

Recent Updates on Biopolymers: Precursors, Process, Properties, Challenge, and Future Perspectives



Aisyah Hanifah, Arfiathi, Melbi Mahardika, Riska Sumirat, Rossy Choerun Nissa, and Yeyen Nurhamiyah

Abstract Fossil sources are common raw materials in the polymer industry because they are cost-effective and ensure a straightforward manufacturing process. However, the insufficient supply of fossil sources failed to afford adequate feedstock for polymer production in the future. Fossil sources are projected to reach a saturation point where supply would be less than demand due to the increasing human population. Another important concern is the fact that fossil-based polymer creates several environmental problems, such as non-degradable products, air pollution, and wastewater contamination (Okkerse and Bekkum 1999). These two main reasons are the main factors why the switch of the raw materials of polymers from fossil to renewable materials is necessary, and the research on biobased polymeric materials becomes an interesting yet urgent topic. In this chapter, we review the current updates on the development of biopolymers. The precursors, technological processes, and updates on the currently available biopolymers are being reviewed. Challenges and future perspectives are also being discussed.

Keywords Biopolymers · Starch · Seaweed · Plant oil · Polymerization

A. Hanifah · M. Mahardika · R. C. Nissa · Y. Nurhamiyah (✉)
Research Center for Biomass and Bioproducts, National Research and Innovation Agency (BRIN), Jl. Raya Bogor KM. 46 Cibinong, Bogor, Indonesia
e-mail: yeye001@brin.go.id

Arfiathi · R. Sumirat
Department of Agricultural Industrial Technology, Universitas Padjadjaran, Jl. Raya Bandung Sumedang KM.21, Bandung, Indonesia

M. Mahardika · Y. Nurhamiyah
Research Collaboration Center for Biomass and Biorefinery between BRIN and Universitas Padjadjaran, Bandung, Indonesia

1 Introduction

Polymer materials are the most widely used applications in everyday life. The production of synthetic polymers continues to grow, such as the use of polycarbonate, polyvinyl chloride, polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), poly(methyl methacrylate), and polystyrene, with an estimated 1.1 billion tonnes in 2050 (Geyer 2020). Increasing awareness of the environment and limited fossil resources have led to the importance of replacing biobased materials (biopolymer) to reduce greenhouse gas emissions. Biopolymers are polymers derived from natural and renewable sources obtained from chemical polymerization reactions (Das et al. 2022; Mohanty et al. 2022). There are classifications of biopolymers: polysaccharides, nucleic acids, polyamides (PAs), polythioesters (PTEs), polyanhydrides, polyphenolic biopolymers, polyisoprenoids, and polyoxoesters (Sharma and Dhingra 2021). The most widely available biopolymers on earth are cellulose, lignin, rubber, and protein (Bayón et al. 2018; Mikus and Galus 2022). The advantages of biopolymer materials are low cost, easy to form, superior properties such as resistance to water, biodegradable, and mechanical properties that can be improved for various applications. However, the increased use of biopolymers is only about 1% of the total industrial materials produced each year (Ranganathan et al. 2020).

This chapter book provides comprehensive information on biopolymers, current research being developed, process, properties, production on a lab or commercial scale, future, and perspective. The first is a summary of the sources of raw materials derived from biomass for the production of biopolymers and bioprocesses. Then, the precursors of biopolymers will be discussed in detail with a focus on current production. The mass production of biopolymers raises concerns about economic and environmental sustainability (Chang et al. 2016; Maraveas 2020). Consequently, the production of biopolymers from renewable biological sources has received great attention during the last decade. Currently, most of the precursors of biopolymers are obtained from biomass sources such as starch, seaweed, and plant oil, which are in direct competition with food production (de Jong and Jungmeier 2015; Popa 2018; Gajula and Reddy 2021). To build a biobased economy, non-edible raw materials must be used for the production of biopolymers. All petrochemical-derived chemicals can be replaced with biopolymer materials produced from biobased materials, which will significantly contribute to the economic progress (Isikgor and Becer 2015; Nanni et al. 2021).

2 Precursor of Biopolymers

2.1 Starch

Starch is a polysaccharide that plants produce to store energy. It is stored intracellularly as spherical granules ranging in size from 2 to 100 μm . The majority of market-available starches are derived from grains such as wheat, rice, and corn or from tubers such as potato and cassava (tapioca) (Jiang et al. 2020). Starch is an amorphous, soft white powder without any sweetness and insoluble in water, alcohol, and ether. The starch granules are densely packed in a semicrystalline structure with a density of about 1.5 g cm^{-3} . Specific shapes, sizes, and surfaces (smoothness or roughness) of starch granules from various botanical sources play a crucial role in functionality and digestibility (Magallanes-Cruz et al. 2017).

Amylose and amylopectin are glucans that combine to form starch; most starches consist of 10–20% water-soluble amylose and 80–90% water insoluble amylopectin (Pokhrel 2015). Amylose is a linear polymer polysaccharide with 1–4-D-glucose units. Amylase's structure contributes to the gelling properties of heated and cooled starches. Amylopectin has a backbone of α -(1 \rightarrow 4) linkages as well, but it is also branched through α -(1 \rightarrow 6) linkages to the extent of 4–5%. Amylopectin is responsible for the thickening during starch preparations, but it does not make a contribution to the formation of a gel (Pokhrel 2015).

Starch has traditionally played a significant role as a food ingredient, but it is finally starting to be used in other applications, such as textiles, paper, pharmaceuticals, and pharmaceuticals. Starch can be applied in various ways, including pure starch as thermoplastics, starch as blends formed by combining other polymers, and copolymers formed by combining synthetic polymers (Pokhrel 2015; Encalada et al. 2018). There have been many studies conducted (Sriroth and Sangseethong 2006; Ibrahim et al. 2017; Area et al. 2019; Mesias and Murillo 2020) related to the development of starch-based products, one of which is thermoplastic starch that can be applied as a raw material for bioplastics. As a result, the use of starch in biopolymers is very promising, especially given that natural starch comes from agricultural sources, which has the advantages of abundant supply, ease of filling, low cost, and a wide range of applications and modifications in non-food products.

2.2 Seaweed

Seaweeds are macroscopic, multicellular, and benthic algae. Seaweed has a rapid growth rate, resulting in a fast accumulation of biomass (Carina et al. 2021; Perera et al. 2021). Edible marine macroalgae, or seaweed, is well-known for being extremely nutrient-rich as both food and culinary additives. Coastal populations all across the world, including Asians (Chinese, Japanese, Indonesian), Europeans (Irish, Icelandic), and South Americans, among others, have harvested wild seaweed

for food and other uses. Although wild seaweeds are still gathered from the coastal areas of several nations, farmed seaweeds make up the majority of the seaweed and seaweed products produced today (Padam and Chye 2020). More than US\$6 billion is thought to be generated by the international trade of seaweed each year. China continues to be the world's largest seaweed producer, producing 35.7 million tons, or roughly 56.75% of the total, followed by Indonesia (27.86%) and Korea (5%) (FAO 2021).

Around the world, there are more than 10,000 different varieties of seaweed. 10 seaweed species are intensively grown globally, out of the 221 species of seaweed that have been commercially exploited (Padam and Chye 2020). Seaweeds remain an unexplored resource with huge potentials such as food ingredients, cosmetics, agri-chemicals, edible foods, fishmeal, biomaterials, and bioenergy molecules, yet also having an important aspect in the ecosystem and economic profits (Padam and Chye 2020; Carina et al. 2021; Chudasama et al. 2021). Based on their color, seaweeds can be divided into three groups: red seaweeds (*Rhodophyceae*), green seaweeds (*Chlorophyceae*), and brown seaweeds (*Phaeophyceae*) (Perera et al. 2021).

Three major polysaccharides that are present in seaweed are alginate, agar, and carrageenan. The majority of polysaccharides can swell in water under ambient conditions or are water soluble (at high temperatures), producing colloidal, highly viscous solutions or dispersions with pseudoplastic flow properties. Due to their natural functional properties, such as thickening, stabilizing suspensions and emulsions, water retention and binding, and gelling, polysaccharides are advantageous in a range of applications. Terrestrial plants do not possess polysaccharides with specific and distinct characteristics that are received from a significant oceanic source (Chudasama et al. 2021).

2.3 Plant Oil

Plant oil is a potential source for biopolymers since it offers availability, low cost, easy processing route, and chemical functionality. Plant oil is a promising source for polymer building blocks as it resembles the hydrocarbon composition of petrochemicals. Globally, plant oil production capacity was 209.42 million metric tons in 2019/2020, and only around 20 million tonnes were used in the chemicals industry (Stempfle et al. 2016; USDA Foreign Agricultural Services 2021).

The total carbon atoms in the chain and the way carbon atoms are joined control the properties of fatty acids. Single carbon atoms may join each other and connect to the hydrogen atom by a single atom. Carbon atoms are also linked by a double bond and joined to only one hydrogen each. The double bond increases the ratio of carbon atoms to hydrogen because of the absence of two hydrogen atoms. The disappearance of hydrogen generates fatty acids that are less "saturated" with hydrogen. This kind of bond is called saturated, while the double bond fatty acid is called unsaturated (Pond 1998). Unsaturated fatty acids are unstable compared with saturated fatty acids. The presence of a double bond makes the carbon atoms in this fatty acid more reactive.

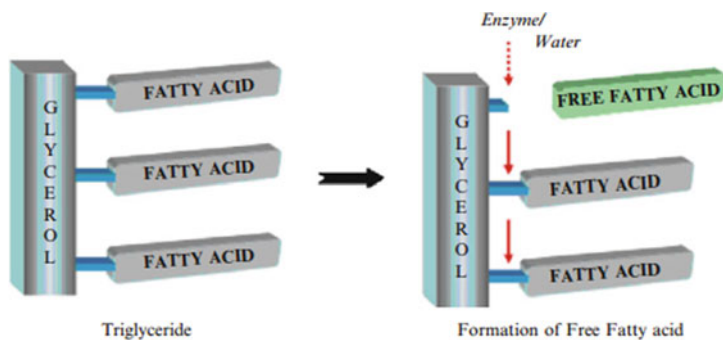


Fig. 1 Ester linkage hydrolysis (Mallakpour and Rafiee 2012)

Double bonds adjust the crystal packs; they limit the rotation of a carbon atom and bend the chain (Gurr et al. 2002) (Fig. 1).

Polymer made from plant oil offers material with beneficial properties such as hydrophobicity, flexibility, low melting temperature, and biodegradability. Polyamide (Fan et al. 1997; Hablot et al. 2010), polyester (Quinzler and Mecking 2010; Testud et al. 2017), polyurethane (Hojabri et al. 2010; More et al. 2013), and self-healing materials (Cordier et al. 2008) are examples of polymers that have been synthesized from fatty acids.

2.4 Others

Classification biopolymers are (1) the agro-polymers that comprise polysaccharides, proteins, and lipids; and (2) bio-polyesters (biodegradable polyesters), such as polyhydroxyalkanoate (PHA), polylactic acid (PLA), and aromatic and aliphatic co-polyesters. Biopolymers classified as agro-polymers are biomass products obtained from agricultural materials, such as polysaccharides, proteins, and lipids. Bio-polyester is subdivided based on its source. The polyhydroxyalkanoate (PHA) group is obtained from activity-derived microorganisms obtained by extraction. Examples of PHAs include Poly(hydroxybutyrate) (PHB) and Poly(hydroxybutyrate co-hydroxy valerate) (PHBV). Another group is the polyesters obtained from biotechnology applications, namely by the conventional synthesis of monomers obtained biologically, called the polylactide group. An example of a polylactide is polylactic acid. The last group is obtained from conventionally synthesized petrochemicals made from synthetic monomers. This group consists of polycaprolactone (PCL), polyester amides, aliphatic co-polyesters, and aromatic co-polyesters.

3 Production Process

3.1 Plasticization

Plasticizers are substances used to improve the flexibility, extensibility, and processability of polymeric materials. Plasticizers have the property of lowering the melting temperature, melt viscosity, and glass transition temperature, as well as having high boiling points, molecular weights ranging from 300 to 600 and elastic modulus of polymers without changing their chemical nature (Drobny 2015; Subramanian and Varade 2017). Plasticizers are classified into three types: polyol (glycerol, polyethylene glycols, and propylene glycol), oils/glycerides (acetylated monoglycerides, castor oil, and fragmented coconut oil), and organic ester (phthalate ester, citrate ester, triacetin, and dibutyl sebacate) (Foroughi-dahr et al. 2017). The amount of plasticizer added to a polymer is determined by the intended result. To improve the workability of the polymer melt, a small amount of plasticizer can be added, contrary to the impression that large additions can completely transform the product's properties (Harrison 2002).

When starch is plasticized, the plasticizers break the inter- and intra-molecular hydrogen bonds existing in the starch, causing it to become thermoplastic. The basic crystalline structure of the starch granules is broken by the plasticizer, which permeates them. Thermoplastic starch (TPS) becomes extremely brittle at low moisture contents while becoming more flexible and softer at high moisture amounts. When wet, it also rapidly loses strength. The effectiveness of TPS in situations with extremely low or high humidity is obviously greatly constrained by its sensitivity to moisture (Janssen and Moscicki 2009).

Plasticizers work by decreasing interactions between molecules and spreading them out. Low viscosities and temperature coefficients of viscosity are characteristics of efficient plasticizers. A polymer with a low molar mass and a higher free volume is frequently used as a plasticizer. A crucial need is that the plasticizer be perfectly blended at the molecular level, either in a homogenous mixture with the polymer or with the plasticizer itself (Janssen and Moscicki 2009). A plasticizer's principal function is to improve process efficiency and flexibility. The glass transition temperature is lowered by the plasticizer (T_g). Due to different environmental issues and rising petroleum product prices, plasticizers are becoming more and more important. So that the process can be made both affordable and biodegradable, plasticizer should be natural, affordable, and renewable (Khan et al. 2017).

The research about TPS and the effect of plasticizer processes obtained by melt processing was carried out by (Carvalho et al. 2006) using 1,4-butanediol (BUT), 1,6-hexanediol, 2,5-hexanediol, glycerol, ethylene glycol (EG), diethylene oxide glycol (DEG), trimethylene oxide glycol (TEG), ethylene glycol monomethyl ether, D-sorbitol (SOR), propylene glycol (PG), polyethylene oxide glycol (PEG) 300 and 600, and polypropylene-oxide glycol (PPG). The results showed that compounds containing OH had a good impact on the characteristics of TPS prepared by melt mixing.

3.2 Polymerization

Similar to fossil-based polymers, polymerization is a common technique to produce biobased polymers. Polycondensation and ring-opening polymerization (ROP) are examples of polymerization to get aliphatic biopolymers. Condensation polymerization is a chemical reaction with the elimination of a small molecule, which results in the repeat units in polymers having less atoms than when they are in the presence of monomers (Young and Lovell 2011). This technique was found by Wallace Carothers who discovered the condensation polymerization technique and linear polymers such as polyamides and polyesters which are still useful today (Carothers 1936, 1937). An example of polycondensation in biopolymers is the polycondensation of poly glycerol sebacate (PGS) which starts from glycerol and sebacic acid. PGS is a biodegradable and bioresorbable polymer which suitable for biomedical applications such as tissue engineering (Rai et al. 2012). Glycerol is a by-product of the saponification process from oleochemical plants meanwhile sebacic acid is originated from fatty acid (Tan et al. 2013). According to Wang et al. (2002), PGS was prepared in two stages: pre-polycondensation and crosslinking. The equimolar amount of sebacic acid and glycerol was mixed under argon at 120 °C for 24 h with the pressure reduced over 5 h. For the crosslinking stage, the pre-polymer is kept reacted at 40 mTorr and 120 °C for 48 h (Fig. 2).

Meanwhile, ring-opening polymerization (ROP) is a polymerization technique of cyclic monomers that produces a polymer with identical molecular formulae to those of the monomers (Young and Lovell 2011). For example, biobased polyamides can be prepared from monomers with cyclic structure (lactams). An example of lactams is ϵ -caprolactone as the precursor of caprolactam for PA6 and ω -lauriolactam for PA12. Evonik produces PA12 on an industrial scale with the tradename Vestamid E Even though the monomer is mostly produced from fossil-based laurin lactam, currently, the alternative laurin lactam is being developed by Evonik from palm kernel through biotechnological process shows the ring-opening polymerization of 12-aminodecanoic acid (laurin lactam) to obtain PA12.

Even though ring-opening polymerization can obtain high-molecular-weight polymers, however, due to few available cyclic monomers (Zhao 2018; Santoro et al. 2020) only limited polymers can be obtained. On the other hand, the polycondensation process brings possibilities and flexibility that are incomparable since could use a variety of monomers.

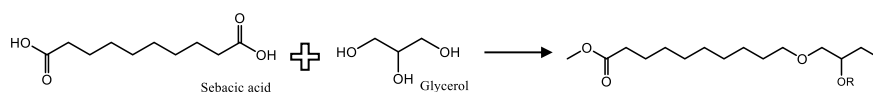


Fig. 2 The polymerization scheme of poly glycerol sebacate (PGS) (Wang et al. 2002)

3.3 *Blending*

To modify the properties of biopolymers to the intended use, various ways are employed for their modifications, including absorption of fillers and reinforcements, blending, plasticization, and impact modification (Rajeswari et al. 2021). Blending is the simple mix of polymeric components without chemical reaction to generate novel materials with appropriate qualities. From an industrial perspective, this procedure can be conducted by employing regular machines, so a costly investment is unneeded. Polymer blends are applied in a wide variety of industrial applications. In comparison to alternative polymerization processes and the production of novel monomers, this technique can obtain a wide range of characteristics, which meet the standard of the targeted application at an efficient cost and time.

The aim of blending might be the optimization of the material performance, reduction of the sensitivity to water, cutting down the cost, and improvement of the application properties. The most significant motivation for mixing could differ from other methods.

3.4 *Fermentation*

Biopolymers which are constructed from microorganisms need certain nutrients and restricted environmental conditions. They are created directly by fermentation or indirectly by chemical polymerization of the monomers produced by fermentation. Most biopolymers are biocompatible and do not negatively affect biological systems. Biopolymers derived from bacteria are considered to be produced due to their defense mechanisms or as storage materials (Mohan et al. 2016). Biopolymers are synthesized by biological organisms and produced by processive enzymes that connect building ingredients such as sugars, amino acids, and hydroxy fatty acids to achieve a high-molecular-weight molecule. Bacteria can produce various ranges of biopolymers, including polysaccharides (composed of sugars and sugar acids linked by glycosidic linkages), polyesters (composed of hydroxy fatty acids linked by ester bonds), polyamides (consisting of amino acids linked by peptide bonds), and polyphosphates (polyPs; composed of inorganic phosphates linked by anhydride bonds) (Fig. 3).

PLA and PHAs are examples of biopolymers that belong to the polyester group and are formed when microorganisms are used in the processing step. PLA is produced from a low molecular weight organic acid synthesized through microbial fermentation called lactic acid (LA). This acid is utilizing renewable sources such as cane sugar, corn, and sugar beets. PHAs are an extensive family of bio-polyesters manufactured by diverse bacteria to store carbon and energy. Fermentation is influenced by several parameters, including the substrate, temperature, pH, oxygen, and bacteria used. The term “substrate” refers to the fermentable material that includes the essential nutrients for the growth and production of fermented products by bacteria. The

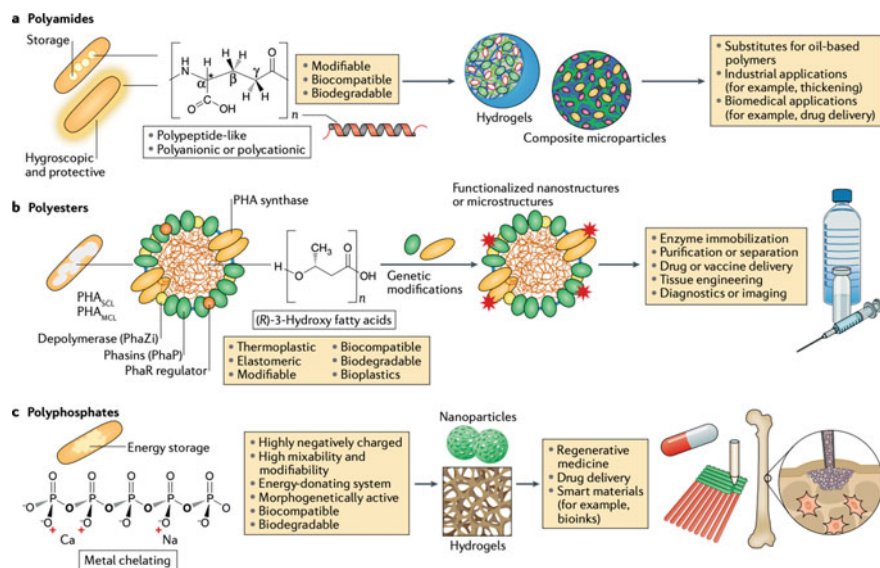


Fig. 3 Bacterial polymer granules as biomaterials (Moradali and Rehm 2020)

bacterial strains used in the fermentation process can be divided into heterofermentative and homofermentative methods. This homofermentative process is constantly utilized in industry.

Lemoigne discovered PHAs in 1943 (Lemoigne and Girard 1943); they are a family of naturally occurring polyesters generated intracellularly by many prokaryotes as carbon and energy storage polymers. In general, PHAs can be synthesized via three distinct carbon source-based steps: step I is mainly applied by poly(hydroxybutyrate) (PHB) PHB-producing organisms such as *C. necator* and *Bacillus sp.*, whereas steps II and III exist in mcl-PHA-producing *Pseudomonas sp.* Different monomers can be produced from different bacterial strains with varying carbon substrates of the microorganisms; consequently, co-polymer proportions can be modified based on the targeted applications of the final product (Fig. 4).

For the synthesis of PLA, raw material starch/sugar is extracted and fermented using lactic acid bacteria (LAB), which results in the generation of lactic acid. The fermentation of starch and other polysaccharides (sugar-containing materials), which are readily available from corn, sugar beet, sugar cane, potatoes, and other biomasses, accounts for 90–95% of the global lactic acid generation. Normal fermentation provides 85–90% of L(+) lactic acid and 70–80% of D(–) lactic acid, depending on the carbon source. During fermentation, anaerobic lactic acid bacteria (LAB) consume pyruvic acid, the last product of the Embden–Meyerhof–Parnas (EMP) route, via glycolysis. Prior to this, the carbon source sugars are converted to pyruvic acid. L-lactate dehydrogenase or D-lactate dehydrogenase can convert pyruvic acid to lactate while influencing the stereospecificity of the lactic acid generated. Lactic acid

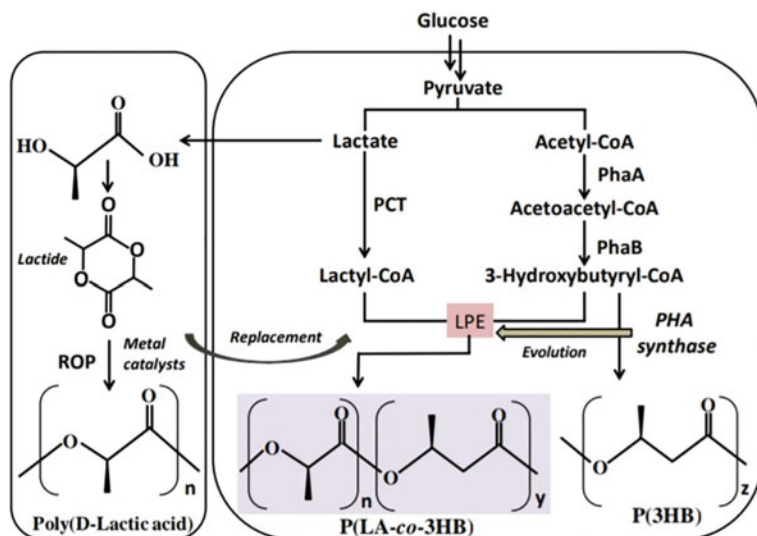


Fig. 4 Schematic illustration of the biosynthetic steps for producing lactate-based polymers (Nduku and Taguchi 2021)

is chemically processed and polymerized to create the final product by polycondensation reaction, ring-opening polymerization, and azeotropic dehydrative condensation. Ring-opening polymerization produces a product with a high molecular weight, making it the most practical method for producing PLA (Fig. 5).

(a) Fermentation and neutralization



(b) Hydrolysis by H_2SO_4



(c) Esterification



(d) Hydrolysis by H_2O



Fig. 5 Lactic acid production by fermentation procedure (Moradali and Rehm 2020)

4 Biobased Polymers

In contrast to fossil fuel plastics, which are produced from petroleum, biopolymers or organic plastics are generated from renewable biomass resources such as starch, seaweed, and proteins. Biopolymers offer the additional advantages of conserving fossil resources and reducing CO₂ emissions, making them an essential invention for sustainable development.

4.1 Thermoplastic Starch

Native starch exists in granular form. Pure starch is hydrophilic, brittle, has a lower thermal decomposition temperature, poor thermal processability, a high melting point (Khan et al. 2017), and rapidly degrades when exposed to water (Janssen and Moscicki 2009). Starch can be processed into thermoplastics by processing under shear of melt extrusion and high temperatures with the addition of plasticizers (Ma et al. 2009). Low-molecular-weight plasticizers are typically used during the gelatinization process to help break up the starch granules (Martin and Gonz 2017). Thermoplastic is a material that may be molded into desired shapes because of its weak physical crosslinks, which can be melted and reshaped in a heating and cooling cycle (Sjoo and Nillsson 2018).

Nowadays, research on the development of TPS continues to increase using various materials due to advances in TPS production technology. The raw materials include wheat starch (Moghaddam et al. 2018), cassava bagasse (Edhirej et al. 2017), cornstarch (Baran et al. 2022), potato starch (Niazi et al. 2015), mango starch (Agwamba 2021), cassava starch (Chotiprayon et al. 2020), rice starch (Prachayawarakorn et al. 2010), and pea starch (Cao et al. 2009). TPS can be processed by extrusion, blowing, thermocompression, or injection molding (Castillo et al. 2013). The advantages of TPS are its low cost, renewable properties, and wide availability. However, TPS has various drawbacks, such as being hygroscopic, hydrophilic, having a high sensitivity to moisture, poor mechanical properties compared with conventional polymers, low gas permeability, and inadequate water barrier characteristics (Bangar et al. 2021). Blending TPS with a different biodegradable polymer and renewable filler are examples of methods of overcoming these drawbacks. TPS can be used for various applications like food packaging, plastic bags, disposable cutlery, etc. (Khan et al. 2017).

4.2 Seaweed Based Polymers

Polysaccharides from seaweed can be used as a potential active agent, a raw material that is rich in polysaccharides, or extracts. The usefulness, sensory qualities, and

sustainability of materials can all be enhanced by seaweed-based products. Seaweed has drawn attention because of its biodegradability, non-toxicity, antioxidant properties, and great film-forming ability. Seaweeds are applied in active packaging (Yildirim et al. 2018), edible films (Tran et al. 2020), and edible coatings (Aayush et al. 2022). Different seaweed polysaccharides' capacities for biocompatibility, gel formation, emulsification, gelation, and foaming are based on their distinctive structural features. In addition to the seaweed's natural qualities, its nutritional value, which includes vitamins, antioxidants, minerals, and calories, is helpful in creating edible coatings and films. When seaweeds are mixed with other polysaccharides, nanoparticles, essential oils, or plant extracts, their barrier, thermal, mechanical, antioxidant, and antibacterial characteristics are improved (Perera et al. 2021).

Active packaging combining sodium alginate and lemongrass oil can inhibit *E. coli* and *L. monocytogenes* growth (de Oliveira et al. 2019). κ -Carrageenan and mulberry polyphenol extracts can improve antioxidant and pH-sensitive properties (Liu et al. 2019). Two seaweed polysaccharides, alginate and carrageenan, are extensively used in the production of edible films and coatings. Film homogeneity and transparency were favored by alginate and glycerol (Paula et al. 2015). Glycerol and κ -carrageenan enhanced the moisture barrier and tensile characteristics (Paula et al. 2015).

Food coatings serve a number of purposes, including changing the functional characteristics of foods, serving as a barrier between the environment and food products, and managing the moisture on the food's surface (Perera et al. 2021; Aayush et al. 2022). The use of agar-based coatings has been beneficial in increasing the storage shelf life of banana fruits by reducing fruit hardness and weight loss (Hussein Ziedan et al. 2018). Carrageenan and chitosan, which are added to dragon fruit that is kept at a temperature of 10 °C and a relative humidity of 90–95%, have been shown to reduce weight loss. Bract chlorophyll concentration and freshness retention for 30 days (Thi et al. 2021).

4.3 *Polylactic Acid*

Poly(lactic acid) (PLA) is a type of biodegradable thermoplastic polyester that is projected to replace conventional petrochemical-based polymers. PLA is a desirable biopolymer due to its processability, sustainability, and eco-friendliness; thus, it has gained popularity in packaging, textile, automotive composites, and biomedical applications. In terms of future industrial uses, the physical characteristics of PLA are crucial, including glossy and translucent, stable at low temperatures, moderately permeable to oxygen and water, and resistant to grease and oil. These characteristics make it an excellent material for the production of film, bottles, cups, and trays (Ranakoti et al. 2022).

PLA can be synthesized through direct lactic acid polycondensation, ring-opening polymerization of lactide, and a lactic acid cyclic dimer. The ring-opening polymerization method is a technique that combines a metal catalyst with lactide to produce larger PLA molecules (Ebnesajjad 2012). Direct polycondensation requires extreme

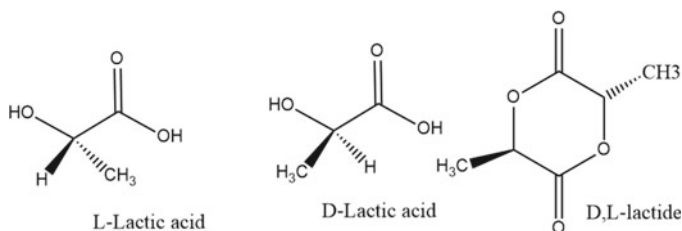


Fig. 6 Chirality structures of PLA

conditions to generate polymer with a high molecular weight at a short reaction time, low pressure of 5 mm Hg, and temperatures as high as 180–200 °C, meanwhile ROP can generate a high-molecular-weight PLA with a controlled molecular weight distribution under mild reaction conditions (temperature of 130 °C at a short reaction time) (Ashothaman et al. 2021). PLA is a kind of polyester that is often made from hydroxy acid, one of the few polymers whose stereochemical form can be easily modified. This is obtained by polymerizing a restricted mixture of L and D isomers, which produces polymers with a high molecular weight that is either crystalline or semicrystalline. Lactic Acid (LA) or 2-hydroxy propionic acid is the main monomer component for PLA which includes an asymmetric carbon that generates two enantiomeric forms, L-LA and D-LA (Fig. 6), which make PLLA and PDLA, respectively. The combination of the two optical isomers results in PDLA. The proportion of D- and L-enantiomers results in various PDLA stereo blocks. The ratio of these isomers, which is the specific chemical composition of PLA, regardless of whether it is PDLA or PLLA, and the structure of the PLA stereo block, may affect essential aspects, such as crystallization extent and thermal properties. However, PLA can be made with many qualities by modifying the polymer chains' molecular weight, composition, and stereoisomeric distribution (Jiménez et al. 2019).

PLA is one of the most potential biodegradable polymers due to its thermoplastic processibility, mechanical properties, and biological properties, such as biocompatibility and biodegradability. Glass transition temperature (T_g) is the most important parameter for amorphous PLA because significant changes in polymer chain mobility occur at the glass transition temperature. The behavior of semicrystalline PLA can be anticipated to influence critical physical characteristics such as T_g and crystalline melting temperature (T_m) (Revati et al. 2016) (Table 1).

4.4 Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHAs) are polyesters of hydroxylic acid (HA) monomers linked by an ester group. PHAs are bacteria-based biodegradable polymers that encourage carbon neutrality and sustainable industry. The monomer composition determines the elastomeric/thermoplastic characteristics of these polymers. Despite

Table 1 Mechanical properties of PLA (Jiménez et al. 2019)

Property	PLA
Density (g/cc)	1.25
Haze (%)	2.1
Tensile strength (MPa)	109.97
Tensile modulus (MPa)	3299.26
Ultimate elongation (%)	160
Tear resistance (g/mm)	0.3810

the significant potential and efforts to build cost-effective fermentative methods, the PHAs production costs are still relatively high (5–10 \$/kg), which hinders the commercialization of these biopolymers as commodities materials (Ortelli et al. 2019). According to ASTM standard, PHAs such as poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-3-hydroxy valerate) (PHBV) are defined as biodegradable in all aerobic and anaerobic environments. They can be used to make soil, marine biodegradable, and compostable products, which is an advantage compared to synthetic non-degradable plastics (Mohapatra et al. 2021).

The main PHAs subcategories are short (3–5 carbons), medium (6–14 carbons), and long (15+ carbons) (Meereboer et al. 2020). Unsaturated fatty acids form short and medium-chain PHAs with double bonds. The common short-chain PHAs are poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-3-hydroxy valerate) (PHBV). Other biodegradable PHAs include poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (PH4B), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHx), and poly(3-hydroxybutyrate-co-3-hydroxyoctanoate) (PHBO) (Fig. 7).

PHAs, such as poly(3-hydroxybutyrate-co-3-hydroxy valerate) (PHBV) and poly(3-hydroxybutyrate-co-3-hydroxy valerate) (PHB), are brittle due to their high crystalline degree. The chemical structure of PHAs is responsible for giving it these characteristics. Therefore, given that these numerous varieties of PHAs each have specific structural, physical, and chemical qualities, it is necessary to categorize them according to those properties and then modify them so that they are simple to use for the purposes that have been described. The general properties of the common types of PHAs are shown in Table 2.

PHAs have various excellent properties, including a high volume-to-surface ratio, a tiny pore size with a high chance of being recycled, biodegradability, and biocompatibility. Recent attention has been drawn to PHAs due to their multiple favorable qualities, such as ease of processing, resistance to UV rays, and insolubility in water. The biodegradable nature and other advantages of polyhydroxyalkanoates, such as high-temperature stability, low degree of surface porosity, improved toughness, and elasticity, result in their use in a variety of industries, including medicine, agriculture, etc. (Chai et al. 2021).

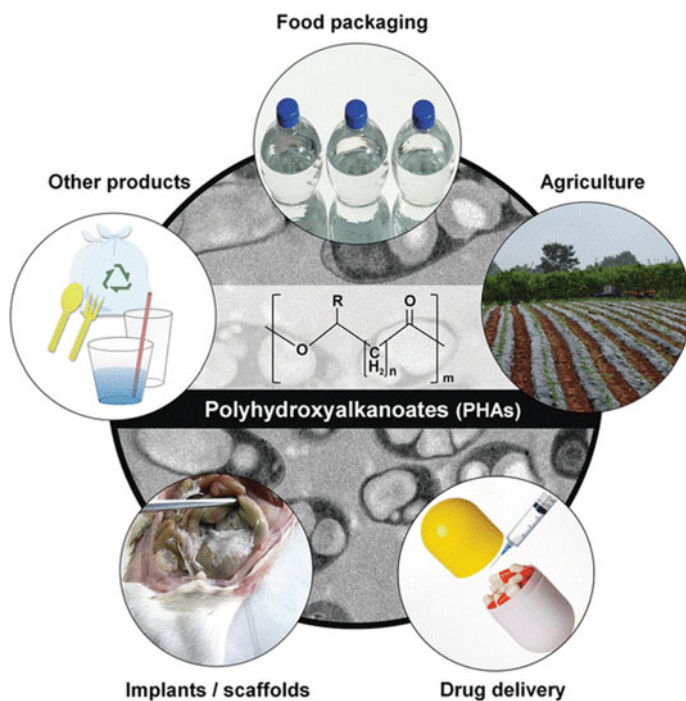


Fig. 7 General chemical structure and various applications of PHAs (Sharma et al. 2021)

Table 2 The general properties of the common types of PHAs (Chai et al. 2021)

Property	P(3HB)	P(3HB-co-4HB)
Glass transition temperature, T_g (°C)	2–4	– 48–4
Melting temperature, T_m (°C)	160–175	50–175
Tensile strength, σ (MPa)	15–40	17–104
Young's modulus (GPa)	1–2	0.07–1.5
Elongation at break (%)	1–15	14–1320
Crystallinity (%)	50–80	34–60

4.5 Plant Oil-Based Polymers

Plant oil has several functional groups coming from fatty acids that are useful for polymer synthesis. Carboxylic acid and alkyl ester are the standard functional groups in the fatty acid. There are also additional groups such as epoxy group (vernolic acid) and hydroxyl (ricinoleic acid). Plant oil can be directly used for polymerization due to these functional groups. Direct polymerization usually converts plant oil to polyol through epoxidation.

Junming and his co-workers (Junming et al. 2012) reported the preparation of polyester polyols from oleic acid, a common unsaturated fatty acid in plant oils. The synthesis consists of three steps: epoxidation, ring-opening reaction, and esterification. The polyols appear as a viscous liquid at ambient temperature with OH number ranging from 307 to 425 mg KOH g⁻¹. Polyester polyol was then used to synthesize polyurethane foams. The polyurethane synthesized from the oleic-based polyols and isocyanate showed an acceptable result and reached the standard of rigid foam in China as shown in Table 3.

The hazardous reaction of phosgene in isocyanates synthesis and the sustainable demand in chemistry generated the development of the phosgene-free method. Plant oils have double bonds and ester that can be synthesized into various new structures including “bio” isocyanates. The major drawbacks of plant oil-based isocyanates are that they are still not able to substitute current isocyanates on the market. Despite that, Henkel Corporation Company and General Mills have commercialized dimer fatty acid diisocyanates from fatty acid containing 36 carbon atoms in the chain. Other raw materials, such as soybean oil, azelaic acid, and oleic acid, also have been attempted to make diisocyanates and used for the synthesis of “green” thermoplastic PU (Caylı and Kusefoglu 2008; Hojabri et al. 2010; More et al. 2013).

Rix et al. used mini-emulsion polymerization in their attempt to prepare non-isocyanates polyurethane (NIPU). A fatty acid diamine, Priamine 1075, was reacted with fatty acid-based bis-cyclic carbonates at 60 °C for several hours. The mini-emulsion process was then prepared to obtain waterborne NIPU latexes with the addition of surfactants and hydrophobic additives. The result obtained was NIPU with a solid content reaching of 30wt%. The molar masses were low compared to bulk NIPUs, and this is because of the existence of partial hydrolysis of the carbonates. The NMR result of PHUs from the mini-emulsion process showed signals at 3.5–4 ppm that are considered equal to protons of hydrolysis compounds (Rix et al. 2016).

Despite direct polymerization being an easy route to obtain plant-oil-based polymer, only few polymers can be obtained through this route, such as bio-polyurethane and epoxy. Other routes such as the dimerization of fatty acid, and self-metathesis of methyl ester are needed to obtain various types of monomers with double functional groups.

Table 3 Physical properties of polyurethane foams (Junming et al. 2012)

Properties	Foam 1 ^a	Foam 2 ^a	Foam 3 ^a	China standard ^b
Thermal conductivity W/(m K)	0.028	0.037	0.076	0.024
Density (kg/m ³)	31.3	40.6	58.1	30–50
Compressive strength (MPa)	150	210	230	150–300
Modulus of compression (MPa)	3.44	4.58	5.66	–
Bending strength (MPa)	0.28	0.34	0.41	–

^a Foam 1 used polyols with hydroxy number 425; foam 2 used polyols with hydroxy number 361; foam 3 used polyols with hydroxy number 307

^b China standard (JC/T 998-2006): Spray polyurethane foam or thermal insulation

Most of the fatty acids have only one functional group and act as a chain terminator in polymer synthesis. Polymerization of fatty acid only occurs in dimer or trimer fatty acids which have two or three functional groups. So, the fatty acid has to be dimerized or trimerized before use (Mallakpour and Rafiee 2012). CRODA has developed various functional dimer and trimer fatty acids for polymer synthesis such as fatty acid, fatty diol, and fatty diamine.

Mecking and his groups (Quinzler and Mecking 2010; Stempfle et al. 2011; Trzaskowski et al. 2011) have investigated the conversion of fatty acid into saturated α,ω -diacid and diol as a preparation of long-chain aliphatic semicrystalline polyester. Oleic acid, erucic acid, or 10-undecenoic acid are modified into diacid through carbonylation and olefin metathesis. Carbonylation converts the internal double bond in the hydrocarbon to terminal ester groups while olefin metathesis coupling of two $=\text{CH}(\text{CH}_2)_n\text{COOR}$ part and then the saturated product being hydrogenated. The reduction mechanism of dicarboxylic acid is used to obtain diols. One of their results has similar properties to low-density polyethylene (LDPE) and polyethylene. The material has a melting temperature (T_m) of 103 °C and crystallize temperature (T_c) of 87 °C while LDPE has T_m 110 °C and T_c 94.09 °C. This material was prepared by the linear incorporation of oleic acid and erucic acid. Equal amounts of dimethyl-1,19-nonadecanoate and nonadecane-1,19-diol were prepared for polycondensation of novel polyester catalyzed by titanium alkoxides (Quinzler and Mecking 2010; Gaska et al. 2017).

Vilela and his groups used erucic acid to generate long-chain aliphatic polyester via self-metathesis for monomer synthesis. Hydrogenation of erucic acid to obtain dicarboxylic acid and reduction of the acid to get diols (Fig. 8). Polycondensation of hexacosane-1,26-diol with α,ω -dicarboxylic acid generates long-chain aliphatic polyesters 26,26 with excellent properties. The polyester has the highest T_m at 104 °C, and the highest degradation temperature (T_d) at 386 °C. The DSC graph of polyester 26,26 exhibits a sharp endotherm and crystallization peak indicating a high degree of the polyesters (Vilela et al. 2012).

A long carbon chain of fatty acids is beneficial for the synthesis of hyperbranched polyester. Testud et al. reported the preparation of hyperbranched polyester (HPBE) from fatty acid methyl ester (FAME) with tunable properties. They use various plant

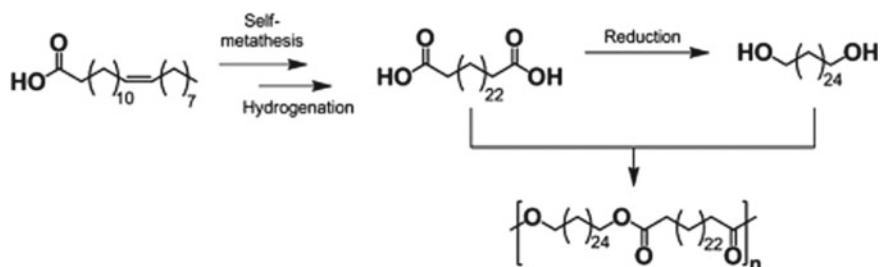


Fig. 8 Conversion of erucic acid to 1,26 diacid and 1,26 diol and polymerization of both (Vilela et al. 2012)

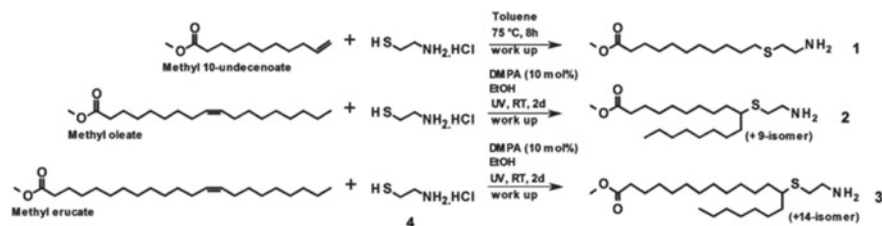


Fig. 9 Thiol-ene scheme of polyamide monomer (Türünc et al. 2012)

oils as starting material for the synthesis of monomers of AB_n type ($n = 2$ or 3) where A is acid and B is diol moieties. The most efficient catalyst system that achieves high molar masses ($3000\text{--}10000\text{ g mol}^{-1}$) is shown by zinc acetate, sodium methoxide, and 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD). The glass transition of the samples varies from -33° to 9°C , with a degree of branching ranging from 0.07 to 0.45 and thermal stability above 300°C . A significant amount of hydroxyl group in HPBE can have further modifications to reach desired properties (Testud et al. 2017).

Falkenburg et al. reported the preparation of polyamide-based fatty acid for the first time in 1945. They synthesized polyamide from difunctional and polyfunctional amines and polymeric fat acid (dimer and trimer). The polyamides result has unique properties including strong adhesion to various surfaces, good water resistance, soluble in alcohol, excellent mechanical properties, and flexible as described in Table 2. It is suitable for resin, coating, elastomer, and hot melting adhesives application (Falkenburg et al. 1945).

Thiol-ene addition was introduced in the synthesis of fatty acid monomers. Thiol-ene addition is an effective method for various transformations because it shows a click reaction behavior. Türünc and his co-workers prepared a fatty acid-based amine monomer through thiol-ene addition to obtain polyamide. Cysteamine hydrochloride addition to double bonds of Methyl-10 undecenoate, methyl erucate, and methyl oleate produced a good multifunctional monomer (Fig. 9). The products were used for polyamides with adipic acid and 1,6-hexamethylene. 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD) was used as a catalysts in copolymerization. The result yields polyamide with excellent thermal and solubility properties. The resulted polyamide gave the highest T_m at 138°C (Türünc et al. 2012).

Nurhamiyah et al. have been synthesized a series of fully biobased polyamides from a fatty acid biobased dicarboxylic acid and biobased diamine, PA36,36, and PA36,9 (Nurhamiyah et al. 2021a, 2021b). PA36,36 was prepared from a facile condensation of Pripol 1009 and Priamine 1075 at 220°C at various times. It was found that the optimum time to synthesize this biobased polyamide is at 24 h. PA36,36 has excellent properties, for example, zero water absorption, high toughness ($14.21 \pm 4.58\text{ MJ m}^{-3}$), and large elongation at break (up to 2286%), and shows autonomous self-healing behavior at room temperature (Nurhamiyah et al. 2021a). Meanwhile, PA36,9 is a semicrystalline fully biobased polyamide elastomer that shows similar

properties to the synthetic medium hardness, prospecting as an alternative substitution. The example is a melting temperature (T_m) of 83.6 °C, a glass transition temperature (T_g) of 17.6 °C, a large elongation at break (1220%), a high tensile strength (31.8 MPa), a medium hardness (Shore A/Shore D = 90/35), and excellent hydrophobicity.

5 Challenges and Future Perspectives

Biopolymer production is growing rapidly, and the production process of precursors of biopolymers (starch, seaweed, and plant oil) from renewable resources continues to increase. This is due to the high demand for biopolymer materials from various industries ranging from packaging, the automotive industry, the agricultural sector, bioplastics, and electronics, as well as biopolymer research and development to increase its capacity in industrialization. In the early stages of the biopolymer industry, biodegradable materials were developed for short-term applications to solve the problem of synthetic polymers. Currently, biopolymer production focuses on the application of durable materials with sustainable bioprocesses using biomass-derived materials in the hope of reducing greenhouse gas emissions and limiting fossil resources. Development of new applications with the advantage of even better properties. In general, the expected development and sustainability of biopolymer materials in the future depend on a variety of applications and the quantity of biobased materials. Particularly, advances in bioprocessing and the utilization of lignocellulosic biomass as a waste product for the production of biopolymers with low production costs, sustainability, and material properties that can be modified according to application based on renewable energy sources are becoming more attractive.

References

- Aayush K, McClements DJ, Sharma S, Sharma R, Singh GP, Sharma K, Oberoi K (2022) Innovations in the development and application of edible coatings for fresh and minimally processed apple. *Food Control* 141:109188. <https://doi.org/10.1016/j.foodcont.2022.109188>
- Agwamba EC (2021) Taguchi optimization of plasticisation process for glycerol and TEA based thermoplastic mango starch biofilms. *Res Sq* 1–13. <https://doi.org/10.21203/rs.3.rs-932373/v1>
- Area MR, Rico M, Montero B, Barral L, Bouza R, López J, Ramírez C (2019) Corn starch plasticized with isosorbide and filled with microcrystalline cellulose: processing and characterization. *Carbohydr Polym* 206:726–733. <https://doi.org/10.1016/j.carbpol.2018.11.055>
- Ashothaman A, Sudha J, Senthilkumar N (2021) A comprehensive review on biodegradable polylactic acid polymer matrix composite material reinforced with synthetic and natural fibers. *Mater Today Proc*. <https://doi.org/10.1016/j.matpr.2021.07.047>
- Bangar SP, Whiteside WS, Ashogbon AO, Kumar M (2021) Recent advances in thermoplastic starches for food packaging: a review. *Food Packag Shelf Life* 30:100743. <https://doi.org/10.1016/j.fpsl.2021.100743>

- Baran A, Fričová O, Vrabel P, Popovič Ľ, Peidayesh H, Chodák I, Hutníková M, Kovačková M (2022) Effects of urea and glycerol mixture on morphology and molecular mobility in thermoplastic starch/montmorillonite-type nanofiller composites studied using XRD and NMR. *J Polym Res* 29:1–12. <https://doi.org/10.1007/s10965-022-03110-6>
- Bayón B, Berti IR, Gagneten AM, Castro GR (2018) Biopolymers from wastes to high-value products in biomedicine. In: *Waste to wealth*. Springer, pp 1–44
- Cao N, Yang X, Fu Y (2009) Effects of various plasticizers on mechanical and water vapor barrier properties of gelatin films. *Food Hydrocoll* 23:729–735. <https://doi.org/10.1016/j.foodhyd.2008.07.017>
- Carina D, Sharma S, Jaiswal AK, Jaiswal S (2021) Trends in food science & technology seaweeds polysaccharides in active food packaging: a review of recent progress. *Trends Food Sci Technol* 110:559–572. <https://doi.org/10.1016/j.tifs.2021.02.022>
- Carothers WH (1936) Linear polyamides and their production
- Carothers WH (1937) Linear condensation polymers
- Carvalho AJF, Gandini A, Curvelo AAS, Ro AL Da (2006) The effect of plasticizers on thermoplastic starch compositions obtained by melt processing 63:417–424. <https://doi.org/10.1016/j.carbpol.2005.09.017>
- Castillo L, López O, López C, Zaritzky N, García MA, Barbosa S, Villar M (2013) Thermoplastic starch films reinforced with talc nanoparticles. *Carbohydr Polym* 95:664–674. <https://doi.org/10.1016/j.carbpol.2013.03.026>
- Caylı G, Kusefoglu S (2008) Biobased polyisocyanates from plant oil triglycerides: synthesis, polymerization, and characterization. *J Appl Polym Sci* 109:2948–2955. <https://doi.org/10.1002/app.28401>
- Chai JM, Amelia TS, Mouriya GK, Bhubalan K, Amirul A-AA, Vigneswari S, Ramakrishna S (2021) Surface-modified highly biocompatible bacterial-poly(3-hydroxybutyrate-co-4-hydroxybutyrate): a review on the promising next-generation biomaterial. *Polymers (Basel)* 13
- Chang I, Im J, Cho G-C (2016) Introduction of microbial biopolymers in soil treatment for future environmentally-friendly and sustainable geotechnical engineering. *Sustainability* 8:251
- Chotiprayon P, Chaisawad B, Yoksan R (2020) Thermoplastic cassava starch/poly(lactic acid) blend reinforced with coir fibres. *Int J Biol Macromol* 156:960–968. <https://doi.org/10.1016/j.ijbiomac.2020.04.121>
- Chudasama NA, Sequeira RA, Moradiya K, Prasad K (2021) Seaweed polysaccharide based products and materials: an assessment on their production from a sustainability point of view. *Molecules* 26. <https://doi.org/10.3390/molecules26092608>
- Cordier P, Tournilhac F, Soulié-Ziakovic C, Leibler L (2008) Self-healing and thermoreversible rubber from supramolecular assembly. *Nature* 451:977–980. <https://doi.org/10.1038/nature06669>
- Das A, Ringu T, Ghosh S, Pramanik N (2022) A comprehensive review on recent advances in preparation, physicochemical characterization, and bioengineering applications of biopolymers. *Polym Bull* 1–66
- de Jong E, Jungmeier G (2015) Biorefinery concepts in comparison to petrochemical refineries. In: *Industrial biorefineries & white biotechnology*. Elsevier, pp 3–33
- de Oliveira JP, Bruni GP, Fabra MJ, da Rosa ZE, López-Rubio A, Martínez-Sanz M (2019) Development of food packaging bioactive aerogels through the valorization of *Gelidium sesquipedale* seaweed. *Food Hydrocoll* 89:337–350. <https://doi.org/10.1016/j.foodhyd.2018.10.047>
- Drobny JG (2015) *Handbook of thermoplastic elastomers*, 2nd edn. Elsevier
- Ebnasajjad S (2012) *Handbook of biopolymers and biodegradable plastics: properties, processing and applications*. William Andrew
- Ehdirej A, Sapuan SM, Jawaid M, Zahari NI (2017) Preparation and characterization of cassava bagasse reinforced thermoplastic cassava starch. *Fibers Polym* 18:162–171. <https://doi.org/10.1007/s12221-017-6251-7>

- Encalada K, Aldás MB, Proaño E, Valle V (2018) An overview of starch-based biopolymers and their biodegradability Una revisión sobre biopolímeros con base en almidón y su biodegradabilidad. *Cienc e Ing* 39:245–258
- Falkenburg LB, Teeter HM, Skell PS, Cowan JC (1945) Polyamides from polymeric fat acids. *Oil Soap* 22:143–148
- Fan X, Deng Y, Waterhouse J, Pfromm P (1997) Synthesis and characterization of polyamide resins from soy-based dimer acids and different amides 305–314
- FAO (2021) Global status of seaweed production, trade and utilization. Food Agriculture Organization United Nations
- Foroughi-dahr M, Mostoufi N, Sotudeh-gharebagh R, De Montre P, Chaouki J (2017) Particle coating in fluidized beds. Elsevier Inc.
- Gajula S, Reddy CRK (2021) More sustainable biomass production and biorefining to boost the bioeconomy. *Biofuels Bioprod Biorefining* 15:1221–1232
- Gaska K, Xu X, Gubanski S, Kádár R (2017) Electrical, mechanical, and thermal properties of LDPE graphene nanoplatelets composites produced by means of melt extrusion process. *Polymers (Basel)* 9:30–40. <https://doi.org/10.3390/polym9010011>
- Geyer R (2020) Production, use, and fate of synthetic polymers. In: *Plastic waste and recycling*. Elsevier, pp 13–32
- Gurr M., Harwood J, Frayn K. (2002) *Lipid biochemistry: an introduction*
- Hablot E, Matadi R, Ahzi S, Avérous L (2010) Renewable biocomposites of dimer fatty acid-based polyamides with cellulose fibres: thermal, physical and mechanical properties. *Compos Sci Technol* 70:504–509. <https://doi.org/10.1016/j.compscitech.2009.12.001>
- Hojabri L, Kong X, Narine SS (2010) Novel long chain unsaturated diisocyanate from fatty acid: synthesis, characterization, and application in bio-based polyurethane. *J Polym Sci Part A Polym Chem* 48:3302–3310. <https://doi.org/10.1002/pola.24114>
- Hussein Ziedan ES, El Zahaby HM, Maswada HF, El Rafh Zoer EHA (2018) Agar-agar a promising edible coating agent for management of postharvest diseases and improving banana fruit quality. *J Plant Prot Res* 58. <https://doi.org/10.24425/122938>
- Ibrahim N, Wahab MKA, Uylan DN, Ismail H (2017) Physical and degradation properties of polylactic acid and thermoplastic starch blends—Effect of citric acid treatment on starch structures. *BioResources* 12:3076–3087. <https://doi.org/10.15376/biores.12.2.3076-3087>
- Isikgor FH, Becer CR (2015) Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers. *Polym Chem* 6:4497–4559. <https://doi.org/10.1039/c5py00263j>
- Janssen L, Moscicki L (2009) *Thermoplastic starch (A green material for various industries)*. Wiley-VCH, Germany
- Jiang T, Duan Q, Zhu J, Liu H, Yu L (2020) Starch-based biodegradable materials: challenges and opportunities. *Adv Ind Eng Polym Res* 3:8–18. <https://doi.org/10.1016/j.aiepr.2019.11.003>
- Jiménez L, Mena MJ, Prendiz J, Salas L, Vega-Baudrit J (2019) Polylactic acid (PLA) as a bioplastic and its possible applications in the food industry. *J Food Sci Nutr* 5:2–6
- Junming X, Jianchun J, Jing L (2012) Preparation of polyester polyols from unsaturated fatty acid. *J Appl Polym Sci* 126:1377–1384. <https://doi.org/10.1002/app.36740>
- JS, Harrison ZO (2002) Introduction Types of Plasticizers. *Encycl Polym Sci Technol* 3:518
- Khan B, Bilal Khan Niazi M, Samin G, Jahan Z (2017) Thermoplastic starch: a possible biodegradable food packaging material—A review. *J Food Process Eng* 40. <https://doi.org/10.1111/jfpe.12447>
- Lemoigne M, Girard H (1943) Reserves lipidiques-hydroxybutyriques chez *Azotobacter chroococcum*. *C. Rmcad Sci Paris* 217:537–558
- Liu Y, Qin Y, Bai R, Zhang X, Yuan L, Liu J (2019) pH-sensitive and antioxidant packaging film based on κ -carrageenan and mulberry polyphenolic extract. *Int J Biol Macromol* 134:993–1001. <https://doi.org/10.1016/j.ijbiomac.2019.05.175>

- Ma X, Chang PR, Yu J, Stumborg M (2009) Properties of biodegradable citric acid-modified granular starch/thermoplastic pea starch composites. *Carbohydr Polym* 75:1–8. <https://doi.org/10.1016/j.carbpol.2008.05.020>
- Magallanes-Cruz PA, Flores-Silva PC, Bello-Perez LA (2017) Starch structure influences its digestibility: a review. *J Food Sci* 82:2016–2023. <https://doi.org/10.1111/1750-3841.13809>
- Mallakpour S, Rafiee Z (2012) Green solvents fundamental and industrial applications BT—Green solvents I: properties and applications in chemistry. Springer, Netherlands
- Maraveas C (2020) Production of sustainable and biodegradable polymers from agricultural waste. *Polymers (Basel)* 12:1127
- Martin L, Gonz A (2017) D-isosorbide and 1, 3-propanediol as plasticizers for starch-based films: Characterization and aging study. *J Appl Polym Sci* 44793:1–10. <https://doi.org/10.1002/app.44793>
- Meereboer KW, Misra M, Mohanty AK (2020) Review of recent advances in the biodegradability of polyhydroxyalkanoate (PHA) bioplastics and their composites. *Green Chem* 22:5519–5558. <https://doi.org/10.1039/D0GC01647K>
- Mesias R, Murillo EA (2020) Properties of the thermoplastic starch/poly(lactic acid) blends compatibilized by hyperbranched polyester. *J Phys Conf Ser* 1587. <https://doi.org/10.1088/1742-6596/1587/1/012001>
- Mikus M, Galus S (2022) Biopolymers from agriculture waste and by-products. In: *Biopolymers*. Springer, pp 111–128
- Moghaddam RA, Mohammad, Mohammad Ali Razavi S, Jahani Y (2018) Optimization of the effects of thermoplastic starch and glycerol concentration on physicomechanical properties of poly(lactic acid)/thermoplastic starch blend by response surface methodology. *J Res Innov Food Sci Technol* 7:309–322. <https://doi.org/10.22101/JRIFST.2018.10.20.736>
- Mohan S, Oluwafemi OS, Kalarikkal N, Thomas S, Songca SP (2016) Biopolymers—Application in nanoscience and nanotechnology. In: Perveen FK (ed) *IntechOpen, Rijeka*, p Ch. 3
- Mohanty AK, Wu F, Mincheva R, Hakkarainen M, Raquez J-M, Mielewski DF, Narayan R, Netravali AN, Misra M (2022) Sustainable polymers. *Nat Rev Methods Prim* 2:1–27
- Mohapatra S, Vishwakarma K, Joshi NC, Maity S, Kumar R, Ramchander M, Pattnaik S, Samantaray DP (2021) A review on PHAs: the future biopolymer. In: *Environmental and agricultural microbiology*, pp 83–100
- Moradali MF, Rehm BHA (2020) Bacterial biopolymers: from pathogenesis to advanced materials. *Nat Rev Microbiol* 18:195–210. <https://doi.org/10.1038/s41579-019-0313-3>
- More AS, Lebarbe T, Maisonneuve L, Gadenne B, Alfos C, Cramail H (2013) Novel fatty acid based di-isocyanates towards the synthesis of thermoplastic polyurethanes. *Eur Polym J* 49:823–833. <https://doi.org/10.1016/j.eurpolymj.2012.12.013>
- Nanni A, Parisi M, Colonna M (2021) Wine by-products as raw materials for the production of biopolymers and of natural reinforcing fillers: a critical review. *Polymers (Basel)* 13:381
- Nduko JM, Taguchi S (2021) Microbial production of biodegradable lactate-based polymers and oligomeric building blocks from renewable and waste resources. *Front Bioeng Biotechnol* 8
- Niazi MBK, Zijlstra M, Broekhuis AA (2015) Influence of plasticizer with different functional groups on thermoplastic starch. *J Appl Polym Sci* 132:1–12. <https://doi.org/10.1002/app.42012>
- Nurhamiyah Y, Amir A, Finnegan M, Themistou E, Edirisinghe M, Chen B (2021a) Wholly biobased, highly stretchable, hydrophobic, and self-healing thermoplastic elastomer. *ACS Appl Mater Interfaces* 13:6720–6730. <https://doi.org/10.1021/acsami.0c23155>
- Nurhamiyah Y, Irvine G, Themistou E, Chen B (2021b) Novel biobased polyamide thermoplastic elastomer with medium hardness. *Macromol Chem Phys* 222:2100218. <https://doi.org/10.1002/macp.202100218>
- Okkerse C, Van Bekkum H (1999) From fossil to green. *Green Chem* 1:107–114. <https://doi.org/10.1039/a809539f>
- Ortelli S, Costa AL, Torri C, Samori C, Galletti P, Vineis C, Varesano A, Bonura L, Bianchi G (2019) Innovative and sustainable production of biopolymers BT—Factories of the future: the Italian

- Flagship initiative. In: Tolio T, Copani G, Terkaj W (eds). Springer International Publishing, Cham, pp 131–148
- Padam BS, Chye FY (2020) Sustainable seaweed technologies. Elsevier Inc.
- Paula GA, Benevides NMB, Cunha AP, Vit A, Morais S, Azeredo HMC, Pinto AMB (2015) Development and characterization of edible films from mixtures of κ -carrageenan, ι -carrageenan, and alginate 47:140–145. <https://doi.org/10.1016/j.foodhyd.2015.01.004>
- Perera KY, Sharma S, Pradhan D, Jaiswal AK, Jaiswal S (2021) Seaweed polysaccharide in food contact materials (Active packaging, intelligent packaging, edible films, and coatings). *Foods* 10:1–22. <https://doi.org/10.3390/foods10092088>
- Pokhrel S (2015) A review on introduction and applications of starch and its biodegradable polymers. *Int J Environ* 4:114–125. <https://doi.org/10.3126/ije.v4i4.14108>
- Pond CM (1998) *Fats of life*. Cambridge University Press, Cambridge
- Popa VI (2018) Biomass for fuels and biomaterials. In: Biomass as renewable raw material to obtain bioproducts of high-tech value. Elsevier, pp 1–37
- Prachayawarakorn J, Sangnitdej P, Boonpasith P (2010) Properties of thermoplastic rice starch composites reinforced by cotton fiber or low-density polyethylene. *Carbohydr Polym* 81:425–433. <https://doi.org/10.1016/j.carbpol.2010.02.041>
- Quinzler D, Mecking S (2010) Linear semicrystalline polyesters from fatty acids by complete feedstock molecule utilization. *Angew Chemie Int Ed* 49:4306–4308. <https://doi.org/10.1002/anie.201001510>
- Rai R, Tallawi M, Grigore A, Boccaccini AR (2012) Synthesis, properties and biomedical applications of poly(glycerol sebacate) (PGS): a review. *Prog Polym Sci* 37:1051–1078. <https://doi.org/10.1016/j.progpolymsci.2012.02.001>
- Rajeswari A, Stobel Christy EJ, Pius A (2021) Chapter 5—Biopolymer blends and composites: processing technologies and their properties for industrial applications. In: Thomas S, Gopi S, Amalraj ABT-B, IA (eds). Elsevier, pp 105–147
- Ranakoti L, Gangil B, Mishra SK, Singh T, Sharma S, Ilyas RA, El-Khatib S (2022) Critical review on polylactic acid: properties, structure, processing, biocomposites, and nanocomposites. *Materials* (Basel) 15
- Ranganathan S, Dutta S, Moses JA, Anandharamakrishnan C (2020) Utilization of food waste streams for the production of biopolymers. *Heliyon* 6:e04891
- Revati R, Majid MSA, Normahira M (2016) Biodegradable poly(lactic acid) scaffold for tissue engineering: a brief review
- Rix E, Grau E, Chollet G, Cramail H (2016) Synthesis of fatty acid-based non-isocyanate polyurethanes, NIPUs, in bulk and mini-emulsion. *Eur Polym J* 84:863–872. <https://doi.org/10.1016/j.eurpolymj.2016.07.006>
- Santoro O, Zhang X, Redshaw C (2020) Synthesis of biodegradable polymers: a review on the use of schiff-base metal complexes as catalysts for the ring opening polymerization (ROP) of cyclic esters. *Catalysts* 10
- Sharma M, Dhingra HK (2021) An overview of microbial derived polyhydroxybutyrate (PHB): production and characterization. *Microb Polym* 143–176
- Sharma V, Sehgal R, Gupta R (2021) Polyhydroxyalkanoate (PHA): properties and modifications. *Polymer (Guildf)* 212:123161. <https://doi.org/10.1016/j.polymer.2020.123161>
- Sjoo M, Nilsson L (2018) *Starch in food (structure, function and applications)*, 2nd edn. Woodhead Publishing
- Sriroth K, Sangseethong K (2006) Biodegradable plastics from cassava starch. *Acta Hort* 703:145–151. <https://doi.org/10.17660/actahortic.2006.703.16>
- Stempfle F, Ortman P, Mecking S (2016) Long-chain aliphatic polymers to bridge the gap between semicrystalline polyolefins and traditional polycondensates. *Chem Rev* 116:4597–4641. <https://doi.org/10.1021/acs.chemrev.5b00705>
- Stempfle F, Quinzler D, Heckler I, Mecking S (2011) Long-chain linear C₁₉ and C₂₃ monomers and polycondensates from unsaturated fatty acid esters. *Macromolecules* 44:4159–4166. <https://doi.org/10.1021/ma200627e>

- Subramanian V, Varade D (2017) Thermoelectric properties of biopolymer composites. Elsevier Inc.
- Tan HW, Abdul Aziz AR, Aroua MK (2013) Glycerol production and its applications as a raw material: a review. *Renew Sustain Energy Rev* 27:118–127. <https://doi.org/10.1016/j.rser.2013.06.035>
- Testud B, Pintori D, Grau E, Taton D, Cramail H (2017) Hyperbranched polyesters by polycondensation of fatty acid-based AB_n-type monomers. *Green Chem* 19:259–269. <https://doi.org/10.1039/C6GC02294D>
- Thi H, Boonyaritthongchai P, Buanong M (2021) Scientia Horticulturae Chitosan- and κ-carrageenan-based composite coating on dragon fruit (*Hylocereus undatus*) pretreated with plant growth regulators maintains bract chlorophyll and fruit edibility. *Sci Hortic (amsterdam)* 281:109916. <https://doi.org/10.1016/j.scienta.2021.109916>
- Tran TTB, Roach P, Nguyen MH, Pristiiono P, Vuong QV (2020) Development of biodegradable films based on seaweed polysaccharides and Gac pulp (*Momordica cochinchinensis*), the waste generated from Gac oil production. *Food Hydrocoll* 99:105322. <https://doi.org/10.1016/j.foodhyd.2019.105322>
- Trzaskowski J, Quinzler D, Bährle C, Mecking S (2011) Aliphatic long-chain C20 polyesters from olefin metathesis. *Macromol Rapid Commun* 32:1352–1356. <https://doi.org/10.1002/marc.201100319>
- Türüñç O, Firdaus M, Klein G, Meier MAR (2012) Fatty acid derived renewable polyamides via thiol–ene additions. *Green Chem* 14:2577. <https://doi.org/10.1039/c2gc35982k>
- USDA Foreign Agricultural Services (2021) Oilseeds: world markets and trade
- Vilela C, Silvestre AJD, Meier MAR (2012) Plant oil-based long-chain C 26 monomers and their polymers. *Macromol Chem Phys* 213:2220–2227. <https://doi.org/10.1002/macp.201200332>
- Wang Y, Ameer GA, Sheppard BJ, Langer R (2002) A tough biodegradable elastomer. *Nat Biotechnol* 20:602–606. <https://doi.org/10.1038/nbt0602-602>
- Yildirim S, Röcker B, Pettersen MK, Nilsen-Nygaard J, Ayhan Z, Rutkaite R, Radusin T, Suminska P, Marcos B, Coma V (2018) Active packaging applications for food. *Compr Rev Food Sci Food Saf* 17:165–199. <https://doi.org/10.1111/1541-4337.12322>
- Young RJ, Lovell PA (2011) Introduction to polymers. CRC Press
- Zhao H (2018) Enzymatic ring-opening polymerization (ROP) of polylactones: roles of non-aqueous solvents. *J Chem Technol Biotechnol* 93:9–19. <https://doi.org/10.1002/jctb.5444>