CHAPTER 1

Polymeric Materials from Renewable Resources

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1.1 INTRODUCTION

Polymers from renewable resources have been attracting ever-increasing attention over the past two decades, predominantly for two reasons: the first being environmental concerns and the second being the realization that our petroleum resources are finite. In addition, this kind of material will provide additional income to those

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Biodegradable Polymer Blends and Composites from Renewable Resources. Edited by Long Yu

involved in agriculture. Generally, polymers from renewable resources can be classified into three groups: (1) natural polymers such as starch, protein, and cellulose; (2) synthetic polymers from bioderived monomers such as poly(lactic acid) (PLA); and (3) polymers from microbial fermentation such as polyhydroxybutyrate.

In this short chapter, various polymers from renewable resources, in particular those that have been used as or have been shown to have potential for use as polymeric materials, are briefly reviewed. The review focuses on the microstructure, general properties and some of the applications for these materials. Some comparisons are also made between natural and conventional synthetic polymers.

1.2 NATURAL POLYMERS

The study and utilization of natural polymers is an ancient science. Typical examples, such as paper, silk, skin and bone artifacts can be found in museums around the world. These natural polymers perform a diverse set of functions in their native setting. For example, polysaccharides function in membranes and intracellular communication; proteins function as structural materials and catalysts; and lipids function as energy stores and so on. Nature can provide an impressive array of polymers that can be used in fibers, adhesives, coatings, gels, foams, films, thermoplastics, and thermoset resins. However, the availability of petroleum at a lower cost and the biochemical inertness of petroleum-based products proved disastrous for the natural polymers market. It is only after a lapse of almost 50 years that the significance of eco-friendly materials has once again been realized. These ancient materials have evolved rapidly over the past decade, primarily due to environmental issues and the increasing shortage of oil. Modern technologies provide powerful tools to elucidate microstructures at different levels and to understand the relationships between structures and properties. These new levels of understanding bring opportunities to develop materials for new applications.

Wide ranges of naturally occurring polymers that are derived from renewable resources are available for various materials applications (Charles et al., 1983; Fuller et al., 1996; Kaplan, 1998; Scholz and Gross, 2000; Gross & Scholz, 2001). Some of them (e.g., starch, cellulose and rubber), are actively used in products today whereas many others remain underutilized. Natural polymers can sometimes be classified according to their physical character. For example, starch granules and cellulose fibers are classified into different groups, but they both belong to polysaccharides according to chemical classification. Table 1-1 lists some natural polymers (Kaplan 1998).

1.2.1 Natural Rubber

One of the best known mature materials is natural rubber, which has been and is widely used in modern life. Although rubber's usefulness was known about in the early seventeenth century, it was not until the early nineteenth century that the rubber manufacturing industry became established. Rubber biosynthesis can occur

TABLE 1-1 List of Natural Polymers (Kaplan, 1998)

Polysaccharides
- from plant/algal: starch, cellulose, pectin, konjac, alginate, caragreenan, gums
- from animal: hyluronic acid,
- from fungal: pulluan, elsinan, scleroglucan
- from bacterial: chitin, chitosan, levan, xanthan, polygalactosamine, curdlan, gellan, dextran

Protein
soy, zein, wheat gluten, casein, serum, albumin, collagen/gelatine
silks, resilin, polylysine, adhesives, polyamino acids, poly(γ-glutamic acid), elastin, polyarginyl-polyaspartic acid

Lipids/Surfactants
acetoglycerides, waxes, surfactants, emulsan

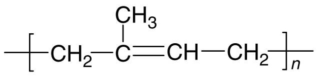
Speciality Polymers
lignin, shellac, natural rubber

in either of two different types of plant cells: specialized latex vessels or parenchyma cells. Latex vessels are the more common route. A number of research groups have investigated ways of transferring the genes responsible for rubber biosynthesis into other species (Backhaus, 1998).

Natural rubber is a *cis*-polyisoprene that occurs as natural latex or a submicroscopic dispersion of the rubber in saplike materials. All such latexes appear milk white and the polyisoprene has the chemical structure shown in Fig. 1-1. Natural rubber can be recovered by coagulation processes. It has a glass transition temperature of about $-70°C$ and a molecular weight of 3×10^6 g/mole (Tanaka, 1991). The central portion of the rubber molecules is marked by extensive *cis*-polymerizations, which denote the structural hallmark of rubber. Rubber from different sources varies most with respect to the number of these condensations, which results in different molecular weight and molecular weight distribution.

Natural rubber is a very reactive polymer because of the presence of olefinic double bonds at every fifth carbon atom. The extensive degree of unsaturation and the close spacing of these double bonds provide a highly vulnerable target for free-radical attack and oxidation. The molecule can also undergo numerous chemical reactions such as hydrogenation, addition, and substitution. Rubber can be made inert by fully chlorinating the double bonds to afford up to 65 wt% chlorine. Natural rubber is soluble in most aromatic, aliphatic, and chlorinated solvents, but its high molecular weight makes it difficult to dissolve.

In practice, natural rubber has limited utility and must be compounded with other ingredients such as carbon black fillers, antioxidants, plasticizers, pigments, and vulcanizing agents to improve its chemical and physical properties. It should be



$$\left[CH_2 - \overset{CH_3}{\overset{|}{C}} = CH - CH_2 \right]_n$$

Fig. 1-1 The chemical structure of natural rubber.

realized that since vulcanized rubber is not biodegradable, natural rubber-based products are not frequently mentioned in the literature on biodegradables even though natural rubber is one of the earliest natural materials to have been used.

1.2.2 Starch

Starch is a polysaccharide produced by most higher plants as a means of storing energy. It is stored intracellularly in the form of spherical granules that are 2–100 μm in diameter (Whistler et al., 1984). Most commercially available starches are isolated from grains such as corn, rice, wheat, and from tubers such as potato and tapioca. The starch granule is a heterogeneous material: chemically, it contains both linear (amylose) and branched (amylopectin) structures; physically, it has both amorphous and crystalline regions (French, 1984). The ratio of amylose to amylopectin in starch varies as a function of the source, age, etc.

1.2.2.1 Chemical Structures Starch is the principal carbohydrate reserve of plants. It is a polymeric carbohydrate consisting of anhydroglucose units linked together primarily through α-D-(1 → 4) glucosidic bonds. Although the detailed microstructures of starch are still being elucidated, it has been generally established that starch is a heterogeneous material containing at the extremes two microstructures according to their chain structure: amylose and amylopectin. Amylose is essentially a linear structure of α-1,4-linked glucose units and amylopectin is a highly branched structure of short α-1,4 chains linked by α-1,6 bonds. Figure 1-2 shows the structure of amylose and amylopectin.

The linear structure of amylose makes its behavior closer to that of conventional synthetic polymers. The molecular weight of amylose is about 10^6 (200–2000 anhydroglucose units) depending on the source and processing conditions employed in extracting the starch, which is 10 times larger than conventional synthetic polymers. Amylopectin, on the other hand, is a branched polymer. The molecular weight of amylopectin is much larger than that of amylose. Light-scattering measurements indicate a molecular weight in millions. The large size and branched structure of amylopectin reduce the mobility of the polymer chains and interfere with any tendency for them to become oriented closely enough to permit significant levels of hydrogen

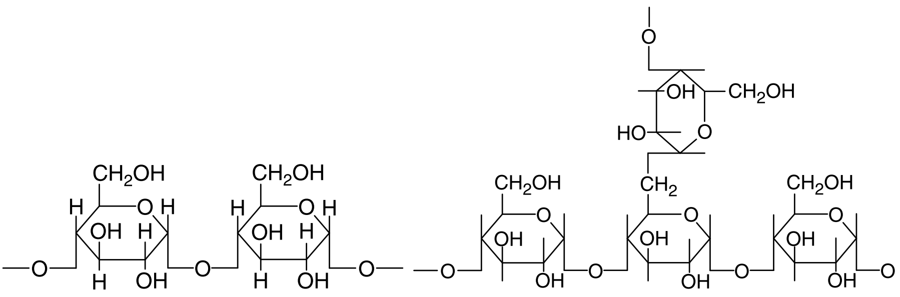


Fig. 1-2 The structures of amylose (left) and amylopectin (right).

bonding. Except the linear amylose and the short-branched amylopectin, starch of a long-branched structure has been detected (e.g., tapioca starch).

1.2.2.2 Physical Structures Most native starches are semicrystalline with a crystallinity of ~20–45%. Amylose and the branching points of amylopectin form the amorphous regions. The short branching chains in the amylopectin are the main crystalline component in granular starch. The crystalline regions are present in the form of double helices with a length of approximately 5 nm. The amylopectin segments in the crystalline regions are all parallel to the axis of the large helix. The amylose/amylopectin ratio depends upon the source of the starch but can also be controlled by extraction processing. Starch granules also contain small amounts of lipids and proteins.

Figure 1-3 shows the wide angle x-ray scattering (WAXS) patterns of cornstarch with different amylose/amylopectin content. The amylose/amylopectin ratios in waxy, maize, G50 and G80 starches are 0/100, 23/77, 50/50 and 80/20, respectively (Chen et al., 2006). It is seen that waxy and maize starches show a typical A-type pattern with strong reflections at 2θ of about 13° and 21° and an unresolved large doublet between them. G50 and G80 give the strongest diffraction peak at around $2\theta = 16^\circ$ and a few small peaks at 2θ values of 18°, 20° and 22°. An additional peak appears at about $2\theta = 4^\circ$. These latter spectra are basically the same as the characteristic B-type. From Fig. 1-3, it is also seen that the crystalline area of amylopectin-rich starches is higher than that of amylose-rich starches, which is to be expected since it is well known that amylopectin in starch granules is considered to be responsible for the crystalline structure.

1.2.2.3 Morphologies and Phase Transition During Processing Starch granules are a mixture of rounded granules from the floury endosperm, and angular granules from the horny endosperm (French, 1984; Chen et al., 2006). In their native state, starch granules do not have membranes; their surfaces consist simply of tightly

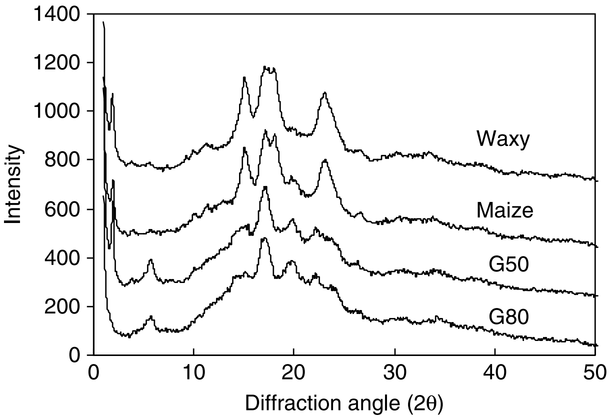


Fig. 1-3 WAXS patterns of cornstarch with different amylose/amylopectin content.

packed chain ends resembling the bottom of a broom with the straws pressed tightly together. Undamaged starch granules are not soluble in cold water but can reversibly imbibe water and swell slightly.

One of the unique characteristics of starch-based materials is their phase transition during processing, which encompasses various chemical and physical reactions including starch swelling, gelatinization, melting, crystallization, decomposition and so on (Lelievre, 1974, 1976; Whistler et al., 1984; Yu and Christie, 2001). It is well known that an order–disorder phase transition occurs when starch granules are heated in the presence of water. When sufficient water is present, this transition—referred to as “gelatinization”—results in near-solubilization of the starch (Lelievre, 1974; Donovan, 1979; Whistler, 1984). The well-accepted concept of gelatinization means destroying the crystalline structure in starch granules. Starch gelatinization is an irreversible process and includes granular swelling, native crystalline melting, loss of birefringence and starch solubilization. The concomitant changes of measurable properties such as viscosity, heat uptake, crystallinity, and size variation of starch granules have been used to detect the extent of starch gelatinization (Yu and Christie, 2001; Liu et al., 2006; Chen et al., 2007; Xie et al., 2008; Xue et al., 2008).

It has been shown that under shearless conditions, full gelatinization of starch requires about 70% water content (Wang et al. 1989; Liu 2006), while gelatinization under shear conditions requires less water since shear stress enhances processing. Extrusion cooking or processing of starch-based materials relies on the proper conversion of starch within the raw materials. In an extrusion environment, gelatinization is typically achieved with low amounts of water under high-shear and high-pressure conditions.

1.2.2.4 Starch Modification In practice, the raw materials of starch are not straightforwardly suitable for any specific nonfood application. Various modified starches have been developed for nonfood applications (e.g., starch graft copolymers, glycosides, cationic starch, or oxidized starch), to meet different specific requirements (Wurzburg, 2000). For example, sodium hypochlorite-oxidized starch which has the advantages of bright white color, easy gelatinization, and high solubility, is more suitable than native starches for applications in the papermaking and textile industries. Cationic starch, which has positive charges, can more easily be attracted by negative charges on fibers and hence is also more effective than native starches in applications in the papermaking and textile industries. Superabsorbent polymers, prepared by grafting acrylonitrile onto starch, can be used in various fields such as hygiene, cosmetics, and agriculture.

Recently, the technology of reactive extrusion has been used for starch modification (Xie et al., 2006). It has been shown that reactive extrusion is a feasible and efficient way to modify starches and to produce more applicable products. The use of an extruder as a chemical reactor allows high-viscosity polymers to be handled in the absence of solvents. It also affords large operational flexibility as a result of the broad range of processing conditions in pressure (0–500 atm [0–50 MPa]) and temperature (70–500°C), the possibility of multiple injections, the controlled residence time (distribution) and degree of mixing.

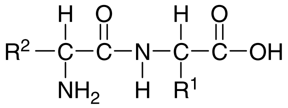
1.2.3 Protein

Proteins are one of three essential macromolecules in biological systems and can easily be isolated from natural resources. Proteins have been studied for decades for their ability to spontaneously form primary, secondary, and higher-order structures that can exhibit biological function and supramolecular protein organization in tissues and organs.

1.2.3.1 Microstructures and Properties of Proteins Proteins are constructed mainly of α-amino acids. These amino acids can be neutral such as glycine, basic (containing one or more additional amines) such as lysine, or acidic (containing one or more additional acid groups) such as aspartic acid. Also, they may contain alcohol or thio functional groups, each representing a chemical "handle" with which chemists (synthetic, inorganic and organic) are able to play their trade on either proteins containing these "available" functional groups or on the amino acids themselves. Figure 1-4 shows the structure of the amide bond linking amino acids.

Proteins have four levels of structural organization: *Primary* structure refers to the sequence of amino acids in the polypeptide chain. Proteins or polypeptides are polymers of amino acids linked by amide linkages (peptide bonds); *Secondary* structure refers to the extended or helically coiled conformation of the polypeptide chains; *Tertiary* structure refers to the manner in which polypeptide chains are folded to form a tightly compact structure of globular protein; *Quaternary* structure refers to how subunit polypeptides are spatially organized. Several interactions and linkages are known to contribute to the formation of secondary, tertiary, and quaternary structures, such as steric strain, van der Waals interactions, electrostatic interactions, hydrogen bonding, hydrophobic interactions, and disulfide cross-links (Cheftel and Cuq, 1985).

Proteins interact with water through their peptide bonds or through their amino acid side-chains. The water solubility of proteins is a function of numerous parameters such as thermodynamic standpoint. Solubilization corresponds to separating the molecules of a solvent/protein molecules and dispersing the latter in the solvent for maximum interaction between the protein and solvent. The solubility of a protein depends mainly on pH value, ionic strength, the type of solvent, and temperature (Cheftel and Cuq, 1985). Protein denaturation is any modification in conformation (secondary, tertiary, or quaternary) not accompanied by the rupture of peptide bonds involved in primary structure. Denaturation is an elaborate phenomenon during which new conformations appear, although often intermediate and short-lived. The sensitivity of a protein to denaturation is related to the readiness with which a denaturing agent breaks the interactions or linkages that stabilize the protein's secondary, tertiary, or quaternary structure. Denaturation agents can be classified as physical



$$R^2-\underset{NH_2}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\underset{R^1}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH$$

Fig. 1-4 Structure of the amide bond linking amino acids.

agents (heat, cold, mechanical treatment, hydrostatic pressure, irradiation, interfaces, etc.) and chemical agents (acids and alkalis, metals, organic solvents, etc.).

The most widely available and highly refined plant proteins are from soybeans. Biotechnology offers the opportunity to modify all four levels of soy protein structure and therefore improve its potential and usefulness for applications as a biomaterials or food protein (Utsumi, 1992). Soybeans have a particularly high protein content, typically $\sim$40%. Processing of soybeans into protein ingredients for food and industrial products involves two major industries: soybean crushing (oil extraction) and protein ingredient processing. The soy proteins are globular, reactive, and often water soluble. The preponderance of polar and hydrophilic amino acids confers unusually good water solubility among plant proteins. Chemically reactive groups in amino acids are the carboxylic, primary and secondary amine, aliphatic and aromatic hydroxyl, and sulfhydryl groups.

1.2.3.2 Processing of Protein-Based Materials Similar to the processing of starch, the processing of protein-based materials (in particular thermal extrusion), is much more complex than that of conventional polymers. Some primary studies on the extrusion of soy protein have mainly focused on food applications. Irreversible and complex changes in the physicochemical interactions of protein molecules such as unfolding and disulfide–disulfide interactions, make it difficult to analyze the melt rheology for biopolymers. Plasticizers are widely used in protein-based materials not only for reducing brightness but also for improving processing properties. Several processes, traditional and new, are currently being developed for protein-based materials. A better understanding of the physical and chemical modifications underlying the various processes will lead to a further improvement in the materials generated by these means.

1.2.3.3 Development of Protein-Based Materials Early research on soy protein-based plastics was conducted in the 1940s. At that time, soy protein was mainly used as a filler or extender to decrease the cost of petroleum-based plastics. The predominant industrial application of soy protein is for coating paper since soy protein has unusual adhesive properties. Recent research work has been aimed at developing soy protein-based biodegradable plastics. The experimental results show that soy protein (alone or mixed with starch) can be molded into plastics items such as disposable containers, utensils, toys, and sporting goods. Soy protein can also be extrusion-blown or cast into films. Soy protein-based films have been shown to be good oxygen barriers and UV-blockers that are useful as packaging materials. With proper processing, soy protein can also be made into foam products. With its biodegradable, nonflammable, and nonelectrostatic properties, soy protein-based plastics provide unique and attractive features.

1.2.4 Cellulose

Natural fibers can generally be classified into several groups according to their resources: (1) wood fibers (such as soft and hard woods); (2) vegetable fibers

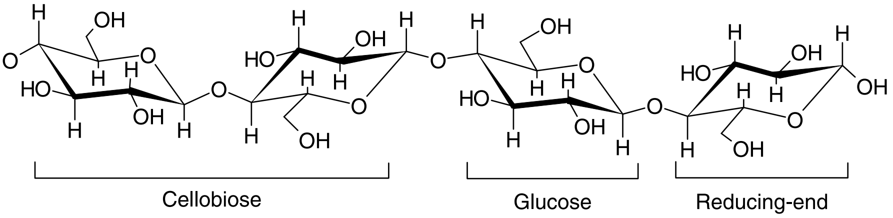


Fig. 1-5 The chemical structure of cellulose.

(such as cotton, hemp, jute, ramie, kenaf); (3) animal fibers (such as wool, silk, spider silk, feather, down); (4) mineral fibers (such as asbestos, inorganic whiskers). Biodegradable fibers usually means wood and vegetable fibers, which consist mainly of cellulose. Cellulose is the most abundant and renewable polymeric resource, but only a small proportion of sources are utilized. Cellulose occurs in all plants as the principal structural component of cell walls. The principal sources of cellulose for industrial processes are wood, cotton fiber, and cotton linters.

Cellulose is a homoglucan composed of linear chains of (1→4)-β-D-glucopyranosyl units (see Fig. 1-5). The essential linearity of cellulose makes it easy for molecules to associate strongly in a side-by-side manner, as occurs extensively in native plant cellulose, especially in trees and woody parts of other pants. Cellulose has both amorphous and crystalline structure. The amorphous regions can be easily attacked by solvents and chemical reagents. However, cellulose is generally insoluble and highly crystalline, and the strong glucosidic bonds ensure the stability of cellulose in such as water, organic solvents etc.

Cellulose has been used since ancient times in such applications as rope, canvas, and sacking made from kenaf. However, because of its crystalline structure, cellulose will not melt upon heating. It is impossible to thermally process cellulose as simply as other conventional polymeric materials. Chemical reactions such as etherification and esterification are conducted on the free hydroxyl group to improve its thermoplastic behavior. Numerous cellulose derivatives have been commercialized including cellulose acetate, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxyalkyl cellulose, carboxymethyl cellulose, fatty acid esters of cellulose, and others (Chiellini et al., 2002; Blackburn, 2005). Various solvent systems have been developed for aqueous processing (Zhang, 2001; Cai et al., 2006). In practice, cellulose has been widely used as a reinforcing agent in various polymer composites, especially for green composites (Baillie, 2004).

1.2.5 Chitin and Chitosan

Chitin is the second most abundant natural polymer after cellulose. Chitin is found widely in nature and is the main structural polysaccharide in many invertebrate animals such as insects and crustaceans. Marine crustaceans such as crabs and shrimps are the source of the most easily isolated chitin. Chitin plays the role of a structural material in many life forms. It is to be found in the cell walls of fungi where it

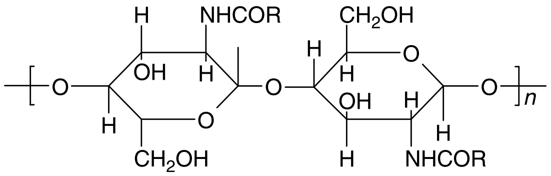


Fig. 1-6 Representative structure of chitin.

contributes stabilizing strength. The biosynthesis of chitin is a very old activity of cells and has survived from the earliest periods of life on this planet. Parrisher has provided a bibliographic listing of specific sources for chitin (Parrisher, 1989).

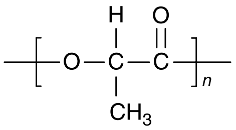
Chitin is essentially a homopolymer of 2-acetamido-2-deoxy-β-D-glucopyranose, although some of the glucopyranose residues are in the deacetylated form as 2-amino-2-deoxy-β-D-glucopyranose. When chitin is further deacetylated to $\sim 50\%$, it becomes soluble in dilute acids and is referred to as chitosan. A representative structure is shown in Fig. 1-6. Chitosan is commonly obtained by the alkaline hydrolysis of the amid group in chitin. The chemistry of chitosan is similar to that of cellulose but also reflects the presence of a primary aliphatic amine. The molecular weight of chitosan is $\sim 0.1-4 \times 10^6$ (Wu et al., 1976). Chitosan reacts readily with carbonyl compounds (i.e., by acylation with acid anhydrides), to form a wide range of ester and amide products. Chitosan's primary usefulness is a result of its ability to act as a cationic polyelectrolyte, its bioactivity and biocompatibility, its use as a thickening agent in water, and its selective chelation properties. Chitosan is also readily converted into fibers, films, coatings, and beads as well as into powders and solutions, further enhancing its usefulness (Hudson, 1998).

1.3 SYNTHETIC POLYMERS FROM BIODERIVED MONOMERS

The development of synthetic polymers using bioderived monomers provides a new direction for the production of biodegradable polymers from renewable resources. One of the most promising polymers in this regard is poly(lactic acid) (PLA) because it is made from agricultural products and is readily biodegradable. Lactide is a cyclic dimer prepared by the controlled depolymerization of lactic acid, which in turn can be obtained by the fermentation of corn, sugar cane, or sugar beat. Although PLA is not a new polymer, better manufacturing practices have improved the economics of producing monomers from agricultural feedstocks and, as such, PLA is at the forefront of the emerging biodegradable plastics industries.

1.3.1 Poly(lactic acid)

PLA belongs to the family of aliphatic polyesters commonly made from α-hydroxy acids, which include polyglycolic acid and polymandelic acid (Garlotta, 2001). PLA is commercially interesting because of its good strength properties, film transparency, biodegradability, and availability. PLA is also manufactured by biotechnological



$$\left[-O-\underset{CH_3}{\overset{H}{\underset{|}{\overset{|}{C}}}}-\overset{O}{\overset{\parallel}{C}}- \right]_n$$

Fig. 1-7 Basic structure of PLA.

processes from renewable resources. Although many sources of biomass can be used, corn has the advantage of providing the required high-purity lactic acid. PLA can be synthesized from lactic acid in two ways: a direct polycondensation reaction or ring-opening polymerization of a lactide monomer. The technique of ring-opening polymerization has the advantage of providing a product with a higher molecular weight.

The basic building block for PLA is lactic acid (2-hydroxypropionic acid) and its chemical structure is shown in Fig. 1-7. The stereochemistry of PLA is complex because of the chiral nature of lactic acid monomers. The stereoisomeric L/D ratio of the lactate units influences the properties of PLA. Poly(D,L-lactic acid), or poly(mesolactic acid), a racemic polymer obtained from a mixture of D- and L-lactic acid, is amorphous with weak mechanical properties.

PLA homopolymers have a glass transition and melt temperatures of about 60°C and 180°C, respectively. PLA is well suited to many conventional thermoplastics processing techniques such as extrusion and injection. In order to avoid degradation, PLA must not be exposed to high temperatures and moisture. PLA undergoes thermal degradation at temperatures $>200°C$ by hydrolysis, lactide reformation, oxidative main-chain scission, and inter- or intramolecular transesterification reactions (Garlotta, 2001). Mineral fillers have been used as nucleation sites for injection products (Bleach et al., 2002), and plasticizers may be employed for films and to improve toughness (Avérous and Martin, 2001; Piorkowska et al., 2006). PLA has been successfully utilized in surgical-implant materials and drug-delivery systems. The application of biodegradable plastics are now attracting much attention with regard to thermoformed products and biaxially-oriented film.

1.3.2 Propanediol

Under aerobic conditions, glycerol can be used as a substrate for the growth of many microorganisms. The glycerol can then be converted by facultative anaerobic bacteria to propanediol, ethanol, butanediol, acetic and lactic acid (Mickelson and Werkman, 1940). Among the fermentation products, propanediol (PDO) is of particular interest as it can be used as a monomer for producing plastics such as polyesters, polyethers, and polyurethanes (Deckwer, 1995).

1.4 POLYMERS FROM MICROBIAL FERMENTATION

In nature, a special group of polyesters is produced by a wide variety of microorganisms for internal carbon and energy storage as part of their survival mechanism

(Hocking and Marchessault, 1994; Scholz and Gross, 2000; Suriyamongkol et al., 2007). Poly(β-hydroxybutyrate) (PHB) was first mentioned in the scientific literature as early as 1901 and detailed studies began in 1925. Over the next 30 years, PHB inclusion bodies were studied primarily as an academic curiosity. The energy crisis of the 1970s was an incentive to seek naturally occurring substitutes for synthetic plastics, which then sped-up the research and commercialization of PHB. This biopolymer has received much research attention in recent years, with a large number of publications concerned with biosynthesis, microstructure, mechanical and thermal properties, and biodegradation through to genetic engineering.

1.4.1 Polyhydroxyalkanoates

Figure 1-8 shows the generic structure of polyhydroxyalkanoates (PHAs). The simplest of the family of PHAs is poly(β-hydroxybutyrate) (PHB). Analogous to starch, the reserve material in plants, these biopolyesters occur as submicrometer inclusions inside the cell. The present commercial development is based on the fermentation technology, but genetic engineers are already cloning the genes that have shown some potential.

1.4.2 Copolymers of the PHA Family

Pure PHB is brittle and has a low extension to breaking. The brittleness of PHB is largely due to the presence of large crystals in the form of spherulites. Interest in copolymers, in particular in copolymers of 3-hydroxybutyrate (3HB) and 3-hydroxyvalerate (3HV) (i.e., poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), stemmed from the fact that they have much lower melting temperatures and are less crystalline, more ductile, easier to mold, and tougher than PHB (Braunegg, 2002; Suriyamongkol et al., 2007). The biosynthetic origin of poly(β-hydroxyvalerate) (PHV) copolymers adds a number of interesting properties, such as full biodegradability and optical activity. Some research shows that the mechanical properties of PHBVs are sometimes similar to those of polypropylene since they have similar morphologies. The tensile strength was reported to be ~45 MPa and elongation was about 10%. PHB is susceptible to thermal degradation at temperatures well below its melting point. Careful control of temperature is required during thermal processing.

Several applications for PHB and PHBVs can be envisaged due to their wide range of specialized properties. One of the simplest applications for PHBVs is as a biodegradable alternative to existing materials. Its gas barrier properties could lead to applications in food packaging. More specialized applications of PHBVs include controlled release and surgical swabs (Hocking and Marchessault, 1994).

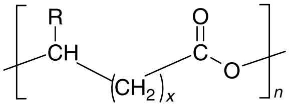


Fig. 1-8 Generic structure of PHAs.

1.5 SUMMARY

Polymers from renewable resources have world-wide interest and are attracting an increasing amount of attention for predominantly two major reasons: environmental concerns and the fact that petroleum resources are finite. Generally, polymers from renewable resources can be classified into three groups: natural polymers, synthetic polymers from bioderived monomers, and polymers from microbial fermentation.

There are some natural polymers that are actively used in everyday products while many others remain underutilized. New and more efficient isolation and purification methods along with chemical and physical modification are future research directions for natural polymers. PLA is a typical synthetic polymer from bioderived monomers. Although it can be processed by many conventional thermoplastics processing techniques, high price is still the major stumbling block to its general application. Biodegradable polymeric materials are now a major research focus and some products are becoming available in the marketplace. However, when it comes to replacing most of the conventional polymers, even in the most promising applications such as packaging and mulch films, it is either poor performance or high cost that is currently preventing the changeover.

Like most polymers from petroleum, polymers from renewable resources are rarely used by themselves. Blending and compositing are common and mature technologies for improving the performance and reducing price. In fact, the history of composites from renewable resources is far longer than that of conventional polymers. In the biblical Book of Exodus, Moses' mother built a basket from rushes, pitch, and slime—a kind of fiber-reinforced composite according to the modern classification of materials. During the opium wars in the mid-nineteenth century, the Chinese built castles to defend against invaders using a kind of mineral particle-reinforced composite made from gluten, rice, sugar, calcium carbonate, and sand.

Fibers are widely used in polymeric materials to improve mechanical properties. Cellulose fibers are the major substance obtained from plant life, and applications for cellulose fiber-reinforced polymers have again come to the forefront with the focus now on renewable raw materials. Hydrophilic cellulose fibers are very compatible with most natural polymers. The reinforcement with filler is particularly important for polymers from renewable resources since most of them have the disadvantage of lower softening temperatures and lower modulus. Furthermore, the hydrophilic behavior of most natural polymers offers a significant advantage since it provides a compatible interface with the mineral filler.

Many natural polymers are hydrophilic and some of them are water-soluble. Water solubility increases degradability and the speed of degradation, and this moisture sensitivity limits application. Blends and multilayers of natural polymers with other kinds of polymers from renewable resources can be used to improve their properties. Blends can also aid in the development of new low-cost products with better performance.

These new blends and composites are extending the utilization of polymers from renewable resources into new value-added products. Various polymeric blends and composites are discussed in the following chapters.

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