *Molded pulp containers* are made from a suspension of mechanical, chemical, or waste pulps by molding into shape either under pressure or vacuum and have good cushioning properties providing good mechanical protection to the contents. (3) *Fiberboard* in solid or corrugated form consists of a layer of paperboard, chipboard, or lined Kraft paper. Solid fiberboard is rigid and resistant to puncturing. Corrugated fiberboard consists of corrugated layers (medium) sandwiched between flat sheets of paperboard (linerboard) by adhesives. The medium may be chipboard, strawboard, or board made from mixtures of chemical and mechanical pulp. They are used as outer containers, to provide mechanical protection to the contents for goods already packaged in pouches, cartons, cans, and glass containers.

(**B**) **Wooden containers** are used when a high degree of mechanical protection is required during storage and transport. They take the form of crates and cases. Wooden drums and barrels are used for liquid products. The role of crates has largely been replaced by shipping containers. Open cases are still used for distribution of food products, although plastic cases are now widely employed. Casks, kegs, and barrels are used for storage of food products [23]. (**C**) **Textile containers** of jute sacks and cotton bags are used for packaging foods. However, multiwall paper sacks and plastic sacks are used, to a large extent, for fresh fruit and vegetables, grains, and dried legumes. Cotton bags were employed in the past for flour, sugar, salt, and similar products, but paper and plastic bags are now mainly used for these purposes. [23].

(D) Modified cellulose: (1) *Regenerated cellulose* (cellophane) films are made from wood pulp by treating bleached sulfite pulp with sodium hydroxide and carbon disulfide to produce cellulose xanthate (viscose), which on passing through an acid bath results in regeneration of cellulose as continuous sheet. The films are clear, transparent, good barriers to gases, and provide general protection against dust and dirt, and some mechanical protection. It is mainly used as coated films or as a component in laminates for food packaging. Films used for food packaging are coated with nitrocellulose or polymer mixtures of PVC-PVdC which improves functional properties. (2) *Cellulose acetate* films are made from waste cotton fibers by acetylation and partial hydrolysis. The film is clear, transparent, highly permeable to water vapor, gases, and volatiles and made by casting from a solvent or by extrusion. They are not used directly in food packaging but can be thermoformed into semirigid containers or as blister packaging.

6.1.1.2 Glass Containers

Glass containers are inert with respect to food products, transparent and impermeable to vapors, gases, and liquids, and are still widely used for food packaging. Glass containers and jars can be washed, sterilized, and reused as food packages, but their uses should not be for pressure processes. However, they are relatively heavy, susceptible to mechanical and thermal damage due to their rigidity and the rapid changes in temperature. The mechanical strengths of glass containers, i.e., their resistance to internal pressure, vertical loads, and impacts, increase with increasing thickness of the glass in the bodies and bases. The resistance of glass containers to changes in temperature is reduced as the thickness of the glass increases. Glass containers become weaker with use, due to abrasion of the outer surface. Treating the glass container surface with titanium compounds and replacement of the sodium ions at the surface with potassium ions can reduce the abrasion problem. Oxygen-absorbing packets are added to glass canning jars filled with dry food, and the jar edge is wiped clean and canned with a new and clean ring lid. When the jars are reused, a new lid should be used. The glass jars are impermeable to moisture, air, and insects and should be stored away from light and in a way that protects them from breakage [23–28].

6.1.1.3 Composite Containers

These containers usually consist of cylindrical bodies made of paperboard or fiberboard with metal or plastic ends, and are widely used for food packaging. Coated or laminated board may be used with aluminum foil to give good barrier properties. Such tubes or cans are used for some food products, while larger containers, as fiberboard drums, are used as alternatives to paper or plastic sacks or metal drums for other food products [5, 23, 24, 29–33].

6.1.2 Synthetic Polymeric Food Packages

The packaging industry is the largest user of common polymers and more than 90 % of flexible packages are made of plastics, because of their unique characteristics. Flexible and rigid polymers are becoming the most important packaging material for food products [34–37]. Most polymers are considered high-barrier packaging materials. They exclude vapors and gases and can be either optically clear or opaque. Polymeric food packages are actually layers of different polymers each layer making a contribution to total package performance. Flexible plastics may contain other additive substances that perform specialized functions as, for instance, antioxidants that prevent oxidation of the packaging plastic, stabilizers to prevent degradation of the packaging plastic when it is heated or exposed to UV radiation, and plasticizers to increase the flexibility of the packaging plastic by lowering its melting point. Plasticizers having relatively low melting points may migrate during sterilization heating. Flexible plastic polymers are used in packaging applications that provide mechanical properties (strength, rigidity, abrasion resistance) at low cost. Barrier polymers provide protection against transfer of gases, flavors, and odors. Adhesive resins bond the structural and barrier plastics together. Heat seal plastics provide package closures in flexible packages.

6.1.2.1 Polymeric Film

Polymeric film materials which are commonly used to package food products include various types made of: (1) *Polyethylene* (PE, polythene), which is made either by polymerization of ethylene at high temperature and pressure in the absence of oxygen, or by polymerization at lower temperatures and pressures in the presence of Ziegler-Natta catalyst. LDPE films are extensively used in food packaging due to their low price featuring the functional properties of clarity, easy processing by extrusion for coating of various substrates, low permeability to water vapor, but not a barrier to gases, oils, or volatiles. They are used in the form of pouches, bags, and sacks, and also used for coating paper and as a component in laminates. HDPE has a higher tensile strength and stiffness, and lower permeability to gases and can withstand higher temperatures. HDPE buckets are oxygen permeable, and serve for dry food products that can be packed for long-term storage. Buckets should be opaque to protect food products from light and are impermeable to moisture and insects when they have a gasketed lid. (2) *Polypropylene* (PP) films have good clarity and gloss, a wide heat-sealing range, printability, high tensile strength, tear strength, stiffness and impact resistance, due to the orientation of the macromolecules by the mechanical processing, low permeability to water vapor and gases. PP films are used in good packaging, but they are usually coated with PE or PVdC-PVC blend to facilitate heat-sealing. PP is used for composite packages in coated or laminated form to package food products. Random PEP shows high clarity, a lower and broader melting range, and reduced flexural modulus, improved impact resistance at low temperatures, and used for blow-molded bottles, cast film, and injection-molded products, such as food storage containers. (3) *Poly*(*vinyl chloride*) (PVC) film is clear, transparent, and brittle. The addition of permitted additives as plasticizers and stabilizers to avoid any hazard to the consumer improves its flexibility and use in food packaging. It has good mechanical and grease-barrier properties, and its permeability depends on the additive. Rigid PVC is used for bottles and packaging sheet, while flexible PVC finds major packaging uses in film, sheet, and bags (e.g., for blood). (4) *Poly*(*vinylidene chloride*) (PVdC) is stiff, brittle, and unsuitable for use as a flexible film. Its copolymer with PVC is used for food packaging with good mechanical properties, barrier to the passage of water vapor, gases and volatiles, and can withstand at high temperatures. (5) *Polyester* films of PET are stable over a wide temperature range and have other beneficial properties as impact resistance, transparency, stiffness, gas-barrier properties, and creep. The desired properties for food packaging applications are attained from the intrinsic properties of PET which eliminate the required addition of additives as antioxidants, plasticizers, heat or UV stabilizers. Low colorant concentrations are used for PET packaging manufacturing which possesses extremely low extractability. Oriented PET has good tensile strength and is often used coated with PE or as PVdC-PVC blend to increase its barrier properties and facilitate heat-sealing. Metallized PET has very low permeability to gases and volatiles. Three major food packaging applications of PET are as containers (bottles, jars, tubs), semirigid sheet (trays, blisters), thin films (bags, snack food wrappers). (6) *Polystyrene* (PS) films are produced by extrusion, are stiff and brittle with a clear appearance, and not useful as food packaging films. Less brittle PS film has an increased tensile strength, high permeability to vapors and gases and is grease-proof, and has few applications in food packaging. PS blends with PEVA or PVdC-PVC is widely used in the form of semirigid containers and blow-molded bottle, and also used in the form of foam for containers. (7) *Aliphatic polyamides* (PAm) films, as Nylon 6,6 and 6,10 are clear and attractive in appearance, mechanically strong, but the permeability to water vapor varies from high to low, they are good barriers to gases, and stable over a wide temperature range. Nylon films are used in the packaging of food products, but they may be combined with other polymers as PE, PEVA, and PEAA by coating, coextrusion or lamination, in order to facilitate heat-sealing or to improve their mechanical and barrier properties. (8) *Polycarbonate* (PC) films are made by the reaction of bisphenol A with phosgene or diphenyl carbonate. They are mechanically strong and grease-resistant, and have a high permeability to vapors and gases. They are stable over a wide temperature ranges, and used for outside food packages. (9) *Poly(tetrafluoroethylene)* (PTFE) films are strong, grease-resistant, and have a relatively low permeability to vapors and gases. They are stable over a wide temperature range and have a very low coefficient of friction. They are not used for food packaging, but may be able to be used for packages where a high resistance to the transfer of vapors and gases is required. (10) *Poly*(*ethylene-co-vinyl acetate*) (PEVAc) films have high impact strength and permeability to water vapor and gases. PEVAc blended with other polymers such as poly(ethylene-*co*-ethyl acrylate) (PEEtA) or PEAA may be used in laminates with PE and PP films for food packaging. PEVAc has very good stretch characteristics and can be used as an alternative to PVC for food-wrap applications [5, 23, 24, 38, 39].

6.1.2.2 Flexible Films and Laminates

Flexible films are nonfibrous thermoplastic materials in continuous sheet form and are usually transparent unless deliberately pigmented to some extent, and have the ability to be heat-sealed. Most flexible films consist of a polymer or a blend of polymers as PE, PP, PVdC, PAA, PAm, PEs as PET, or PEVAc, to which additives are mixed to give them particular functional properties, for altering their appearance or to improve their handling characteristics. Such additives may include plasticizers, stabilizers, coloring materials, antioxidants, antiblocking and slip agents. (1) *Extrusion* is commonly used to produce films through feeding the mixture of polymer and additives into the extruder which consists of a screw revolving inside a close-fitting, heated barrel. The combination of the heat applied to the barrel and that generated by friction, melts the mixture which is then forced through a die in the form of a tube or flat film. The extrudate is stretched to control the thickness of the film and rapidly cooled. It is possible to coextrude two or more different polymers simultaneously and fuse them together to form a single web. (2) *Calendering* is another technique used to produce polymeric films and sheets by squeezing the heated polymer between a series of heated rollers with a progressively decreasing clearance and the film formed then passes over cooled rollers, e.g., calendering of PVC, PEVAc, PEP copolymer films. (3) *Solution casting* is also used to a limited extent to produce polymeric films. The solvent is driven off by heating and the resulting films have a clear, sparkling appearance, e.g., solvent casting of cellulose acetate and ethyl cellulose films. (4) *Orientation* is a technique applied to produce oriented forms of the polymeric films in order to increase their strength and durability, improve their flexibility and clarity, and lowering their permeability to water vapor and gases, compared to nonoriented polymeric films. The orientation process that causes the polymer chains to line up in a particular direction may be of two types: (a) *uniaxial orientation* that involves stretching the film in one direction, or (b) *biaxial orientation* that involves stretching the film in two directions at right angles to each other. The process involves heating the flat films to a softening temperature between heated rollers and then stretched and passed over a cooling roller, e.g., oriented form of PET, PP, LDPE, nylon films. Films in the form of tubes are stretched by increasing the air pressure within the tube. When stretched to the correct extent they are cooled on rollers. Oriented films tear easily and are difficult to heat-seal.

Some food products are usually positioned on a tray made of paperboard or foamed plastic, with an absorbent pad between them and the tray, where flexible polymeric films may be used to overwrap items of food. The film is stretched over the food and under the tray. It may be heat-sealed on a heated plate or held in position by clinging to itself. Films may also be made into preformed bags which are filled by hand or machine and sealed by heat or other means. Heavy-gauge materials, such as PE, may be made into shipping sacks for handling large amounts of foods as grains or powder. However, films and laminates are most widely used in the form of sachets or pillow packs. A sachet is a small square or rectangular pouch heat-sealed on all four edges. A pillow pack is a pouch with a longitudinal heat seal and two ends sealed. These are formed, filled, and sealed by a sequential operation, a form-fill-seal system. Pillow packs are more economical than sachets as a packaging material which must be thin and flexible, have good slip characteristics, and form a strong seal, even before cooling. Sachets are made from stiffer materials and can be used for a wider range of product types. They are usually employed in relatively small sizes, e.g., for individual portions of sauce or salad dressing [5, 23, 24, 39–41].

When considering a packaging material for a particular food product it is necessary to balance the barrier properties with the suitability for the form of package, the method of preservation, and any subsequent handling after purchase. Such a balance is often not achieved by the use of a single polymeric layer, hence it is necessary to combine several polymeric materials or incorporate special barrier layers. Flexible laminates can be applied as combination of two or more flexible film materials, which are used for packaging food products when a single paper or polymeric film does not provide adequate protection to the product. In this laminate form, the functional properties of the individual layers combine to achieve the suitable film requirements for packaging a particular food product. The materials involved in the laminate may include papers or paperboards, films, and aluminum foil. The paper or paperboard provides stiffness, protects the foil against mechanical damage, and has a surface suitable for printing. The polymeric film contributes to the barrier properties of the laminate, provides a heat-sealable surface, and strengthens the laminate. The foil acts as a barrier material and has an attractive appearance. Laminates may be formed from paper-paper, paper-film, film-film, paper-foil, film-foil, and paper-film-foil combinations. The layers of a laminate may be bonded together by adhesive, which must be compatible with one layer. Thus, when one of the laminate layers is hydrophilic, i.e., permeable to water vapor, an aqueous adhesive may be used. Otherwise, nonaqueous adhesive is used when one of the laminate layers is lipophilic. The thermoplastic layers of the laminate may be bonded together by heated rollers or by coextrusion, e.g., regenerated cellulose-PE foil for wrapping butter and margarine, and for vacuum-packed cheese, PET-PE for coffee, paperboard-foil-PE for milk, fruit juice cartons, laminate typically consisting of PET-foil-PP or PET-foil-HDPE [5, 23, 24, 39].

Plastic garbage bags are another important application of polymers in packaging waste food products for disposal. They have the advantage of light weight, strength, and the capability to retain odors as a deterrent to rodents. Plastic garbage cans are lighter in weight than those fabricated from metals and also resist damage effectively. Many household chemicals are packaged in containers made from polymers, in which the resistance to breakage is an important advantage especially when the contents are corrosive or toxic.

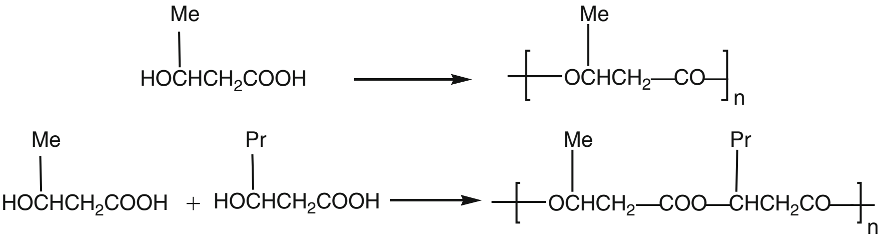
6.1.2.3 Rigid and Semirigid Plastic Containers

In addition to the use of polymeric films or coatings as packaging materials for food products, many of them are used as thermoplastic or thermosetting materials for food packaging which can be classified as rigid or semirigid food containers. The most common plastics used are being LDPE, HDPE, PVC, PP, PET, and PS. Acrylic plastics are also used for this purpose, including PAN and poly(acrylonitrile-butadiene-styrene). UF resins as thermosetting polymeric materials are used to make screw-cap closures for glass and plastic containers. Various methods are used to convert these polymeric materials into packages or containers for food products. (1) *Thermoforming*: in which the thermoplastic sheet is clamped in position above a mold and heated until it softens and then pressed to take up the shape of the mold by (a) having an air pressure applied above the sheet, (b) having a vacuum created below the sheet, or (c) sandwiching the sheet between the mold sides. The hard, cooled sheet is ejected from the mold, e.g., thermoformed plastic materials PS, PP, PVC, HDPE, PET, ABS; as trays: PVC, PEs, and PS; tubs and containers: PS, PVC, PE, PP, and ABS [42]. (2) *Blow molding*: in which a mass of molten thermoplastic is introduced into a mold and compressed to take up the shape of the mold. The hard, cooled plastic is then ejected from the mold. Blow molding is mainly used to produce narrow-necked containers as squeezable bottles for liquid food products. Blow-molding materials include LDPE, PP, PVC, PS, PET, and PAN. (3) *Injection molding*: in which the molten thermoplastic from an extruder is injected directly into the mold, taking up its shape. The hard, cooled material is then ejected from the mold. Injection molding is mainly used to produce wide-mouthed containers, but narrow-necked containers can be injection-molded in two parts which are joined together by a solvent or by welding. Materials such as PS, PP, and PET may be processed by injection molding into cups, tubs, vials, and jars for a variety of food uses. (4) *Compression molding* is used to form thermosetting resins, such as urea-formaldehyde resins. The prepolymeric powder is held under pressure between heated mold sides. It melts and takes up the shape of the mold, then cooled and the item ejected from the opened mold. The main application for this method is to produce screw caps [5, 23, 24, 39, 43–45].

6.1.2.4 Biopolymers and Metallized Films

Many types of food packages can be made from natural biopolymers. The physical characteristics required in packaging polymeric materials depend on their chemical structure, molecular weight, crystallinity, and processing conditions, as well as the packaged food and the storing environment. Poly(3-hydroxybutyrate) which is made by microbial synthesis, is crystalline, thermoplastic polyester, whereas its copolymer with 3-hydroxyvaleric acid increases the percentage of amorphous regions due to the steric hindrance in the produced copolymer poly(3-hydroxybutyrate-co-3-hydroxyhexanoate), Scheme 6.1. Thus, it is readily attacked by hydrolytic degradation, thereby increasing degradation rates [46, 47]. The properties of the copolymer make it suitable either for use in foods packaging and disposable items.

Other biodegradable polymeric blend materials acceptable to produce destroyable food packaging consists of either blends of starch as biodegradable polymer and nondegradable polymers as PE and PAA [48], or blends of starch and



Scheme 6.1 Preparation of homo- and copolymer of 3-hydroxybutyrate [46]

degradable polymer as PET [49]. The technique formulation used in the blend preparation depends on either using starch gel as the continuous phase with synthetic polymer as dispersed additive, or synthetic polymers as the continuous phase with starch as dispersed additive. The blend of PE–starch treated with a silane coupling agent and an unsaturated ester (soy or corn oil) as autooxidant reacts with metal salts in soils to form peroxide radicals that degrade the PE chains [50]. The stability of PE–starch film can be regulated by the amount of photosensitizer used which can absorb photons to produce free radicals. This treated PE can thus be timed and used for mulching the soil in vegetable growing to decompose and disappear at the end of the time of harvesting.

Metalized polymeric films are extensively being used to package food products. They are flexible and highly resistant to the passage of water vapor and gases and can be used as coatings for decorative purposes of food packages. They are made from aluminum vaporized and deposited onto PET, PP, PA, PS, PVC, and PVdC film or regenerated cellulose [5, 39, 41].

6.1.3 Selection of Polymeric Packaging Materials

The quality of a food product depends on its moisture content, extent of oxidation, concentration of flavor and odor components, and combinations of these factors. Maintenance of these factors at acceptable levels is governed by the permeability of the packaging system and the conditions of transport, storage, and marketing considerations. However, the choice of a packaging material or container for particular food storage is affected by several factors.

6.1.3.1 Permeability

Permeability is the permeation of a penetrant (liquid, vapor, gas, or volatile odor) through a polymeric membrane barrier which may be film, laminate, or coating. The rate of transmission at which a penetrant will pass through a polymeric membrane is governed by different factors. Some of these factors are dependent on the properties of the permeating species and the properties of the membrane, whereas the others are controlled by the degree of interaction between the membrane and the penetrant or environmental conditions. Permeation of a penetrant through a polymeric membrane is generally of the activated diffusion type, the presence of cracks, pinholes, and voids leading to loss of barrier properties. The permeability through a polymeric film is governed by the following four stages: (a) *absorption* onto the surface of the polymeric membrane, (b) *dissolution* into the matrix of the polymeric membrane, (c) *diffusion* through the membrane wall along a concentration gradient, and (d) *desorption* from the other surface of the polymeric membrane.

(A) **Permeability characteristics**. The rate of permeation of water vapor, gases (O_2, CO_2, N_2), and volatile odor compounds into or out of the package is an important consideration. Foods with high moisture contents tend to lose water to the atmosphere which results in a loss of weight and deterioration in appearance and texture. Food products with low moisture contents tend to pick up moisture, while dry food powders may cake and lose their free-flowing characteristics. Packaging materials with a low permeability to water vapor and effectively sealed decrease the water activity of the dehydrated food product that prevents microbiological spoilage. In contrast, fresh food products as fruit and vegetables use up oxygen and produce water vapor, carbon dioxide, and ethylene because they continue to respire after harvesting. In such cases, it is necessary to allow for the passage of water vapor out of the package. Thus, packaging materials which are semipermeable to water vapor are used to decrease the humidity inside the package when the temperature fluctuates. The shelf life of foods may be extended by creating an atmosphere in the package which is low in oxygen, and can be achieved by vacuum packaging or by replacing the air in the package with carbon dioxide or nitrogen. In such cases, the packaging material should have a low permeability to gases and be effectively sealed. If a respiring food is sealed in a container, the oxygen will be used up. The rate at which this occurs depends on the rate of food respiration, the amount in the package and the temperature. It is necessary to select a packaging material which permits the movement of oxygen into and carbon dioxide out of the package, at a rate which is optimum for the contents. Ethylene is produced by respiring fruits which can accelerate the ripening of the fruit. The packaging material must have an adequate permeability to ethylene to avoid this problem. To retain the pleasant odor associated with foods, it is necessary to select a packaging material that is a good barrier to the volatile compounds which contribute to that odor, and also prevent the contents from developing taints due to the absorption of foreign odors. Metal, glass, and flexible laminated film containers may be used in the cases where the movement of gases and vapors is to be minimized, because they are good barriers to vapors and gases. Semipermeable films may be used in the cases where movement of vapors or gases is desirable. Microperforated films may be used for products with high respiration rates.

(B) **Factors affecting permeability**. The factors which can affect the permeability of the polymer film may be divided into those associated with the polymer itself and those affecting the diffusion and solubility determined by the nature of the penetrant [51]. (1) *Polymeric barrier material.* The composition and macromolecular structure of the polymer play an important part in determining the barrier permeability. Specific molecular structures give rise to good barrier properties in polymers [52]. The selection of polymeric barrier properties may be governed by: the polymer chemical structure which must possess polarity, high chain stiffness, inertness to the penetrant molecules, bonding or attraction between chains, crystallinity, i.e., chain packing [53]. In addition to control of the polymeric barrier properties through chemical composition, the materials selection will be governed by consideration of the physical properties of the materials and package requirements in terms of strength, rigidity, cost, film performance, and processability. It is also possible to extend package shelf life by selection of the food processing technique or storage conditions [54–56]. (a) Polymers with polar structures are good barriers (impermeable) for gas but poor barriers (permeable) for water vapor, because the water plasticizes the hydrophilic polymeric barrier, whereas nonpolar hydrophobic polymers have excellent water-barrier but poor gas-barrier properties. (b) Crystalline polymers have a high degree of molecular packing that may be impermeable to a diffusing molecule and diffusion can occur in the amorphous regions of the polymers due to the free volume content of the structure. Crystalline polymers have a high degree of molecular packaging that are good barriers, whereas the amorphous regions of the polymers are sufficiently permeable to a diffusing penetrant due to the free volume content of the structure. (c) A crosslinking structure of a polymer barrier decreases the permeability due to the decrease in the diffusion coefficient. (d) Inert additives incorporated into polymeric packages, as plasticizers or impact modifiers to modify properties, may act as filler or reinforcements that can either decrease or increase barrier properties, depending on the degree of adhesion and compatibility between the polymer matrix and additive. (e) Copolymerization can also decrease barrier properties or increase permeation, especially in the use of flexible or poor barrier comonomers. (f) The permeability is independent of barrier thickness, but the permeation rate is inversely proportional to the thickness of the polymer film and the number of pores. Although polymeric films may be considered relatively free of pinholes they may still be present in very thin films [57, 58]. Packaging polymeric materials may consist of coated layers, films, or laminated multilayered structures [59–61]. Polymeric barriers used in coatings in a multilayer structure have different characteristics which depend on the barrier thickness and the number of pinholes. Rigid stiff containers of plastics have considerably lower moduli than metals and glass and are molded in thicker wall sections to compensate for the difference. (2) *Pentrant molecules*: The molecular structure of the penetrant gas or liquid molecules is of importance in the permeability which depends on their steric hindrance and their interaction with the polymeric membrane. Small penetrant molecules diffuse faster than large or bulky molecules, whereas nonpolar pentrants diffuse more rapidly in nonpolar barriers and are less diffuseable in polar barriers, and penetrant solubility greatly increases permeation [62–64]. In the packaging of fatty foods, it is necessary to prevent the egress of grease or oil to the outside of the package, where it would spoil, lose its appearance and possibly interfere with the printing and decoration labels. (3) *Temperature and pressure*: The permeability of polymers that show no interaction with the gases and vapors is independent of the pressure of the diffusing gas. However, the permeability of polymers that show strong interactions with the gases and vapors is found to be pressure-dependent and generally increases as pressure increases. This is due to the increase in the diffusion caused by the plasticizing effect of the absorbed gas or vapor and an increase in the solubility caused by the shape of the sorption isotherm. The permeability always increases rapidly when the temperature increases [65, 66].

However, in the design of packaging containers, it is desirable to minimize the three factors: solubility, diffusivity, and transport of the coatings or films used in these structures.

(C) **Solubility**. It is important to minimize the solubility of the polymeric barriers, coatings, or films, of the package components, because the increase in the solubility will plasticize the polymer with a consequent increase in the diffusion of all components of the food mixture. Major factors affecting solubility of a penetrant are the relative chemical compositions which affect polymer chain segmental mobilities and temperature and the concentration of the penetrant. The effects of these factors are well established for amorphous polymers, but it is not clear for glassy, semicrystalline, and multiphase polymers. The difficulty in these systems is the presence of excess free volume or voids in glassy and semicrystalline polymers, interactions in polar and H-bonding systems, domain structures in multiphase polymers of structure or composition which lead to the occurrence of sorption interaction between the penetrant and the polymeric matrix. The excess volume in such systems favors the transport of penetrants of small molecular size and shape. The overall sorption process in a glassy polymer involves two different processes of interaction of the penetrant with the polymer: (1) penetrant adsorption process, (2) penetrant sorption process. The absorbed material may affect the physical properties of the polymer by plasticizing action. Crosslinking in container coatings has a major effect on solubility. The presence of a crosslink network decreases the amount of absorbed penetrant due to its restraint on swelling of the polymer. The crosslink density varies in domains throughout the volume of the coatings' membrane due to nonhomogeneous distributions of reactants and other factors affecting the curing process. The heterogeneous structure of the network, varying in density, must affect both the solubility and diffusion of penetrants.

(D) **Diffusivity.** The molecular mobility of penetrant molecules in a polymeric matrix is affected by at least four factors. (1) *Polymer-chain segmental mobility* is governed by the inherent flexibility of the polymer chain (chemical composition, chain sequence distribution, inter- and intrachain interactions, etc.), effects of crosslinking and crystalline domains, interactions with penetrant (plasticization), and any other factor which affects the free volume content in the polymer-penetrant system such as temperature. Any decrease in polymer-chain segmental mobility will decrease the diffusion rate of penetrant through the membrane. Polymers containing highly polar chain substituents, e.g., PAN, give membranes with excellent barrier properties. PVC and PVF membranes have good barrier properties. The substitution of two halogen groups on the same carbon, e.g., in PVdF and PVdC, lowers the net polar vector by partial cancellation of the two opposing dipoles, but the regularity of the structure allows partial crystallization to occur which aids in reducing both solubility and diffusion to give excellent barrier properties. The presence of H-bonding groups along the polymer chain gives good barrier properties when the membranes are dry. The presence of hydrogen-bonding groups causes a great increase in permeation of the penetrant species via plasticization of the polymer. The presence of H-bonding acceptor groups also improves barrier properties due to their polar nature. The incorporation of aromatic or cyclic rings into the polymer backbone structure (PET, polyimides) gives membranes with good barrier properties. These materials also often display good chemical and water resistance. (2) *Diffusion path length modification* through the membrane is often used to increase the effective barrier properties of the coatings or packaging materials. The use of impermeable fillers of disk or plate shape to lower the net transport of penetrants through a membrane has been utilized to offer the greatest hindrance to diffusion of penetrant through the polymeric film barrier applications. The penetrant molecules are required to circumvent the obstructing filler or crystalline regions in order to traverse the film thickness. This way of reducing transport has been used by the application of polymer-blend technology. A direct approach is to use film laminates of differing properties including one film laminate component of very low permeability. Cellophane is coated with PVCVdC to protect the cellophane from water attack. (3) *Defect structures in the coating*, such as pinholes, cracks, down to fluctuations in polymer crosslinking and density, have profound effects on diffusion through the membrane. The difficulty is the sensitivity of diffusion to the size scale of the defect. (4) *Localization of penetrant within the polymer matrix*: the mechanisms for localization include dual mode sorption, solvation of polar and ionic groups in the polymer matrix, and physical clustering due to incipient phase separation of absorbed penetrant.

(E) **Transport.** The usual driving force for transport-causing diffusion is the gradient of chemical potential of the penetrant. In the case of gases, the transport of mixture components obeys the relation with the driving force for each gas being its individual partial pressure gradient. In the case of vapor and liquid transport, where one or more of the absorbed penetrants may swell the polymer membrane, the diffusion of all penetrants is enhanced due to the increase in free volume and increased chain segmental motion in the polymer. There are factors operating into modifying the simple driving force concept. This includes effects of a gradient of concentration of another penetrant on a given penetrant, a gradient in temperature or imposed mechanical stress, or a gradient in the composition of the polymer itself across the membrane. Thus, the net flux of the penetrant is affected by its own concentration gradient and also by the other types of gradients in the system.

6.1.3.2 Compatibility

The packaging polymeric materials should not leach toxic substances to the food contents that result in health hazards to the consumer. Such toxic substances may be residual monomers or additives as stabilizers, plasticizers, and coloring materials. To control the safety of the packaging materials, it is desirable to reduce the extent of migration or to use nontoxic monomers and additives in the polymer preparation and formulations, which depend on the chemical compatibility of the packaging material and the food contents of the package. Interactions between the packaging materials and the food contents should be avoided because they affect the quality and shelf life of the food and causing a health hazard to the consumer. This results in the deterioration and a change in the appearance and the color of the food. These interactions between the packaging materials and the food contents can also be avoided by interposing another barrier substance between the packaging material and the food [23–26].

6.1.3.3 Mechanical Damage

Mechanical damage to processed and manufactured foods may result from sudden stress as impacts, shock, vibration, or compression loads imposed during handling, transport, or storage. Appropriate packaging, handling, and transport procedures can reduce the extent of such mechanical damage. The selection of a packaging material of sufficient strength and rigidity can also reduce the damage due to compression loads. Metal, glass, and rigid polymeric materials may be used for primary or consumer packages. Fiberboard and timber materials are used for secondary or outer packages. The incorporation of cushioning materials, corrugated paper and boards, pulp board, and foamed plastics, into the packaging can protect against impacts, shock, and vibration. Restricting movement of the product within the package by tight- or shrink-wrapping may also reduce damage.

6.1.4 Factors Affecting Packaging Materials

The deterioration rate of food products is related to their composition, processing, and environmental factors that determine microbial growth which in turn are affected by direct and indirect factors. The direct factors result from the food and packaging interactions that affect the physical, biochemical, and microbial integrity of packaged food products leading to immediate food spoilage, e.g., off-taste or color, and to termination of shelf life. The indirect factors result from external effects, such as time, temperature, moisture, light, gases, and pressure that bring changes in the food product and does not necessarily render it useless. Thus, food changes are chemical changes caused by deterioration that can result from: (a) interactions with heat and light, (b) interactions with the container surface either as catalyst or coreactant, (c) permeation of molecules from the environment through the package wall to enter the food, (d) migration of molecules from the package, which are derived from the polymer itself or from the coating additives to the food, (e) the transfer of flavor molecules to the food by permeation into and through the plastic walls of the package (transport of aromas).

6.1.4.1 Effect of Time and Temperature

Foodstuffs require time before the effects of deterioration is noticed, which may be delayed by protecting the food product against spoilage caused by microorganisms and chemical reactions catalyzed by enzymes. Food preservation techniques can be achieved by destroying the microorganisms by heating or reducing their activity by a number of processes such as cooling, freezing, drying, vacuum or gas flushing, pickling or fermenting, adding chemicals. Lower temperatures or freezing cause slowing down of the bacterial growth and chemical activity while at increased temperatures bacterial growth is increased significantly and finally terminates at high temperatures during the preservation cycle. Light can catalyze adverse reactions such as oxidation in foods, which may lead to discoloration, loss of nutrients, or the development of off-odors.

6.1.4.2 Permeation of the Package Wall

Food packages made from polymeric coatings or films possess the ability to transmit liquids, gases, or vapors to a greater or lesser extent. This permeability is an important factor in determining the suitability of a particular polymer for packaging. The effects of package permeation on the shelf life of food products are of considerable economic importance as the shift to plastic packaging continues. The ideal situation is to package products in materials which will protect foods for maximum shelf life desired in the marketplace.

6.1.4.3 Effect of Moisture and Oxygen

It is necessary to prevent the intrusion of moisture in packages of dried products, while it is necessary to prevent the loss of moisture through the package for moist products. The inside humidity conditions of the package can be determined by the water vapor permeability of the packaging polymeric barrier. The humidity of packaged food products can provide a biologically active medium significantly promoting mold growth and hence food deterioration. The packaging material is therefore selected to provide an arid atmosphere around the product so as to preserve palatability. In order to select a suitable packaging material for protection against permeation of water vapor it is necessary to consider the following factors: (a) the hygroscopic nature of the food product, (b) the humidity of the atmosphere, and (c) the effectiveness of the selected package material as a barrier to moisture vapor.

Oxygen is absorbed strongly and irreversibly held to the food product, whilst water is lightly and reversibly held by hydrogen bonding. The ingress of oxygen leads to a permanent change in the nature of the food product. Packaging materials with relatively poor barrier function to oxygen are useful for fresh vegetables since they can breathe inside the pack; respiration would consume oxygen in the pack and if this is not replaced by permeation through the packaging material, bacteria will flourish and decomposition will set in. It is also desirable for fresh vegetables to retain water in the product since loss of water causes wilting and loss of texture. Thus the ideal packaging material for fresh fruit and vegetables is one having high permeability to oxygen but low permeability to water vapor. Also, for the preservation of fresh food products, air in the package is evacuated and replaced with gases which inhibit bacterial growth within the package and good-quality barrier material is used to prevent loss of vacuum.

Oils and fats (vegetable and animal) are affected by oxygen, which alter their nature and flavor making them rancid [67]. Thus, protection of food products containing fats and oils against the effects of oxygen and light is required to improve the degree of protection by packaging polymers of fats in terms of oxygen and moisture transmission rates. This protection to inhibit rancidity is usually achieved by various ways: (a) increasing the thickness of the packaging polymer layer, (b) improving water and oxygen barrier properties by introducing crystallinity into the polymer that is achieved by orientation, by introduction of suitable fillers, by using polymer blends or copolymers, by coating with another polymer, or by lamination of polymeric multi-layers via adhesive, extrusion, or coextrusion processes.

An essential requirement for the use of polymeric barriers in food packaging is the absence of any additive or residual monomers which can transfer potentially toxic components in any way to the contents of the package and impart an off-flavor to the product or present a health hazard. They must have little or no extractives which is particularly important to avoid odor or taste being imparted to food in the coated container. A variety of special purpose additives, which must be acceptable for use in food-contact applications, are used in coating systems. These additives include pigment dispersants, suspension agents, defoamers, emulsifiers, and rust prevention concentrates.

6.2 Polymeric Coatings in Metal Food Cans

6.2.1 Metal Food Cans

The most common metal materials used for metal food cans are aluminum, tinplate, and electrolytic chromium-coated steel. The traditional cylindrical can is a three-piece can widely used for heat-processed foods, which consists of the can body and two ends sealed by welding or by PAm adhesive, while the drawn can is a type of two-piece container consisting of the can body with a base and a can end. The can end is applied by seaming to the top of the can body with the base after filling the can with the food product, which is used in the production of tin cans meeting criteria such as: environmentally safe, robust, good storage capability, and also cheap to produce. Other metal containers used for packaging foods include: cylindrical cans with a friction plug closure at the cans end, rectangular or cylindrical containers with push-on lids, rectangular or cylindrical containers incorporating apertures sealed with screw caps, or metal drums [29–33, 46–52]. (a) *Aluminum foil* is produced from aluminum ingots by a series of rolling operations. Aluminum is used in the form of foil or rigid metal. Most foil used in packaging contains aluminum with traces of silicon, iron, copper, chromium, and zinc. Foil used in semirigid containers also contains up to 1.5 % manganese. After rolling, foil is annealed in an oven to control its ductility. This enables foils of different tempers to be produced from fully annealed (dead folding) to hard, rigid material. Foil is a bright, attractive material, tasteless, odorless, and inert with respect to most food materials. For contact with acid or salty products, it is coated with nitrocellulose or other polymeric material. It is mechanically weak, easily punctured, torn, or abraded. Coating or laminating it with polymeric materials will increase its resistance to such damage and improve its barrier properties. Relatively thin foil will contain perforations and will be permeable to vapors and gases. Foil is stable over a wide temperature range. Foil is used as a component in laminates, together with polymeric materials and paper. These laminates are formed into sachets or pillow packs. Foil is included in laminates used for retortable pouches and rigid plastic containers for ready meals. It is also a component in cartons for liquid foods. Foil is used for capping glass and rigid plastic containers. Plates, trays, dishes, and other relatively shallow containers are made from aluminum foil. These are used for frozen pies, ready meals, and desserts which can be heated in the container. (b) *Tin cans* are the most common food cans. They consist of a low-carbon, mild steel sheet or strip, coated on both sides with a layer. The mechanical strength and fabrication characteristics of tinplate depend on the type of steel and its thickness. Four different types of steel with varying levels of constituents (C, Mn, P, Si, S, Cu) are used for food cans. The corrosion resistance and appearance of tinplate depend on the tin coating. There are two types of tinplate: single- (or cold) reduced electroplate and double-reduced electroplate which is stronger in one direction than single-reduced plate and can be used in thinner gauges. The thickness of tinplate used for food-can manufacture is at the lower end of the range given above. Usually, lacquer may be applied to tinplate to prevent undesirable interaction between the food product and the container. Such interactions arise with: (1) acid foods which may interact with tin dissolving it into the food, (2) colored products reacting with the tin, causing a loss of color in the product, (3) sulfur-containing foods reacting with the tin, causing a blue-black stain on the inside of the can, (4) food products sensitive to traces of tin. Lacquers can also provide certain functional properties, such as a nonstick surface to facilitate the release of the contents of the can. A number of lacquers are available, including natural, oleoresinous materials and synthetic materials. (c) *Chromium-coated steel* is made electrolyticaly and is now more widely used for food cans. It consists of low-carbon steel coated on both sides with a layer of metallic chromium and chromium sesquioxide, applied electrolytically. Chromium-coated steel is less resistant to corrosion than tinplate and is normally lacquered on both sides. It is more resistant to weak acids and sulfur staining than tinplate. It exhibits good lacquer adhesion and suitable for a range of lacquers. However, the problem of the ready oxidation of carbon steel can be solved by coating and different kinds of polymeric coatings have been used to fulfill this need. The production of polymer-coated steel cans consists of the following steps: (1) steel sheets are laminated with a polymer coating, which can be attached to the steel using direct extrusion or by heating the steel to attach the polymer sheets, and the laminate is quenched in order to keep the polymer coating amorphous. (2) The steel is cut in circular disks which are shaped by deep-drawing. (d) *Aluminum alloy* (1.5–5 % Mg) is used for food cans. Gauge for gauge, it is lighter but mechanically weaker than tinplate. It is less resistant to corrosion than tinplate and needs to be lacquered for most applications. A range of lacquers suitable for aluminum alloy is available, but the metal surface needs to be treated to improve lacquer adhesion.

6.2.2 Polymeric Coatings

Food cans are metal containers or packaging used to hold any type of food products. Contact between the metal cans and the food products can lead to corrosion of the metal container, which can then contaminate the food. This is particularly true when the food contents of the metal can are acidic in nature, as tomato-based products or soft drinks. The food safety and shelf life of a canned food product are the important specific factors behind the attempts to develop alternative processes for protection of metal-can packages for foods. Can coatings are applied to eliminate the interactions between the metal package and the food contents, which prevent perforation defects in the can that would allow bacteria and microorganisms to enter. The coatings of the food can protect against food poisoning caused by microbiological contamination. The methods generally involve coating the cans with a composition comprising polymeric materials. The application of various coatings to the interior of metal food cans prevent the food contents from contacting the metal of the container that retard or inhibit corrosion. The coatings applied to the interior of food cans prevent also corrosion in the headspace of the cans, which is the area between the fill line of the food product and the can lid, corrosion in the headspace is particularly problematic with food products having a high salt content. For each of the wide variety of food items available in metal packaging, a variety of factors must be assessed in determining the right coating material for the metal package. These specific factors involved in selecting the coatings used for protection of metal-can packages include: food type, sterilization process, and metal substrate and performance characteristics. But the most important factor is the ability of the coating to protect the food content and to provide the highest level of safety characteristics available [68].

Epoxy resins of bisphenol A and bisphenol A diglycidyl ether (BADGE) have been used safely in metal food packaging. They offer superior performance in a number of critical coating performance characteristics, including corrosion resistance, minimal environmental impact, resistance to a wide range of chemical changes found in food products, and no incidences of food-borne illness resulting from a failure of metal packaging. Their superior performances enable long-term preservation in a durable, resistant package and high-temperature sterilization process, which eliminates the dangers of food poisoning from microbial contaminants. Metal packaging reduces the potential for serious illness and provides a high level of confidence for consumers that their canned products are safe. However, epoxy-based can coatings have negative health effect thus there is a need for food packagings that are free from bisphenol A. Various PVC-based coatings have been used to coat the interior of metal food cans to prevent negative health effects of the epoxy-based coatings. However, PVC-based coatings or related halide-containing vinyl polymers can generate toxic by-products, and these polymers are typically formulated with functional plasticizers.

Polyester coatings are highly flexible but subject to hydrolysis in acid environments, while polyacrylics are good for providing resistance to hydrolysis but are inflexible [69]; thus, both have drawbacks. Combining them requires compatibilization. Compatible compositions of polyester–polyacrylic coatings for inside food cans can be achieved either by blending or forming graft copolymer techniques [70]: (a) Grafting has been achieved either by grafting the polyacrylic to the polyester, or by grafting the polyester to the polyacrylic, and the graft copolymer reacts with the phenolic resole or novalac crosslinker to form a film. (b) Blending of polyester and polyacrylic has been achieved either by using polyacrylic containing *N*-(*N*-butoxymethyl)acrylamide as compatibilizing functional groups, or by using appropriate compatibilizer such as coupling solvents, e.g., EG-monobutyl ether. The polyesters used for coatings the inside of food cans are made from butanediol, EG, *c*-hexane dicarboxylic acid, isophthalic acid, and maleic acid. The polyacrylics are obtained from styrene, butyl acrylate, ethylhexylacrylate, methacrylic acid, and maleic acid [71]. The PET laminate technology which involves the application of PET for coating the inside of the food metal containers has been used as alternative to the epoxy-based coatings with bisphenol A as an adhesive to the metal. In fact, combination of nearly all coating specifications have been used and free from the negative health effects of the epoxy-resin coatings [72, 73]. Coatings based on aqueous dispersions of PVC-PVdC butyl rubber have been employed which possess the physicochemical properties required to ensure the biochemical processes required for the maturing of cheese [74].

The majority of food cans are now made without lead or tin solder, thus metal cans are no longer manufactured by tin-coated three-piece and side-soldered techniques. Modern cans are made either from two pieces (body and one end piece) or from three pieces with a welded side seam. This necessitated the utilization of improved can interior coating. Polymeric materials are used as barriers for coating metal containers to provide protection for various food substrates from attack by aggressive components of ambient environments. The fundamental function of the inside coatings on cans and ends is to protect the packed product for maintaining its nutritional value, texture, color, and flavor when purchased and used by the consumer. To meet these requirements, the polymeric film must be free of any material which might extract into the packed product and must protect the food product from spoilage to maintain its integrity over the product recommended shelf life. The ingredients in the can must not make contact with the metal surface. Current commercial coating compositions for cans and ends have met all these performance criteria. Packaging food substances inside polymeric materials (coated cans or flexible wrappers) always leads to concern that the packaging may impart some odor, flavor, color, or undesired characteristics to the contents. Thus, in protective coating applications there is an additional requirement that the coating material system must not affect the packaged food material. Relevant sorption and transport processes are described in terms of their dependence on the relative compositions and structures of coating materials, i.e., on the fundamental and applied aspects of solution, diffusion, and permeation in polymeric materials [75–79], and components of the substrates and packaged substance.

The coatings may be safely used as the food-contact surface of articles intended for use in producing, manufacturing, packing, processing, preparing, treating, packaging, transporting, or holding food. Although coatings are in direct contact with the food, they are not considered as direct food additives but rather as indirect food additives. Direct food additives are intended for use in or on food and are intended to accomplish a physical, nutritive, or other technical effect in food. Indirect food additives are substances such as adhesives and components of coatings used in articles that contact food in packages or containers, in which their purpose is to provide a functional barrier between the container substrate and the food. Primarily, the restrictions on volatile organic compounds generated the impetus for the trend in coatings to move toward low solvent, high solids formulations, thereby increasing use of water-borne (thinable) coatings, and solvent-free (powder) and radiation-cured coating systems. Radiation curing has had limited success in the metal-coating area because of adhesion problems. However, the other reduced or nonsolvent curing systems are growing in use for many applications including can coatings.

The type of container coating chosen is usually dictated by several factors, such as the packaged product, the type construction of the container, and the filling procedure of the container. A good coating must be resistant to punctures and dents, have good adhesion properties, be flexible, and have little or no extractives which are particularly important to avoid any transfer of odor or taste from the coated container to the packaged food. A variety of special-purpose additives are used in coating systems, which include pigment dispersants, suspension agents, defoamers, emulsifiers, and rust prevention concentrates. These additives must be acceptable for use in food contact applications. An impermeable film is needed for the following reasons: (1) the components used in food products to provide flavor should not be extracted by contact with the film, (2) to prevent the lubricants contained in coatings of a metal surface from passing through the film and contaminate the food and spoiling the flavor.

Herbs and spices are added to canned foods in the form of dispersions in a gel thereby preventing spice or herb particles from floating on the top of the liquid in which the foods are kept and avoiding subsequent interference with the sealing of the cans. Suitable materials for preparing the gel consists of cellulose derivatives which are tasteless and nontoxic, such as cellulose ether and carboxymethyl cellulose [80]. Seal integrity is critical for assuring the safety of shelf-stable products. Many new plastic container types utilize heat to seal a lid to a container body. Heat-sealed containers may employ a peelable or fusion (nonpeelable) seal. The latter, which will generally result in greater seal strength, can be utilized on packages. In order to prevent the entrapment of air during the sealing of containers which would result in deterioration of the contents, such as pickles, it is a common practice to overfill the containers with liquid. This has the disadvantage that part of the herbs or spices which float on the liquid will flow over the rim and deposit thereon. The result is defective sealing as a consequence of which the contents will deteriorate after a shorter period of time. Weak or incomplete seals can result from causes such as sealing head pressure or temperature drops, inadequate sealing dwell time, head misalignment, or product contamination on sealing surfaces.

Standard peelable flexible lidding constructions are generally laminated structures with a foil barrier layer, polymeric inner (food contact) and exterior layers, and appropriate adhesives. The development of water-based coating compositions for use as internal adherent sanitary liners for metal containers has received considerable attention [81]. In this case, a metal container contains a food having its internal surface coated with a cured layer of water-based coating composition consisting of acrylamide or methacrylamide. These cured coatings are characterized by improved impermeability to lubricants and flavor components and also better resist water at elevated temperature so as to be useful as an exterior coating [82]. In general, coating systems are alkyd resins of crosslinked polyesters and acrylic, acrylate ester copolymer coatings of styrene-acrylic and vinyl-acrylic systems, partial phosphoric acid esters of polyester resins, PVF resins, resinous and polymeric coatings, poly(VAc-crotonic acid), and PVdC coatings. Other coating systems are epoxies, vinyls, polyesters, polyurethanes [83].

The widely used coating compositions for the inside of cans are essentially based on aqueous dispersions of acrylated epoxies combined with a phenolic resin which essentially are reaction products of acrylated copolymers with bisphenol A [84]. This primary film former is added to provide the required adhesion, hardness, flexibility, corrosion protection, and chemical resistance. The exterior coating is required to provide water-white clarity, adhesion, flexibility, toughness, and resistance at specific food processing conditions. The composition should be compatible to that of the interior in order to avoid any defect to the interior coat which is generally applied afterwards. The commercial coatings are based essentially on TiO_2 pigmented vinyl organosols crosslinked with phenolic or alkoxylated melamines/benzoguanamines. The inside coatings for can ends are based on either solution- or dispersion-type PVC. The precoated metal sheets are subjected to severe elongative and compressive stresses during can-forming process or the fabrication of can ends.

The integrity of the respective coating must be maintained during all the specific fabrication operations.

The unique properties of epoxy-resin coatings have made them predominate thermosetting resins for the interior of hard and chemical-resistant cans. Epoxy-resin container coatings are used to protect the metal of the container from corrosion, and to protect the flavor of the contents which can be affected by direct contact with metal. Epoxy resin-based container coatings offer the advantages of excellent: (1) adhesion, (2) chemical resistance, (3) corrosion protection, (4) organoleptic properties, i.e., they do not impart taste or odor. The excellent adhesion property of epoxy-resin coatings to a very broad range of substrates and reinforcements is needed to prevent the contents of the container from penetrating between the coating and the metal. With the advent of aluminum and tin-free steel cans epoxy-resin coatings again became popular, because of the very poor adhesion of hydrocarbon resins to these substrates. Epoxy resin-based coatings have excellent overall performance characteristics compared to the other coating systems. Phenolic resins offer excellent chemical and solvent resistance, but they suffer from poor flexibility, poor taste characteristics, and high bake requirements. The vinyl-based coatings have excellent chemical resistance, better flexibility, and poor heat and sterilization resistance, but they suffer from environmental attack, which severely restricts their use. The interior linings of all food containers and packaging are of the water-borne type based on poly(epoxy-*g*-acrylic) cured with an aminoplast crosslinker, but can interiors for food packagings are based primarily on phenoplast crosslinkers [84]. The polymer backbone of epoxy-phenoxies is resistant to hydrolysis and has proven performance with a wide range of food packs especially when crosslinked with phenolic resins. However, they are not easily modified by simple additives to adjust T_g. Crosslinked melamine-, urea-, and phenol-formaldehyde resins are also used in container coatings. Oleoresinous container coatings, which are the original interior food-can coatings, have good acid resistance making them suitable for packaging many vegetables and fruits, but they are unacceptable for other foods because of their poor taste characteristics. The ester linkages of the linear polyester thermoplastic material whose T_g can be formulated to be similar to that of amorphous PVC, are commonly considered to be a weakness due to the possibility of hydrolysis. This can be overcome by careful selection of diacids and diols. Introduction of some crystalline character to the polymer by incorporating hard-soft block structures into the polyester are complicated by limitations on the choice of monomers. Introduction of a low level of branching allows curing reactions to have greater influence on the thermo-mechanical behavior.

6.2.3 Factors Affecting Polymeric Coatings

Food products in metal-can packaging provide a way for consumers to maintain food safety and nutrition. They are cleaned, packed, and thermally processed at their peak of flavor, freshness, and nutritional content and can help bring nutritional quality to the diet similar to their fresh counterparts. Metal-can packaging increases the shelf life of packaged food and decreases food waste due to product expiration, enabling the convenient and safe distribution of nutritive food. Metal packages enable high-temperature sterilization of food products when initially packaged, which is critical in maintaining the sterility of the food product. They have made nutritive, high quality, and shelf-stable food available to consumers and changed the way of food production, preservation, and consumption. Different varieties of food products are packed in metal packaging, making seasonal foods available in all seasons of the year. Metal cans are recyclable without losing strength or quality and the recycling rate is higher than that of most other packages [85].

The metals and polymers used in laminate coatings have different mechanical properties, with the metal having a much higher modulus and the polymer having a lower yield strain than the metal. The mechanisms for plastic deformation in both materials are also entirely different. During plastic deformation this mismatch in properties may lead to compatibility problems for the microscopic deformation near the interface. On the metal side, the macroscopic imposed plastic strain induces dislocation movement on favorably oriented slip systems within grains. Generally, this will lead to roughening of the interface as the dislocations escape the grains. In fact, the roughening at the interface due to the deformation of the metal determines the deformation of the polymer near the interface. The polymer, while it has to deform to the applied strain, must also adapt to the displacements imposed to it by the metal at the interface. In the process of plastic deformation the evolution of the roughness is an important parameter, increase in surface roughness of the metal, a reduction of roughness at the free polymer surface, local delamination of the polymer, and the reduction of coating thickness.

Characteristics of the work of adhesion include polymer deformation, surface roughness, and metal deformation [86, 87]. At the interface of the polymer-coated metal, the displacements imposed by the metal will decrease the adhesive energy. The deformations at the polymer-coated metal are partly elastic deformation and partly plastic deformation expressed in shear bands. The deformation will increase the elastic stored energy in the coating and decrease the adhesive energy. The deformation is the characterization of the behavior of the coating. The plastic deformation of polymer-metal laminates specifically addresses the role of the evolution of roughness at the interface and its impact on the adhesion. Thus, the simultaneous roughening and stretching of the metal-polymer laminate determine the mechanical performance of metal-polymer laminates, especially the impact of plastic deformation on the work of adhesion at the interface. The adhesion strength and the deformation at the interface between the metal and the polymer are described by the interface energy, i.e., the interaction energy at the surface of the substrate [88]. Increasing pressure leads to delamination of adhering polymer at the polymer-metal interface [89]. The polymer coating includes an elastic part, yield stress, softening and hardening with increasing strains

6.3 Polymeric Biodegradable Packages

The recycled disposal wastes of traditional polymeric materials exhibit a serious environmental pollution issue because of their long time of decomposition causing ecological imbalance. Relatively large amounts of such recycled polymeric waste originates from food packaging materials. One possible solution the use of food packages from natural or synthetic biodegradable polymers because they are environment friendly and their deterioration products do not cause pollution. Biodegradable green packages have good packaging performance and do not affect food product safety besides promoting the removal of waste disposal problems. This type of packaging products have the unique characteristic that microbes (bacteria, fungi, algae) can decompose the polymer macromolecules completely into carbon dioxide and water [90, 91].

Packages used for storing food products were designed to balance cost and performance during their useful life, and responsible disposal at the end of use. With the number of approved landfills diminishing each year, the costs of disposal at remaining sites will escalate annually. That is why recycling and composting have a useful place in an overall solid-waste strategy. This has provided impetus for the development of biodegradable and compostable polymeric products. However, the biodegradable packaging materials usually have problematic processing characteristics and lower mechanical properties, which can be reduced by blending of two polymers or by chemical grafting, where the properties are a combination of the individual components. Polymer blends based on polycaprolactone and starch were prepared from polycaprolactone which exhibits good processing stability, high price, and low melting point, and corn starch which is a cheap and very brittle biopolymer. Poly(hydroxybutyrate) (PHB), as biopolymer produced from renewable resources by biotechnological synthesis has good tensile strength, poor processability, and high brittleness, and is modified for use in recycled food packages by the addition of plasticizer. Polycaprolactone, corn starch, and PHB have been blended together for preparation of fully biodegradable blends, suitable for environmental friendly packaging materials [92].

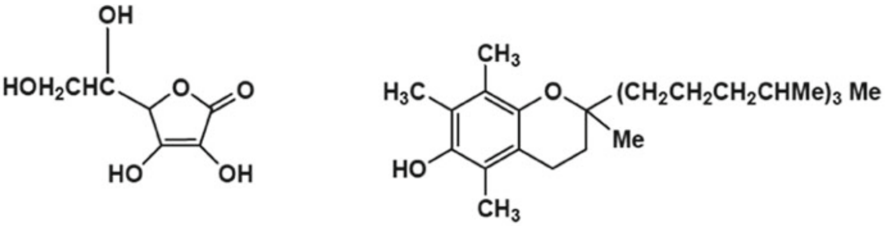
Incorporation of starch, as biodegradable natural polymer, into synthetic polymers imparts bio-degradability, e.g., shopping bags containing starch in a matrix of PE, where microbes digest the starch and leave PE that disintegrates mechanically. A biodegradable polymer made by the use of different starch types and nontoxic biodegradable polymers can be formulated to provide a wide range of properties and biodegrade completely in biologically active environments, yielding carbon dioxide, water, and minerals, and leaving no toxic, hazardous, or synthetic residues [36]. PVA does not exhibit an environmental pollution problem, because it dissolves in water and is readily biodegradable, and makes ideal packaging. PHB is biodegradable and an ideal food for microbes. Its copolymers with another hydroxyacid, as 3-hydroxypentanoic acid, can be tailored to take it suitable either for molded articles or film for packaging food products. Poly(butylene adipate-*co*-terephthalate) is another type of biodegradable polyester, which is more flexible and has high elongation at break, and therefore it is more suitable for food packaging films [93, 94]. Poly(lactic acid) (PLA) as a biobased polymer for packaging, is extensively being used as recyclable bottles, that help to collect the food scraps from events for plastic contamination [95].

6.4 Polymeric Preservative Food Packages

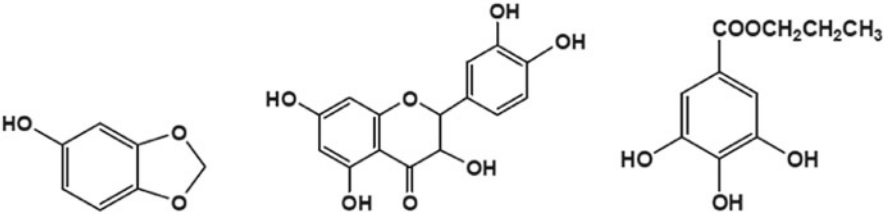
The preservative agents in antimicrobial, antioxidant, and insect repellent packaging may be applied to packaging films in such a way that only low levels of the preservatives come into contact with the food. Films or coatings with preservative properties are attractive for extending the shelf life of a wide range of food products and considered to be highly effective. Some commercial antimicrobial films and materials have been introduced, e.g., silver zeolite has been incorporated directly into food contact packaging film. The purpose of the zeolite is to allow slow release of preservative silver ions into the surface of the food products [96]. Many other synthetic and naturally occurring preservatives have been proposed for preservative activity in food packaging films [97–99]. Functional polymers containing active moieties as antimicrobials and antioxidants are used in a wide range of food applications for inhibition of microorganisms in fresh foods and for long-term reduction of lipid oxidation in processed foods. Traditionally, these active polymers are incorporated into initial food formulations, however, once the active moieties are consumed in reaction, protection ceases and food quality decreases rapidly. New controlled-release packaging can release the active moieties at predetermined rates suitable for a wide range of food applications including inhibition of microorganisms in fresh foods and reduction of lipid oxidation in processed foods. Thus, the controlled-release packaging can overcome the limitations of using traditionally additives by continuously replenishing the consumed additive in the inhibition of microorganisms via controlled release from packaging to enhance food quality and safety [100, 101]. Other natural and synthetic preservatives include sorbic acid, benzoic acid, heptyl-/ethyl-/methyl-*p*-hydroxybenzoate, sulfur dioxide, sodium sulfite/hydrogen sulfite, *o*-phenylphenol, thiabendazole have been introduced into packaging films or coatings.

6.4.1 Polymeric Antioxidant Packages

Antioxidant substances are used to reduce the deterioration of food products caused by the contact with atmospheric oxygen. Natural antioxidants have been incorporated into polymer blend films at various levels of loadings. The blend films are from two or more polymers in various ratios mixed homogenously. Various polymers of LDPE, LDPE-PP, and EVA-LDPE have been used in polymer blended combinations of antioxidant packaging films containing mixed active compounds of tocopherol-sesamol (3,4-methylenedioxyphenol) and tocopherol-quercetin



Ascorbic Acid **α-Tocopherol**



Sesamol **Quercetin** **Propyl-gallate**

Fig. 6.1 Natural food antioxidants

(2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxy-4*H*-chromen-4-one) formed by casting or extrusion processes. The effectiveness of the packaging films to retard the oxidation in food products that enhance the quality and safety of food is determined by the controlled release of tocopherol and quercetin from the packaging films. Release rates of active compounds from the polymer films with release rates suitable for a wide range of foods were determined by the relationships between release kinetics of active compound and their polymer composition and film morphology. These relationships between these important variables of composition, structure, properties, and processing are also useful for designing controlled-release packaging films. Active compounds used as antioxidants and as acidity regulators include ascorbic acid (vitamin C), esters of ascorbic acid, α-tocopherol (vitamin E), and propylgallate (propyl 3,4,5-trihydroxybenzoate) (Fig. 6.1).

The use of antioxidant packaging films has been driven by two interests: (a) the consumer demand for reducing antioxidants and other additives in foods, (b) the interest in using natural food antioxidants, e.g., vitamin E (α-tocopherol), for food stabilization instead of synthetic antioxidants. Butylated hydroxytoluene (3,5-di-t-butyl-4-hydroxytoluene) and butylated hydroxyanisole (mixture of 2- and 3-*t*-butyl-4-hydroxyanisole) antioxidants released from waxed paper liners into food products has been applied for evaporative migration of antioxidants into foods from packages (Fig. 6.2). Packaging films incorporating natural vitamin E as a safer, yet effective alternative to synthetic antioxidant-impregnated packaging films have been used for food products where the spoilage that limits shelf life has led to rancid odors and flavors [102–106]. Effective synthetic polymer antioxidants are used for inhibiting packaging film degradation during film extrusion or blow molding and for food products where the development of rancid odors and flavors often limits shelf life (see Sect. 6.5.2).

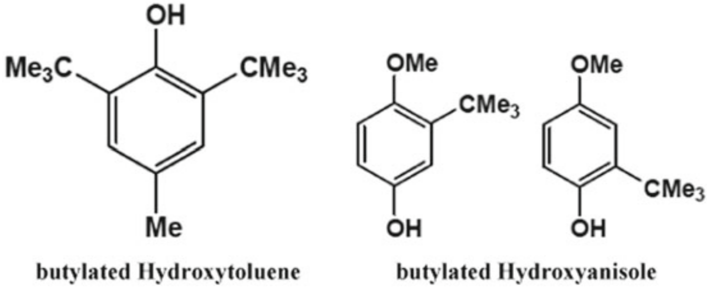


Fig. 6.2 Synthetic food antioxidants

6.4.2 Polymers in Insect Repellent Packages

Insects (as moths and beetles) and mites are the main pests infesting foods and food products leading to spoilage and loss especially of fresh food products, as they are often included in viable form as the foods are being packed. The control of insect infestation is mostly by fumigation with methyl bromide or contact insecticides. However, there is an urgent desire to phase out the use of these chemicals as insecticidal fumigants because they contribute to the depletion of the Earth's ozone layer [107]. Another disadvantage of using insecticidal fumigants is that dead insect carcasses remain in the package, thus reducing its general appeal. There are a number of options for insect-repellent packaging that effectively reduce the presence of insects and the requirement for chemical fumigants.

The controlled release of insect repellents or insecticides is desirable to prolong the effect of repelling insects from food and other consumable food products [108]. Particles of a highly crosslinked macroporous hydrophobic polymer are able to entrap insect repellents. The repellent needs to be compatible with the unexpanded plastic resinous material [109]. Macroporous PS beads (20 % wt DVB) entrapping pine oil as an insecticide were used for indoor or outdoor use. Sulfonated PS-(15 % DVB) and PE pellets entrapping an insecticide were screw-extruded into sheets, and the resulting sheets were cut into strips and used as animal collars, and as insecticidal strips employed in homes and other buildings. A hydrophobic porous copolymer of EG-dimethacrylate and lauryl methacrylate monomers as a powder consisting of unit particles, agglomerates, and aggregates was isolated. This polymeric composition containing a macroporous structure is used to release the entrapped insect repellent in the polymer.

With the exception of metal and glass packages and containers, insects can penetrate or gnaw many other packaging materials, such as paper, paperboard, and regenerated cellulose materials. Thick packaging films are mostly resistant to penetrating and gnawing insects. Laminated films, particularly those containing foil, usually offer good resistance to penetrating insects. The use of adhesive tape to seal

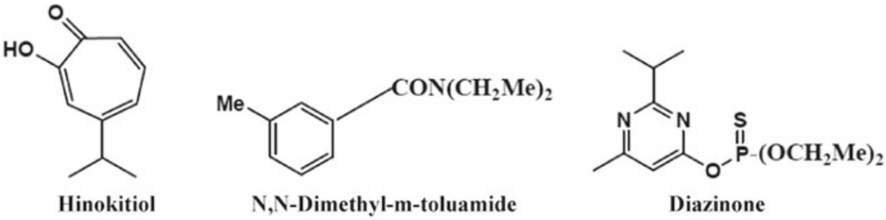


Fig. 6.3 Some insect repellents

any openings, as possible cracks, crevices, and pinholes in corners and seals, can help in limiting the ingress of invading insects. The application of insecticides to some packaging materials to a limited extent can protect the packaging from these insects. However, the incorporation of these insecticides into the outer layers of sacks can only be done if regulations allow [110, 111]. The use of package-entrapped insecticides or rodenticides contributes significantly to the prevention of infestation through the controlled release of these active compounds over long periods.

The incorporation of controlled-release insect repellent [112–115] and insecticides [116–119] into paper-based packaging materials has been described [108, 120]. Two paperboard packaging products have been marketed for their insect-repellent properties that incorporate methyl salicylate in the coating [108]. Papers and adhesive tapes that are surface-treated with a combination of plant substances, as *hinokitiol* (2-hyroxy-4-isopropylcyclohepta-2,4,6-trien-1-one), have gained widespread use to act as insect repellents (Fig. 6.3). For paper-based packaging, insect repellents have been applied on carton board (for breakfast cereal, confectionery, and pet food), bags/sacks (for grains, stock feed, milk powder), and container board (food produce). The use of natural plant extracts in this application may facilitate acceptance by food regulators as well as by public consumers. Many of the repellents are highly volatile and are readily lost from carton board unless they are partially immobilized. Citronella (3,7-dimethyloct-6-en-1-al) as one of five commercial plant extracts (citronella, garlic oil, neem extract, pine oil, and pyrethrum) was found to be effective in deterring the infestation of cartons containing muesli and wheat germ by red flour beetles [121, 122] (Fig. 6.3). Paperboard coatings as carriers of citronella-treated have been developed and used as persistent insect-repellent packaging cartons which deter beetle infestation [123].

A preferred insect repellent is liquid *N*,*N*-diethyl-*m*-toluamide (*N*,*N*-diethyl-3-methylbenzamide) for indoor or outdoor use. Other such chemicals include: dimethylphthalate, 2-ethyl-1,3-hexanediol, stabilene, indalone, di-Bu-phthalate, citronyl, alicyclic piperidines, permethrin, di-Bu-succinate, hexahydrodibenzofuran carboxaldehyde-butadiene-furfural copolymer, *t*-Bu-*N*,*N*-dimethyldithiocarbamate, 2-hydroxyethyl *n*-octyl sulfide, pyrethrins, *diazinon* (*O*,*O*-diethyl-*O*-[4-methyl-6-(propan-2-yl)pyrimidin-2-yl]-phosphorothioate), *aldicarb* (2-methyl-2-(methylthio)-propanal-*O*-((methylamino)carbonyl)-oxime), pine oil, and anthrahydroquinones

(Fig. 6.3). Such chemicals are effective against various kinds of mosquitos, ticks, chiggers, and cockroaches.

6.4.3 Polymeric Antimicrobial Packages

Surface growth of microorganisms is one of the leading causes of food spoilage and contamination. Food surfaces can be contaminated by such microorganisms during handling, processing, and packaging. A variety of processing and preservation technologies have been used to control surface contamination. One of these concepts is the incorporation of antimicrobial substances into packaging materials to control or inhibit the growth of microorganisms by direct contact of the package with the surface of the food. Preventing or limiting the contamination of the food contents by microorganisms (bacteria, viruses, fungi, parasites) from sources outside the package is most important in the case of foods that are not heat-sterilized in the package, where postprocess contamination does not occur. Control of food-spoiling microorganisms, particularly during processing, preserving, storage, and distribution of foodstuffs, requires various approaches such as postfill sterilization, washing in antimicrobial solutions, modified atmosphere packaging, addition of acceptable additives. Antimicrobial packaging technologies can play a role in extending the shelf life of foods and reducing the risk from pathogens. The antimicrobial package interacts with the product or the headspace between the package and the food system, to reduce, inhibit, or retard the growth of microorganisms that may be present in the packed food or the packaging material itself [11]. Antimicrobial packaging materials are treated with antimicrobial agents or bacteriocins to prevent these microbes from flourishing and to combat the spread and severity of many diseases. The antimicrobial agents can either be incorporated into the packaging material itself, or coated onto the package surface. The antimicrobial packaging materials used to control microbial growth in a food product include food packaging films or edible film coatings that contain and control antimicrobial agents to modify the atmosphere within the package. Antimicrobial packaging has attracted much attention because of the increase in consumer demand for processed, preservative-free products. Antimicrobial chitosan has been used as an active packaging material to maintain the microbial safety of a food product [124–127].

6.4.3.1 Antimicrobial Compounds

The antibacterial compounds used in packaging materials are either synthetic or of natural origin and include: (a) Organics: allyl isothiocyanate, propionate, benzoate, sorbate, ethanol, linalool, methyl chavicol (1-allyl-4-methoxybenzene), citral (3,7-dimethylocta-2,6-dienal:), methylcinnamate, methyleugenol, geraniol, 1,8-cineole, *trans*-α-bergamotene, carvacrol (5-isopropyl-2-methylphenol), thymol (2-isopropyl-5-methylphenol), 1-octen-3-one, 3-octanol, ethyl pyruvate (ethyl

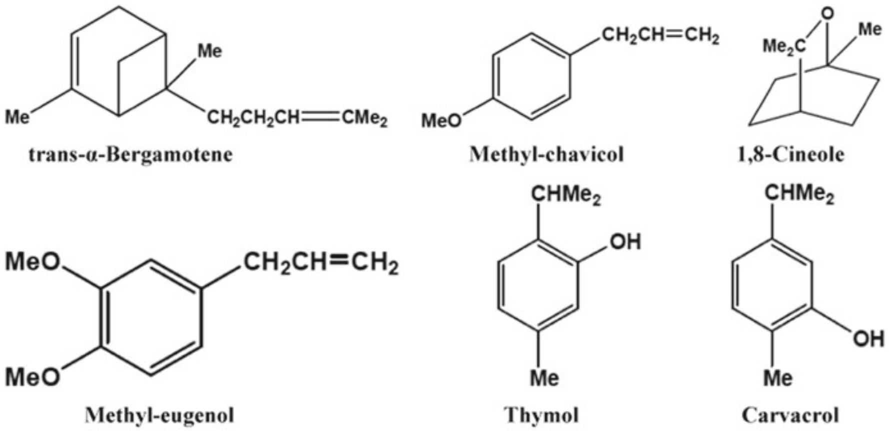


Fig. 6.4 Antimicrobial compounds

2-oxopropanoate), *trans*-3-octen-2-one (Fig. 6.4). Antimicrobial packaging polymers incorporating quaternary ammonium and phosphonium salts are used as delivery systems for antimicrobial compounds into the headspace of active packages [128]. Certain plant extracts with antimicrobial activities have been approved for use with foods, such as allyl isothiocyanate which, however, has a repelling smell causing unacceptable off-flavors. The use of potassium sorbate on LDPE for cheese packaging, calcium sorbate in carboxymethylcellulose/paper constructions for bread wraps, benzoic acid anhydride in LDPE for fish packages; imazalil in LDPE for bell peppers and cheeses; and grapefruit seed extract in LDPE for lettuce and soybean sprouts. (b) Bacteriocins (such as nisin, pediocin, and sakacin-A) are produced by certain bacteria and kill or inhibit the growth of other bacteria; they can be employed on the surface of foods to extend the shelf life and reduce the risk from pathogens, through the controlled migration of the active molecule from the film to the food [129]. Packaging treated with bacteriocins as biopreservatives makes direct contact with the enclosed food items and reduces the use of chemical preservatives while bringing down the intensity of heat treatments, which kill some of the beneficial food organisms along with the harmful ones. The result is more naturally preserved, fresh tasting, nutritious food, closer to its natural state. Nisin, which is a polycyclic antibacterial peptide, was incorporated into a cellulose-based coating and coated onto LDPE film to inhibit the growth of common food-borne microorganisms. Nisin was incorporated into binder solutions of PAA and PEVAc, and coated onto paper. Diffusive migration of the incorporated nisin and the antimicrobial activity of the active polymeric coatings on LDPE film in a methylcellulose carrier, control nisin migration and the extent of microbial suppression by the coated paper. PAA and PEVAc exhibited a high degree of migration into aqueous food solutions and also exhibited a high degree of suppression against microbial activity [130]. (c) Inorganics: metal-chelating agents (EDTA), silver ion, sulfur dioxide, chlorine dioxide, and ozone. Chlorine dioxide is effective at treating the entire package contents of freshly harvested fruits and vegetables, cheeses, and other foods. Ethanol has been incorporated into zeolite or silica in sachets; the release of ethanol is by evaporation in contact with foodstuffs [131]. (d) Natural oils: cloves, horse radish, mustard, cinnamon, thyme, carvacrol, and spices as vanilla and herb extracts as hinokitiol and rosemary oil (Fig. 6.4). Basil oil is volatile and exhibits activity against bacteria, yeasts, and molds, has a weak odor which may be lost during mixing of the packaging material and processing of the packaging containers and hence special precautions have to be followed.

Antimicrobial polymers can be used in several food applications, including packaging. They should promote safety and thus extend the shelf life by reducing the rate of growth of specific microorganisms by direct contact of the package with the surface of the solid foods. The antimicrobial packages can be self-sterilizing, reducing the potential for recontamination of the products and simplify the treatment required to eliminate product contamination. A package system that allows for slow release of an antimicrobial agent into the food could significantly increase the shelf life and so improve the quality of a large variety of foods [132]. While passive packages simply provide a barrier able to protect the product, active packages play an active role in maintaining the quality of the enclosed food to provide an increased margin of safety and quality. Other categories of active substances generally incorporated in the polymer matrix of the active packaging material useful for a better preservation or maintenance of the organolectic qualities may include: antibiotics, antioxidants, antimycotics, dyes substances, stabilizers, and plasticizers.

6.4.3.2 Antimicrobial Packages

Antibacterial packaging materials are made by adding a certain amount of antibacterial agents to the materials which are used to make food packages. The different types include: bacterial membranes, antibacterial hollow containers, antibacterial turnover box packages, and food antimicrobial packaging films which are most widely used. The incorporation of antimicrobial substances into polymeric packaging materials can take several forms, such as: (i) addition of sachets or pads containing volatile antimicrobial agents into packages that have been considered for the control of pathogens in meat trays; (ii) incorporation of volatile and nonvolatile antimicrobial agents directly into polymers. The agent may be added at the extruder when the film or coextrusion is produced. High temperatures and extruder shear can cause deterioration in the performance of the antimicrobial additives; (iii) using polymers that are inherently antimicrobial; (iv) adsorbing antimicrobials onto polymer surfaces by soaking the polymer component in the solution of the antimicrobial followed by evaporation of the solvent; or (v) immobilizing antimicrobials to polymers by ion or covalent linkages which require the presence of other functional groups on the antimicrobial agent and the polymer [133–135].

(A) **Antibacterial masterbatch**. It is possible to combine masterbatches of antimicrobial resin layer produced by extrusion or salvation and prepared on a surface layer with another layer of antibacterial composite film. Films obtained by antimicrobial masterbatch require relatively small particle size antibacterial distribution, or use of dissolved resin in the organic antibacterial agent. The printing properties of the films obtained by antimicrobial masterbatch are not adversely affected, but some of the barrier properties to a certain extent, so it is important to select the appropriate antimicrobial agent to ensure that the performance of the packaging meets the requirements. An example of an antimicrobial packaging film for food products consists of an LDPE film blended or coated with the masterbatch of an antimicrobial polymeric material as volatile basil oil incorporated into P(EtA-MMA). The blend mixture of masterbatch and LDPE was extruded and blown into a film. To minimize the volatilization of the volatile oil into the atmosphere through the PE matrix, a high gas barrier material has been laminated to the outside of the packaging material. The inclusion of a binder as PEG to the blend improves the retention rate of the volatile oil in the polymer during processing and controls its release. By using a low-temperature processable polymer composition, the loss of the volatile oil and also the risk of denaturing the oil constituents are reduced. Other polymers used for the masterbatch include PEVA, P(EtA-MMA), ionomers, nylons, hydrophilic polymers, or polymers possessing functional groups capable of anchoring the additives. A preferred film-forming polymer is LDPE blended with a PEVA masterbatch containing the active additive.

(B) **Antimicrobial coatings and film deposition**. Antimicrobial packages can be designed as polymeric films or paper systems containing natural plant extracts as immobilized antimicrobials or as coatings or vapor deposits to film that release the antimicrobial at controlled rates for extending the food's shelf life. The barrier properties of the plastics affect the quality of the final product. The surface properties of plastic films, i.e., polarity, substrate surface pretreatment, surface roughness, surface oxygen content, and the percentage of nitrogen will affect the film bond strength which all affect the antibacterial properties. For coating or packaging film, the employed deposition substrates are PET, PA, PVC, BOPP, LDPE, EVA, or cellulose.

(C) **Types of antimicrobial food packaging films**. (1) *Inorganic antimicrobials* are silver, copper, zinc, titanium, and certain other metals. Organic-coated steel food packaging with silver antibacterials is potentially usable in food packaging. Zeolite carrier containing silver ions as active component has been directly applied to food-contact packaging film. The zeolite causes slow release of silver ions into the surface of the food products. Films of TiO_2 can be added to slow the release of silver. (2) *Organic antibacterial films* inhibit the propagation of microorganisms through anionic binding to the surface of cells. (3) *Natural polymeric antibacterial films* made of sorbic acid, turmeric root alcohol, or chitosan adhere to flexible packaging films and thereby avoid migration and reduce bacterial activity [136]. (4) *Composite antibacterial films* of triazine fungicides and antibacterial pyridine have been used for food packages.

6.5 Polymeric Active Packages

Traditional food packaging involves the use of a covering material vehicle characterized by inherent insulation to protect the product from external contamination, and to provide ease-of-handling that preserves and delivers an adequate nutrition quality of the product [137]. *Active packaging* usually refers to packaging films characterized by active functions via incorporated additives that control or react with contaminants inside the packaging to provide safe food and to maintain and extend product shelf life, and to perform some desired role in food preservation other than providing an inert barrier to external conditions [8, 9, 11, 138, 139]. Active packages can be classified into: (1) *Active scavenger* systems which are packages containing active functions as absorbers for oxygen, ethylene, moisture, carbon dioxide, and odor taints. (2) *Active emitter* systems that release carbon dioxide, ethanol, flavors, or preservatives. (3) *Active controller* systems which are packages controlling the temperature inside the packaging or controlling the moisture levels to extend the shelf life without the need of additives. The active packaging technology has been used with many kinds of foods. Important parameters include: delayed oxidation, controlled respiration rate and moisture migration, prevention of microbial growth, absorption of odors, carbon dioxide, removal of ethylene, aroma emitters, reducing the need for additional preservative additives, and maintaining the freshness of the food products [140].

Release and consumption of agents is described by three aspects of the packaging: (1) the polymer package being impermeable to the active agent, and the polymer sheet containing the active agent with a uniform concentration; (2) the agent diffuses through the polymer sheet and is released into the food; (3) the agent reacts with the microorganisms, and a part of the agent is consumed. The release kinetics of the agent may be controlled either by diffusion through the polymer sheet or by convection into the food. Also the kinetics of the agent by the microorganisms located in the food may be described by a first-order reaction with respect to the concentration of the agent. The active functional substance may be immobilized in the polymeric material with covalent or ionic bonds, intercalated or absorbed on the surface, or dispersed inside the matrix of a lamellar structure. The polymeric matrices used in active packages which are compatible and interact with the active substances may be synthetic thermoplastic and thermosetting polymers or biodegradable natural polymers as: PEG, polyesters, polylactones, polylactides, polyanhydrides, poly(vinyl pyrrolidones), PUs, polysiloxanes, poly(amino acids), poly(acrylate-methacrylate)s, polyanilines, PANs, poly(ether ketone)s, poly(amide-imide)s, HDPE, LDPE, PP, PS, gelatin, cellulose, chitin, chitosan, pectin [131, 141].

Passive polymeric barrier materials that provide protection from external elements such as air and moisture act as a flexible high-barrier between the environment and the food products that greatly reduce the rate of oxygen and moisture transfer to the food. Such materials are often mixed layers of different plastics so as to take advantage of the final desired properties, such as two layers of PP attached to an inner barrier polymer layer of PEVA. Other passive materials, such as plasticized PVC, slow moisture loss while allowing oxygen to pass through. Polyesters or PP metallized with a thin coat of aluminum are being used as packages to ensure good flavors are retained inside and bad flavors kept out. There are numerous other food packaging combinations as PET, polyamides, and PP coated with silicon or aluminum oxide to create barriers for oxygen and organics, clay-polyimide as barrier materials for oxygen, carbon dioxide and water vapor, poly(ethylene naphthalate) and poly(ethylene naphthalate)-PET blends as high-barrier films or rigid containers [132].

6.5.1 Gas Scavenging Packages

Polymeric materials incorporating active groups within the packaging allow to control humidity, oxygen, carbon dioxide, ethylene via permeation across the membrane to absorb or release these gases that avoid the driving force for the ripening process and the formation of low-molecular-weight fragments as well as to extend shelf life of packaged food products. Optimum gases within the food packaging can be achieved by incorporating substances to absorb or release such gases or vapors or by permeation across a membrane for controlling humidity and changes in temperature in the packaging to extend shelf life of the packaged food products.

6.5.1.1 Oxygen Scavenging Packages

The presence of oxygen in a sealed food package has considerable detrimental effects limiting the shelf life of the food product. Oxidative reactions result in food deterioration and favor the growth of aerobic microbes and molds. These oxidative reactions lead to off-odors, off-flavors, undesirable color changes, and reduced nutritional quality of the food. Therefore, removal of oxygen from the package's headspace and from the solution in liquid foods is a necessity in food packaging.

Oxygen scavengers (absorbers) can help to remove oxygen from a sealed package, diminishing oxidative reactions and maintaining food product quality by decreasing food metabolism, reducing oxidative rancidity, inhibiting undesirable oxidation of unstable pigments and vitamins, controlling enzymatic discoloration, and inhibiting the growth of aerobic microorganisms. Oxygen scavengers are an important aspect of active packaging and are usually directly incorporated into packaged foods or added in different forms, such as on cards or contained in small packets or sachets, or can be built into package films or molded structures. Packaging which scavenges oxygen either from the atmosphere or the food products is based on chemical reactions. Oxygen-scavenging polymers avoid formation of low-molecular-weight fragments. Oxygen scavengers can be used alone or in combination with modified-atmosphere packaging. However, it is usually more common to remove most of the atmospheric oxygen by modified-atmosphere packaging and then use a relatively small and inexpensive scavenger to mop up the residual oxygen remaining within the food package. Oxygen scavenger technology has been successful for a variety of reasons, including the hot and humid climate during the summer months which is conducive to mold spoilage of food products, and the acceptance by consumers of innovative packaging [142, 143]. It should be noted that discrete oxygen-scavenging sachets suffer from the disadvantage of possible accidental ingestion of the contents by the consumer. However, this problem has been overcome by the development of oxygen-scavenging adhesive labels that can be adhered to the inside of packages, or by the incorporation of oxygen-scavenging materials into laminated trays and plastic films, which have enhanced and help the commercial acceptance of this technology. For example, oxygen-scavenging adhesive labels are used for a range of food products which are particularly sensitive to deleterious light and oxygen-induced color changes.

Oxygen scavengers such as metallic iron powder, iron carbonate, ascorbic acid, catechol, ascorbate-metallic salts as ferrous oxide, ascorbate sulfite, photosensitive dye, photosensitive dye-organic compounds, and enzymes incorporated into packaging polymeric film react with the oxygen to reduce its content in food packages. Metallic iron powders or iron(II) carbonate are used as oxygen scavengers to remove the oxygen from the surrounding atmosphere in PET bottles, bottle caps, and crowns [142, 144, 145]. These chemical systems often react with water supplied by the food to produce a reactive hydrated metallic reducing agent that scavenges oxygen within the food package and irreversibly converts it to a stable oxide. The iron powder is separated from the food by keeping it in a small, highly oxygen-permeable sachet that is labeled. The main advantage of using such oxygen scavengers is that they are capable of reducing oxygen, which is much lower than the residual oxygen levels achievable by modified atmosphere packaging. Powdered iron(II) as an oxygen scavengers is fixed to cards or contained in small packets or sachets, or can be included in package films or molded structures, which is reduced to the iron(III) form.

Iron-based label and sachet scavengers cannot be used for wet foods because their oxygen-scavenging capability is rapidly lost. Instead, various nonmetallic reagents and organometallic compounds which have an affinity for oxygen have been incorporated into bottle closures, crowns, and caps or blended into polymer materials so that oxygen is scavenged from the bottle headspace in case of ingression. The oxygen-scavenging bottle crowns, oxygen-scavenging plastic (PET) bottles, and light-activated oxygen-scavenger materials are just three of many oxygen-scavenger developments aimed at the beverage market but also applicable to other food applications [142, 143]. It should be noted that the speed and capacity of oxygen-scavenging plastic films and laminated trays are considerably lower than iron-based oxygen-scavenger sachets or labels. Nonmetallic oxygen scavengers have also been developed to alleviate the potential for metallic taints being imparted to food products. The problem of inadvertently setting off inline metal detectors is also alleviated whilst retaining high sensitivity for ferrous and nonferrous metallic contaminants [146]. Nonmetallic scavengers include organic reducing agents such as ascorbic acid, ascorbate salts, or catechol, sulfites, photosensitive dyes, ligands, and enzymatic oxygen-scavenger systems such as polymeric immobilized yeast or glucose oxidase and ethanol oxidase which can be incorporated into sachets, adhesive labels, or immobilized onto packaging film surfaces. A number of different oxygen-scavenging chemicals have been incorporated into tubes, sachets, and packaging: solid granules impregnated with $KMnO_4$, activated charcoal impregnated with bromine, bentonite, zeolite, or electron-deficient tetrazine embedded in films [147]. The polymeric oxygen scavengers consist of an oxygen-absorbing component as the polymer melt blend of nylon with PET and cobalt salt catalyst that triggers the oxidation of the nylon, cobalt catalyst/nylon polymer, to provide protection to oxygen-sensitive food products throughout their shelf life. Polymers with double bonds can react with free oxygen, catalyzed by transition-metal salts as cobalt. Oxygen scavenging and antimicrobial packaging of absorbate-releasing LDPE films have the potential to extend the shelf life of cheese foods while at the same time improving their quality by reducing the need for additives and preservatives.

6.5.1.2 Carbon Dioxide Scavenger and Emitter Packages

Carbon dioxide is used in certain food products for beneficial effects as suppressing microbial growth decreasing the respiration rate of fresh products, to overcome package collapse or partial vacuum caused by oxygen scavengers. There are many devices that can be used as either carbon dioxide scavenger or emitter. The use of carbon dioxide scavengers is particularly applicable for food products that absorb moisture and oxygen and lose desirable volatile aromas and flavors. However, the carbon dioxide released builds up within the packs and eventually causes them to burst. Carbon dioxide generators result in the production of carbon dioxide, e.g., tartaric acid/$NaHCO_3$. Two solutions are currently used: by the first use, packaging with one-way valves that allow excess carbon dioxide to escape, or by the use of carbon dioxide scavengers or a dual-action oxygen and carbon dioxide-scavenger systems. A mixture of CaO and activated charcoal has been used in PE pouches to scavenge carbon dioxide, but dual-action oxygen- and carbon dioxide-scavenger sachets and labels are more common and are commercially used for canned and foil-pouched products [148]. These dual-action sachets and labels typically contain iron powder for scavenging oxygen and $Ca(OH)_2$ which scavenges carbon dioxide and converts it to $CaCO_3$ under sufficiently high humidity conditions. The development of a partial vacuum can also be a problem for foods packed with an oxygen scavenger. To overcome this problem, dual-action oxygen scavenger/carbon dioxide-emitter sachets and labels have been developed which absorb oxygen and generate an equal volume of carbon dioxide. These sachets and labels usually contain $FeCO_3$ and a metal halide catalyst although nonferrous variants are available. Commercial food applications for these dual-action oxygen scavenger/carbon dioxide-emitter sachets and labels have been with snack food products, e.g., nuts and sponge cakes [149].

6.5.1.3 Ethylene Scavenger Packages

Ethylene is a natural plant hormone that accelerates the respiration rate and subsequent senescence and ripening of fruits, vegetables, and flowers. Ethylene is being liberated during respiration and the driving force of ripening processes. Liberation of ethylene inside a package during storage or transportation promotes respiration and ripening and thus accelerates senescence, leading to significant deterioration of organoleptic and physical properties of produce prior to reaching its destination. Many of the effects of ethylene are necessary to suppress its effect of inducing the onset of flowering and color development in fruits and vegetables as tomatoes, but it is desirable to remove ethylene by the incorporation of ethylene scavengers into fresh produce packaging and storage areas [150]. Ethylene-scavenging technologies, by $KMnO_4$-impregnated alumina pellets, activated carbon, activated carbon/Pd catalyst, or activated carbon/Br_2 zeolites, aim to reduce the undesirable build up of ethylene in plastic packages. Effective ethylene scavenger systems utilize $KMnO_4$ immobilized on an inert mineral substrate as alumina or silica gel, oxidizing ethylene to acetate and ethanol, and changing color from purple to brown. Some packages are designed to contain $KMnO_4$ adsorbed onto silica to absorb ethylene and retard ripening. Ethylene scavengers absorbed onto activated charcoal or zeolite, or based on chemical removal with $KMnO_4$, are available in sachets to be placed inside produce packages or inside blankets or tubes that can be placed in produce storage warehouses [150]. Activated carbon-based scavengers with various metal catalysts can also effectively remove ethylene. They have been used to scavenge ethylene from produce warehouses or incorporated into sachets for inclusion into produce packs or embedded into paper bags or corrugated board boxes for produce storage. A dual-action ethylene scavenger and moisture absorber containing activated carbon, a metal catalyst, and silica gel is capable of scavenging ethylene as well as acting as a moisture absorber [150].

Activated earth-type minerals such as clays, pumice, zeolites, coral, and ceramics embedded or blended into PE film have the ability to absorb ethylene and to emit antimicrobial far-IR radiation and are used to package fresh produce. Such bags extend shelf life for fresh produce partly due to the adsorption of ethylene by the minerals dispersed within the bags, and the reduction of headspace ethylene in mineral-filled bags. However, the gas permeability of mineral-filled PE bags is much greater and consequently ethylene will diffuse out of these bags much faster, as is also the case for commercially available microperforated film bags. In addition, a more favorable equilibrium-modified atmosphere is developed within these bags, especially if the produce has a high respiration rate. Therefore, these effects can improve produce shelf life and reduce headspace ethylene independent of any ethylene adsorption [150].

6.5.2 Flavor and Odor (Absorbers) Removing Packages

The interaction of packaging with food flavors and aromas has been recognized through the undesirable flavor scalping of desirable food components, e.g., the scalping of a considerable proportion of desirable limonene in aseptic packs of orange juice. Commercially, very few active packaging techniques have been used to selectively remove undesirable flavors and taints by adsorbing compounds as activated charcoal or zeolites. Some varieties of oranges are particularly prone to bitter flavors caused by limonene, a tetraterpenoid liberated into the juice after orange pressing and subsequent pasteurization. Processes for debittering such juices are by passing them through columns of cellulose triacetate or nylon beads, or by using active packaging material including limonene absorbers, such as cellulose triacetate or acetylated paper [151, 152].

Two types of taints amenable to removal by active packaging are amines with an unpleasant smell, which are formed from the breakdown of proteins, and aldehydes that are formed from the autoxidation of fats and oils. Amines can be removed by various kinds of acidic bags that are made from polymeric film containing a ferrous salt and an organic acid as citrate or ascorbate to oxidize the amines [153]. Removal of aldehydes, as hexanal and heptanal, from package headspaces is [154] based upon porous molecular sieves that remove or neutralize aldehydes [154, 155]. A range of synthetic aluminosilicate zeolites adsorb odorous gases within their highly porous structure. Their powder can be incorporated into packaging materials, and odorous aldehydes are adsorbed in the pore interstices of the powder [155].

6.5.3 Polymeric Moisture Control (Absorbers) Packages

Excess moisture causes food spoilage and soaking up moisture by using various absorbers or desiccants is very effective at maintaining food quality and extending shelf life by inhibiting microbial growth and moisture-related degradation of texture and flavor. Desiccants as hygroscopic substances in porous pouches placed inside of a food package are used to actively control the moisture in a closed package to extend the shelf life of moisture-sensitive foods. Moisture absorbers in the form of sachets, pads, sheets, or blankets for packaged dried food applications are typically silica gel or activated clays contained within permeable plastic sachets. For dual-action purposes, these sachets may also contain activated carbon for odor adsorption or iron powder for oxygen scavenging [156, 157]. Moisture-absorber sachets are commonly utilized in a number of dried food products and cereals which need to be protected from humidity damage. Moisture drip-absorbent pads, sheets, and blankets for liquid water control are also being used and consist of two layers of a microporous nonwoven plastic film, such as PE or PP, between which is placed a superabsorbent polymer that is capable of absorbing high amounts of water. Typical superabsorbent polymers include polyacrylate salts, carboxymethylcellulose–starch blends. Moisture drip-absorber pads are often used for absorption of melted ice from cooled seafood during transportation or for controlling transpiration of produce.

Another approach for the control of excess moisture in foods is to intercept the moisture in the vapor phase to decrease the water activity on the surface of foods by reducing in-pack relative humidity. Placing one or more humectants between two layers of water-permeable plastic film can achieve this. The film consists of a layer of humectant, carbohydrate, and PG, sandwiched between two layers of PVA plastic film. After wrapping in this film, the surface of the food is dehydrated by osmotic pressure, resulting in microbial inhibition and shelf-life extension. Microporous sachets of desiccant inorganic salts as sodium chloride have been used for the distribution of tomatoes. Fiberboard box functions as a humidity buffer on its own without relying on a desiccant insert. It consists of an integral water-vapor barrier on the inner surface of the fiberboard, a paper material bonded to the barrier which acts as a wick and an unwettable but highly permeable to water vapor layer next to the foods. This multilayered box is able to take up water in the vapor state when the temperature drops and the relative humidity rises. Conversely, when the temperature rises, the multilayered box releases water vapor back in response to a lowering of the relative humidity [158].

6.5.4 Ethanol Emitter Packages

The use of ethanol as an antimicrobial agent is particularly effective against molds but can also inhibit the growth of yeasts and bacteria. Ethanol can be sprayed directly onto food products just prior to packaging. However, a more safe method of generating ethanol is the use of ethanol emitting films and sachets that contain absorbed or encapsulated ethanol in a carrier material to allow the controlled release of ethanol vapor. Ethanol emitters are adsorbed onto silica gel powder and contained in a sachet made of a paper and PEVAc laminate. The size and capacity of the ethanol emitting sachet used depends on the weight of the food and the shelf life required. Ethanol emitters are used extensively to extend the mold-free shelf life of high-moisture products to inhibit mold growth [159]. Hence, ethanol vapor exerts an antistaling effect in addition to its mold-inhibiting properties. Ethanol-emitting sachets are also widely used for extending the shelf life of semimoist and dry products. To mask the odor of alcohol, some sachets contain traces of vanilla or other flavors.

6.5.5 Temperature Control Packages

Temperature indicators give a visual signal at a specified temperature, while time-temperature indicators give signal when a specified temperature deviation over time has been recorded throughout the shipment. Time-temperature indicators can be used to predict product degradation and to determine the suitability of products for normal sale. Thermochromic inks are used to signal temperature change, which have reversible or permanent color change, which show signal when the desired food temperature is achieved [160]. Gel packs are often used to actively keep the temperature of the contents within specified acceptable temperature ranges. Passive packaging can help to control the temperature fluctuations seen even with controlled cold chains. In addition, gel packs are often used to actively keep the temperature of the contents within specified acceptable temperature ranges. Temperature-control active packaging includes the use of insulating materials, self-cooling and self-heating cans, which are available for several products [160]. Some packages have the ability to heat or cool the product for the consumer. These have segregated compartments where exothermic or endothermic reactions provide the desired effect.

6.5.6 Polymers in Microwave Susceptors for Food Packages

Microwave ovens are used for food heating and usually result in nonuniform heating because they generally have one temperature output with no temperature regulation, and often do not generate enough heat to achieve adequate browning and crisping of cooked foods. Unfortunately, there is no reliable way to control the temperature in the microwave oven other than by its exposure time, and often the food product becomes browned and burned on the outer surface, and also overcooked and dried out in the interior. Two spaced susceptor layers in a single composite structure are being used to control the amount of energy received by the food product while still heating the surface to a high enough temperature for browning, the interior gets cooked, but remains moist without drying out. Thus, to allow heating of a food product in a uniform manner using microwave energy, heat susceptors are employed which serve to minimize and overcome the nonuniformity in heating larger food products. The amount of microwave energy reaching food products packaged in microwave food packages containing heat susceptors can be adequately controlled. Thus, the primary cooking objective of the susceptor material is to decrease the amount of microwave energy reaching the food product, while the amount of microwave energy absorbed by the susceptor is increased to brown the surface of the food products [161, 162].

Heat susceptors are made of electrically conductive materials such as metallized film or metals (aluminum flakes) that absorb electromagnetic energy delivered from microwave radiation (radiofrequency energy) during the microwave cooking cycle and convert this to thermal energy [163–166]. The heat susceptors in disposable microwave packages for microwave ovens are not reused because the adhesives that hold the susceptor to the package may be damaged by the original use and the material may migrate into the food. Microwavable food-heating packages consist of: an outer container body formed from the composite susceptor material which generates heat by absorption of microwave energy, including: (1) **Dielectric substrate**. This is the primary structural layer of non-microwave-interactive substance and comprises microwave-transparent coated or uncoated paperboard, as polyester-coated paperboard or clay-coated paperboard, on the outer surface of the laminate to provide structural rigidity and support for the physical shape of packages. It is porous and is printed on one surface with a susceptor-ink composition (electrically conductive layer). The paperboard as dielectric substrate contains a surface coating of polyester and is coated with inorganic pigment clay, $CaCO_3$, and TiO_2 [167]. (2) **Thermal barrier layer**. A laminated adhesive layer holds the printed susceptor film to the substrate, i.e., is applied to the upper surface of the substrate, between the microwave dielectric substrate and the printed susceptor-ink composition, to insulate the substrate from excess heat generated by the susceptor-ink composition when the container and its food products are heated in a microwave oven. It is a non-microwave-interactive layer prepared from a sodium silicate coating solution applied to dielectric sheet material (insulating substrate). It serves as a protective support for the electrically conductive layer and should be thermally stable at temperatures encountered in a microwave oven, usually made of polyester, silicones, PUs, polysulfones, fiberglass, polyamides (aramids: Kevlar-X), fluoropolymers, polyimides, phenolics, and inorganic pigments to provide voids in the coating for releasing bound moisture associated with the sodium silicate during the microwave heating process. The use of sodium silicate, which is a mix of silica (SiO_2) and soda ash (Na_2O), as thermal barrier coating and vehicle in the susceptor-ink formulation has the advantage of compatibility with the susceptor-ink composition and improving fire-retardant properties to packaging paperboard used in microwave ovens [167, 168]. (3) **Electrically conductive layer**. This is the composite susceptor material which generates heat by absorption of microwave energy to achieve crisping and browning of the food product without overheating other parts of the package on the exposure to microwave radiation, i.e., to control the rate of heating and temperature reached when exposed to microwave radiation. The susceptor-ink composition consists of a dispersion of electrically conductive coating of microwave-interactive material, such as metal oxides or carbon (graphite or carbon black), dispersed in a printable-ink vehicle printing as sodium silicate binder. It is press-printed on the package dielectric substrate only in the areas of the package which contact the food surface, i.e., printed on an exposed surface of the thermal barrier layer, which generates heat by absorbing microwave energy to provide heat for the food products. It is an adhesively bonded polymeric film located between primary structural layer and inner food contact layer. The composite susceptor material comprises two layers in a single composite susceptor material, each having its own transmittance and reflectance characteristics, to control the total amount of energy absorbed for heating [169, 170]. (4) **Inner food product contact layer**. This is the protective coating layer of the container body applied over the printed electrically conductive layer (susceptor-ink layer made up of: polyesters, acrylics, or silicones) and directly contacts the surface of the packaged food product. The coatings for the food contact layer (polyesters, acrylics, nitrocellulose or sodium silicate) serve several purposes: to protect the underlying layers from moisture penetration during storage and cooking, to protect the food products packaged with the susceptor material from possible contaminants which might migrate from the underlying layers, and to prevent sticking of food products, i.e., the food products may be easily removed from the susceptor packages after cooking [161].

Susceptor types. Currently there are three microwave susceptor types.

1. **Metallized-film susceptor** is electrically conductive metal, such as aluminum, antimony, bronze, chromium, copper, gold, iron, nickel, tin, and zinc (in powder or flake form), which has the tendency to convert electromagnetic energy to heat, because soft polymeric materials are not safe for use in the microwave oven [171]. The lack of control of the heat output across the entire surface results in overcooking certain areas of the food while undercooking the center. Additionally, the amount of heat generated is not sufficient to compare with traditional cooking methods. The metallized film may be a polyester film with a vacuum-deposited aluminum layer [172, 173]. The beneficial properties of PET, such as impact resistance, transparency, stiffness, and creep, and excellent thermal properties, allow it to be chemically inert, providing good gas barrier properties, and can processed and used over a wider temperature range required in the sterilization processes based on steam, ethylene oxide, and radiation. Trays made from semirigid PET sheet are used in precooked meals for reheating in either microwave or conventional ovens. Blending of PET with other polymers by coinjection, coextrusion, laminating, or coating technologies can be used to extend its applications for achieving additional protection against oxygen and moisture, thereby preventing rancidity and similar off-flavors.
2. **Demetallized film susceptors** reduce the heat in areas that tend to overcook. While this can be effective, the result is slower preparation time and improper browning. The heat area is reduced by removing metal (demetallizing) in the areas where the food is being overcooked, resulting in less browning. While demetallization can provide balanced cooking results for some foods, the results still fall short of traditional cooking methods because thin film-metallized susceptors do not provide the heat required to properly brown foods.
3. **Printed susceptors** mostly lack the temperature regulation to assure that the package does not runaway heat, which can result in the package catching fire and lack the natural thermostat that is inherent in film susceptors. That is, when a metallized film reaches a certain temperature it naturally cracks and reduces its heat output. In contrast, printed susceptors absorb energy as long as microwave energy is applied. The result can be package ignition [171].

6.6 Polymeric Modified Atmosphere Packaging (MAP)

The internal atmosphere of a package is drawn out and replaced with a mixture of gases prior to sealing. Once the package is sealed, no further control is exercised over the composition of the in-package atmosphere. However, this composition may change during storage as a result of respiration of the food contents or solution of some of the gases in the product. The aim is to reduce the level of oxygen to prevent growth of aerobic microorganisms which may spoil food, and hence to extend the shelf life, particularly of fresh food products, by reducing the rate of food deterioration achieved by modification of the initial gas concentrations of oxygen and carbon dioxide inside the package, which change with time. Also, for some foodstuffs the absence of oxygen can affect freshness and flavor perception and encourage the growth of harmful anaerobic microorganisms. Nitrogen is an effective replacement, but for cases where a more acidic environment is desirable, carbon dioxide can be used to give an inert atmosphere at lower pH. The gases involved in MAP, as applied commercially, are carbon dioxide, nitrogen, and oxygen. MAP applies by one of two methods: (a) in trays the air is removed by a vacuum pump and the appropriate mixture of gases is introduced prior to sealing, (b) in flexible packages, as pouches, the air is displaced from the package by flushing it through with the gas mixture before sealing.

Nonrespiring products require high barrier films, preserving the initial atmosphere. However, for respiring products, the film must be permeable to allow for oxygen and carbon dioxide transfer. In the case of horticultural products, a modified in-package atmosphere may develop as a result of respiration of the food. The concentration of oxygen inside the package replaced by carbon dioxide depends on the rate of respiration of the food and the permeability of the packaging material to gases. Carbon dioxide reacts with water in the food product to form carbonic acid which lowers the pH of the food and inhibits the growth of certain microorganisms, mainly molds and some aerobic bacteria. Lactic acid bacteria and most yeasts are resistant to carbon dioxide and may replace aerobic spoilage bacteria in MAPs. Anaerobic bacteria, including food poisoning organisms, are little affected by carbon dioxide. Consequently, there is a potential health hazard in MAP products from these microorganisms. Strict temperature control is essential to ensure the safety of MAP foods. Molds and aerobic bacteria are inhibited by carbon dioxide. In general, the higher the concentration of the gas, the greater is its inhibitory power. The inhibition of bacteria by carbon dioxide increases as the temperature decreases. Bacteria in the lag phase of growth are most affected by the gas. Nitrogen has no direct effect on microorganisms or foods, other than to replace oxygen, which can inhibit the oxidation of fats. As its solubility in water is low, it is used as a bulking material to prevent the collapse of modified packages when carbon dioxide dissolves in the food. This is also useful in packages of sliced or ground food materials, such as cheeses, which may consolidate under vacuum. Oxygen is included in MAPs to maintain the red color, which is due to the oxygenation of the myoglobin pigments. Other gases have antimicrobial effects as sulfur dioxide which has been used to inhibit the growth of molds and bacteria in some soft fruits and fruit juices [174].

With the exception of packages for fresh produce, MAP trays or pouches need to be made of materials with low permeability to gases (CO_2, N_2, O_2). Laminates made of various combinations of polymer as PET, PVdC, PE, and polyamides such as nylons should have low oxygen permeability [175–178]. Respiration in fruits and vegetables leads to a build-up of carbon dioxide that may reduce the rate of respiration and help to prolong the shelf life of the product; a reduction in the oxygen content by anaerobic respiration will set in and the product will spoil. The effect of the build-up of carbon dioxide varies depending on the product. Selection of a packaging film with an appropriate permeability to water vapor and gases can lead to the development of this optimum composition. Hard cheese may be packaged by flushing with carbon dioxide before sealing, which will be absorbed by the cheese, creating a vacuum. Cheese packaged in this way may have a long shelf life; to avoid collapse of the package, some nitrogen may be included with the carbon dioxide. Mold-ripened cheese may be packaged in nitrogen. The shelf life of some other food products can be significantly increased by packaging in carbon dioxide or nitrogen–carbon dioxide mixtures. Oxygen and carbon dioxide levels in MAPs change as a function of the respiration rate of the produce, temperature, the characteristics of the film, and especially the oxygen and carbon dioxide permeability coefficients of the package materials. High-moisture-content pasta placed in a carbon dioxide–nitrogen atmosphere within a moisture-barrier package has an extended shelf life; such packages include packets containing iron-based compounds, which rust and thus absorb oxygen out of the package. MAPs with high oxygen and carbon dioxide permeability increase shelf life. The package also has to be breathable, because the product continues to respire, emitting gases, and when these gases build up inside, they would spoil the produce, so they have to permeate through the package [132, 179].

6.7 Polymeric Smart and Intelligent Food Packages

Polymeric smart packages are used to monitor freshness, extend shelf life, display information on quality, improve the safety of foods, and improve convenience [8, 17, 180]. The goal is to be able to sense or measure an attribute of the product, the inner atmosphere of the package, or the shipping environment information. There is a growing need for packaging information about the food product to become available to the consumer to make adequate decisions regarding the discarding and recycling of the packages after consumption. This information requirement has led to the development of the concept of smart food packages for the ingredients and components of packed foods that are stored and used over a longer period of time. Smart packages may be able to affect consumer demand for more convenient, fresher, and better-tasting foods. These packages are recyclable and environmentally friendly, i.e., they are ecological materials which are also degradable at the end of their service life. Smart packages possess microbial growth indicators, along with physical shock indicators, and leakage or microbial spoilage indicators and may also serve to prevent the spoilage of foods by maintaining integrity, to retain flavor and taste, and to enhance the appearance of the product, to act in the changing environment of temperature and weather, to give clear information on the product, calorie details, ingredients, and be sealed properly to maintain integrity. Smart packages potentially can sense, monitor, and indicate changes in color and temperature when nearing the expiry date. Smart colors such as thermochromic inks are used in packaging as temperature indicators. These packages are made from synthetic or natural polymers as proteins or polysaccharides (e.g., starch). Consumer-driven developments are based on the growing need for information on packaging for consumer security assurance particularly for perishable food products, the consumers need to know the ingredients or components in the product and how the product should be stored and used, printed labels for communicating directly to the customer to provide information, safety, and disposal instructions regarding the contained food products to tell the consumer how to use the disposed packages after consumption, and information for adequately separating the packaging materials from the waste streams for use in the recycling industry.

Smart packages automatically regulate the ingression of oxygen and egression of carbon dioxide, which helps in creating an optimal temperature and environment around the food product thus preventing its spoilage. While conventional film packaging is not suitable to cope with the high respiration rates of precut vegetables and fruit, leading to early product deterioration, breathable polymer films are already in commercial use for fresh-cut vegetables and fruit. Packaging films have been made of acrylic side-chain crystallizable polymers tailored to change phases reversibly at various temperatures. As the side-chain components melt, gas permeation increases dramatically, and by further tailoring the package and materials of construction, it is possible to fine-tune the carbon dioxide to oxygen permeation ratios for particular products.

Hydrogels can be employed as polymeric smart materials because their properties exhibit volume changes or phase transitions in response to differences and variations in the surrounding environment, such as temperature, pH, pressure, electricity, or light and can be used in a wide range of applications [181]. Intelligent polymeric materials of poly(*N*-isopropyl-AAm) and poly(vinyl methyl ether) exhibit unique thermoshrinking properties when heated in aqueous solution above the lower critical solution temperature where they become insoluble and phase separation occurs. Below the lower critical solution temperature, the polymers are soluble in the aqueous phase, as the chains are extended and surrounded by water molecules. The exact temperature is a function of the detailed microstructure of the macromolecule and the reversible transitions are repeated thermal switching. These thermoresponsive polymers, made of three layers of P(N-i-Pr-AAm), PAAm, and an inert spacer, can be useful as polymeric tools to pick up a target compound in aqueous solution by raising the temperature above the lower critical solution temperature and to release the compound below the lower critical solution temperature. The monomer *N*-i-Pr-AAm can be grafted onto polymer substrates to achieve modification of polymer surfaces, e.g., it is grafted on porous LDPE, PP, or polyamide films in order to prepare novel films for separations [182, 183].

Smart polymers employ three different techniques: (1) The *capacitive principle* uses a capacitor chemical sensor composed of two electrodes separated by a dielectric material sensitive to a certain chemical. The capacitive detection relies on the change of dielectric constants or on the thickness of the dielectric layer due to swelling. (2) The *resonating principle*, when combined with a chemical sensitive layer, becomes an extremely sensitive transducer. The sensitivity of the device is proportional to the square of its resonance frequency. The addition of small foreign mass over the surface will shift its resonance frequency. (3) The *field-effect principle* uses a transducer made of a transistor that operates at constant voltage. If a signal induced by stimuli alters the potential distribution in the device or the semiconductor mobility, this will modify the output current. Sensors and "smart packaging" devices capable of detecting food-borne pathogens could be useful in food monitoring.

Smart packages have been used as self-heating or self-cooling packages for foods [184, 185]. In beverage cans self-cooling is achieved in that the water is bound in a gel layer coating a separate container and is in close thermal contact with the beverage. The consumer twists the base of the can to open a valve, exposing the water to the desiccant held in a separate, evacuated external chamber. This initiates evaporation of the water at room temperature. The correct temperature can be indicated by a thermochromic-ink showing the correct serving temperature following microwave heating or following refrigeration of the cold drink.

Polymeric intelligent packaging switches on and off in response to changing external or internal conditions, giving information for the consumers about the status of the ingredients and the components of the packed food products and how these should be stored and used for longer time [15, 16, 186]. They also contain information on proper discarding of the packing after consumption as well as health-related information. The factors as food safety, food wastage, traceability, and sustainability concerns are the major factors that drive the development of intelligent packages. Thus, intelligent packaging senses and monitors the condition of packaged foods to give information about the quality of the packaged food during transport and storage. Intelligent food packaging devices feature visual indicators based on physical, chemical, or enzymatic activity in the food as indication of product quality, safety, and shelf-life condition [187, 188].

A number of different polymeric indicator are used in packagings with different benefits such as: radiofrequency indicators, ripeness indicators, time-temperature indicators, biosensors, gas-sensing dyes, microbial growth indicators, physical shock indicators, and color indicators on the outside of packaging films to monitor the freshness of seafood products. Freshness indicators currently used across the food industry usually take the form of labels inserted in a package but these come at a significant cost. The indicator works on the basis of a color change when the freshness of the food deteriorates. The indicator is used as part of an MAP, keeping the food in specially created conditions prolonging its shelf life. Intelligent and smart packages include the following types. (1) *Gas indicators* are reversible oxygen indicator consisting of a redox dye laminated in a polymeric film, in which the color changes between the reduced and oxidized state of an indicator, e.g., from white or pink to blue. They are designed to show and monitor the performance of the packaging. (2) *Moisture indicators* use thermochromic, photochromic, and liquid crystal inks for monitoring quality deterioration of moisture-sensitive foods. Hydrochromic inks are available in both reversible and irreversible forms, and have great potential for demonstrating that food products have not been exposed to excessive moisture. (3) *Temperature indicators* are used to monitor products shipped in a cold chain, to measure and record the temperature history of food shipments through temperature control packaging. They sometimes have temperatures displayed on the indicator or have other outputs, such as light. They document the thermal history of the food products based on encapsulated thermochromic inks, which are liquid crystals or leuco dyes that change their color on cooling, but become transparent on warming. Temperature indicators contain a bimetallic sensing element which permanently changes from clear to red when exposed to a damaging temperature. (4) *Time-temperature indicators* for monitoring food product quality integrate the time and temperature by the indicator that indicates the degree of a physical color change due to the probable food degradation through chemical reactions [189]. The rate of food degradation is dependent on both time and temperature, and the indicators are placed on temperature-sensitive packages to track their exposure to high temperature conditions during shipment and storage, and develop a visible change when kept above a certain temperature. (5) *Radiofrequency indicators* are applied to food packages for supply control and have shown a significant benefit in allowing food producers and retailers to create full real-time visibility of their supply chain. Smart or electronic labels are very thin and consist of an integrated microchip and antenna for contact-free transfer of data used to track and trace packages and unit loads throughout distribution. Labels or tags are either active and battery-powered or passive without internal power supply and powered by signals from an external source. The simplest forms of radiofrequency indicator systems are electronic tags consisting of four components: (a) base material and adhesive, (b) antenna, (c) transmitter that can be programmed to a specific frequency and range, (d) microchip that can store, add, or subtract information depending upon size and type. (6) *Food spoilage indicators* incorporated into packaging for monitoring microbial quality deterioration are based on a solid-phase colored immunobead assay and antibody sandwich principles, modified to allow the continuous flow and exposure of products and contaminating microorganisms. The system of microbial growth sensors depends on the biological activity change in foods which can lead to off-tastes and odors and hence may lead to serious illness. They bind to colored immunobeads that migrate to be captured by a second specific antibody attached to a membrane-forming part of the barcode system. This allows the reaction of the antibody to be indicated by modification of the barcode using thermochromic inks. (7) *Rancidity indicators* are used for monitoring quality deterioration of oxygen-sensitive foods. The system consists of a matrix polymer, as nylon–PET blend, an oxygen-absorbing component, and a catalyst as cobalt salt that starts the oxidation of the nylon. It provides protection to oxygen-sensitive products throughout their shelf lives, e.g., absorbate-releasing LDPE film for cheese. (8) *Chemical change indicators* are used as ripeness indicators. Food degradation results from chemical reactions which in turn result in food that is unfit for consumption: often this is associated with specific changes in pH. Chemical indicators in packaging can effectively cause a color change when the foods are perfect for eating [190]. However, the color changes for these chemicals are dependent on both temperature and the presence of other ionic species. Their reliability as freshness indicators in uncontrolled environments is limited. Another limitation is that the presence of additional chemicals in the proximity of foodstuffs gives rise to public and legislative concerns. Polyaniline can be employed as a chemical indicator for pH changes: it has a green color in the protonated and blue color in the unprotonated form. Acids forming in spoiled foods, such as lactic acid (from sour milk), change polyaniline from blue to green, while amines change polyaniline from green to blue. Freshness indicators have also been employed in electronic noses for food [191].

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Abbreviations

AA	Acrylic acid
Agarose	3,6-Anhydro-L-galactose
Agaropectin	L-Galactose-6-sulfate
Agarobiose	D-Galactose + L-3,6-Anhydro-α-galactopyranose
Aldicarb	2-Methyl-2-(methylthio)-propanal-O-[(methyl-amino) carbonyl]-oxime
Amberlite XE-258	Polystyrene macroporous/macroreticular beads
Amberlite IRA-401S	Poly(styrene ammonium salt) gel resin
Amberlite IRA-900	Poly(styrene ammonium salt) macroreticular resin
Bayer-73	5,2-dichloro-4-nitro-salicylanilide
Chloropyrifos	O,O-Diethyl-O-(3,5,6-trichloro-2-pyridyl)-phosphorothioate
CMC	Carboxymethylcellulose
CMPA	4-Chloro-2-methylphenoxyacetic acid
Cyanuric chloride	2-Amino-4,6-dichloro-s-triazine
2,4-D	2,4-Dichlorophenoxyacetic acid
DAA	Diallyl adipate
DADMAC	Diallyldimethylammonium chloride
DCC	Dicyclohexylcarbodiimide
DEGMA	Diethylene glycol methacrylate
Dichlorvos	2,2-Dichlorovinyldimethylphosphate
Diflubenzuron	N-[(4-Chlorophenyl)aminocarbonyl]-2,6-difluorobenzamide)
Diazinon	O,O-Diethyl-O-2-(2-isopropyl-4-methyl-6-pyrimidinyl) phosphoro-thioate, N,N-diethyl-m-toluamide, N,N-diethyl-3-Me-benzamide
DNMP	2,4-Dinitro-6-methylphenol

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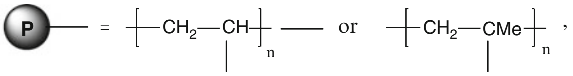
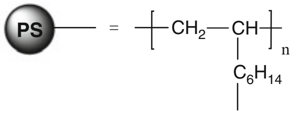
DNSA	[2-(2,4-Dinitrophenylazo)-6-(N-Me-N-(2-hydroxysulfonyloxyethyl-sulfonyl)-amido]-1-naphthol-3-sulfonic acid
DVB	Divinylbenzene
EP	Epichlorohydrin
EVAc	Ethylenevinylacetate
Famphur	O-[p-(Dimethylsulfamoyl)phenyl]-O,O-dimethylphosphorothioate
Fenvalerate	Cyano(3-phen-oxyphenyl)methyl-4-chloro-α-(1-methylethyl)benzene acetate
GRP	Glass reinforced polymer
HDPE	High density polyethylene
HEMA	2-Hydroxyethylmethacrylate
Hinokitiol	2-Hyroxy-4-isopropylcyclohepta-2,4,6-trien-1-one
HMDA	Hexamethylenediamine
HMDI	Hexamethylenediisocyanate
H-PAN	Hydrolyzed-polyacrylonitrile
H-PVAc	Hydrolyzed-poly(vinyl acetate)
HSPAN	Hydrolyzed starch–polyacrylonitrile
IAA	Indole-3-acetic acid
Larvicide diflubenzuron	1-(4-Chlorophenyl)-3-(2,6-difluorobenzoyl)urea
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
MA	Methyl acrylate
MBAA	N,N-methylenebisacrylamide
Methoprene	Isopropyl-(E,E)-methyloxy-3,7,11-trimethyl-2,4-dodecadienoate
MF	Melamine-formaldehyde resin
MMA	Methyl methacrylate
MMAA	Methyl methacrylic acid
MMT	Montmorillonite
MPEGMA	Methoxypolyethyleneglycol methacrylate
NAA	1-Naphthylacetic acid
NaPAA	Poly(sodium acrylate)
NBR	Acrylonitrile–butadiene rubber
Neem Extract	3-Nitro-4-hydroxyphenyl arsenic acid
Niclosamide	5,2-dichloro-4-nitro-salicylanilide
NR	Natural rubber
OcEGMA	Octaethylene glycol methacrylate
OEGMA	Oligoethylene glycol methacrylate

OOEMA	Oligooxyethylene methacrylate
PAA	Poly(acrylic acid)
PAAm	Polyacrylamide
PAAmAA	Poly(acrylamide-acrylic acid)
PAAm-NaA	Poly(acrylamide-sodium acrylate)
PAAVA	Poly(acrylic acid-vinyl alcohol)
PAASBR	Poly(acrylic acid-styrene–butadiene rubber)
PAcEI	Poly(N-acylethylenimine)
PAEI	Poly(N-alkylethylenimine)
PAm	Polyamide
PAMA	Poly(acrylate-co-methacrylate)
PAN	Polyacrylonitrile
PAn	Polyaniline
PC	Polycarbonate
PCMS	Poly(chloromethylstyrene)
PCP	Pentachlorophenol
PCS	Polycarbamoylsulfonate
PDADMAC	Poly(diallyldimethylammonium chloride)
PE	Polyethylene
PEAA	Poly(ethylene-acrylic acid)
PEG	Poly(ethylene glycol)
PEGDMA	Poly(ethyleneglycol dimethacrylate)
PEGMA	Poly(ethyleneglycol methacrylate)
PEGPG	Poly(ethyleneglycol-propyleneglycol)
PEOPO	Poly(ethylene oxide-propylene oxide)
PEN	Poly(ethylene naphthalate)
PEO	Poly(ethylene oxide)
PEP	Poly(ethylene-propylene)
Permethrin	3-Phenoxyphenylmethyl-3-(2,2-dichloroethyenyl)-2,2-dimethylcyclopropane carboxylate
PEs	Polyester
PET	Poly(ethylene terephthalate)
PEt	Polyether
PEVA	Poly(ethylene-vinyl alcohol)
PEVAc	Poly(ethylene-vinyl acetate)
PF	Phenol-formaldehyde resin
PHA	Poly(β-hydroxyalkanoate)
Phantolid	1-(2,3-Dihydro-1,1, 2,3,3,6-hexamethyl-1H-inden-5-yl)ethanone
PHB	Poly(3-hydroxybutyrate)
PHBHH	Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)
PHC	Propylhydroxy-cellulose
PHEMA	Poly(2-hydroxyethylmethacrylate)
PiBMA	Poly(isobutylene-co-maleic acid)
PIC	Polyisocyanate

PiPAAm	Poly(N-isopropyl acrylamide)
PKAAAm	Poly(pot acrylate-acryl amide)
PKPPAm	Poly(pot propenoate-co-propenamide)
PLA	Poly(lactic acid)
PLGA	Poly(lactic-co-glycolic acid)
PMAAmS	Poly(methacrylamide-styrene)
PMASBR	Poly(methacrylic acid-styrene–butadiene rubber)
PMEGMA	Poly(methoxyethyleneglycol methacrylate)
PMMA	Poly(methyl methacrylate)
P-MMT	Polymer-g-montmorillonite nanocomposite
PNAEA	Poly(2-(1-naphthylacetyl)ethyl acrylate)
POE	Poly(oxyethylene)
POP	Poly(oxyphenylene)
PP	Polypropylene
PPCPA	Poly(pentachlorophenyl acrylate)
PPCPMA	Poly(pentachlorophenyl methacrylate)
PPG	Poly(propylene glycol)
PPO	Poly(propylene oxide)
PS	Polystyrene
PSB	Poly(styrene-butadiene)
PSMA	Poly(styrene-co-maleic anhydride)
PSu	Polysulfone
PTFE	Polytetrafluoroethylene (Teflon)
PU	Polyurethane
PVA	Poly(vinyl alcohol)
PVAc	Poly(vinyl acetate)
PVAcMA	Poly(vinyl acetate-co-maleic acid)
PVAm	Poly(vinyl amine)
PVC	Poly(vinyl chloride)
PVCa	Poly(N-vinyl-carbazole)
PVCVAc	Poly(vinyl chloride-vinyl acetate)
PVCVdC	Poly(vinyl chloride-vinylidene chloride)
PVdC	Poly(vinylidene chloride)
PVdF	Poly(vinylidene fluoride)
PVF	Poly(vinyl fluoride)
PVME	Poly(vinyl methylether)
PVMEMA	Poly(vinyl methylether-maleic anhydride)
PVP	Poly(4-vinylpyridine)
PVPd	Poly(vinyl pyrrolidone)
Rabon	2-Chloro-1-(2,4,5-trichloro-phenyl)vinyl-dimethyl-phosphate
SA	Sulfasalazine
SAPs	Super absorbent polymers
SBR	Styrene–butadiene rubber
TEGMA	Tetraethylene glycol methacrylate

Temephos	O,O,O’,O’-Tetramethyl-O,O-thiodi-p-phenylenephosphorothioate
TMPTMA	1,1,1-Trimethylolpropane trimethacrylate
TPP	Tripolyphosphate
UF	Urea-formaldehyde resin





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