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Overview of Biobased Polymers

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Abstract Awareness of the environmental issues results in increasing attention paid to biobased polymers as their development and commercialization can help to limit exploitation of fossil resources and global warming. The article presents an overview of biobased polymers comprising most abundant natural polymers, bio-engineered polymers, and polymers synthesized fully or partially from biobased substrates,

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including analogs of petrochemical resins. The structure, important properties, synthesis, and applications are addressed.

Keywords Biobased polymers · Biodegradability · Properties · Structure

1 Introduction

The term “biobased” is used to describe polymers produced from natural renewable resources, that is, biomass, which is the only source of available renewable carbon. The regeneration time of biomass carbon is measured in decades, whereas that from fossil resources reaches several million years [1]. Humankind has been using biomass since Stone Age, but converting it into substrates used for production of “biobased” polymers started in the nineteenth century. In fact, early technologically important discoveries in the field of polymer materials concerned biobased polymers. Goodyear empirically discovered the vulcanization of natural rubber in 1839, Schönbein obtained nitrocellulose in 1845, and the Hyatt brothers produced celluloid as a substitute for ivory in 1869 [2]. At the end of the nineteenth century, many polymers were available on the market including fully synthetic ones, and this period is considered as the beginning of polymer science and technology. Since that time tremendous development in both polymer science and technology resulted in a huge increase of production and broadening of polymer applications. Nowadays, it is difficult to imagine everyday life without polymer products. However, durability of polymer materials, which contributed to their success, created a serious impact on the environment as they can remain in water, soil, and landfill for many years. Nevertheless, many waste problems in agriculture, marine fishery, and construction industries, among others, were solved by the development of biodegradable polymers, driven by an increasing awareness of environmental issues [3, 4]. “Biodegradable” polymers, which include both naturally derived polymers and artificially synthesized ones, are degraded by microorganisms to biomass, water, and, depending on aerobic or anaerobic conditions, carbon dioxide or methane, respectively. It must be noted that biodegradable polymers are sometimes defined as biocompostable polymers, that is, those intended to be decomposed in industrial and municipal composts after their service life.

Biobased polymers are either biodegradable (e.g., polyhydroxyalkanoates) or non-biodegradable (e.g., bio-polyolefins). Although not all biobased polymers are biodegradable, biodegradability was an important motivation for their progress. Nowadays, the development of biobased polymers is a subject of intensive research [e.g., 5–10] as it plays a vital role in struggling with carbon dioxide emissions causing global warming and in diminishing still growing dependence on fossil resources. Initially, many biobased polymers were derived from agricultural products such as corn, potatoes, and other carbohydrate-containing resources. However, in recent years, the focus moved away from food-based feedstocks, due to desire to save the land for food production but also because of biotechnology development. In 2016, the worldwide production capacity for biobased polymers amounted to 2% of the global polymer market and was expected to increase further [11].

Nowadays biobased polymers are classified into three groups:

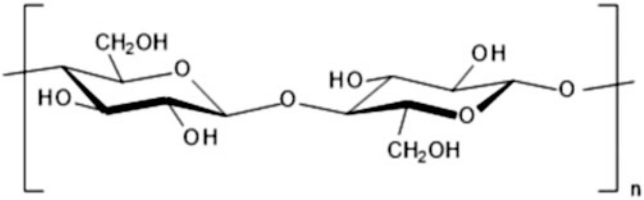
- The first class: natural polymers directly derived from biomass, including those modified chemically, such as starches, modified starches, chitin, chitosan, cellulose, cellulose acetate, and natural rubber
- The second class: bio-engineered polymers, synthesized by microorganism and plants like polyhydroxyalkanoates
- The third class: polymers synthesized from monomers obtained from renewable resources, like polylactide, poly(butylene succinate), bio-poly(ethylene terephthalate), and bio-polyolefins [12, 13]

The polymers of the first and second group, with defined chemical structures, are directly used, which enables their efficient production but limits versatility. Monomers for the polymers of the third group are obtained from naturally synthesized molecules. Due to diversity of those bio-substrates, the third group comprises numerous polymers differing in structure and properties. It includes biodegradable and non-biodegradable polymers, like bio-polyolefins and bio-poly(ethylene terephthalate). The third group of polymers is in fact the most promising. The main advantage of their production and use is reduction of exploitation of the fossil resources and limiting atmospheric carbon dioxide.

In the review the most abundant natural polymers are briefly described. However, extensive research on natural polymers like cellulose, native starch, or natural rubber has been going on for a long time and led to accumulation of vast knowledge, easily accessible. Therefore, the review recalls only the most important features and applications of those materials. In more detail, the most promising polymers, bio-engineered or synthesized from monomers of natural origin, especially biodegradable polyesters, are presented. Routes to obtain biobased analogs of fossil-based commercial polymers are also briefly described.

2 Cellulose

Numerous natural biodegradable polymers occur in living organisms on Earth: proteins, DNA, natural rubber, cellulose, lignin, chitin, pectin, etc. The most abundant natural polymer on Earth is cellulose – a biodegradable polysaccharide present in plant cell walls (15–50% of the dry weight of plant biomass) [14]. Natural cellulose-based materials, including wood, cotton, hemp, and also cellulose derivatives, are widely used. Cellulose is a linear polymer composed of D-glucose (β-D-glucopyranose) units linked through covalent β(1 → 4) glycosidic bonds, as shown in Scheme 1.



Scheme 1 Chemical structure of cellulose repeating unit: two β-D-glucopyranose units linked through covalent β(1 → 4) glycosidic bond

The intramolecular hydrogen bonds between hydroxyl groups and oxygens of neighboring rings stabilize the structure and result in linear configuration of cellulose macromolecule [15, 16]. Van der Waals and inter-chain hydrogen bonds between hydroxyl groups and oxygens of adjacent chains stimulate formation of cellulose elementary microfibrils having 2–20 nm in diameter [15–17]. In the fibrils there are differently ordered regions: highly ordered crystalline, low order, and amorphous regions. The intra- and inter-chain hydrogen bonding network is a reason of stability and axial stiffness [17]. The physical and chemical properties of cellulose depend on the number of inter- and intramolecular hydrogen bonds, the chain lengths, the chain length distribution, the crystallinity, and also the distribution of functional groups within the repeating units and along the polymer chains as well as on the isolation process employed [17–19]. The number of D-glucose rings in the chain varies in a broad range and depends on cellulose source, production process, and treatment; it is in the 800–10,000 range for cellulose in plant fibers [17]. Native cellulose generally exhibits higher molar mass than regenerated cellulose or cellulose processed by pulping. Cellulose exhibits high tensile strength of 63–500 MPa and elongation of 4% [20, 21]. The glass transition temperature (T_g) of cellulose derivatives ranges from 53 to 180°C [22]. Four principal cellulose polymorphs have been identified: I, II, III, and IV. Native cellulose I with parallel chain ordering is composed of triclinic Iα and monoclinic Iβ forms, and irreversibly transforms into stable monoclinic cellulose II with antiparallel chain arrangement upon regeneration or alkali treatment [15, 16, 23].

Although insoluble in water, cellulose is hydrophilic. Because of its high energy of cohesion, cellulose does not melt but decomposes at elevated temperatures. The cellulose has to be dissolved or chemically modified to obtain it in the liquid state. Its derivatives, cellulose xanthogenate and carbamate, are soluble in aqueous sodium hydroxide, and pure cellulose is regenerated in a wet spinning step forming viscose fibers or cellophane. The direct solvents, e.g., N-methylmorpholine N-oxide, are also used for that purpose. Owing to its thermal stability and modulus, regenerated cellulose is the largest biobased polymer produced for fibers and films widely used in numerous applications [7, 24]. In addition to pure cellulose, cellulose derivatives like cellulose acetate, cellulose nitrate, and carboxymethyl, methyl, ethyl, hydroxyethyl, and carboxyethyl cellulose are commercially important and used [25]. Cellulose esters, acetate and nitrate, are applied as films and fibers. Functional thermoplastic derivatives of cellulose were reviewed recently in [26]. A certain type of aerobic bacteria (mostly studied is *Gluconacetobacter xylinus*) produces high-purity and high-strength bacterial cellulose [16, 27], which is mainly used in food and biomedical applications.

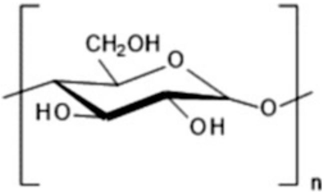
Numerous reports on using cellulose-containing fibers as reinforcement for other polymers were published, both natural fibers and regenerated cellulose fibers [28, 29]. Recently, cellulose nanomaterials, including net-forming nanofibers and rod-shaped nanocrystals, isolated from native cellulose, draw increasing attention. Due to their abundance, low weight, high strength and stiffness, and renewability, numerous studies have been reported on the isolation of nano-cellulose nanomaterials from different sources, their morphology and properties, as well as their use in high-performance applications, including polymer nanocomposites [16, 30, 31].

3 Starch

Starch, a natural polysaccharide, consisting of D-glucose (α-D-glucopyranose) units predominantly linked by α(1 → 4) glycosidic bonds (Scheme 2), is present in many food feedstock like potato and wheat seeds, as green plants produce starch by photosynthesis.

Native starch forms small granules of various shapes, with size ranging from 0.5 to 175 µm, consisting of amylose and amylopectin [32]. Amylose, of a molar mass of 10^2–10^3 kg/mol, is sparsely branched, whereas amylopectin is a highly multiple-branched polymer of a molar mass of 10^4–10^6 kg/mol [33]; the branches in amylopectin constitute about 5% of the molecule [34]. Moreover, starch can contain traces of lipids, gluten, or phosphate after industrial isolation and processing. The composition and structure of starch depend on its origin; starch can contain 20–25 wt.% of amylose and 75–80 wt.% of amylopectin. The starch granule is composed of alternating concentric amorphous and crystalline zones; crystallinity varies in the range of 17–50 wt.% [34]. Amylopectin is the dominating component of crystalline phase in the form of thin lamellae, whereas amylose and the branching regions of amylopectin form the amorphous phase. The crystals are formed by short, external chain segments of amylopectin with a degree of polymerization (DP) approx. 10–20 [34]. Different starch crystallographic forms exist: monoclinic A, hexagonal B, and C being a combination of A and B [34, 35]. In both A and B polymorphs, macromolecules are in a double helix conformation with six glucose monomers per turn. The monoclinic A form is synthesized in cereals in dry and warm

Scheme 2 Repeating unit of starch



conditions, whereas the hexagonal B form in tubers, and occurs in starch with high amylose content. The A and B unit cells contain 8 and 36 water molecules per cell, respectively. The C form is synthesized in some vegetables [34, 35].

In food or noon-food applications, usually chemically and/or physically destructured starch is used, with the exception of the application as a filler for other polymers [35, 36]. T_m of neat dry starch is in the 220–240°C range, whereas starch decomposition begins at 220°C [35, 37]. Gelatinization with water and heat treatment disrupt most of inter-macromolecular hydrogen bonds and reduces both the melting temperature (T_m) and T_g. At a high level of destructuring and low water content, plasticized starch, also called "thermoplastic starch" (TPS), is obtained, which is processed using conventional plastic processing equipment. At water content decreasing below 20 wt.%, T_m approaches the degradation temperature. To overcome this problem, plasticizers, like glycerol or other polyols, like sorbitol or poly(ethylene glycol) or their mixtures, are added to decrease both T_m and processing temperature. Other compounds can also be utilized like those containing nitrogen (urea, ammonium derived, amines) [35].

TPS exhibits reduced crystallinity, composed of residual crystallinity from the native state (A, B, and C types) and processing-induced crystallinity, the latter influenced by processing parameters. During processing, amylose single helices recrystallize into crystals with orthorhombic or hexagonal unit cells (V and E types) with different levels of hydration [38].

Being dependent on its formulation, TPS thermal and mechanical properties can vary in a wide range. T_g of TPS is between −50 and 110°C, and its elastic modulus can be similar to that of polyolefins [39]. For instance, TPS with 10 wt.% of glycerol and 10 wt.% of water exhibits T_g of 43°C and elastic modulus of 1,144 MPa, whereas for TPS with 35 wt.% of glycerol, the respective values are −20°C and 11 MPa [33]. However, after processing, TPS exhibits aging, which leads to increased brittleness and stiffness [35]. Below T_g it undergoes physical aging accompanied with densification, whereas above T_g retrogradation occurs with crystallinity increasing over time. Van Soest [38] proposed a complex mechanism of such post-processing crystallization, involving both amylose and amylopectin.

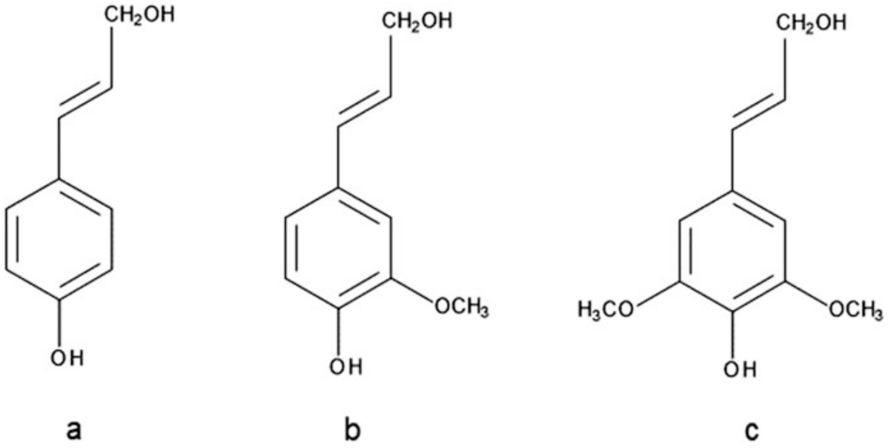
Although exhibiting water permeability, TPS is less permeable to oxygen than most polyesters. To alter its properties, starch can be chemically modified, for instance, by esterification. Moreover, to improve its mechanical performance, TPS was reinforced with various types of natural cellulose fibers, lignins, mineral microfillers, and nanofillers, like cellulose whiskers, starch nanocrystals, or nanoclays. The different starch-based formulations are suitable for a range of short-lived applications, for instance, packaging [40, 41]. However, starch is still mostly used in paper, cardboard, cosmetics, pharmaceuticals, and paints [7].

4 Lignin

The second most abundant natural polymer in plant biomass is lignin – the main renewable source of aromatic structures on Earth. It is found in plant cell walls and binds cells together imparting rigidity and impact resistance. Lignin is amorphous, relatively hydrophobic, and rich in aromatic units. It is a complex cross-linked phenolic polymer built of heterogeneous phenylpropane units, so-called monolignols, p-coumaryl (p-hydroxyphenyl), coniferyl, and sinapyl alkohols (Scheme 3), differing by the degree of substitution by methoxyl groups on the aromatic ring. The structure of lignin depends on its source and is a product of radical polymerization of monolignols, which results in a variety of inter-unit linkages [42]. The proportions of the three monoligols determine the type of inter-unit bonds, which is decisive for the degree of branching and also reactivity [42–45]. Softwood lignins are almost entirely built of coniferyl units, hardwood lignin of coniferyl and sinapyl units, and grass lignins of all three types [42]. Lignin decomposes slower than cellulose and in a broader temperature range, 200–500°C [46].

Traditionally, lignin is obtained as a by-product of cellulose in the paper production. The main lignin derivatives are kraft lignins, lignosulfates, soda lignins, and organosolv lignins.

Lignin has rather low added-value applications, primary as biofuel, and only 1–2% is used for more demanding applications, although the high carbon content makes it an interesting precursor for all kinds of carbon materials, including carbon fibers. Promising opportunities are also in the field of adsorbing materials [42]. Lignin phenol groups are well-known antioxidants acting as hydrogen donors [47, 48]. Moreover, different possibilities have been investigated to blend unmodified lignins with other polymers [42, 49], although they are chemically modified to increase their potential applications in polymeric materials. In addition



Scheme 3 Monolignols: (**a**) p-coumaryl alcohol, (**b**) coniferyl alcohol, and (**c**) sinapyl alcohol

to molar mass and functionality, T_g of lignin is of importance for its properties. Depending on lignin source and processing, its T_g varies in a broad temperature range, 113–174°C [49].

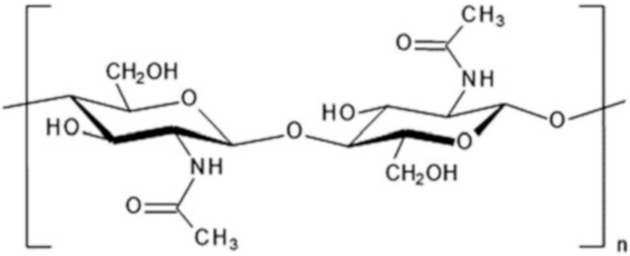
Lignin nano- and microstructures include aerogels, functionalized lignin beads, nanoparticles, and also lignin-based micro- and nanocapsules for encapsulation [42].

Due to their chemical structure, lignins are a potential source of renewable phenolic groups to replace phenol in thermoset resins, such as phenol-formaldehyde resins, and also as a source of hydroxyl groups to react with diisocyanates to form polyurethanes (PUs) [42]. The synthesis and properties of thermosets and thermoplastic polymers obtained from biobased aromatic compounds potentially derived from lignins were recently reviewed [10].

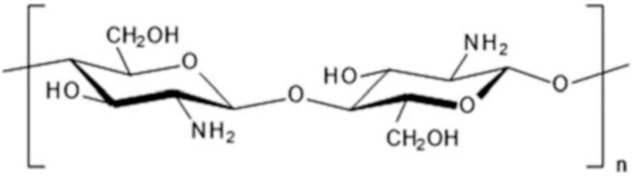
5 Chitin and Chitosan

Chitin is an abundant natural amino polysaccharide mainly present in the exoskeleton and internal structure of invertebrates. It is a biodegradable polymer of N-acetylglucosamine (2-acetamido-2-deoxy-β-D-glucopyranose) units linked with β(1 → 4) glycosidic bonds [9, 50, 51] (Scheme 4), although some of the glucopyranose residues are in the deacetylated form, as 2-amino-2-deoxy-β-D-glucopyranose.

The potential applications of chitin are related to its crystalline structure and thermal properties [51, 52]. Natural chitin forms ordered crystalline microfibrils [9, 53]. As a result of the differences in the inter- and intra-molecular hydrogen bonds in the structure, natural chitin occurs in three crystalline forms: α-, β-, and γ-chitin [54–56]. Chains in the α-chitin and the β-chitin are aligned antiparallel and parallel, respectively [57–59]. The γ-chitin is a combination of the α- and β-chitin [60], although it was also claimed to be a different form of the α-crystals [9, 61]. Chitin is highly hydrophobic and insoluble in water and most organic solvents [51, 62]. T_g of chitin is very high. It was estimated to be at 236°C [63], although recently a value of 165°C for Antarctic krill chitin was reported [54]. The weight-average molar mass of chitin is 10^3–2.5×10^3 kg/mol, but the deacetylation decreases it to 5×10^2 kg/mol [9]. On an industrial scale, chitin and chitosan are



Scheme 4 Repeating unit of chitin, polymer of N-acetylglucosamine (2-acetamido-2-deoxy-β-D-glucopyranose) units linked with β (1 → 4) glycosidic bonds



Scheme 5 Chemical structure of polymer of 2-amino-2-deoxy-β-D-glucopyranose units linked with β(1 → 4) glycosidic bonds

derived from waste of shrimps, prawns, and crabs by chemical extraction based on demineralization by acid, deproteination by alkali, and finally deacetylation into chitosan [7]. It is also possible to produce chitin by enzymatic processes or fermentation, but these methods are not economically viable on a large scale [7, 64]. Chitosan is a deacetylated derivative of chitin, in which acetamide groups are replaced with amino groups as shown in Scheme 5. In fact, the degree of deacetylation (DD) usually ranges from 50 to 95%, and glucopyranose residues with amido and amino groups are present in the same chain.

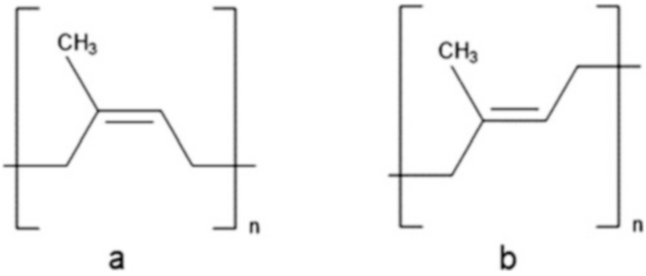
The presence of amino groups in chitosan modifies properties of this polymer compared with chitin. Chitosan is more soluble in diluted acids, and it can form complexes with metal ions, acids, and polyanions. Characteristics of films, fibers, and chitosan-based materials differ depending on their composition, solvents used for preparation, and conditions of formation. The physical properties of chitosan depend on its molar mass, DD, purity, and sequence of the amino and the acetamide groups [9, 65]. Chitosan is a semicrystalline polymer exhibiting polymorphism, described in detail in a recent review [66]. Orthorhombic unit cell was reported for hydrated chitosan (known also as tendon chitosan) from lobster or crab tendon (DD of 100%) and also for dehydrated chitosan, whereas films of chitosan obtained from solutions exhibited orthorhombic or monoclinic unit cells [66]. The orthorhombic polymorph of hydrated chitosan [67] is formed by chains in helical conformation with intramolecular hydrogen bonds, directed parallel to the b axis. The neighboring chains are antiparallel and connected by hydrogen bonds. Water molecules, one per polymer repeating unit, form interlayers between the chains and contribute to stability of the structure linking the chains through hydrogen bonds. The transformation to anhydrous form by removing the stabilizing water molecules occurs above 200°C due to destabilization of hydrogen bonds [68]. Motions of chains to the regions previously inhabited by water molecules result in the decrease of orthorhombic unit cell parameters, a and especially b, which is reduced by half [66]. T_g of amorphous phase of chitosan (DD 96%) was found at 203°C [69].

Owing to the presence of reactive amino side groups, a variety of beneficial chitosan derivatives can be created, as described in [9]. The advantages of chitosan include not only biodegradability, biocompatibility, and bioactivity, including antimicrobial activity, but also chemical inertness, low toxicity, high mechanical strength, good film-forming properties, and low cost [7]. Pharmaceutical and biomedical applications include treating burns, tissue engineering, preparation of artificial skin, contact lenses, artificial blood vessels and blood dialysis membranes, dental therapy, and also gene and drug delivery [9]. It is also applied in cosmetic products for hair and skin care [70]. In agriculture chitosan is used as a coating fertilizer and fungicide [71, 72]. Water engineering takes advantage of its adsorbing ability to recover different elements and compounds from wastewater [9]. Chitosan is also applied in the food industry as a preservative and an antioxidant, and emulsifying as well as stabilizing and thickening additive, and also to reduce lipid adsorption [9].

6 Natural Rubber

Natural rubber (NR), also called India rubber or caoutchouc, is the most abundantly used biopolymer, together with cellulose and starch, because of its valuable characteristics combining very large elastic strain with high tensile strength and crack growth resistance. It is the most important raw material used in the production of elastomers. Although more than 2 500 plant species are known to produce NR, currently, the tropical *Hevea brasiliensis* is its main commercial source (99% of the world market) [73–75]. NR latex is collected from the trunks, coagulated, and dried. Dried NR consists mainly of poly(1,4-cis-isoprene) (Scheme 6) with a molar mass of 10^2–10^3 kg/mol and contains a few percent of other substances, such as proteins, fatty acids, resins, and inorganic materials [73–77].

NR obtained from the *Hevea* species contains two trans-isoprene units in the terminal region of the macromolecule followed by several hundred to a few thousand cis-isoprene units and long-chain fatty acid groups linked to the rubber molecule through phospholipids [74–76]. The Guayule rubber of *Parthenium argentatum* (1% of the world market) [75] is important because of its hypoallergenic properties as it does not contain proteins causing allergy. Only a few species synthesize poly (1,4-trans-isoprene) (Scheme 6), a structural isomer that has similar but not identical properties [75, 76].



Scheme 6 Repeating unit of (**a**) poly(1,4-cis-isoprene) and (**b**) poly(1,4-trans-isoprene)

Macromolecules of NR are long, flexible, and practically linear. T_g of NR is near $-70°C$, whereas maximum crystallization rate is approx. at $-25°C$ [78–80]. Various lattice parameters for either monoclinic or orthorhombic structure of NR crystals were proposed with the value of β angle being the only difference between these two systems [79]. The outstanding properties of NR are partly attributed to its strain-induced crystallization (SIC) as the strain-induced crystallites are supposed to slow down, deviate, and even stop crack growth [81]. The SIC of NR was reviewed recently in [78]. When stretch ratio exceeds four, SIC starts almost instantaneously and can continue for days. The thus-formed crystallites are aligned in the stretching directions. Crystallization rate increases with the maximum stretch ratio. SIC is accompanied by a stress decrease due to the relaxation of amorphous chains. SIC of NR is not very sensitive to a strain rate, although its hardening effect decreases at very small strain rates $<10^{-3}$/s. Moreover, SIC diminishes with temperature increase and disappears above 80°C [79].

In 1839, Goodyear empirically discovered the vulcanization of NR with sulfur, which could dramatically improve properties. During the vulcanization, the macromolecules are cross-linked by bridges containing one to several sulfur atoms; the number of atoms in the cross-link strongly affects the physical properties of the final material. Although NR can be vulcanized also with organic peroxides or radiation [82], those vulcanized NRs exhibit worse long-term stability because the polymer chains are cross-linked solely by carbon bonds [74]. The basic vulcanizing ingredients include not only vulcanizing agents but also accelerators, activators, antidegradants, fillers such as carbon black, and processing aids [73].

The ability of NR to crystallize is not affected by vulcanization [79]. The diffraction patterns of vulcanized and unvulcanized NR are very similar, and the crystal structure is not changed in NR vulcanizates containing carbon black fillers [83, 84]. The influence of cross-linking and carbon black fillers on SIC of NR is addressed in [7]. In general, the number of crystallites increases, whereas their size decreases with increasing cross-link density. There exists an intermediate cross-link density, at which the volume crystallinity reaches a maximum value. However, the stretch ratio inducing the onset of SIC is roughly independent of the cross-link density. Contrary to that, carbon black fillers decrease macroscopic stretch ratio inducing SIC because they enhance the local stretch [79].

Nowadays numerous applications of rubbers take advantage of their flexibility, relative gas impermeability, resistance to water and most chemicals, as well as electrical resistance. Besides NR, various types of synthetic rubber are produced: polyisoprene, styrene-butadiene rubber, acrylonitrile-butadiene copolymers, ethylene-vinyl chloride copolymers, polybutadiene, and polychloroprene [73, 75]. Nevertheless, about 40% of rubber is of natural origin, and most of NR (75%) is used for automobile tires [73, 75, 76]. It is worth noting that the so-called isoprene rubber (IR) is a polymer with molecular structure similar to NR, with predominant cis-isoprene units bonded by 1,4-linkages although it can contain up to 10% trans-isoprene units [73].

Biodegradation of NR was recently reviewed, e.g., in [73, 75, 76]. It can be degraded by bacteria and fungi although the process is slow. Examination of the biodegradation products of NR and synthetic rubbers indicates oxidative cleavage of the double bond in the polymer backbone [75, 76]. Degradation of vulcanized rubber by microorganisms is also possible, although more difficult due to cross-linked structure, and is also influenced by additives present in the rubber [73, 75].

7 Other Natural Polymers

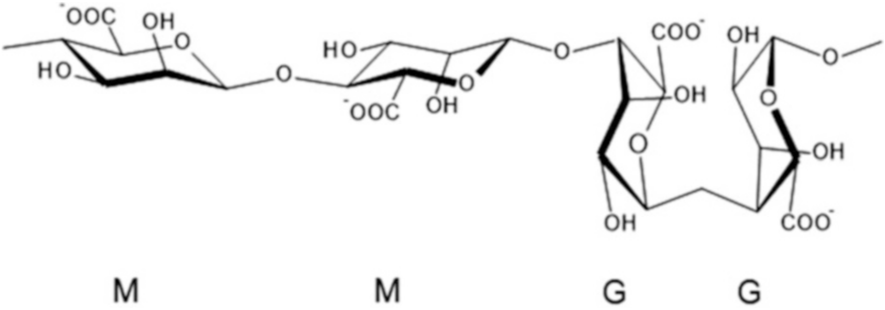
7.1 Collagen

Collagen, insoluble and fibrous, is the most abundant protein present in connective tissue and extracellular matrix in the animal kingdom. Although 27 different types of collagen have been identified, type I prevails in the connective tissue. Collagen macromolecules are composed of three α-chains forming the triple helix mainly stabilized by intra- and inter-chain hydrogen bonds [85]. The sources of collagen for industrial purposes are pig skin, bovine hide, and pork and cattle bones, although the use of non-mammal collagen increases in importance [7, 85]. Biocompatibility, biodegradability, and weak antigenicity [86] make collagen a very useful biomaterial, applied for drug delivery and tissue engineering [87]. Chemical pretreatment and warm-water extraction of collagen permits to obtain gelatin [85], which applications take advantage of its gel-forming ability, mainly in the food industry. It is worth noting that a range of applications of gelatin broadens with increasing tendency to use natural substances and includes also foaming, emulsifying, and stabilizing agents, as well as microencapsulating and biodegradable film-forming materials [7, 85].

7.2 Alginates

Alginates, linear polysaccharides, are anionic heterogeneous copolymers built of blocks of (1 → 4) linked α-L-guluronate (G) and β-D-mannuronate (M) residues (Scheme 7) and also blocks comprising alternating GM residues. They are synthesized by bacteria, for instance, *Azotobacter* and *Pseudomonas*, and brown algae [88]. Alginates are mainly obtained by alkali solution treatment of algae, although bacterial biosynthesis may be a source of these polymers with more defined chemical structures and physical properties than the alga-derived alginates. Commercially available are sodium alginates [88].

The content and length of G and M blocks, as well as molar mass, vary depending on the source of extraction. These factors are responsible for properties of alginates and alginate-based hydrogels [89]. Only the G-blocks participate in intermolecular cross-linking with divalent cations resulting in the formation of hydrogels [88]. The mechanical properties of alginate gels are enhanced by increasing the G-block length and molar mass. Molar mass of commercial alginates ranges from 32 to 400 kg/mol.



Scheme 7 MMGG sequence of alginate

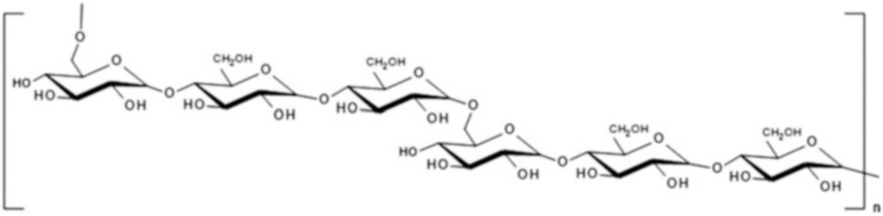
However, solutions of high molar mass alginates polymer are highly viscous, which is often a disadvantage for processing [90]. Upon heating alginates decompose, alginic acid above 150°C, whereas sodium alginate above 175°C [91]. Nowadays, more than 200 different alginates are produced with different chemical structures. Alginates have some unique properties such as non-toxicity, biocompatibility, biodegradability, and hydrophilicity and have a relatively low cost. They are used as viscosifiers and stabilizing, gel-forming, film-forming, and water-binding agents in various industrial applications [7]. Owing to their biocompatibility and good gelation ability, alginates are attractive for pharmaceutical and food applications [92].

Alginates are typically used in biomedicine in hydrogels, that is, cross-linked three-dimensional networks built of hydrophilic polymers with high water content. The most common method to prepare alginate-based hydrogels is to combine an aqueous alginate solution with ionic cross-linking agents, such as divalent cations, for instance, Ca^{2+} from $CaCl_2$. They bind to G-blocks and connect the G-blocks of neighboring alginate chains. Another way is covalent cross-linking, interesting because of its inability to dissociate. However, unreacted reagents, if toxic, have to be removed from the gels [89]. The other possible ways, being explored, are thermal gelation and cell cross-linking [93, 94].

7.3 Pullulan

Pullulan, first isolated in 1958 [95], is a linear polysaccharide, with structure being a succession of α(1 → 6)-connected (1 → 4)-α-D-triglucosides, i.e., maltotrioses (Scheme 8).

Pullulan is produced extracellulary by a yeast-like fungus *Aureobasidium pullulans* and other microorganisms by fermentation of feedstocks containing sugars as an amorphous slime on the surface of microbial cells [96]. Owing to the presence of hydroxyl groups, it can be chemically modified to induce pH sensitivity by introducing functional reactive groups, to decrease solubility in water or to obtain



Scheme 8 Structure of pullulan repeating unit: two maltotrioses linked with α(1 → 6) bond

water-insoluble polymer [7]. Pullulan can be molded into articles with transparency, strength, and toughness [97] similar to those made of conventional polymers such as polystyrene. Although pullulan is brittle, it is odorless and tasteless and exhibits good moisture retention and barrier property for oxygen. Owing to these features, it is an interesting material for food preservation [98]. Its commercial and industrial applications include healthcare, pharmaceutical, food, and cosmetic industries and even lithography. In recent years, pullulan has also been examined for various biomedical applications [99].

7.4 *Pectin*

Pectins, known also as pectin polysaccharides, are a group of hetero-polysaccharides abundant in cell walls of terrestrial plants. Pectin macromolecule is very complex as it can be composed of 17 different monosaccharides containing more than 20 different linkages [100]. However, all pectins are built of the same repeating units, although their amount and chemical structures differ, being dependent on pectin origin. Pectins mainly contain galacturonic acid residues, in which carboxyl groups are mostly esterified to methoxyl esters. In addition, in pectin macromolecule, certain amount of neutral sugars might be present as side chains [101]. Main applications of pectin polysaccharides are in the food industry, primarily as gelling, stabilizing, or thickening agents. Most of the pectin used in food products is obtained from citrus peel and apple pomace [100].

7.5 *Galactomannan*

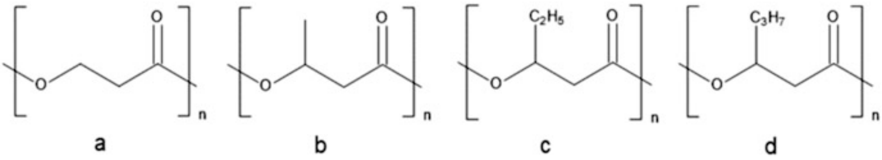
Galactomannans are natural polysaccharides having β-(1–4)-D-mannan backbone with single α-(1–6)-linked D-galactose branches [102], which are able to form stable viscous solutions in water. The main sources of those polysaccharides are locust bean gum, guar, tara plant, and fenugreek [103]. The physicochemical properties of galactomannans depend to a great extent on the mannose/galactose ratio (M/G) and on the distribution of D-galactose groups along the main chain. For instance, the galactomannans with M/G from 1.3 to 5.6 exhibited T_g ranging from −70 to −65°C, tensile strength from 1.4 to 6.9 MPa, and elongation at break of 37–70% [104]. The structural features responsible for properties are related to galactomannan origin and extraction method used [104, 105]. Their capability to moisture retention as well as thickening, binding, gelling, emulsifying, suspending, and film-forming ability makes galactomannans useful in food, paper, textile, pharmaceutical, biomedical, and cosmetics industries [106].

8 Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHAs) are thermoplastic semicrystalline polyesters of 3-, 4-, 5-, and 6-hydroxyalkanoic acids, which are synthesized by microorganisms, and are materials with a potential to replace conventional fossil-hydrocarbon-based polymers. PHAs are biocompatible and biodegradable; it is worth noting that they are able to biodegrade in the environment [107, 108]. More than 150 PHA monomers have been identified [109]. The repeating unit of PHA polymers is –O–CHR–$(CH_2)_m$–CO–. For $m = 1$ and R being hydrogen, methyl, ethyl, propyl group the polymer is called poly(3-hydroxypropionate), poly(3-hydroxybutyrate) (P3HB), poly(3-hydroxyvalerate) (P3HV), poly (3-hydroxyhexanoate), respectively. Examples of PHAs structure are shown in Scheme 9.

Depending on the number of carbon atoms in the repeating unit, PHAs are classified as short-chain-length (scl-PHA), medium-chain-length (mcl-PHA), and long-chain-length (lcl-PHA) with up to 5, 6–14, or more than 14 carbon atoms, respectively, the latter uncommon and least studied. P3HB and P3HV are scl-PHA, whereas mcl-PHA include poly(3-hydroxyhexanoate), poly(3-hydroxyoctanoate), and poly(3-hydroxydecanoate). Due to the presence of chiral carbon atom in the repeating unit, PHA polymers can exhibit different chirality, but naturally obtained PHAs are stereospecific with the carbons in the backbone in the R configuration. The first discovered PHA was P3HB. The French scientist Lemoigne extracted it from *Bacillus megaterium* in 1927 [110].

Microorganisms synthesize PHA for energy storage in the form of granular submicron inclusions, with the average size approx. 0.2–0.5 μm. To collect PHA it is necessary to destroy the bacterial cell and remove the protein layer on the granules. PHA production involves synthesis of the polymer by bacteria, requiring minimum



Scheme 9 Repeating units of (**a**) poly(3-hydroxypropionate), (**b**) poly(3-hydroxybutyrate), (**c**) poly(3-hydroxyvalerate), and (**d**) poly (3-hydroxyhexanoate)

of 48 h, followed by its isolation and purification. Depending on the PHA required, feedstocks include cellulosics, sugars, starch, alcohols, vegetable and other plant oils, fatty acids, organic waste, and even municipal solid waste [7, 111]. The recovery methods for the isolation and purification of PHA from the cells were recently reviewed in [112]. The methods include solvent extraction, mechanical disruption, and chemical and enzymatic digestion. Research on PHA production and optimization was recently reviewed in [113]; the academic studies focused on seeking cost-efficient carbon sources and also on improving productivity by genetic engineering. More than 300 different microorganisms synthesize PHAs, but only a few are sufficiently effective for large-scale production [113]. Some bacteria are able to synthesize PHA as much as 90 wt.% of dry cells when the feedstock is depleted of essential nutrients such as nitrogen, phosphorus, or magnesium [113, 114]. Different PHAs are produced by different bacteria. Typically, copolymers of 3-hydroxybutyrate with other comonomers contain 80–95% of the first comonomer [7]. The molar mass of PHAs depends on the type of microorganism and its growth conditions and may range from 200 to 3,000 kg/mol [114].

In general, PHAs are insoluble in water and relatively resistant to hydrolysis. They exhibit good resistance to UV but poor to acids and bases [115]. PHAs are thermoplastics with T_g from −50 to 4°C and T_m from 40 to 180°C [7, 111]. Similarly to T_g and T_m, other features of PHAs like thermodegradation temperature, crystallinity, mechanical properties, and barrier properties for vapor and oxygen depend on their chemical structure [115]. Exemplary mechanical and thermal properties of PHAs are shown in Table 1. P3HB is brittle, with tensile strength of 30–40 MPa, and elongation at break of a few percent. T_m of P3HB is high, near 177°C [108, 116, 117]. P3HB crystallizes from melt in the orthorhombic α-form, whereas metastable

Table 1 Examples of thermal and mechanical properties of biodegradable biobased polyesters

Polymer	Glass transition temperature (°C)	Melting temperature (°C)	Tensile strength (MPa)	Tensile strain at break (%)	Tensile modulus (MPa)	References
P3HB	10	177	40	4	3,500	[113]
	5–9	173–180	40	3–8	3,500–4,000	[116]
PHBV						
(15.5)	−1	140	34	12	2,500	[117]
(20.1)	−5	114	26	27	1,900	[117]
(24)	−6	138	Nr	Nr	Nr	[137]
(25)	Nr	Nr	70	30	1,370	[137]
(28.4)	−8	102	30	700	1,400	[117]
PBS	−32	114	62–59	660–710	470–540	[126]
	−32	115	31	24	337	[129]
PLA	59	154	56	13	3,740	[168]
	55	165	59	7	3,500	[169]

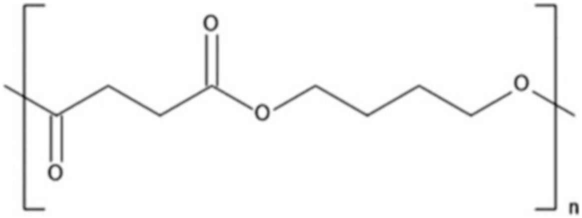
Numbers in brackets indicate mol% content of 3HV in PHBV. *Nr* not reported orthorhombic β-form is strain-induced [117]. Crystallization from melt is slow, in the form of large spherulites, whose size can be decreased using nucleating agents. A relatively low thermal decomposition temperature of PH3B is also a problem as well as ageing at room temperature [115]. To overcome those disadvantages, research efforts focused on finding effective nucleating agents and plasticizers to shorten crystallization, to improve flexibility and drawability, and to reduce T_m. Also biosynthesized copolymers of 3-hydroxybutyrate with other hydroxyalkanoate comonomers can exhibit improved mechanical performance and decreased T_m, which permits to avoid degradation during processing. For instance, copolymers of 3-hydroxybutyrate and 3-hydroxyvalerate (PHBV) are less crystalline, less stiff, and brittle and can exhibit increased tensile strength and toughness compared to P3HB [113, 116], as exemplified in Table 1, although their properties and structure are related to their chemical composition. Moreover, PHBV melt viscosity is higher, which is advantageous for extrusion and blow molding. Nowadays, besides P3HB, PHBV, and poly(4-hydroxybutyrate) (P4HB), copolymers of 3-hydroxybutyrate and 4-hydroxybutyrate, as well as copolymers of 3-hydroxybutyrate and 3-hydroxyhexanoate, are produced on a large scale [117, 118]. It is worth noting that also modification by blending with other biodegradable polymers and fillers, including those based on cellulose and lignin, can modify PHAs [115–117, 119, 120]. Moreover, different methods such as epoxidation, carboxylation, chlorination, hydroxylation, and pyrolysis were used to alter the properties [121]. PHA applications include biomedical uses (drug delivery, development of scaffolds, implants, and biosensors) but also food coating, paper coating, packing, agriculture, molded goods, non-wovens, fabrics and other textiles, performance additives [108, 121]. Owing to PHA biocompatibility and biodegradability, their medical uses were recently extensively investigated [122].

9 Poly(Butylene Succinate)

Poly(butylene succinate) (PBS) is a thermoplastic polyester synthesized from succinic acid (SA) and 1,4-butanediol (BDO), named also as poly(tetramethylene succinate), with chemical structure shown in Scheme 10.

SA is obtained through hydrogenation of maleic anhydride, derived from oxidation of butane or benzene, followed by hydration. However, SA can be also

Scheme 10 Repeating unit of poly(butylene succinate)



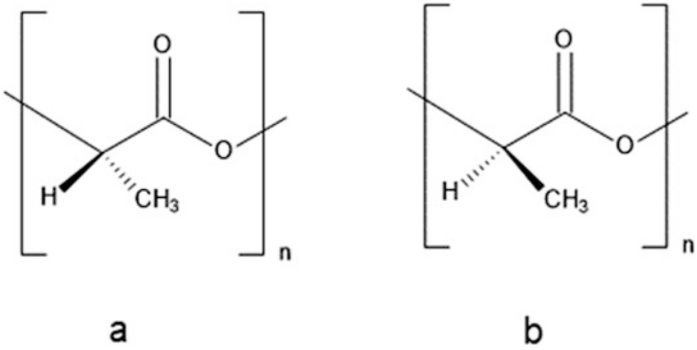
produced by bacterial fermentation of renewable feedstock, like starch or glucose. Several bacterial strains are able to produce SA [123]. BDO can be obtained via different chemical processes but also by catalytic reduction of purified SA, obtained by fermentation of corn-derived glucose [124, 125]. In addition, genetically modified *Escherichia coli* is able to ferment sugar into BDO [124]. Synthesis of PBS involves esterification of SA and BDO or transesterification of dimethyl succinate and BDO to obtain oligomers, which are subjected to polycondensation yielding high molar mass PBS [126].

PBS is a semicrystalline polymer with crystallinity level of 35–45 wt.% [126, 127], although higher values were also reported, 65 wt.% for raw PBS, and nearly 72 wt.% for extruded fibers [128]. Exemplary properties of PBS are shown in Table 1. T_m of PBS is near 115°C, heat distortion temperature near 95°C, and T_g below −30°C [124, 126, 129]. Crystallization of PBS occurs in the monoclinic α-form [130, 131]. The transition of α-form to monoclinic β-form occurs reversibly upon stress application and removal [132, 133]. In both polymorphs hydrogen bonds were revealed by Raman spectroscopy [134]. Crystallization of PBS from the melt is spherulitic, and its temperature depends on a cooling rate; a decrease of crystallization peak temperature from 80°C at 5°C/min to 62°C at 25°C/min was reported [135]. PBS is featured by good thermal stability; significant weight loss during TGA experiment occurs above 300°C [136, 137]. PBS exhibits similar mechanical properties to polyethylene. Its elastic modulus is approx. 0.4–0.5 GPa, and it can exhibit relatively high tensile strength and large elongation at break, as shown in Table 1. PBS is hydrophilic but insoluble in water. PBS can be processed using extrusion, injection molding, and thermoforming [126]. To tailor physical properties, random copolymerization with different types of comonomer units has been studied, including adipic, terephthalic, methyl succinic, 2,2-dimetyl succinic and benzyl succinic acids, ethylene glycol, and 1,3-propanediol [124]. It is also worth noting that PBS and its copolymers are biodegradable in soil, water, and compost, also in lipase solution and activated sludge [124].

Linear structure of PBS may result in low melt strength and viscosity, which might be disadvantageous during processing, for instance, foaming; chain extenders and also branching enable to overcome this drawback [138]. Improvement of PBS properties can be also achieved by modification with other biodegradable polymers [7, 124, 139–142], fillers, and nanofillers [140, 143–147]. PBS and its blends have found commercial uses in many fields like agriculture, fishery, forestry, and construction, for instance, as mulch film, packaging, foaming, and flushable hygiene products [7]. The biomedical applications of PBS were recently reviewed in [126].

10 Polylactide

The most promising biobased polyester for replacement of conventional thermoplastics is polylactide (PLA), termed also as poly(lactic acid). The repeating unit of polylactide is $CHCH_3$–CO–O– (Scheme 11).



Scheme 11 Repeating units of (**a**) poly(L-lactide) and (**b**) poly(D-lactide)

PLA can be synthesized through polycondensation of lactic acid (2-hydroxypropanoic acid), which results in polymer with secondary alcohol and carboxylic end groups. Depolymerization of lactic acid oligomers leads to cyclic dimers of lactic acid called lactide (LA). Ring-opening polymerization (ROP) of LA permits to obtain PLA with secondary alcohol and ester end groups, and allows to reach high molar mass [148, 149]. In industrial processes, the latter method of synthesis is mostly used. Lactic acid can be obtained through fermentation of hexoses by a group of lactic acid bacteria, other bacteria, fungi, or yeasts. Sugarcane, beet, and corn have been used for industrial production of lactic acid. However, there is a growing demand for low-cost and non-food sources for production, including starchy wastes, molasses, and lignocellulose [150].

Lactic acid is optically active, and lactic acid bacteria can produce either or both L and D (S and R) stereoisomers [148, 150]. This results in a diversity of chemical structures of PLAs, which can be optically pure poly(L-lactide) (PLLA) or poly(D-lactide) (PDLA), or copolymers containing repeating units of both chiralities [151].

Rheological properties of PLA melt were recently reviewed in [152]. PLA can be cooled to the glassy state without crystallization; in this way wholly amorphous glassy material is obtained [153, 154]. Examples of thermal and mechanical properties of amorphous PLA are shown in Table 1. T_g of amorphous PLLA and PDLA with high molar mass is similar, at around 60°C [153]. Both the enantiomeric composition of PLA and its molar mass influence T_g. T_g increases with increasing molar mass in accordance with the Flory-Fox equation and becomes nearly constant for PLA with molar mass exceeding 100 kg/mol [153, 154]. The presence of comonomers of different chirality decreases T_g; for a copolymer with equal contents of L-lactide and D-lactide, T_g decreases by about 10°C [154].

Crystallization and crystal structures of PLA were recently a subject of extensive reviews [154–157]. Ability of PLA to crystallize strongly depends in its enantiomeric composition. Optically pure PDLA and PLLA exhibit the best ability to crystallize reflected in the fastest spherulite growth rate and high crystallinity, even 60–70 wt.% [154, 156], although dependent on crystallization conditions and molar mass. Also T_m of optically pure PLA is higher, up to approx. 180°C. The presence of comonomers of different chirality decreases the spherulite growth rate, diminishes crystallinity, and lowers T_m; the highest the content, the stronger the decrease [154]. For the copolymers, T_m decreases linearly with increasing minor fraction content; at 10% content T_m can be lowered even by approx. 25 K. T_m of PLA increases with increasing molar mass but levels off for molar masses above 50 kg/mol [154]. The crystallization is spherulitic. The spherulite growth rate dependence on temperature is bell-shaped with a maximum in the 115–130°C range [154]. However, an additional maximum is visible near 110°C, as the plot diverges from the typical bell-shaped curve below 120°C [158], which is most possibly related to crystallization in a different crystallographic modification. The orthorhombic phase of PLA crystallizes in two variants: the ordered α-phase (termed also as the δ-phase) and the less ordered α′-phase that form at high and at low crystallization temperature, respectively [157, 159, 160]. It was observed [157] that the α-form crystallized at 120°C and above, the α′-form below 100°C, whereas both modifications formed in the intermediate temperature range. The orthorhombic γ-phase was found in PLLA crystallized epitaxially on hexamethylbenzene [157, 161]. The frustrated trigonal β-phase of PLLA was first observed in stretched fibers, but recently also in thin films [157]. Moreover, the mesophase formed during strain-induced crystallization of PLA [162].

In semi-crystalline PLLA, two distinct mobile amorphous fractions exist: a bulk-like totally mobile fraction and a slightly constrained mobile fraction, which vitrify/devitrify in the region of the bulk T_g, whereas at the crystal–amorphous interface, a rigid amorphous fraction is located, which vitrifies/devitrifies above the bulk T_g [153, 163]. The thermal properties of PLLA were extensively described in recent reviews [153, 154]. Because of slow crystallization, cooling of PLA, even optically pure, may result in fully amorphous glass, which can cold-crystallize above T_g during subsequent heating. The crystallinity developed during cooling and/or heating depends on molecular characteristics of PLA, cooling rate and/or heating rate, and thermomechanical history. Shearing of PLA melt can induce crystallization during cooling even in slowly crystallizing PLA containing a significant fraction of D-lactide [164]. The enantiomeric PDLA and PLLA form stereocomplex (scPLA) due to weak multicentered hydrogen bonds [165, 166], which significantly improves PLA properties [5, 167]. T_m of scPLA is in the range of 220–230°C.

Barrier properties of PLA have been recently reviewed in [152]. Oxygen permeability of PLA, 1.3–2 $\times$ 10^{-18} m^3 $m/(m^2$ s Pa) at 30°C, is similar to that of polystyrene but higher than in the case of poly(ethylene terephthalate). However, the barrier property of PLA for water vapor is worse than that of many polymers including polyolefins, PS polystyrene, poly(ethylene terephthalate), and PHBV.

Owing to its T_g, amorphous PLA is stiff and brittle at room temperature, with modulus of elasticity of about 3.5 GPa, yield strength near 60 MPa, and strain at break of few percent [152, 168, 169]. Examples of tensile properties of amorphous PLA are given in Table 1. In the amorphous PLA, crazing and shear banding are observed during drawing. Crystallinity increases the modulus but further decreases the strain at break; specimens frequently fracture before the yield. For instance, PLA with 43 wt.% of crystallinity fractured during tensile test before the yield at the stress of 43 MPa and strain of 6%, and exhibited the modulus of 4,250 MPa [168]. With increasing temperature the drawability of PLA improves. Strain-induced crystallization during tensile drawing leads to the formation of the mesophase or α′-crystals, depending on temperature and strain rate [162].

Recently star-shaped polymers attract increasing attention. The syntheses, properties, and selected applications of star-shaped polymers with arms composed of homo- or copolymers of polylactide were recently reviewed [170]. Crystallization of 6-arm PLLAs with high molar mas was compared with their linear counterparts in [171].

After their service life, PLA products can degrade in compost under appropriate conditions via hydrolysis and enzymatic biodegradation. The hydrolytic degradation is the most important stage of biodegradation. Degradation processes occurring during processing and also in compost are comprehensively reviewed in [172].

In order to improve properties of PLA polymers, including crystallizability; mechanical performance; rheological, electrical, and barrier properties as well as stability and inflammability, various modification routes are applied, including copolymerization, chain extension, plasticization, and blending with other polymers, fillers, nanofillers, fibers, and nucleating agents [151, 152, 168, 173–181].

PLA is suitable for processing by various techniques, and nowadays PLA products are widely used, from biomedical applications to packaging, daily appliances including textiles, items used in agriculture and engineering, water treatment, car parts, electric appliances, etc. [7, 151].

11 Bio-polyethylene

Polyethylene (PE) is obtained by catalytic polymerization of ethylene under appropriate temperature and pressure conditions. Bio-PE is produced from bio-ethylene. Ethanol can be obtained by anaerobic fermentation of extracted sugarcane juice with high sucrose content and distilled to remove water and to yield azeotropic mixture of anhydrous ethanol. Although industrial-scale production is based on sugarcane, other feedstocks including sugar beet, starch crops, wood, and plant wastes can be also used. Bio-ethylene is obtained by dehydration of ethanol at high temperatures over a solid catalyst followed by polymerization [182, 183]. Bio-PE has the same properties as PE produced from petrochemical sources.

12 Bio-poly(Ethylene Terephthalate)

Poly(ethylene terephthalate) (PET) production is normally carried out through prepolymer synthesis which is mainly bis(2-hydroxyethyl) terephthalate (BHET) followed by polycondensation. The first step is the esterification of terephthalic acid

(TPA) and ethylene glycol (EG) or the transesterification of dimethyl terephthalate and EG. The synthesis of bio-PET requires biobased monomers. One of them, bio-EG, is obtained by oxidation of biobased ethylene or through hydrogenation of products of sugar pyrolysis [184]. Use of bio-EG allows to synthesize 30% biobased PET. Fully biobased PET can theoretically be produced from bio-EG and bio-TPA. Synthesis of the latter was recently reviewed in [5, 185]. Bio-TPA is a product of oxidation of *p*-xylene, resulting from cyclization of two molecules of isooctane, the latter obtained from iso-butanol produced by dehydration of sugars. Another way leading to bio-TPA is a series of reactions beginning with muconic acid produced by chemical processes and biorefinery; from the muconic acid, tetrahydroterephthalic acid is obtained and dehydrogenated to bio-TPA. Bio-TPA can also be produced from limonene-derived building blocks or from furan derivatives, especially the furan derivative such as 2,5-furandicarboxylic acid. In addition, fermentation of sugar and starches yield biobased 1,3-propane diol (bio-PDO) [186], which is used to produce biobased poly(trimethylene terephthalate) [187]. Development of the production of biobased butanediol will lead to biobased poly(butylene terephthalate) [188].

13 Bio-polyamides

Biobased polyamides (bio-PAs) include PA4, PA4.4, PA4.10, PA6.10, PA10.10, PA11, and PA12 [5, 189]. Some of them, for instance PA11 used for high-performance applications, synthesized from castor oil, are known for decades. Triglycerides in castor oils are subjected to a transesterification or a saponification to give ricinoleic acid or the corresponding methyl ester, respectively. Pyrolysis of the acid yields undecanoic acid and then 11-aminoundecanoic acid. Polycondensation of the latter with water extraction results in PA11. Another route of synthesis of bio-PAs utilizes sebacic acid derived from ricinoleic acid. PA6.10, PA10.10, and PA10.12 are polymerized from sebacic acid and hexamethylene diamine (HDMA) obtained petrochemically from butadiene. However, decamethylene diamine can be produced from bio-sebacic acid and used to synthesize bio-PAs. Besides polycondensation of dicarboxylic acids and diamines, another way of synthesis of PAs is ROP of lactams. Although starting materials to obtain bio-PAs by polycondensation are castor oil, fatty acids, carbohydrates, terpenes, and roisin acids, it is also possible to use terpenes and fatty acids to derive lactams and synthesize bio-PAs by ROP. Recent advances in biobased PAs and their synthesis are comprehensively reviewed in [189]. Properties of biobased and petrochemically obtained PAs are compared in [5]. Although bio-PAs occupy only 5% of the current biopolymer market, they are becoming increasingly important as they are applied as high-performance polymers [189].

14 Thermosetting Bio-materials

Thermosetting materials are highly cross-linked polymers that are cured at elevated temperature, also under elevated pressure, and/or by irradiation. Owing to their high cross-linking density, thermosets are high-performance materials featured by high elastic modulus, strength, durability, and resistance to thermal stresses and chemicals. The potential opportunities and drawbacks of the use of renewable feedstock in the design of some commonly used thermosets including phenolics, epoxy, polyester, and polyurethane resins were extensively reviewed in [190].

Phenolic resins, synthesized from phenol and formaldehyde, are widely applied because of superior mechanical strength, dimensional stability, heat and flame resistance, as well as high resistance against various solvents, acids, and water. Alternatively, hexamethylenetetramine can be used as a replacement for formaldehyde. A range of phenolic resins, more flexible than the conventional ones, can be obtained by reactions of cardanol with formaldehyde. The source of bio-cardanol is a cashew shell liquid, which is an agricultural by-product [190].

Owing to its structure and abundance, lignin is considered as a potential source of phenol for phenol-formaldehyde-based thermosets [10, 190]. However, because of steric hindrances, lignin reactivity with formaldehyde is limited, and in order to enhance it, lignin has to be chemically modified through acid hydrolysis and acetosolv and organosolv processes [191, 192]; recently environmentally friendly enzymatic approaches have been also developed [193]. Other raw bio-materials considered in the design of phenolic resins are tannins and pyrogallol derived from hydrolysable tannins.

Epoxy resins are formed from precursors having epoxy groups. The reaction between bisphenol A (2,2-bis(4′-hydroxyphenyl)propane) and epichlorohydrin, resulting in diglycidyl ether of bisphenol A (DGEBA), is a basis for nearly 90% of the world production of epoxy resins [190]. The so-called curing agents, reacting with epoxy groups, include amines, anhydrides, and amides; in some cases catalysts are required. To obtain bio-epoxy resins, epoxidized plant oils and fatty acids have been used [194, 195]. Depending on the oil type, the comonomers (divinylbenzene or styrene), and the stoichiometry, a range of thermosets, from elastomers to rigid materials, can be obtained by thermal or cationic copolymerization. Some of them are potentially (bio)degradable in soil. Moreover, the use of novel phosphorous-containing derivatives of fatty acids permitted to obtain epoxy thermosets with good flame-retardant properties [196]. Co-reactants (or hardeners) of natural origin are also expected to be valuable in epoxy thermosetting materials, for example, cis-9,10-epoxy-18-hydroxyoctadecanoic acid present in birch tree [197]. Another example is alcoholysis lignin that has been used as hard and hydrophilic segments in epoxy resins [198]. To reinforce oil plant-based epoxy resins, different inorganic or organic fillers were used, including glass, carbon, mineral fibers, and various nanofillers [190, 199–202].

An important class of versatile materials for flexible and rigid foams, and thermoplastics, with variety of applications, are polyurethanes (PUs). PUs, with marked contents of urethane groups, are obtained through reactions of various polyols and isocyanates, usually catalyzed with tin derivatives [203], which permits to alter the product properties. Biopitches, soy flours, and castor oil have directly been applied as raw polyols in synthesis of bio-PUs; while isocyanate is mainly petroleum-based, recent development in biotechnology should allow to obtain biobased isocyanate compounds in the near future [190]. Among other renewable resources, plant oils, other than castor oil, have a potential to be a source of polyols for polyurethanes [204]. Other ways were also explored, for instance, oxypropylation of natural cork [205] or the use of cardanol derivatives [206].

Polycondensation of a polyol and a polyvalent acid or acid anhydride yields unsaturated polyester resins, which can be cured in the presence of unsaturated monomers, for instance, styrene. Acid anhydrides, phthalic or maleic anhydrides, are usually used, while polyols are (di)pentaerythritol, glycerol, ethylene glycol, trimethylolpropane, and neopentylglycol [207]. Polyester resins are used in decorative coating and also composites having a broad range of applications. In the design of bio-polyester resins, isosorbide, sorbitol derivative obtained from starch, can be used as a polyol, whereas fatty acids or oils are used as polyacids [190]. The design of polyester thermosetting resins was reviewed recently in [208].

15 Other Polymers

It must be noted that besides the biobased polymers described above, there are others being studied and developed. Biodegradable poly(ethylene succinate) is synthesized from SA and EG and could also be produced from biobased substrates [5]. Owing to the good barrier properties for oxygen, and elongation, it can be used in film applications. Other succinic polymers include copolymers of SA and other dicarboxylic acids, such as poly(butylene succinate-co-butylene adipate), poly(butylene succinate-co-butylene terephthalate), and poly(butylene succinate-co-butylene furandicarboxylate) [209–211] with relatively long aliphatic sequences, suitable for packaging applications. As mentioned above, bio-PDO is used to produce biobased poly(trimethylene terephthalate), and it is envisaged that biobased poly (butylene terephthalate) will also be available [5]. Other examples are biobased poly (ethylene 2,5-furandicarboxylate), with high oxygen barrier properties, and terpene-derived polymers [5, 212]. Synthesis of biobased poly(ether-ether-ketone) was also described [213]. Performance of certain recently developed biobased polymers can surpass that of conventional fossil-based materials; for instance, biobased liquid crystalline polymer derived from natural phenol, 4-hydrocinnamic acid, exhibits the mechanical strength of 63 MPa and elastic modulus of 16 GPa, and high softening temperature [214, 215]. Superstrong transparent bio-PAs with phenylenecyclobutane repeating backbone [216] and esters of poly(α-glucan) [217, 218] with outstanding thermal properties were recently reported.

16 Concluding Remarks

In the review biobased polymers were described including natural polymers, bio-engineered polymers produced by microorganisms, and those synthesized from biobased monomers. The increasing interest in biobased polymers is driven by awareness of environmental issues, that is, struggle with carbon dioxide emissions causing global warming and with still increasing dependence on fossil resources. However, it must be remembered that production of plastics consumes only a few percent of oil, whereas the rest is mainly used for fuels and asphalt. It is important that many biobased polymers are able to degrade in the environment or in compost, which is helpful in solving the plastic waste problem. It must be noted, however, that biodegradation results in irreversible loss of material, which otherwise could be re-used through recycling or burn to recover energy. Moreover, although biodegradability in the environment or compost can be helpful in decreasing the impact of the plastic waste on the environment, it is not always desirable, for instance, in the case of applications demanding durability in water or soil.

Naturally occurring polymers are abundant and can be directly used, but they are not versatile, and bio-engineered polymers also have this disadvantage to some extent. However, chemical and physical modifications of those polymers allow to obtain materials with improved properties and a broad range of applications. It must be noted that the development of biotechnology plays an important role in increasing diversity of bio-engineered polymers. Nevertheless, the most versatile are polymers synthesized from bio-substrates. It is worth noting that naturally occurring polymers also serve as a source of substrates for synthesis of other biobased polymers. For example, lignin is a potential source of phenol for phenol-formaldehyde-based thermosets. Polymers synthesized from bio-substrates are a broad range of materials including thermoplastic polyesters, polyolefins, PAs, and thermosetting resins, differing in properties and applications. This group of polymers comprises resins produced currently on industrial scale, like PLA, PBS, bio-PE, bio-PET, and some bio-PAs. Not all of them are fully biobased, like 30% biobased PET, although there is a perspective of substitution of non-biobased substrates used so far with biobased ones. Other materials, for instance, thermosets, are being developed and studied. It is worth noting that some of the newly synthesized biobased polymers exhibit better properties than the conventional fossil-based ones. Nevertheless, it is rather obvious that expansion of production of biobased polymers and increase of their share in the global plastics production require further efforts focused on improvement of their performance and also economic viability.

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