General Structure and Classification of Bioplastics and Biodegradable Plastics

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Abstract

The term "bioplastics" refers to chemically unrelated products that are manufactured exclusively or partially from renewable biomass sources such as agricultural products or microbes such as bacteria, yeast, and sometimes several nanometre-sized carbohydrate chains (polysaccharides). Bioplastics prepared from renewable means can be naturally recycled by biological processes, thus limiting the use of fossil fuels and shielding the environment. Biodegradable plastics are categorized as agro-polymers (starch, chitin, protein) and bio-polyesters (polyhydroxy-alkanoates, polylactic acid). Usually, foodstuffs with limited shelf life including fresh vegetables and fruits as well as those with long shelf life like cooked food items which are not in the need of increased oxygen supply are parceled using these bioplastics. Mainly, the enzymatic actions of microorganisms cause bioplastics polymers to decay into CO_2, H_2O, and other inorganic compounds. This current effort provides a general idea about bioplastics, aiming their production methods from biomass-based resources. Similarly, it will discuss the origin and classification of bioplastics. Furthermore, the details about the structure and components of bioplastics including polymers and the ways how these polymers are biochemically converted into bioplastics will also be reviewed. Moreover, different biopolymers currently under research will also be explored. With further improvements in the biopolymer area of

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research in the coming future, it can be more effectively utilized in various fields of life.

Keywords

Biopolymers · Bioplastics · Biodegradable · Classification · Biochemical synthesis · Renewable resources

2.1 Introduction

Bioplastic simply means the use of living organisms such as plants, animals, and microorganisms for the production of plastic. This type of plastic is different in many ways from fossil fuel-derived plastics. The bioplastic derived from biomass sources is also known as bio-based plastic. These are usually biodegradable because they are derived from renewable sources and can degrade by direct hydrolysis. A wide range of oil-based polymers are now utilized in many industries as packaging material. Plastic leftover is one of the most important issues in the present world because the plastic derived from fossil fuels is nondegradable and difficult to recycle, so this type of plastic is a major contributor to solid waste. To overcome the nondegradable plastic waste, scientists have now introduced bioplastics that are derived from living organisms (Kumar and Thakur 2017). According to the European Bioplastics Organization (EBO), bioplastics are referred to as plastics which are biobased and are biodegradable and/or compostable. These bioplastics are decomposed into carbon dioxide and water and biomass of inorganic nature under natural or unnatural conditions mainly by the degradation caused by the enzymes of microorganisms (Song et al. 2009). Furthermore, it is also required that these materials should be almost 50% organic in nature by composition. The developed polymer should be cut down during 6 months under-stimulated composting state by at least 90% of its weight/volume (Ezeoha and Ezenwanne 2013).

In recent years, bio-based polymers are extensively utilized for packaging purposes in various industries. The use of bio-based polymers has encouraged researchers to support ecological development because of diverse disposable options (Kumar and Thakur 2017). The major interests behind the production of bioplastics are mainly two in number: the first interest is the making bioplastic in bulk quantity, and the second is the proper disposal of bioplastic. Fossil fuel-based plastics are very slowly degraded in the environment that is why they are considered nonbiodegradable. There is a variety of biodegradable polymers such as lignin, starch, and cellulose that are actively involved in the production of bioplastics (Ross et al. 2017). The major drawback of the use of nondegradable plastics obtained from petrochemicals involves the emission and long-period accumulation of carbon dioxide in the environment. This accumulated carbon dioxide affects the ozone layer and is also a major contributor to climate change. Therefore, the world is seeking the sustainable use of plastic (bioplastic) that can be easily degradable and are environment-friendly (Tokiwa et al. 2009). To move toward a sustainable environment and prevent the disposal of plastic waste in the environment, the production of bioplastic has gained a lot of interest due to its high biodegradable ability. Bioplastics obtained from biomass or renewable resources include polyhydroxyalkanoate (PHA) and polylactic acid (PLA) in contrast to the plastics obtained from fossil fuels (like polybutylene succinate, PBS) that put a negative impact on the environment (Mekonnen et al. 2013). Although bioplastic is considered to be environment-friendly, it may have some limitations such as poor mechanical properties and high production cost. High production costs can be tackled by utilizing agriculture waste that is a low-cost renewable resource. Polylactic acid (PLA) is a type of bioplastic that has some unique properties like high tensile strength and modulus, but polyhydroxyalkanoate (PHA) lacks some mechanical properties when compared with polylactic acid (Tabasi and Ajji 2015).

These bioplastics can be degraded very easily in the environment and can be recycled easily. The degradation of polymer is completed in three steps in the environment: (1) biodeterioration, the microorganisms grow in or on the surface of the polymer, which changes the chemical, physical, and mechanical properties of the polymer; (2) bio-fragmentation, the microorganisms act on the large polymer unit and convert it into oligomers and monomers, the smaller units; and (3) assimilation, after the breakdown of polymer into smaller unit monomers, there is a release of a large amount of carbon, energy, and nutrient sources that are used by the microorganism and convert them into the water, carbon dioxide, and biomass (Lucas et al. 2008). Some factors actively involved in the degradation of plastics in the environment are the polymer chain, the chemical structure of the polymer, and the complexity of a polymer formula along with crystallinity. The specific functional group is selected and can be processed by using an appropriate enzyme. The polymers that have a more amorphous part, a shorter chain, and a less complex formula are more easily degraded by microorganisms (Massardier-Nageotte et al. 2006).

2.2 Types of Bioplastics

There are mainly three types of bio-based polymers which have been designed depending upon their source and manufacturing process (Ezeoha and Ezenwanne 2013): (a) polymers obtained from biomass, i.e., polysaccharides (starch and cellulose) and proteins (casein and gluten); (b) polymers obtained via renewable bio-based monomers. Polylactic acid is a good example here, which is obtained from monomers of lactic acid. The monomers themselves may be made via fermentation of carbohydrate feedstock and (c) polymers obtained from microorganisms. To date, bio-based polymers of this group consist primarily of polyhydroxyalkanoate, but advancement with bacterial cellulose is in progress.

2.3 Sources of Bioplastic

Plastic plays a very significant role in our daily life because there are a lot of things that we use today are directly or indirectly made up of plastic. But too much plastic use in our world makes plastic a major contributor to solid waste due to its nondegradable ability. That is why the world is seeking the alternative use of plastic that must be easily degraded and should be environment-friendly. So, bioplastics have their importance due to their degradable property and can be easily recycled. They are acquired from several biological foundations such as plants, microorganisms (bacteria), and algae. The plant and microbial products are the major contributors to the production of bioplastics (Reddy et al. 2003).

2.3.1 Plants as a Source of Bioplastics

The main plant source that is responsible for the production of bioplastic is starch. Starch is a naturally occurring polysaccharide consisting of two types of polymers: amylose and amylopectin. Starch is abundantly present in wheat, corn, sweet potato, barley, rice, etc. Along with starch, cellulose is also of key importance in bioplastic production. Thermoplastic starch is very common and widely used in the synthesis of bioplastic. The pure form of starch has a unique humidity-absorbing property; that is why pure starch is commonly used as bioplastic and is used in synthesizing drug capsules in pharmaceutical companies. Polylactic acid (PLA) is also a widely used bioplastic that is commonly obtained from cane sugar. There is a lot of genetic engineering practices that are being done on plants to get next-generation bioplastics (Rajendran et al. 2012).

2.3.2 Bacteria as a Source of Bioplastic

Bacteria are the most studied organism for the production of bioplastic. There are a lot of bioplastics that are directly or indirectly synthesized from bacteria. Many bacterial species contain intracellular polyhydroxyalkanoate (PHA) granules as a source of carbon and energy in their cells. The PHA that is extracted from gram-negative and gram-positive bacteria shows similar properties to polypropylene (Braunegg et al. 1998). *Bacillus megaterium* is an important bacterial species for the production of PHA because this bacterium contains 20% w/v of PHA content. The bacteria produce acetyl coenzyme A, which is converted into poly-3-hydroxybutyric acid (PHB) by the activity of three enzymes: acetoacetyl-CoA reductase, 3-ketothiolase, and PHB synthase (Ross et al. 2017).

2.3.3 Algal Sources

Algae are one of the diverse groups of organisms that range from unicellular to multicellular photosynthetic organisms. The by-products of many algae are used in the production of bioplastics. *Spirulina dregs* are microalgae commonly used in bioplastic manufacturing, but this alga is difficult to harvest. But macroalgae like seaweeds have many advantages over microalgae. The seaweeds produce high biomass, are cost-effective with the capability to grow up in a wide range of environments, and can be easily cultivated and harvested in a natural environment. Seaweeds produce polysaccharide that is commonly used in the field of microbiology, food technology, biotechnology, medicine, and now plastic industries. Bioplastic is now produced from the polysaccharide of seaweeds, this bioplastic is low-cost, environment-friendly, and nontoxic. The bioplastic derived from seaweeds has high tensile strength and much better in all aspects than the conventional plastic that is being used today (Rajendran et al. 2012).

2.4 Classification of Bioplastics

The bioplastics also known as biodegradable polymers are obtained from biomass, microorganisms, are petrochemicals and are biotechnologically derived. The bioplastics are majorly divided into two main categories that are agro-polymers and bio-polyesters (Fig. 2.1). Agro-based polymers are derived from natural renewable sources that may be polysaccharides, starch, cellulose, lignin, pectin, animal, and plant proteins and oils, while the bio-polyesters are obtained from microorganisms, petrochemicals, and biotechnological means. In agro-polymers, the main source is biomass that is obtained from plants and animals. Biopolymers that are derived from starch have many key features like renewability, high biodegradability, and good oxygen barrier property that make it more suitable than ordinary plastic (Thuwall et al. 2006). Most of the proteins that are obtained from animal and vegetable sources are used as a raw material for the production of bioplastics. Proteins are a well-known source used in the plastic manufacturing industries (Kumar and Thakur 2017).

2.4.1 Bioplastic from Biomass Products

Biomass is the material obtained from plants and animals, and these materials are used for the synthesis of bioplastic. The bioplastic obtained from biomass is also known as agro-bioplastics. The biomass products include polysaccharide, starch, cellulose, chitin, lignin, pectin, and proteins derived from plants and animals. These substances are directly obtained from plants and animals, and these are the major contributors to the production of various types of bioplastics (Kumar and Thakur 2017).

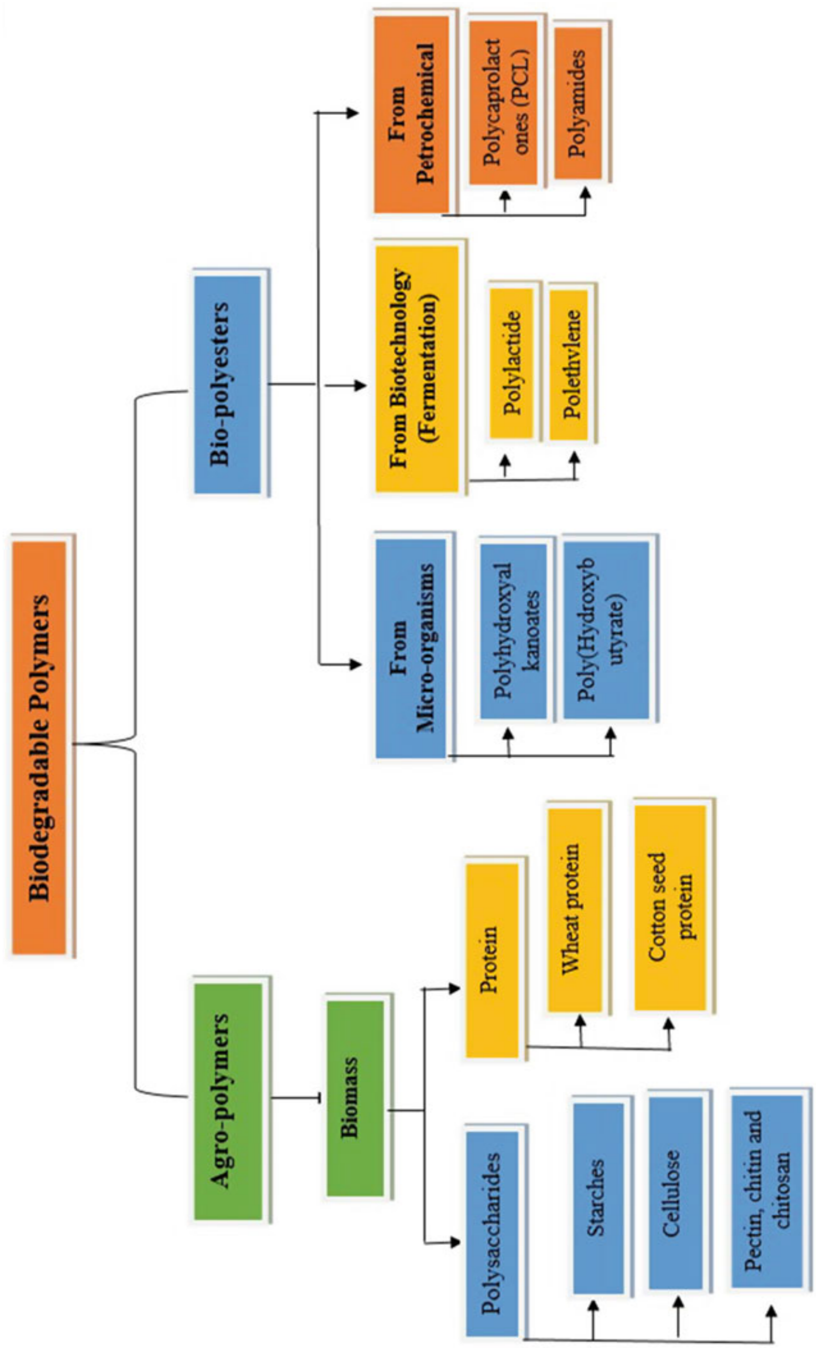


Fig. 2.1 Classification of biodegradable polymers (Kumar and Thakur 2017; Palanisamy et al. 2019)

2.4.1.1 Bioplastic-Based on Polysaccharide

There have been variously reported polysaccharides that are involved in the production of bioplastics. Polysaccharides are a long chain of carbohydrate molecules that bind with one another through glycosidic linkages. There are a lot of polysaccharides that have unique properties, which is why they are used in bioplastic production (Mali et al. 2002).

2.4.1.2 Bioplastic Obtained from Starch

Starch is one of the best-known polysaccharides that is formed by the combination of amylose and amylopectin (Fig. 2.2). The specific ratio of these two glucose-based polymers makes its unique physiochemical properties. If starch has a high content of amylose, this contributes to the film strength of the polymer, and if the starch contains branched amylopectin, then this will lead to a film with low mechanical properties. This low mechanical property of polymer can be upgraded by means of plasticizers such as glycerol and sorbitol (Mali et al. 2002). Different biopolymers that are manufactured by blending conventional polymers with granular starch will increase the strength, permeability of film, and water absorption and decreases the cost of production of the polymeric film (Kumar and Thakur 2017).

Bioplastic from the Modified Form of Starch

The starch molecules are manipulated for their physiochemical characteristics by adding the ester group. This manipulation improves the thermal stability, moisture absorption, and water vapor transmission rate and also increases the barrier properties for different gases. Starch has a good biodegradable property, which is why starch molecules are used in conventional polymers to increase its biodegradable ability. Scientists have successfully proved how starch mixed with a conventional polymer like low-density polyethylene to improve the biodegradable property (Albertsson and Karlsson 1995).

2.4.1.3 Bioplastic Obtained from Cellulose

Cellulose is naturally occurring biodegradable polysaccharides in plant cells. Cellophane is a chemically synthesized biodegradable material that is made by dissolving the cellulose in the mixture of carbon disulfide and sodium hydroxide and obtained product is cellulose xanthate (Fig. 2.3) which is further dipped into the acid solution (H_2SO_4), and the final product produced is cellophane film (Jabeen et al. 2015). Another method is adopted to obtain the derivatives of cellulose by the process of the esterification and etherification of the hydroxyl groups (Cyras et al. 2007). To make the cellulose as bioplastic material in the form of thermoplastic materials, further additives are added as cellulose diacetate and cellulose triacetate. These chemicals enhance the extrusion molding and laminating process, and finally, cellophane exhibits good film properties (Zepnik 2010).

2.4.1.4 Bioplastic Obtained from Pectin

Pectin is a linear biomacromolecule which is based upon the linear configuration of α-(1-4)-linked D-galacturonic acid. Many chemical changes are produced in the

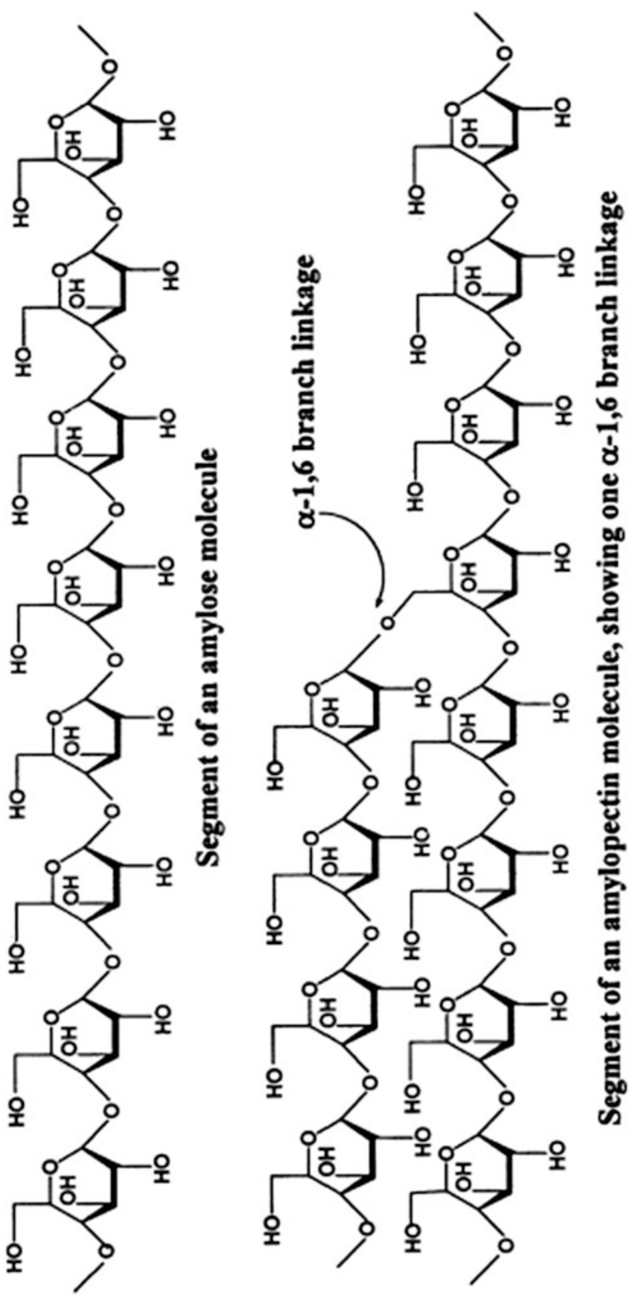


Fig. 2.2 Structure of starch, showing a segment of amylose and amylopectin (Robyt 2008)

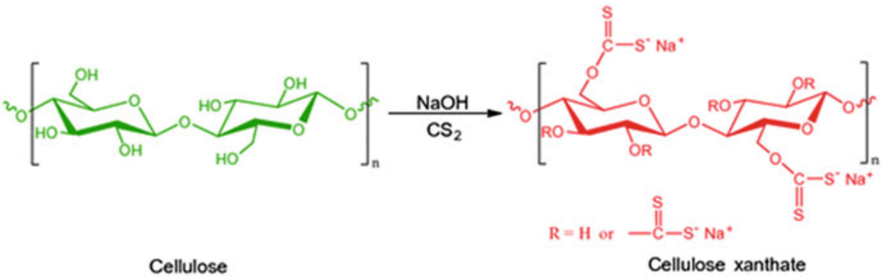


Fig. 2.3 Synthesis of cellulose xanthate from cellulose (Boy et al. 2018)

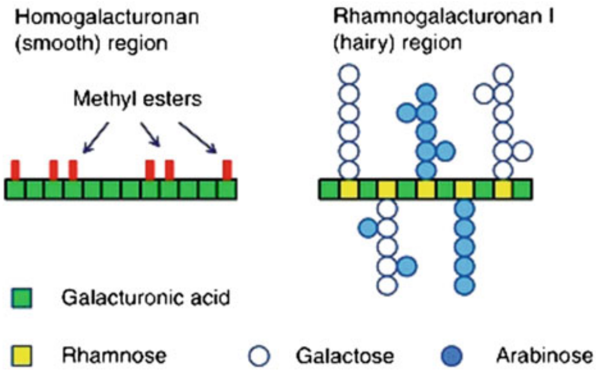


Fig. 2.4 Rhamnogalacturonan I and rhamnogalacturonan II as bio-polymers (Jaskolski 2013)

pectin by the partial replacement of monomer units like an α-(1-2)-L-rhamnose leading to a new structure rhamnogalacturonan I (Fig. 2.4). Rhamnogalacturonan II is the third type of new structure which is common, except highly for branched and complex polysaccharide structure (Fig. 2.4) (Thakur et al. 1997). In nature, ~80% esterification of the galacturonic acid carboxyl group is based on the methanol; this condition is based on the proportion of extraction. In food applications, the behavior of pectin depends upon the ratio of esterified and nonesterified galacturonic acid. Based on esterification, pectin is classified as high- and low-ester pectin (Malathi et al. 2014; May 1990).

2.4.1.5 Bioplastic Obtained from Chitin and Chitosan

Chitin is one of the most familiar agro-polymer after the cellulose in nature that is produced in rich quantity. It mainly exists in nature in the form of an orderly crystalline microfibril structure. Chitin is also the main component of the exoskeleton in many arthropods and also a component of the fungal and yeast cell wall (Rinaudo 2006). It is naturally occurring polysaccharides that are biodegradable, nontoxic, and biocompatible (Itoh et al. 2002). Flieger et al. (2003) identified that usually, the extraction of naturally occurring chitin is based on the crab crumb during

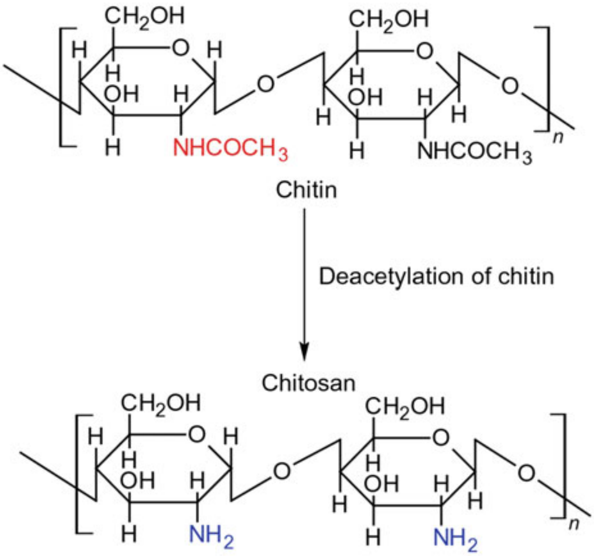


Fig. 2.5 Synthesis of chitosan from chitin (Królczyk et al. 2020)

pretreatment; dilute solution of sodium hydroxide (pH 13.5) is used for the prevention of microbial infection of the flesh of crab and protection of shell degradation. The isolated crushed shell passes into the rector for the further process where they are treated with hydrochloric acid (HCL) to gasify the materials (Flieger et al. 2003). In the third step of the process, produced chitin and liquefied proteins go into the washing procedure before ingoing into another NaOH solution, following a slightly high temperature. After completion of the whole procedure, 12% of chitin yield is obtained from crushed crab crumbs. Chitin is used to produce chitosan from various chemical processes (Fig. 2.5). In the process, chitin is washed and put under the boiling condition until acetate is removed from the molecules. After the hydrolysis, the resulted material chitosan is shifted for the following procedure, washed, dried, ground, weighed, and packed for sale.

2.4.2 Bioplastic Obtained from Proteins

Proteins have vast and empirical importance for the production of bioplastics. The main sources of protein are plants and animals that act as a raw material in the synthesis of bioplastics. Proteins play a significant role in thermosetting modifications of plastics due to their denaturation ability. The protein-based bioplastics are well-known for their high degradability and also make them a fast degrading polymer. A certain number of proteins have gained maximum attention due to their biodegradable polymer nature, but only a few of them have an impact due to their definite industrial scale-up, high assembly cost, and low product performance. There are certain plant proteins which are the main potential source such as com protein (zein), soy protein, and wheat protein (gluten) (Sorrentino et al.

2012). Some animal-based proteins also act as biodegradable polymers such as gelatin or collagen protein and casein. These are purely animal-based proteins. Some proteins inside the bacteria also play an effective enzymatic role such as lactate dehydrogenase, fumarase, and chymotrypsin (Itoh et al. 2002).

2.4.2.1 Bioplastic from Wheat Gluten Protein

There is a protein known as wheat gluten, a by-product that is produced from the bio-ethanol industry also used for packaging purposes in the baking industry. This wheat gluten has many advantages over other proteins like abundantly available, relatively inexpensive, and mechanical and biodegradation ability. Wheat gluten also has other unique properties such as gas barrier, film formation, and biodegradation ability. The properties of polymers developed from wheat gluten depend upon the two types of proteins: gliadins, and glutenins (Fig. 2.6). The wheat gluten is usually thermoplastic and it has been utilized for manufacturing natural fiber-based bio-composite and biofilms (Muneer et al. 2014).

2.4.2.2 Bioplastic from Cottonseed Protein

Cottonseed is also an important source of plant protein. It has a unique amino acid combination that increases its nutritional value and commonly used in cattle feeds but not as much used in nonfood industries. The protein-based bioplastics have low mechanical properties as compared to synthetic polymers. Its inferior mechanical properties are due to its hydrophilic nature, complex composition, and environmental sensitivity. To overcome these issues, protein requires different modifications like

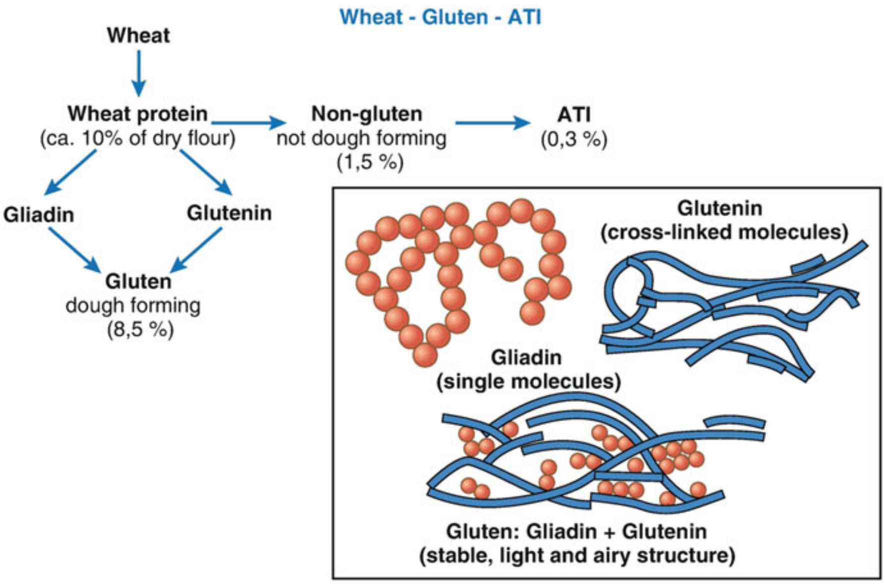


Fig. 2.6 An overview of wheat gluten composition (Schuppan and Gisbert-Schuppan 2019)

plasticization, denaturation, and cross-linking. Cottonseed protein is used to produce bioplastic. The protein obtained from cottonseed undergoes some modifications like denaturation and cross-linking with aldehyde and urea. This modified form of cottonseed protein is capable to produce bioplastics (Yue et al. 2012).

2.5 Bioplastics from Microorganisms

Bioplastic is a special type of biomaterial. They are usually polyester in nature and can be produced in microbes under different nutritional and environmental conditions. Most of the polyesters are produced inside the microbes under the lack of some important nutrients. They are usually a storage substance that is produced by microbes under stress conditions. The number of granules, size of granules, and physicochemical properties vary from species to species (Calero-Bernal et al. 2020).

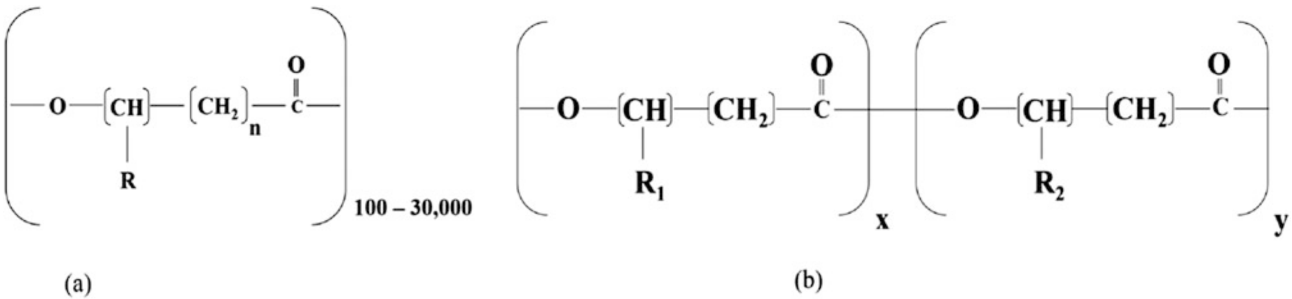
2.5.1 Polyhydroxyalkanoate (PHA)

Polyhydroxyalkanoate (PHA) is a biopolymer that is well-known for its biodegradability, usually present inside microorganisms as a source of energy. PHA obtained from more than 90 genera of both gram-negative and gram-positive bacteria under anaerobic and aerobic conditions. Bacteria can be divided into two groups based on conditions required for PHA production. The first group needs some nutrients such as oxygen, nitrogen, phosphorus, and magnesium for the accumulation of PHA, but this group does not accumulate PHA during the growth phase. The second group does not require any limitation of nutrients and can accumulate PHA during the growth phase (Muhammadi et al. 2015).

Suszkiw (2005) explained polyhydroxyalkanoates are linear and are produced as a by-product by the bacterial fermentation of lipids and sugar. Bacteria produce polyhydroxyalkanoates as the product to store the maximum amount of energy in the form of carbon. On the large scale of the industrial level, the optimum conditions provide the bacteria to obtain the purified polyester by the fermentation of sugar. During the fermentation, more than 150 types of monomers are combined in this polyhydroxyalkanoate production, and these monomers change the whole properties of this family (Fig. 2.7). PHA is a less elastic material and more ductile than plastic material, and it is also biodegradable. Due to the efficiency of these materials, they are more extensively used in the medical industry (Suszkiw 2005).

2.5.2 Polyhydroxybutyrate (PHB)

Polyhydroxybutyrate (PHB) is a macromolecule present inside the bacteria, which acts as inclusion bodies. These are energy reserves that are used by bacteria under unfavorable conditions. They are polymers, and their properties are similar to synthetic plastic like polypropylene. These properties make this polymer a valuable



n	*R* group	IUPAC Nomenclature	Abbreviation
1	hydrogen	poly(3-hydroxypropionate)	(3HP)
1	methyl	poly(3-hydroxybutyrate)	(3HB)
1	ethyl	poly(3-horoxyvalerate)	(3HV)
2	hydrogen	poly(4-hydroxybutyrate)	(4HB)
2	methyl	poly(4-hydroxyvalerate)	(4HV)
2	ethyl	poly(4-hydroxycarpoate)	(4HC)
3	hydrogen	poly(5-hydroxyvalerate)	(5HV)
3	methyl	poly(5-hydroxycarpoate)	(5HC)
3	ethyl	poly(4-hydroxyheptanoate)	(5HH)

Fig. 2.7 Homo- and heteropolymer of polyhydroxyalkanoate (PHA). (**a**) Homopolymer PHA (**b**) Heteropolymer PHA (Mudenur et al. 2019)

product for the synthesis of bioplastic that can replace the petro-based plastic (Kumar and Thakur 2017). A major hurdle in the production of PHB is its high production cost as compared to petro-based plastic. Different techniques such as optimizing fermentation, recovery process, and development of efficient bacterial strain have been used to reduce the production cost of PHB. PHB generally accumulates in the bacteria under a high level of carbon and low levels of nitrogen, oxygen, and phosphorus (Verlinden et al. 2007). The PHB is produced by the activity of acetyl coenzyme-A that is completed in three steps. In the first step, two acetyl-CoAs are converted into acetoacetyl-CoA by the activity of acetyl-CoA acetyltransferase. In the second step, acetoacetyl-CoA is converted into 3-D-hydroxybutyryl-CoA with the help of acetoacetyl-CoA reductase, and in the last step, the final polymerization step is catalyzed by PHB synthase (Peoples and Sinskey 1989).

Suszkiw (2005) stated that the production of the biopolymer poly-3-hydroxybutyrate (PHB) is based on the processing of the bacteria that utilize the raw substrate in the form of glucose, corn starch, or wastewater (Suszkiw 2005). The production of poly-3-hydroxybutyrate by bacteria increases every year, and the properties of the PHB are quite similar to the petro-plastic polypropylene (Gouda et al. 2001). Chen and Patel (2012) also stated that the South American sugar industry is surely going to enhance PHB production at the industrial level. At the primary level, on the industrial scale, isolation of the PHB is based on the physical characteristics, and after that, it can be developed into an apparent film with a high melting point of more than 130 °C (Chen and Patel 2012).

2.6 Bioplastics Obtained from Biotechnological Inventions

Biotechnology plays a significant role in the invention of various methods to get a product in bulk quantity within a short period. By using biotechnology, we can alter the product according to our needs, and product quality can be enhanced. There are a lot of biotechnological methods through which we can obtain our desired product. Biotechnology involves converting plant sugar into plastic, growing plastic in various crops, and producing plastic inside microorganisms. The effort of biotechnology makes bioplastics a more useful and environment-friendly product as compared to conventional plastic (Kumar and Thakur 2017).

2.6.1 Polylactic Acid (PLA)

Polylactic acid is an aliphatic biodegradable polymer that is made from hydroxyl acids mainly polyglycolic acid. Polylactic acid is one of the most important renewable monomers of bioplastic material which are derived from the fermentation of agricultural by-products such as starch-rich substances like sugar or wheat and corn starch. The fermentation process is followed for the conversion of corn and another carbohydrate into the dextrose and finally into the lactic acid (Fig. 2.8). PLA is

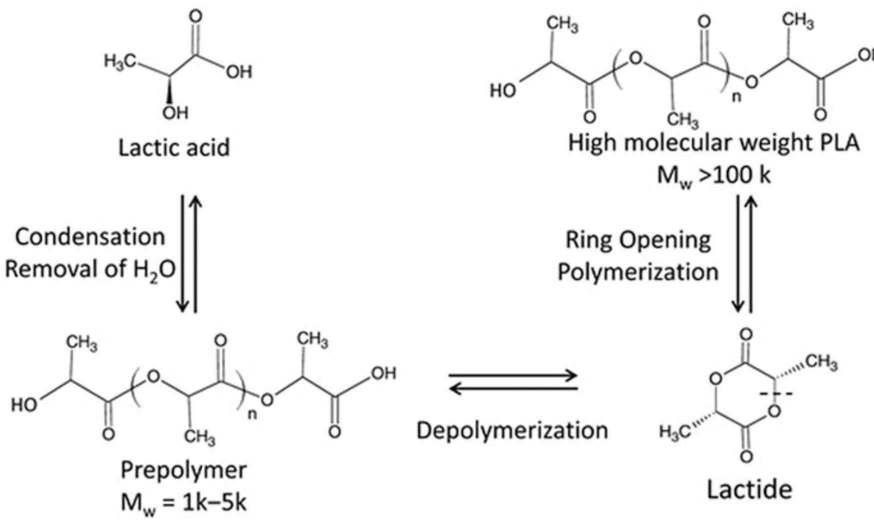


Fig. 2.8 Synthesis of polylactic acid (Ding et al. 2018)

obtained from lactic acid by two different methods. In the first method, the lactic acid cycle produces cyclic lactic acid dimer lactide that further produces PLA with high molar mass. The second method is direct polymerization of lactic acid, usually condensation polymerization, which yields PLA polymer with low molar mass (Polyesters and Albertson 2001). There are two stereo-regular forms of lactic acid: L-lactic acid and D-lactic acid. The lactic acid obtained from petro-chemical is D-lactic acid, while L-lactic acid is obtained from the fermentation of starch. PLA obtained from lactic acid is also called thermoplastic that is a result of biodegradable aliphatic polyester having sufficient potential for the application of packaging (Rhim et al. 2009). PLA pellet formation is directly based on the lactic acid monomers polycondensation or ring-opening polymerization of lactide (Jabeen et al. 2015).

PLA is a packaging material most commonly used for the packing of different materials. The strength of packing material depends upon the ratio of isomers of lactic acid monomers. PLA is the first more safe biobased material that fulfills the requirements of packaging material on a huge scale. Due to its safety and eco-friendly nature, PLA is most actively used in large-scale coatings, film, and injection-molded objects (Rasal et al. 2010). PLA is also modified with low-density polyethylene (LDPE), high-density polyethylene, and polyethylene terephthalate to be used as packaging material. PLA is well-known for its biodegradability in nature due to the presence of ester bonds which act as its backbone. It is much similar to polyolefins and can be converted into plastic by some standard methods such as extrusion and injection molding. PLA is commonly used for packaging purposes as the PLA is present in our body as a nontoxic material. So, when the PLA is used in packaging, food contamination is neglected. By increasing brittleness and thermal properties, PLA requires various modifications such as blending with other polymers and copolymerization. PLA is also copolymerized with polyethylene glycol (PEG) because PEG is well-known for its hydrophilic and biocompatible ability. In this way, PLA improves its hydrophilic property and can be later used in drug delivery systems (Ross et al. 2017).

2.6.2 Polyethylene

Ethylene is the main constituent for the development of polyethylene (Fig. 2.9). The source of ethylene is ethanol, and it has many similar properties. Fermentation is the main process for the synthesis of polyethylene from agricultural feedstocks such as corn or sugar cane. Although bio-derived, polyethylene is nonbiodegradable but has chemical and physical similarities with traditionally synthesized polyethylene. Bio-ethylene is a bioplastic material, and it can also eliminate greenhouse emissions (Shiramizu and Toste 2011).

2.7 Bioplastics Obtained Chemically

The chemical method is one of the most applicable and conventional methods for the synthesis of polymers; there is one suitable method for the production of "bio-polyesters" in a huge quantity. By adopting the chemical method, a large number of "bio-polyester" are produced; however, in the class of "bio-polyester," polylactic acid (PLA) is one of the materials which can be synthesized commercially in a huge quantity for the production of renewable packaging material (Jamshidian et al. 2010). In the present time, all types of classical packaging materials derived from mineral oil-based renewable resources are derived from the fermentation process.

2.7.1 Polycaprolactones

Polycaprolactone is a crude oil-based bioplastic material that is chemically synthesized by adopting thermoplastic polymer methods. Polycaprolactones contain oil, solvent, water, and chlorine resistance due to these ingredients Polycaprolactones is used as thermoplastic polyurethanes, resins for the synthesis of leather, fabrics, and surface coating due to its adhesive nature (Mousa et al. 2016).

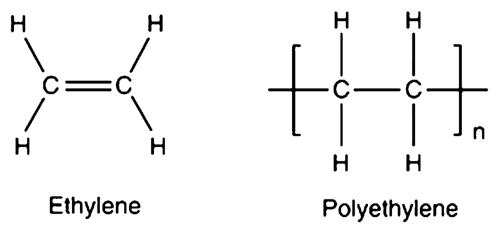


Fig. 2.9 Structure of ethylene and polyethylene (Sherazi 2014)

2.7.2 Polyamides

Aliphatic polyamides, also considered nylons (Fig. 2.10), are among the most significant product polymers. Polyamides also contain amide groups in the backbone of the macromolecule, which makes polyamides heterochain polymers. These are thermoplastic due to wide-ranging presented properties which are actively utilized in the creation of fibers and films, molding compounds (Page 2000). There are three main methods which are used for the synthesis of polyamides: (1) the first method is amino carboxylic acid polycondensation as bifunctional monomers, (2) diamines and dibasic acids both are polycondensed, and (3) the third method is lactams—cyclic amides ring-opening polymerization method and amide monomers contain three to seven ring atoms (Rulkens and Koning 2012). Literature well covers all synthetic pathways as well as polyamide copolymers of various compositions and structures (Hashimoto et al. 2004). Recently, the researches are fully focused on the more significant class of bio-based polyamide thermoplastics, which are partially or entirely manufactured from renewable resources of low cost (Stevens 2013). In the fabrication of bio-based polyamide thermoplastics, castor oil is used as a bio-based monomer and also mass-produced by the fermentation process. The process of synthesis of bio-based polyamides and synthetic polyamide are the same, and there are several profitable yields accessible in the market (Rilsan®11 of Arkema (Colombes, France), Ultramid Balance® of BASF (Ludwigshafen, Germany), Vestamid Terra® of Evonik (Essen, Germany), etc.) (Thielen 2010). The latest research includes the most well-known and fast-developing family of thermoplastic poly-(ester amides) that contain the most effective and valued characteristics of both polyesters and polyamides, i.e., polyesters naturally originated by bio-based castor oil so that is biodegradable and also shows the properties of high tensile strength and high thermal stability (Fonseca et al. 2014). Recently, all consideration is being given to the production of poly-(ester amides) that contain α-amino acids which are actively participated in the biomedical materials (Rodriguez-Galan et al. 2011). The

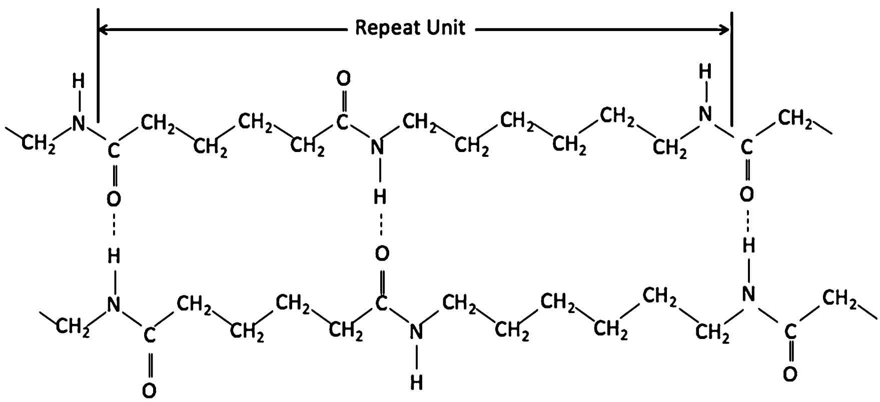


Fig. 2.10 Structure of nylon (Baker 2018)

role of the α-amino acid enhances polymer-cell interactions and also contributes to the addition of functional groups. This whole process is actively involved in the biodegradability of the material.

2.7.2.1 Polyamide (PA11)

Natural oil is the main source of biopolymer polyamide 11 (Fig. 2.11). PA11 is not biodegradable and belongs to a family of technical polymers, and it is also known as tradename Rilsan B and at a commercial scale by the name of Arkema PA11. The properties of PA11 are quite similar to PA12, although, during the production of PA11, emission of greenhouse gases and utilization of nonrenewable assets are depleted. PA11 is superior to PA12 and thermally resistant. Due to extraordinary properties, it is the most commonly used in pneumatic air brake tubing, automotive fuel lines, flexible oil and gas pipes, electric cable anti-termite sheathing, control fluid umbilicals, sports shoes, electric device components, and catheters. PA410 polyamide is another closely related bioplastic material extracted from castor (Levchik et al. 1992).

2.8 Role of Petrochemical Products in the Synthesis of Bioplastics

Petrochemical products played a very effective role in the synthesis of bioplastic materials. Polycaprolactone and polyvinyl alcohol are the main synthetic (petroleum) source product. The origin of polycaprolactone is based on crude oil and chemically synthesized biodegradable thermoplastic polymers. Polycaprolactone shows the properties of the good solvents, and chlorine resistance used in thermoplastic, resin for surface coating, and synthesis of leather and fabrics. Polycaprolactone and polyvinyl alcohol both have limited use, due to low glass transition and melting temperature of 60 °C actively used in the starch-blends.

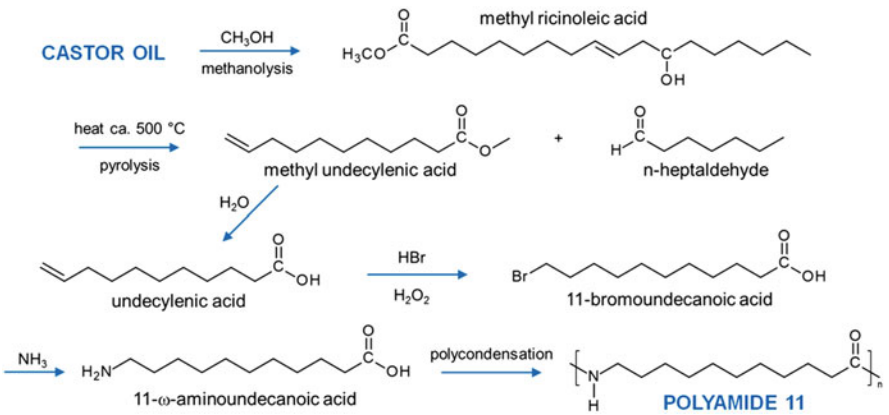


Fig. 2.11 Synthesis of polyamide 11 (Jariyavidyanont et al. 2019)

Polyvinyl alcohol (POVH) is another polymer used in packaging applications. The preparation of POVH is based on the hydrolysis of polyvinyl acetate. The method is based on the starch control over the water solubility, and finally, resin products are formed—although the PVOH biodegradability is still disputed further. Starch and PVOH blends are sensitivite to water, both can be water-soluble (Kumar and Thakur 2017).

2.9 Conclusion and Future Perspective

Production of bioplastic material at the commercial level is costly in the current situation, but the future advancements in the technologies play an effective and viable role in the production of these biomaterials. Researchers are already doing a great job in this field, and some positive results have been obtained. The utilization of bioplastic material in the market is minimal due to rare uses for special purposes such as food items, medical items, and consumable packages. In the future, there will be more possibilities which will eliminate all environmental hurdles we are facing currently due to the petroleum hydrocarbon-derived plastics. To date, the number of polyesters with plastic material is 160, and the number of this bioplastic material increases exponentially by the genetic modification and metabolic genetic engineering techniques. However, some limitation is observed about original microbial strains as compared to the recombinant microbes for the synthesis of novel polyesters. Thus, by utilizing appropriate organisms, many other bioplastic materials could be obtained with different properties and structures. In conclusion, bioplastic materials, due to special characteristics and broad biotechnological application, offer an extremely promising future.

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