

Renewable Resource-Based Polymers



Ahmed Sharif and Md Enamul Hoque

Abstract There are growing concerns that a significant reliance on fossil resources is not sustainable for the production of polymers. The all-out transition toward renewable resources for polymer production is inevitable. Polymers from renewable resources include cellulose, starch, chitosan, lignin, proteins, oils, common commodity polymers (e.g., polyethylene, polyethylene terephthalate), and microbial poly(ester)s. Fundamental research in the production, modification, property enhancement, and new applications of these materials is an important undertaking. In this chapter, existing advances in the exploitation of renewable resources to produce polymers are summarized.

Keywords Renewable · Polymer · Fossil · Cellulose · Starch · Chitosan
Lignin · Proteins

1 Introduction

There are growing concerns over the sustainability of materials and chemicals from petrochemical-based resources for the threat to welfare, health, and the ecosystem (Kanagaratnam et al. 2013; Mac Kinnon et al. 2017; Koutinas et al. 2014; Sahoo et al. 2018). It is an enduring need to substitute polymers from fossil fuel-based resources with the more environmental congenial renewable resources (Gandini and Belgacem 2013). Contemporary progresses in the production and properties of polymers from renewable resources with better characteristics and possibly small

A. Sharif

Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology (BUET), Dhaka 1000, Bangladesh

M. E. Hoque (✉)

Department of Biomedical Engineering, Military Institute of Science and Technology (MIST), Mirpur Cantonment, Dhaka 1216, Bangladesh
e-mail: enamul1973@gmail.com

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expenses have stimulated the optimism of replacing the traditional petrochemical-based polymers (Kumar et al. 2017; Saikia and Karak 2017; Nilsson et al. 2015). With the latest innovations in production technologies and the invention of new exploitable chemical building blocks, investigation in ecological polymers from renewable resources has increased dramatically (Lindblad et al. 2002).

The term “renewable” has become a major attention among the industries and citizens. The used feedstock may be termed as renewable when it is mobilized from resources which are biologically refilled on a human timescale; on the other hand, petrochemical resources take thousands of centuries to be built naturally (Gandini and Lacerda 2015), provided that new harvest balances cultivating bio-based feedstock can be called renewable. For instance, peat is not judged renewable due to sluggish restoration rate, and on the other hand, tropical hardwood can be termed as renewable when appropriately governed. Sustainability is becoming immensely important leading to create an attention in the use of renewable resource in polymer application (Tsanaktsis et al. 2015). Renewable resource-based polymer is a new era, which is entirely based on natural resources, significantly creating a paradigm shift in the properties of polymer-based materials (Wu 2015; Yan and Chen 2015; Das et al. 2015; Han et al. 2016; Zia et al. 2016; Lligadas et al. 2014). The environment is protected due to reduction in emission of harmful gases by replacement of the fossil fuel and gas by green agricultural resources. Thus, the objective of this chapter is to present the contemporary research achievements by emphasizing the wide possibility of the renewable polymers for a huge number of functions.

Historically, the attainment of fossil fuels depended on cost-effective extensive manufacturing (Bruijninx et al. 2015). The cheap refining competences offered an economical supply of building block compounds in the petroleum-based industry (Imre and Pukánszky 2015). Similarly, improvements in the development of renewable feedstocks (e.g., cellulosic) for biofuels should facilitate the production of low-cost elementary units for beneficial chemical and polymeric developments (Thakur et al. 2014).

Another aspect is that approximately 1.3 billion tons of waste are being generated all over the world each year and is expected to escalate to 4 billion tons by 2100 (Zhang 2016). Disposing of waste jeopardizes the people life and environment. Incineration of waste like plastic has tremendous impact on the environment, as burning of plastic tends to produce dioxin-like noxious substances (Baeumler et al. 2012). Hence, throwing away of waste resources and materials denotes ruining of huge amount of money (Vestapen et al. 2017). In case of traditional petroleum-based plastics, durability, which makes it a viable candidate, renders it vulnerable after disposal. Having immense resistance to microbial degradation, these materials are not biodegradable and substantially accumulate above the ground creating waste (Botello-Álvarez et al. 2018). The polymers from agro-based resources could conquer the restrictions of the petrochemical resources which are widely used.

2 Renewable Polymers Classifications

A wide spectrum of materials from renewable resources is already potentially available. Most importantly these resources are sustainable to provide a wealthy variety of building blocks and polymers that are presently offered from fossil fuel-based industry. Based on the source and synthesis technology, renewable polymers are classified into four major groups. Figure 1 represents a classification of renewable polymer which is based on synthesis source.

- (i) Polymers from vegetable resources, for example, agro-polymers (cellulose or starch)
- (ii) Polymers obtained from animal resources, for example, chitin and chitosan
- (iii) Polymers obtained from microbial action, for example, the polyhydroxyalkanoates (PHAs)
- (iv) Polymers from monomers which is chemically and conventionally synthesized (obtained from agro-resources), for example, polylactic acid (PLA), biopolyethylene (PE), biopolyethylene terephthalate (PET).

3 Some Polymers from Renewable Sources

An assessment of the contemporary polymer field dealing with renewable resources reveals an enormous global activity in both academic and industrial arena. Some renewable resource-based polymers are described on the basis of their preparation, processing, properties, and performance below.

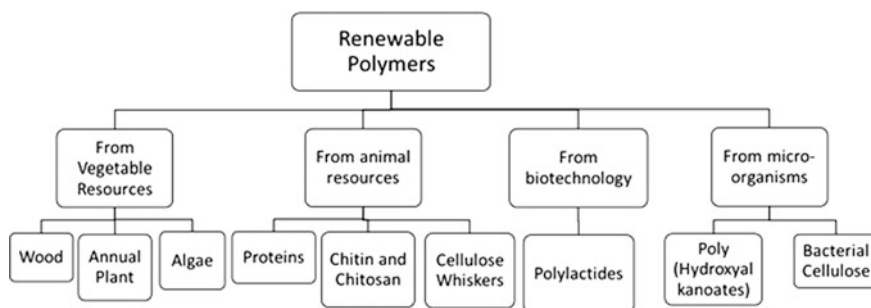


Fig. 1 Classification of renewable polymers

3.1 Cellulose

Cellulose represents, by far, the most appealing candidate in terms of availability. Cellulose is the most abundant natural resource on earth since it represents the chief constituent of plant cell walls (French et al. 1993; Ketabchi et al. 2015, 2016; Hoque et al. 2016). For example, cellulose nanoparticles (CNPs) can abundantly be isolated from Kenaf fiber (Ketabchi et al. 2016). As the most plentiful biopolymer on earth, with some 1012 tons, cellulose is readily renewed. It also possesses unique properties and chemical reactivity. This polymer constituted of D-glucose residues as monomeric units (Fig. 2) (Chiellini et al. 2002a, b). Cellulose molecules are unbranched chains of up to 17,000 1,4 linked β -D-glucose residues, but shorter chains occur under other circumstances. The two end groups of cellulose are not chemically matching, since one exhibits the “normal” C4–OH group (non-reducing end), while the other has a C1–OH component in equilibrium with the conforming aldehyde function (reducing end) (Gandini 2011a, b).

Cellulose is the dominant integral of woods which are used in an extensive variety of basic materials for buildings and furniture. Clean cellulose is usually branched out from plants exploiting various pulping procedures. Fibers from pulp are exploited in printing papers, industrial papers, household essentials such as toilet papers, paper towels, handkerchiefs, facial tissues, napkins, and so on.

This structure is responsible for the exclusive characteristics of cellulose. Because of the equatorial positions of the hydroxyls on the cellulose chain, they protrude laterally along the extended molecule and are readily available for hydrogen bonding. These hydrogen bonds cause the chains to group together in a highly ordered structure. The interchain hydrogen bonds in the crystalline regions are strong, giving the resultant structure good strength, corresponding high surface energy, high hydrophilic character, and insolubility in most solvents. They also prevent cellulose from melting (nonthermoplastic). Of course, the marked reactivity of cellulose is associated with the three OH groups present in each anhydroglucose units (AGU) (Petersen et al. 1999).

Most celluloses have a high degree of polymerization both as a function of the species and of the isolation and purification procedures. The latter operations often introduce other functionalities, like carbonyl and carboxyl groups, into the macromolecular backbone (Gandini 2011a, b). The glycosidic bonds in cellulose are strong, and this polymer is stable under a wide variety of reaction conditions. The purification step is also known to provide specific features to cellulose, including surface charge and additional chemical reactivity (Petersen et al. 1999).

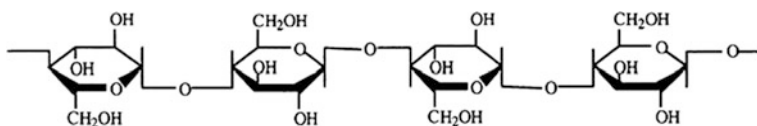


Fig. 2 Chemical structure of cellulose (Chiellini et al. 2002a)

Modified cellulose was the first polymer developed prior to the advancement of modern synthetic plastic industry. Celluloid from nitrocellulose was the first thermoplastic material invented in the nineteenth century (Shi et al. 2011). Technically, worthy chemical modifications of cellulose polymer generally engage reaction (i.e., characteristic of alcohols) with free hydroxyl groups in 2, 3, and 6 positions (Simon et al. 1998). Etherification and esterification of individual hydroxyl groups, of the polysaccharide backbone, are of specific significance for cellulose. The alteration of chemical nature of cellulose enables its synthesis with the same environments exercised for thermoplastic polymers. Several cellulosic derivatives are industrially handy such as cellulose acetate, ethyl cellulose, hydroxyethyl cellulose, and hydroxypropyl cellulose. These derivatives have been widely exploited for the fabrication of membranes and hollow fibers capable of immobilization of enzymes and in the practice of hemodialysis reverse osmosis and chromatographic supports (Lagoa et al. 1999; Hoenich and Stamp 2000). Furthermore, hydroxyalkyl cellulose and carboxymethyl celluloses are being used as a media for drug delivery and as wound dressing (Vert 2001).

The period of nanocellulose can be acknowledged with the inauguration of the third millennium (Klemm et al. 2011; Einchhorn 2011; Einchhorn et al. 2010; Dufresne 2017; Missoum et al. 2013; Habibi 2014). Some noticeable illustrated cellulosic nanoscale substances are enthusiastically investigated because of their exceptional characteristics and innovative functions in materials science: cellulose nanocrystals (CNC) (Habibi et al. 2010), nanofibrillated cellulose (CNF) (Siró and Plackett 2010), and bacterial cellulose (BC) (Pecoraro et al. 2008). For instance, the nanocellulosic fibrils are isolated from cellulose through high-pressure, high-temperature, and high-velocity impact homogenization, grinding, or microfluidization.

Cellulose xanthate in sulfuric acid or sodium sulfate solution is used to produce regenerated cellulose by extrusion or spinning (Shi et al. 2011). Cellophane film and rayon fiber are two important regenerated celluloses. Biodegradable cellophane is a transparent film with a low permeability to air, oil, and grease. Cellophane is still exploited these days in some specialized packaging films such as candy wraps, and industrial films as a base film for tapes. Rayon is an artificial redeveloped cellulose fiber formulated from a range of cellulosic natural resources such as wood, cotton, hemp, and bamboo (Kauffman 1993). Rayon fiber is employed mostly in apparels, bedding products, disposable personal sanitary objects including feminine pads and liners, furnishings, window treatment, medical products, tire cords, lighter fillings, and so on. Cellulose can also produce nanocomposites consisting of carboxymethyl cellulose, chitosan, and hydroxyapatite (HA) that can be used for load-bearing biomedical devices (Michael et al. 2016). Jiang et al. (2008) prepared a three-dimensional scaffold consisting of HA, chitosan, and carboxymethyl cellulose where the mechanical properties were seen to increase due to enhanced dispersion of HA in the polymer matrix.

3.2 Starch

Starch is the chief form of carbohydrate packing in green plants. It is the primary constituent of seeds, tubers, and roots. Starch is manufactured commercially from corn, wheat, rice, tapioca, potato, sago, and other sources. Starch contains six-membered ring glucose units (glucopyranose). There are two major types of starch molecular structure. In one type of structure, starch molecules are highly branched, known as amylopectin. It constitutes the major part of starch (i.e., up to 100% in waxy starches, 72% in normal maize starch, and 80% in potato starch). Amylopectin molecules are composed of chains of glucose units linked by α -1-4 linkages with branches of double helical α -1-6 linkages which gives the crystallinity of starch (Chauhan et al. 2000). The average branch chain length is 20–30 glucosidic units (Zdrahala 1997). The other type of starch structure is arranged by repeating units of 1-4- α -glucose with very few branches and is known as amylose. Both amylopectin and amylose structures are shown in Fig. 3.

Apart from use in food applications, starch is utilized considerably as surface modifying agents in paper and textile industry, as adhesive in corrugated board industry. Other applications of starch include laundry, baby powders, oil production, and production of bioplastics or biodegradable polymers (Bemiller 1997; Hoque et al. 2013a). Relatively cheap polyhydroxy compounds were developed from starch for industrial applications. A suitable mixture of chemical reagents permits for the introduction of ionic charge into the starch molecules (Doane et al. 1992). Starch can be readily transformed to glucose from which a variety of cyclic and acyclic polyols, aldehydes, ketones, acids, esters, and ether can be attained with the introduction of anionic or cationic charge by adding suitable chemical reagents (Tharanathan 2005). Lately, cornstarch was utilized to produce adhesive by cross-linking with polyvinyl alcohol and hexamethoxymethylmelamine together with citric acid as catalyst (Imam et al. 1999).

Aqueous esterification of starch can be generated at low alkalinity, under controlled pH. These reactions can be controlled by regulating the temperature for a range of degree of substitution ($DS = \leq 0.2$ to ≥ 2.4) (Tessler and Billmers 1996; Sagar and Merrill 1995; Mormann and Spitzer 2001). Starch ester can be produced in nonaqueous medium with the use of solvents such as pyridine. Here, pyridine is used to serve the dual purpose of catalyst and solvent (Maim et al. 1951). The reaction of

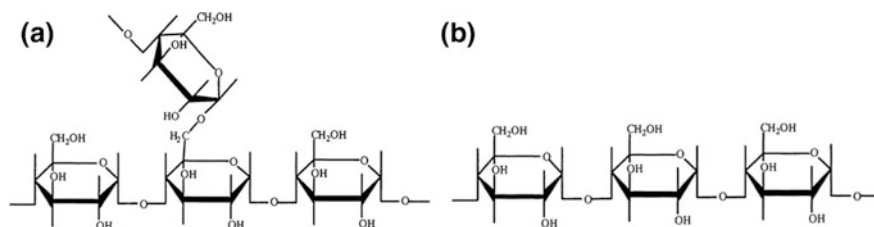


Fig. 3 Schematic representation of **a** amylopectin and **b** amylose structure (Chiellini et al. 2002a)

starches with several oxidizing reagents (such as hypochlorite, permanganate, hydrogen peroxide, persulfate, periodate, and dichromate) reduces molecular weight and also increases the solubility of starch for paper and food applications (Thoma and Stewart 1965; Kruger 1989; Vikso-Nielsen et al. 2009). These oxidized starches have found a large application in adhesive manufacturing.

A high carboxyl and carbonyl containing starch-modified water-soluble products can be developed by a reactive extrusion process with hydrogen peroxide in the presence of ferrous-cupric catalyst (Wing and Willett 1997, 1999). In graft polymerization technique, a free radical is initiated on the starch backbone and then allowed to react with polymerizable vinyl or acrylic monomers with chemical or radioactive induction (Jyothi 2010; Meshram et al. 2009). Such starch graft polymers were suggested for the application as thickeners for aqueous system, flocculants, clarification aids for wastewaters, retention aids in paper making, and many other uses (Labet et al. 2007).

3.3 Lignin

Lignin is the second most plentiful natural polymer surpassed only by cellulose in nature. Naturally, lignin acts as a cement and has a supportive structural function by establishing hydrophobic structure to defend highly hydrophilic cellulose and hemicellulose segments. Free lignin is insoluble even in strong mineral acids and hydrocarbons (Goheen and Royt 1981; Pollak 1952). Lignin in wood can be made soluble in water by changing its polymerization state with physical or chemical treatment (Calvo-Flores and Dobado 2010). Lignin exhibits a complicated three-dimensional aromatic molecule composed of phenyl groups, depending on its origin (Adler 1977). The irregular molecular mass of this biopolymer is an outcome of the random cross-linked polymerization of phenolic moieties by at least ten types of C–C and C–O–C bonds, initiating from radical-coupling reactions between phenolic radicals. It is commonly acknowledged that there are three basic phenol products that are known as monolignols: 10 p-coumaryl alcohol (M1H), coniferyl alcohol (M1G), and sinapyl alcohol (M1S) (Vanholme et al. 2008). Each monolignol produces p-hydroxyphenyl, guaiacyl, and syringyl residues in the polymer (Fig. 4).

The lignin polymer is synthesized by peroxidase-mediated dehydrogenation of monolignol units, giving a heterogeneous structure formed by basic units linked by C–C bonds and aryl–ether linkages with aryl–glycerol and β -aryl ether (dos Santos Abreu et al. 2007). In general, lignin is obtained from biomass with an organic solvent/water/reagents mixture at a high temperature and pressure. The most abundant monolignol in hardwoods is sinapyl alcohol, and this leads to syringyl S-units in the lignin polymer (Lora and Aziz 1985). Lignin is separated by acid precipitation. However, only Alcell and Organocell lignins are commercially available (Piccolo et al. 1997). A partial hydrolysis of lignin can be carried out by treating wood with steam at high temperature and pressure (i.e., about 200 °C),

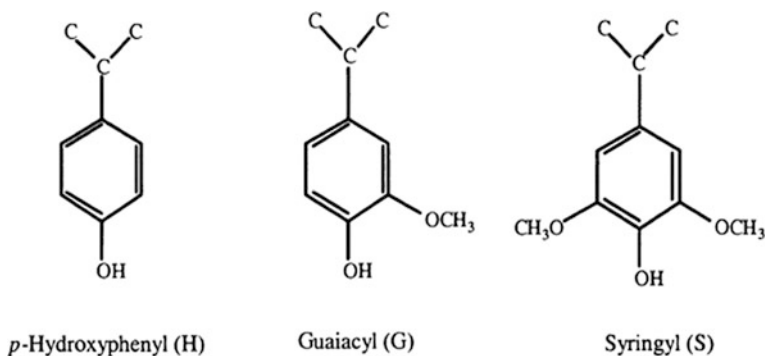


Fig. 4 Representation of typical subunits of lignin

followed by a sudden decompression in the presence of some chemicals (Focher et al. 1991). Under these circumstances, a water-insoluble lignin material with a low level of carbohydrate and wood-extractive impurities develops. Liquefaction of lignocellulosics was earlier performed by several hours of treatment at 300–400 °C in aqueous or organic solvents. Subsequently, liquefaction in organic solvents at temperatures of 240–270 °C without catalyst or at temperatures around 80–150 °C with acidic catalysts was developed with very high yield (90–95%) (Shirashi 1992). Lignin is used as dispersant, binders, humectants, emulsion stabilizers, sequestering agents, fuel source, concrete admixtures, and so on (Northey 1992).

Lignin surface and solubility characteristics can be modified with a wide range of reactions: alkylation, dealkylation, oxyalkylation, amination, carboxylation, acylation, halogenation, nitration, hydrogenolysis, methylation, oxidation and reduction, sulfomethylation, sulfonation, silylation, phosphorylation, and nitroxide formation (Wang et al. 1992). The glass transition temperature, T_g , of lignin varies widely depending on the method of isolation and molecular weight. Chemical modification of lignin has mainly been used to dissolve lignin into organic solvents and to determine the functional groups of lignin in the synthesis of copolymers with modified lignins (Thielemans and Wool 2005).

The sulfite-pulping procedure is used to employed to produce ligninsulfonates from waste liquid from softwood with salts of sulfurous acid (sulfites or bisulfites) (Lindsey and Tollens 1892). Ligninsulfonates can be used as binders, dispersant agents for pesticides, emulsifiers, and heavy-metal sequestrants (Mathiasson and Kubat 1994; Browning 1955; Wetzel et al. 2006). Low-cost binders from ligninsulfonates are commonly used in coal briquettes or ceramics, briquetting of mineral dust (fines, shavings, turnings), and wood-related material such as plywood or particle boards (Lora and Glasser 2002). In craft pulping of wood, the lignin is made water soluble through the introduction of alkaline solution. Kraft lignin is a good precursor for the preparation of char and active carbon (Carrott and Carrott 2007). Furthermore, lignin is an economical basic material for carbon fiber production. Several synthetic methods exist for preparing carbon fiber from lignin (Kadla et al. 2002).

3.4 Chitin and Chitosan

Chitin, an important structural polysaccharide, is well known to consist of 2-acetamido-2-deoxy- β -D-glucose through a β (1 \rightarrow 4) linkage (Rinaudo 2006) (Fig. 5). In fact, chitin exists in three different polymorphic forms (α , β , and γ) (Blackwell 1982; Rudall and Kenchington 1973; Tong and Yao 1997). Recent studies have confirmed that the γ form is a variant of α family (Atkins 1985). This naturally abundant mucopolysaccharide can be found in the cell walls of lower plants and fungi, insect cuticles and in the exoskeleton of arthropods and mollusks. An estimated billion tons of chitins are synthesized every year in nature (Singh and Ray 2000). It is highly hydrophobic and is insoluble in water and most organic solvents. It has low chemical reactivity. For its inertness, it gained less attention with respect to cellulose, remaining an almost unutilized resource. It is soluble in hexafluoro isopropanol, hexafluoroacetone, chloroalcohols in conjugation with aqueous solutions of mineral acids (French et al. 1993) and dimethylacetamide containing 5% lithium chloride.

Chitosan is the fully or partially *N*-deacetylated derivative of chitin (Fig. 6) (Sahoo and Nayak 2011). Chitosan is soluble in acetic acid and other organic solvents. It is more favorable in many applications than chitin. Chitin and chitosan are of commercial interest due to their high percentage of nitrogen (6.89%) compared to synthetically substituted cellulose (1.25%). Because of the presence of the amino functionality, chitin and chitosan could be suitably modified to impart desired properties and distinctive biological functions including solubility (Tharanathan and Kittur 2003; Kurita 2001; Gorochovceva and Makuška 2004).

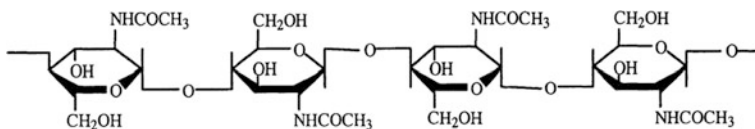


Fig. 5 Representation of typical chitin structure

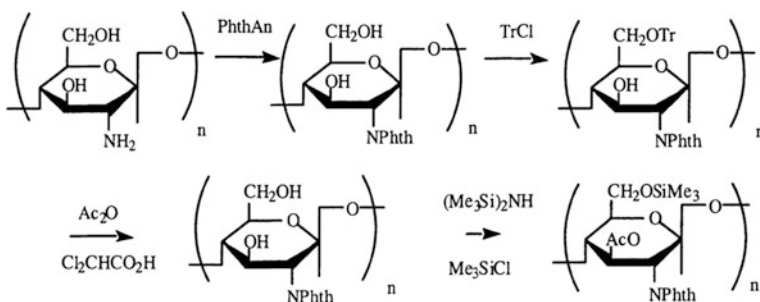


Fig. 6 Representation of typical chitosan structure

Water-resistant adhesive proteins used by marine animals (mussels) to adhere to wet or submerged surface have stimulated the studies to confer water-resistant adhesive properties to semidilute solutions of chitosan. High viscosities and water-resistant adhesive strength of chitosan semidilute solutions have been obtained by tyrosinase catalyzed reaction with 3,4-dihydroxyphenethylamine (dopamine) or by reaction with glutaraldehyde (Nakajima et al. 1984). The deacetylation process is rarely complete, and most commercial and laboratory products tend to be a copolymer of *N*-acetylglucosamine and *N*-glucosamine repeat units. The ratio of the two repeating units depends on the source and preparation conditions of chitosan, but in many cases, the glucosamine units predominate.

Fibers made of chitin and chitosan are useful as absorbable sutures and wound dressing materials (Nakajima et al. 1984). Novel methods have been recently devised for the preparation of chitin threads for the fabrication of absorbable suture materials, dressings, and biodegradable substrates for the growth of human skin cells (keratinocytes and fibroblasts) (Tamura 2004). It has also been claimed that wound dressings made of chitin and chitosan fibers have applications in wastewater treatment. Here, the removal of heavy metal ions by chitosan through chelation has received much attention (Muzzarelli 1997). Yannas et al. proposed a design for artificial skin, applicable to long-term chronic use, focusing on a nonantigenic membrane, which performs as a biodegradable template for synthesis of neodermal tissue (Yannas et al. 1982).

Artificial kidney membranes prepared from modified and albumin-blended chitosan membranes were found to be potential candidates for dialysis applications (Reinhart and Peppas 1984). Chitosan can provide ionic conductivity when dissolved in acetic acid. The transport of protons which gives conductivity in chitosan is thought to occur through many microvoids in the polymer. The choice of a more suitable electrode material may produce a better battery system (Arof et al. 1995).

3.5 *Proteins*

Proteins are built up of chain of amino acid residues joined by amide linkages with the presence of reactive groups such as amino, carboxyl, amido, hydroxyl, thiol, and imidazole groups. Proteins have a wide variety of applications in fermentation processes, coatings, encapsulant in the pharmaceutical and food industries, adhesives, surfactants, and plastics (De Graaf and Kolster 1998). Proteins can be used for making of slowly degrading packaging or mulching films (Chiellini et al. 2002a, b). Examples of industrial proteins are plant proteins, such as wheat and corn gluten, soy, pea, and potato proteins; and animal proteins, such as casein, whey, keratin, collagen, and gelatin. Recently, gelatin gets much technological appreciation for its solubility in hot water, polyampholyte character, availability in a wide range of viscosity, and thermally reversible gel formation. Gelatin is currently used in a variety of applications comprising manufacturing of pharmaceutical products, X-ray and photographic films development and food processing (De Graaf and Kolster 1998; Feughelman 2002).

Collagen is used as the basic material for the manufacturing of leather products (Yannas 1972). Proteins are also used for the fabrication of materials such as edible films, films and coating, adhesives, thermoplastics, and surfactants (Cuq et al. 1998; Kester 1986). Chemical modifications of proteins improve its economic consideration as thermoplastic or thermosetting materials (De Graaf et al. 1998). Esterification of protein carboxyl and amide groups by fatty alcohol that lead to a protein derivative with improved functional properties can result into a lower water sensitivity. In this case esterified protein becomes less soluble at basic pH compared to native proteins, indicating a hydrophobation effect (Ayhllon-Meixueiro et al. 2001).

3.6 Polylactic Acid (PLA)

Polylactic acid (PLA) is a biodegradable aliphatic polyester. Most importantly, PLA can be synthesized from bio-derived monomers. Lactide monomer is produced from lactic acid, which is produced by fermentation of a renewable agricultural source corn (Auras et al. 2004). Lactic acid is a chiral molecule available in the L and D stereoisomer forms (Fig. 7). Lactide is a cyclic dimer of lactic acid that has three possible stereoisomers: (i) L-lactide (LLA), which is composed of two L-lactic acids, (ii) D-lactide (DLA), which is composed of two D-lactic acids, and (iii) meso-lactide (MLA), which is composed of an L-lactic acid and a D-lactic acid (Kulkarni et al. 1971). Lactic acid in the L-form is actually produced by fermentation from nearly any renewable resources.

To produce lactic acid (2-hydroxy propionic acid) which is the single monomer of PLA, fermentation or chemical synthesis is used. Its two optically active configurations, the L(+) and D(-) stereoisomers, are produced by bacterial (heterofermentative and homofermentative) fermentation of carbohydrates. PLA can be made through a polymerization process from the lactic acid by polycondensation or ring-opening polymerization or can be made by direct methods such as azeotropic dehydration or enzymatic polymerization (Fig. 7) (Lasprilla et al. 2012). The direct polymerization and ring-opening polymerization methods are commonly exploited. Polycondensation reaction produces low molecular weight poly(lactic acid). Lactide ring-opening polymerization provides a direct and easy access to the corresponding high molecular weight polylactide. Industrially important high molecular weight PLA with a controlled optical and crystal property is formed with vacuum distillation of L-lactide, by ring-opening polymerization. Stannous octoate (bis 2-ethyl hexanoate, SnOct₂) for the L-lactide ring-opening polymerization is used as active initiator, which in turn causes a low degree of racemization at high temperature (Pang et al. 2010).

Some unique properties (such as high mechanical strength, good appearance, good barrier, and low toxicity) of PLA have broadened its application. PLA exhibits rapid loss of molecular weight at processing temperature while undergoing thermal treatment. PLA is thermally unstable, and during thermal processing or under hydrolytic conditions, the ester linkages of PLA tend to degrade (Cheng et al.

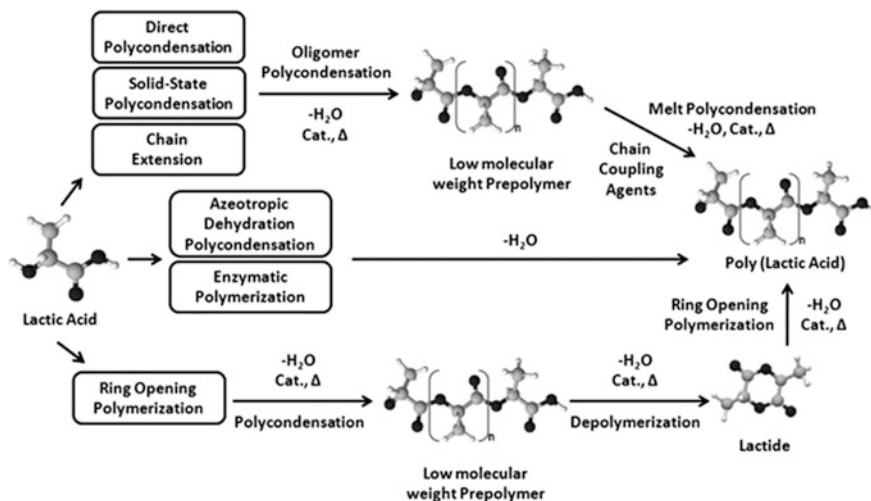


Fig. 7 Synthesis of PLA from L- and D-lactic acids. Adapted from Auras et al. (2004)

2009). The degradation rate of PLA rapidly increases above the melting point, although it undergoes thermal degradation at temperatures lower than the melting point of the polymer. PLA films have good tensile strength, lower than polyethylene terephthalate (PET) but higher than polystyrene (PS). The permeability coefficients of O_2 and CO_2 are lower than PS and comparable to those of PET, in the context of barrier properties of PLA. PLA has the highest value in comparison to high-density polyethylene (HDPE), polypropylene (PP) and PS for tensile modulus and flexural modulus (Akbari et al. 2015).

Crystallinity influences many polymer properties including modulus, stiffness, tensile strength, hardness, melting point, and crease point. The crystallization rate of PLA at temperatures between 100 and 118 °C is very high (Drumright et al. 2000). It was also concluded that the high crystallization rate of PLA below 120 °C has to be ascribed to the high rate of radial growth of the spherulites (spherical semicrystalline regions inside nonbranched linear polymers) after measuring crystallization rates of PLA over a wide temperature range (Müller et al. 2015).

PLA applications include a wide variety of biomedical products (Hutmacher et al. 2008; Yousefi et al. 2015; Hoque et al. 2018), food packaging for meat and soft drinks, films for agro-industry, and nonwoven materials in hygiene products. PLA is approved by the US Food and Drug Administration (FDA) for the biomedical applications in the orthopedic area that include fixation screws, suture anchors, meniscal darts, suture reinforcements, and skin replacement materials (Jagur-Grodzinski 1999; Nair and Laurencin 2007). Tormala et al. proposed fully resorbable composites by reinforcing matrices with resorbable PLLA fibers and calcium phosphate-based glass fibers (Törmälä et al. 1991). One of the first commercially available fiber-formed bioresorbable medical products is based on copolymers of glycolic acid (GA) in combination with L-lactide (Vicryl)

(Albertsson and Varma 2003). Porous PLA scaffolds have been found to be potential reconstruction matrices for damaged tissues and organs (Södergård and Stolt 2002; Avinc and Khoddami 2010; Nainar et al. 2014; Hoque et al. 2018). The capability of PLA to produce hybrid paper plastic packaging that is compostable and to recycle back to lactic acid by alcoholysis or hydrolysis has made it suitable for various applications. As a “green” food packaging polymer, PLA is now considered as the growing alternative. It has a wide range of application in the field of fresh products as thermoformed PLA containers are being used in retail markets as containers (Lunt 1998). Besides, PLA/natural fiber composites have been known for its potential applications in the areas of automotive parts, construction materials, food packaging, and medical devices (Asha et al. 2017).

3.7 Vegetable Oil-Derived Polymer

Vegetable oils, such as soybean oil, palm oil, and rapeseed oil, are extracted primarily from the seeds of oilseed plants and have a wide variety of applications: as foods, fuels (biofuels), lubricants, paints, cosmetics, pharmaceuticals, plasticizers, and construction materials (Hoque and Gee 2013). They are also attractive monomers for polymer chemistry due to their natural abundance and reactive functionality (Wang and Schuman 2013). From seeds of certain plants, vegetable oils are extracted, the mainstream of which are oil palm (*Elaeis*), soybean (*Glycine max*), sunflower (*Helianthus*), and oilseed rape (*Brassica napus*). These seeds have a wide range of applications and are produced on a very large scale (i.e., 156 megatons in 2012) (Zhu et al. 2016). Majority of them are used as food, biofuels, and chemical feedstocks. The key chemical building blocks of vegetable oils are triglycerides which is the triesters of glycerol and fatty acids. Of the five commonly occurring fatty acids, two are saturated (palmitic and stearic) and three are unsaturated (oleic, linoleic, and linolenic).

Triglyceride structure consisting of glycerol esterified by three long-chain aliphatic acids with variable number of carbon atoms (Fig. 8). During esterification, the number of C=C unsaturation in the chain makes the main difference for different types of fatty acid structures including the hydroxyl moieties (Pagliaro et al. 2007). Fatty acids account for 95% of the total weight of triglycerides and their content varies depending on the plant, the crop, the season, and the growing conditions (Fig. 8). The structures of some frequently studied fatty acids are depicted in Fig. 8 (ii). By transesterification reactions, they are commonly processed to produce glycerol and fatty esters. In terms of polymer production, glycerol is used as a precursor for the production of monomers such as epichlorohydrin and lactic acid. It is a widely used building block in polymer science finding application in the synthesis of polyurethanes, polyesters, or telomeres (Behr et al. 2008). On the other hand, fatty acids have been used for a long period for the development of polymeric structures, both directly and as building blocks for the synthesis of more sophisticated monomers (Behr et al. 2008).

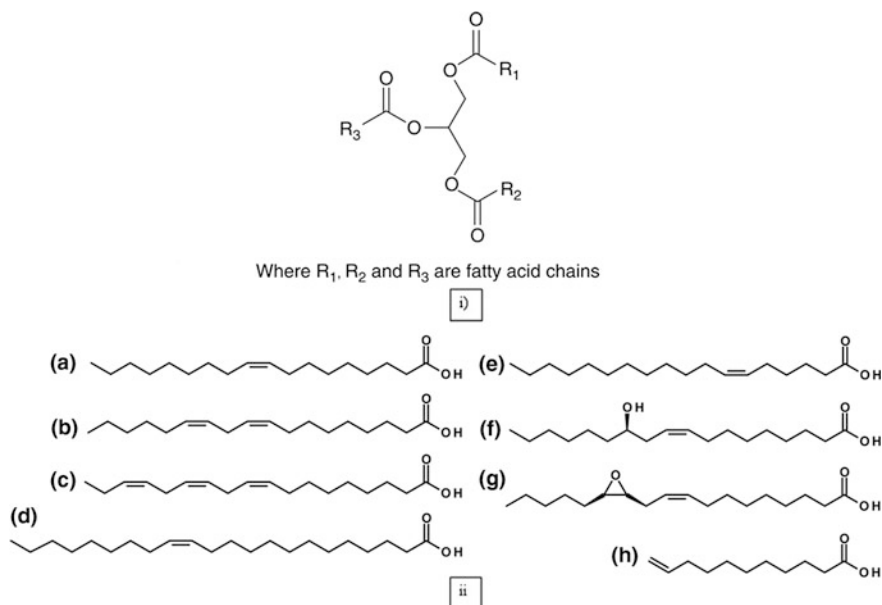


Fig. 8 (i) General triglyceride structure and (ii) fatty acids commonly used in polymer chemistry: **a** oleic acid, **b** linoleic acid, **c** linolenic acid, **d** erucic acid, **e** petroselinic acid, **f** ricinoleic acid, **g** vernolic acid, **h** 10-undecenoic acid

The triglyceride oils need to be functionalized and separated to make well-defined polymers and monomers. By reactions at the olefin functional groups for unsaturated fatty acids, functionalization is achieved. Commonly used olefin functionalization reactions include epoxidation, isomerization, hydroformylation, reduction, and metathesis reactions to produce polyol (Williams and Hillmyer 2008). The polyurethanes are prepared by the reaction between a vegetable oil-derived polyol and various isocyanates. These polyurethane materials are characterized with particular attention being paid to their degradability and biocompatibility. The epoxy resin formation with epoxidized plant oils and fatty acids was the most vividly studied topic (Maisonneuve et al. 2013). The epoxidation of unsaturated fatty acids or triglycerides can be achieved in a straightforward reaction with, e.g., molecular oxygen, hydrogen peroxide as well as by chemo-enzymatic reactions. Additionally, acrylated epoxidized soybean oil as well as maleinized soy oil monoglyceride and maleinized hydroxylated oil were used to prepare composite materials with glass fibers as well as natural flax and hemp fibers (Maisonneuve et al. 2013).

Vegetable oils symbolize an excellent foundation for obtaining aliphatic diacids or diesters and diamines for polyamides production. Partially fatty acid-based polyamides from azelaic acid (PA-6,9 and PA-6,6,9), sebacic acid (PA-6,10), dimer fatty acids, and brassylic acid have been synthesized from different researchers (Meier et al. 2007). Polyamide synthesis from plant oils already found industrial application in the preparation of Nylon-11, since the necessary monomer,

11-amino-undecanoic acid, can be obtained from castor oil by further chemical modification of 10-undecenoic acid (Maisonneuve et al. 2013).

The radical polymerization of acrylated or maleinized plant oil derivatives was investigated to produce plant oil-based thermosets. Another way is the direct cross-linking of soybean oil with polybutadiene or p-dinitrosobenzene and of linseed oil with phenolic resins. In this regard recently, the synthesis of polyurethane foams and the development of biocompatible adhesives were also carried out from plant oil (Meier et al. 2007; Yilmaz and Kusefoğlu 2005; Mutlu and Kusefoglu 2009). Moreover, the great potential of fatty acids as building blocks for olefin metathesis polymerization (ADMET) is now materialized commercially (de Espinosa and Meier 2011). On the other hand, the production of monomers and polymers by thiol-ene coupling reactions with fatty acid derivatives is a newly growing area (Black and Rawlins 2009). These multifunctional thiols and enes were synthesized by ring opening of epoxidized soybean oil with polythiols or allyl alcohol, respectively. These products with high functionality provided good coating film properties by UV curing in the presence of petrochemical-based enes or thiols.

3.8 Terpenes

Terpenes and terpenoids are derived from plants. Both terpenes and terpenoids have a common isoprene unit (2-methyl-1,4-butadiene) as a common carbon skeleton building block in their chemical structures. The best-known polyterpene is natural rubber. Other types of terpenes are being investigated as monomers for polymer production, although on a much smaller scale. One of them is turpentine, which is extracted from pine trees (*Pinus* spp.) and is composed mainly of α -pinene (45–97%) and β -pinene (0.5–28%), and limonene, which is extracted from the peel of citrus fruits (De Carvalho and da Fonseca 2006). The general formula of monoterpene is $C_{10}H_{16}$ (Erman 1985). Among the huge variety, α -pinene, β -pinene, limonene, and myrcene are the most common types of terpenes which can be readily isolated in viable amounts from turpentine.

Among terpenes, β -pinene is by far the most sustainable monomer because of the unhindered availability of its alkenyl unsaturation. Its cationic polymerization has been extensively studied, first with classical Lewis-acid initiators and then using quasi-living systems (Silvestre and Gandini 2008). Myrcene was polymerized through a double mechanism consisting of a cyclization step through ring-closing metathesis followed by its cationic activation to give a high molecular weight polymer (Kobayashi et al. 2009). The synthesis of polyamides and polyurethanes was also done from limonene-based diamines and diamides prepared by a similar click strategy involving thiolamine-hydrochlorides (Firdaus and Meier 2013). Monomer limonene oxide was copolymerized with CO_2 using β -diiminate zinc complexes to yield polycarbonate structures (Byrne et al. 2004). A polyester network, with ultra-small pores exploited for gas separation application, was synthesized from triterpene as monomer by the isolation of betulin (which bear two OH

groups) from birch bark and its polycondensation with 1,3,5-benzenetricarbonyl trichloride (Jeromenok et al. 2011).

3.9 *Furans*

Furan derivatives are present in nature in a wide category of structures. Furan is one of the major representatives of the five-member unsaturated heterocycle family. Furan displays the lowest aromatic and the highest dienic character. In furan chemistry alkylation, halogenation, sulfonation, and nitration occur regioselectively at C2 and/or C5. A typical consequence in macromolecular synthesis is the ease with which furan, and some of its derivatives undergo the Diels–Alder (DA) reaction as dienes (Gandini and Belgacem 1997; Moreau et al. 2004; Gandini 2010, 2011a, b; Manfredi and Rivero 2012; Hou et al. 1998; Sutton et al. 2013).

Some of the novel furan monomers displayed characteristics entirely compatible with their conventional petrochemical alternatives. 2-Furyl oxirane monomer can take part in anionic polymerization with the initiation by a very weak nucleophiles like amines and alcohols, for the synthesis of block, star, and grafted copolymers (Gandini and Belgacem 1997; Moreau et al. 2004; Gandini 2010, 2011a, b; Manfredi and Rivero 2012; Hou et al. 1998; Sutton et al. 2013).

Polyamides were made by “direct condensation” through the polycondensation of both 2,5- and 3,4-dicarboxylic acids with a number of aromatic diamines (Gandini and Belgacem 1997; Moreau et al. 2004; Gandini 2010, 2011a, b; Manfredi and Rivero 2012; Hou et al. 1998; Sutton et al. 2013). These polyamides showed regular structures, high molecular weights and interesting crystallization and thermal properties. Furans resulting from furfural (F) can be condensed with aldehydes and ketones to produce difuran monomers bearing different terminal functionalities. Polyesters, polyamides, and polyurethanes were prepared with these monomers by step-growth polymerizations. When hydroxymethylfurfural (HMF) was used to prepare novel furan monomers, a new family of polycondensation structures arose and their macromolecules displayed remarkable properties (Gandini and Belgacem 1997; Moreau et al. 2004; Gandini 2010, 2011a, b; Manfredi and Rivero 2012; Hou et al. 1998; Sutton et al. 2013). Other materials based on the polymerization of furan monomers include photosensitive macromolecules with applications in the printing industry, conjugated semiconducting polymers with luminescent features, polymer electrolytes for solid-state batteries based on the combination of furan and chitosan chemistries, and insulating foams (Gandini and Belgacem 1997; Moreau et al. 2004; Gandini 2010, 2011a, b; Manfredi and Rivero 2012; Hou et al. 1998; Sutton et al. 2013).

3.10 Polyhydroxyalkanoates

Biodegradable polyhydroxyalkanoates (PHAs) plastics are produced by bacteria in several grades with the difference in composition and molecular weight (Braunegg et al. 1998). The bacteria produces the PHAs from a carbon source that is when overfed, the PHA polymer is formed and on the contrary the polymer is consumed when the bacteria are short of a feeding source. PHAs have properties similar to those of some polyolefins. They are fully and rapidly biodegraded under appropriate conditions. The simplest PHA is polyhydroxybutyrate (PHB) polymer and the only type of PHAs relevant for practical applications (Braunegg 2002). The first step of bacterial synthesis of PHB consists in the conversion of a selected carbon source to acetate. Then, an enzyme cofactor is attached via the formation of a thioester bond. The enzyme, called coenzyme A (CoA), is a universal carrier of acyl groups in biosynthesis, and acetyl-CoA is a basic metabolic molecule found in all PHA-producing organisms by the sequential action of three enzymes, 3-ketothiolase, acetoacetyl-CoA reductase, and PHA synthase (Choi and Lee 1999). A dimer acetoacetyl-CoA is formed via reversible condensation and subsequently reduced to a monomer unit (R)-3-hydroxybutyryl-CoA. PHB is formed via the polymerization of the latter, maintaining the asymmetric center (Macrae and Wilkinson 1958).

Appropriate exchanged propiolactones can be used to produce PHAs chemically using aluminum or zinc alkyl catalysts with water as the cocatalyst. In terms of stereoregularity, synthetic PHAs can be made almost identical to the corresponding biopolymers (Chodak 2008). This resemblance results even in the excellent biodegradability of the material (Araki and Hayase 1979). However, high lactone monomer costs are the major limitation for industrial application of the synthetic PHAs (Philip et al. 2007).

The structure of PHAs is based on polyester macromolecules bearing optically active carbon atoms. The crystalline structure of PHB is orthorhombic with dimensions of the basic crystalline cell $a = 5.76 \text{ \AA}$, $b = 13.20 \text{ \AA}$, $c = 5.96 \text{ \AA}$. A partially planar zigzag structure can be formed as a result of the mechanical uniaxial load from the amorphous phase between lamellae (Yamane et al. 2001; Orts et al. 1990). PHB is a completely biodegradable, highly hydrophobic thermoplastic, containing almost 80% crystallinity, with high melting temperature, resistance to organic solvents and possessing excellent mechanical strength and modulus resembling that of polypropylene (Pollet and Avérous 2011). Noticeable brittleness, very low deformability, high propensity to a rapid thermal degradation, difficult processing by conventional thermoplastic technologies (mainly due to fast thermal degradation), and rather high price compared to other high-volume plastics may be named as the major factors hindering a wider application of PHB (Follain et al. 2014).

In order to improve properties of PHB, random copolymers have been prepared by replacing the methyl group on the PHB main chain by ethyl or longer substituents with the help of changing the substrate on which the bacteria grow (Doi et al. 1987). Bacterial synthesis using sodium octanoate as a sole carbon source was

reported to result in a formation of copolymer with the majority of polyhydroxy-octanoate segments (Gagnon et al. 1992). An application of epoxidized soybean oil has been reported recently for plasticizing blends of PHBV and cellulose acetate butyrate for packaging applications. The material with longer side chains is claimed to be suitable for using as degradability enhancers for poly(olefins) (Marchessault et al. 1990). In another study, it is claimed that the ductility of PHB can be improved significantly by hot rolling treatment (Barham and Keller 1986). In case of chemical modification, poly(hydroxy ether) prepared from Bisphenol A was reported to react with PHB by transesterification during annealing at 180 °C (Yuan and Ruckenstein 1998). In another case, grafting of acrylic acid onto PHB and PHBV was initiated by gamma irradiation (Mitomo et al. 1996).

Injection blow-molded bottles for packaging of biodegradable containers for hair shampoo or motor oil and disposable razor handles were produced with PHB (Ramsay and Ramsay 1990; Dalev et al. 1998). Excellent barrier properties against gas permeation of isotropic PHB foils may be considered for application in food-stuffs packaging (Basta 1984). PHB-coated paper has been shown to be completely biodegradable and also easier to recycle than conventionally coated paper (Chodak 2002). A direct electrostatic coating technique is possible to use for depositing PHB on a low dielectric substrate such as paper (Marchessault et al. 1993). PHB fibers were considered to be mainly used for the production of scaffolds (Van de Velde and Kiekens 2002). PHB composites with apatite can be used as biodegradable bone fracture fixations or even as bone repair materials (Ni and Wang 2002).

3.11 Polycarbonates

As carbon dioxide (CO₂) is abundant and inexpensive, it is an interesting synthetic feedstock for the production of polymers. CO₂ fixation through reaction with the highly reactive three-membered epoxide ring to afford cyclic or polymeric carbonates is an extensive field of research (Kember et al. 2011; Miao et al. 2008). The copolymerization involves the alternating insertion of carbon dioxide and epoxide in the growing polymer chain. The use of a catalyst is required in order to achieve the selective synthesis of polycarbonates with high yield and under relatively mild conditions of temperature and CO₂ pressure. In the copolymerization cycle, a Lewis acidic metal species binds and ring opens an epoxide, generating a metal alkoxide species. CO₂ introduces into the metal alkoxide bond giving a metal carbonate, and this group can combine and ring open a further molecule of epoxide; duplication of the cycle ultimately directs to the production of high molecular weight polycarbonate (Coates and Moore 2004). A variety of homogeneous and heterogeneous Lewis acidic metal complexes initiate the polymerization, including Zn(II), Co(II), and Cr(III) alkoxides, carboxylates, and carbonates (Cohen et al. 2005). It was also found that the addition of phenylphosphonic acid [PhP(O)(OH)₂] or phosphoric acid [H₃PO₄] as chain transfer agent in CO₂-PO copolymerization catalyzed by a cobalt salen complex produced flame-retarding poly(propylene carbonate)s (Cohen et al. 2005).

The mechanical properties of polycarbonates can differ significantly as a function of the nature of the epoxide used in the copolymerization with CO₂. Poly(cyclohexene carbonate) is a brittle material at room temperature, whereas poly(ethylene carbonate) displays rubber-like properties (Taherimehr and Pescarmona 2014). The low thermal degradation temperature of polycarbonates is problematic for processing by common thermoplastic techniques such as molding, mixing, or extrusion. The use of co-monomers and end groups has improved the thermal stability (Hwang et al. 2003).

Polycarbonate polyols of low molecular weight may be suitable to prepare foams, coatings, and adhesives, whereas high molecular weight polycarbonates may be used as rigid plastics or elastomers (Zhu et al. 2016). Recently, it was shown in a discovery that poly(propylene carbonate) (PPC) could be used in the application as organic filler in packaging material and containers as with some modification it exhibited good adhesion, smooth processability, and better thermal degradability (Allen 2014). PPC has potential application in medical implants for its production of nontoxic consequences by enzymatic degradation in the body (Kim et al. 2008). PPC can also be used in combination with other polymers (such as starch) to make biodegradable plastics (Luinstra 2008).

3.12 *Biopolyethylene (PE) and Biopolyethylene Terephthalate (PET)*

Polyethylene (PE) is an important engineering polymer traditionally produced from petroleum-based resources. PE is now being manufactured from dehydration of ethanol produced by microbial fermentation of plant-based renewable resources. Bioethanol is developed from sugar cane, sugar beet, maize, wood, wheat, corn, and other plant wastes through microbial strain and biological fermentation process (Babu et al. 2013). At the end of the fermentation process, ethanol is distilled in order to remove water and to yield azeotropic mixture of hydrous ethanol. Ethanol is then dehydrated at high temperatures over a solid catalyst to produce ethylene and, subsequently, polyethylene (Chen et al. 2007). Polyethylene from natural resources has exactly the same chemical, physical, and mechanical properties as petrochemical polyethylene. These bio-based PE grades are mainly targeted toward food packing, cosmetics, personal care, automotive parts, and toys.

For partially bio-based polyethylene terephthalate (PET) (30 or 70%) production, one of the two fossil precursors {e.g., ethylene glycol (EG) and purified terephthalic acid (PTA)} is substituted with a bio-based material. Distinctively for a fully bio-based PET, both precursors are produced from biomass (Tuck et al. 2012). PTA accounts for approximately 70% of the weight of PET resin, while EG contributes to the rest. In the case of bio-based PET, para-xylene is produced from bioisobutanol by fermentation of cellulosic materials. PTA is currently produced from the oxidation of aromatic para-xylene. Then, PTA is condensed with ethylene

glycol to make PET. Bio-based versions of PTA and EG can be produced from a variety of biomass materials (Mülhaupt 2013). Currently, PET is being used for clothing and beverage bottles on a huge scale.

4 Conclusions and Future Perspectives

Undoubtedly, renewability of polymer material is an increasing new point to maintain the sustainability of ecosystem. As the foreseeable limit of fossil feedstocks and the increasing the environmental concerns, it is necessary to develop novel bio-renewable resource-based polymer materials on a large scale. Therefore, readjusting in carbon cycle is taken into serious consideration by the researchers. In this process, renewability of polymers is an escalating new fact to uphold the sustainability of the ecosystem. Polymers from renewable resources will perform a continual growing task in the common plastic goods as well as in medical products. Apart from economic and environmental advantages, the new property outcomes are evitable in the renewable base polymers. Essential research attempts in this field are set to persist. It is obligatory at this stage in the development of this renewable research field to assemble an abundant database in preparation for the gradual declining of fossil resources. This will eventually enable us to pick wise decisions and choices for industrial implementation.

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