

Chapter 1

Introduction to Biodegradable Polymers



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1 Introduction

In our continuously ever-growing society, polymers play a vital role in our day-to-day applications. Some of them do not persist in our ecosystem for too long as they are degraded away by microorganisms and other natural factors. But many others tend to remain in our environment and get accumulated as waste. Most of them are reprocessible, whereas some are not. Economically, it is relatively easier to manufacture materials from petroleum-based sources. Majority of the non-biodegradable polymers that are used today are plastics made up of polyethylene, polypropylene, polystyrene, etc. lead to waste-disposal problems. These plastics tend to stay in our environment because there is hardly any microorganism that may feed them. Due to their adaptability in modeling, durability, and simplicity of use, across a range of manufacturing and production processes, plastics are widely used and since then rate of production of plastic products has increased since 1970s. The production of plastic waste was manageable in 1970s but in early 1990s the plastic waste production was more than tripled. Today the generation of plastic waste is more than 400 million tons [1]. The increase in plastic waste has become a serious problem for the environment. Most of this plastic waste includes single use plastic bottles, food wrappers, plastic grocery bags, cigarette filters, etc. Millions of tons of plastic waste are introduced to the environment; these plastics waste sometimes are shipped to thousand kilometers and dumped or burned which in turn affects our ecosystem. It has been studied that polyethylene may need 100–1000 years for its degradation in nature depending on

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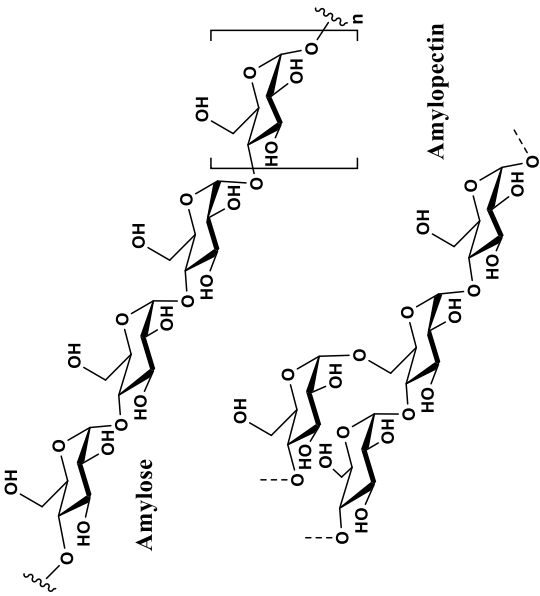
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the product [2]. These non-biodegradable polymers on burning produce greenhouse gases which further cause global warming and severe respiratory problems. As these polymers are non-biodegradable, they stay in environment in form of microscopic plastic and contaminate our soil and water bodies. Despite the efforts being made to overcome these issues, 75–200 million tons of plastic wastes are found in our ocean. On the other side, plastics are causing the planet serious challenges by either clogging the water system or interrupting the food chain system. Almost 79% of the plastic waste are dumped in landfills [3]. Also, our petroleum source is limited, so it is highly expected those non-biodegradable polymeric materials should be replaced with recyclable and biodegradable alternatives.

Biodegradable polymers are either extracted from renewable sources or obtained via polymerization in laboratory and degrade easily in nature. On their own, their shelf life and service life both are less because they degrade more easily than non-biodegradable polymers, but with continuous advancement in polymer technology this can be improved. Common biodegradable polymers—starch, cellulose, gelatin, chitosan, Polyhydroxy alkanoate (PHA), Polyvinyl alcohol (PVA), Polybutylene succinate (PBS), Polylactic acid (PLA), Polyurethanes (PU), Polycaprolactone (PCL), and Poly(ortho ester) (POE) are being widely used in several sectors. The chemical structure and applications of these polymers are tabulated in Table 1. The reason for their appreciable biodegradability is the presence of heteroatom in the backbone of the polymer as C–X linkages (X=O, N, S, etc.). The bond energies [C–O(~67 kcal/mol) < C–N(~72 kcal/mol) < C–C (~85 kcal/mol)] prove C–X bonds can be easily cleaved by environmental factors [4–6]. These polymers possess unique properties of degradation in the environment either by the microbial action or by the effect of natural factors [7]. The polymer degradation can happen in multiple ways—(1) chemical degradation which includes hydrolysis and oxidation; (2) Physico-chemical degradation which occurs via photodegradation, thermal degradation, and mechanical degradation; and lastly (3) degradation via enzymatic pathway [5]. Besides these factors, molecular weight, morphology, crystallinity, tacticity, branching, and nature of side groups also affect the rate of degradation [8].

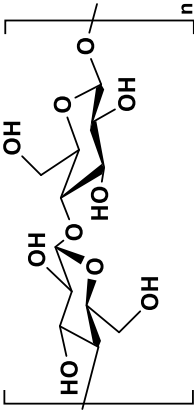
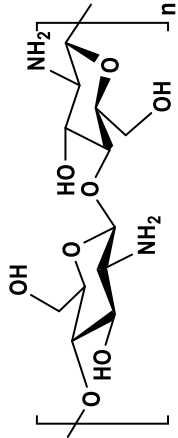
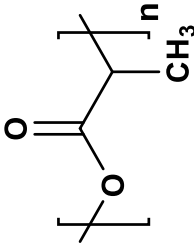
The easiest methods to evaluate the degradation of biodegradable polymers are—visual observation (formation of cracks or color changes with time), weight loss measurements by GPC (Gel Permeation Chromatography), HPLC (High Performance Liquid Chromatography), GC–MS (Gas Chromatography- Mass Spectrometry), clear-zone formation NMR (Nuclear Magnetic Resonance), and XRD (X-ray Diffraction) [6, 7]. Lastly, the most effective method is CMR (cumulative measurement respirometric) or DMR (Direct measurement respirometric) which measures the amount of CO₂ released with respect to certain reference materials [8].

Table 1 Different biodegradable polymers, their structures, and applications

Polymer	Chemical Structure	Applications	Refs.
Starch	 <p>The image shows two chemical structures of starch components. On the left is Amylose, a linear chain of alpha-D-glucopyranose units connected by alpha-1,4 glycosidic bonds. On the right is Amylopectin, a branched chain of alpha-D-glucopyranose units with alpha-1,4 glycosidic bonds in the main chain and alpha-1,6 glycosidic bonds at the branch points. Both structures include wavy lines indicating the continuation of the polymer chains.</p>	Used in food and pharmaceutical packaging industries, water treatment, and emulsion stabilization	[9, 10]

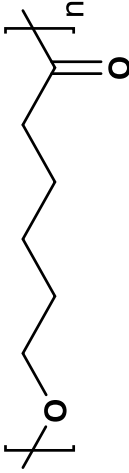
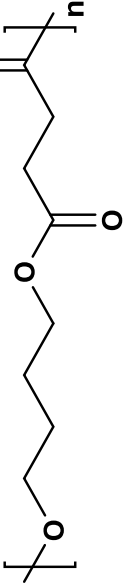
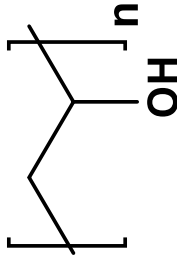
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Table 1 (continued)

Polymer	Chemical Structure	Applications	Refs.
Cellulose		Used in paper industry, metal industry, packaging industries. Also used in tissue engineering, and agricultural fields	[11–16]
Chitosan		Due to its exceptional biocompatibility, it is used in wound healing, blood hemostasis, and therapeutic delivery (drug/vaccine delivery)	[17–20]
PLA		Large applications in kitchen appliances (disposable bags, cutlery, microwavable trays), in electronic gadgets (laptops, mobile devices), in feminine hygiene products and diapers. It is also used for upholstery and automotive parts (floor mats, panels, and coverings). PLA is also used in biomedical field as implants (suture, anchors, screws, fixation pins) drug delivery carrier, and scaffold	[21–23]

(continued)

Table 1 (continued)

Polymer	Chemical Structure	Applications	Refs.
PCL		PCL is used as orthopedic sutures, dermal fillers, and drug carriers	[24, 25]
PBS		PBS is used as food packaging material, mulch film, plant pots, fishing nets, and hygiene products	[26, 27]
PVA		It is used as adhesives, surfactants, and film-forming material	[28–30]

(continued)

Table 1 (continued)

Polymer	Chemical Structure	Applications	Refs.
PHA	<p style="text-align: center;">R = Alkyl</p>	It is used to make biomedical implants—scaffolds, screws, sutures, and pins	[31, 32]

2 Classification of Biodegradable Polymers

Biodegradable polymers can be classified with respect to many factors, i.e., sources, composition, synthesis procedure, processing method, applications, etc. Among all, the most important categorization is source and application based. Conventionally, biodegradable polymers are categorized into three major divisions—natural, semi-synthetic, and synthetic biodegradable polymers (Fig. 1). Natural polymers are those which are directly obtained from biomass, and when monomers are obtained from natural source and polymerized in laboratory is called semi-synthetic polymers. Synthetic polymers are purely synthesized in laboratory through chemical routes [33, 34]. Natural, semi-synthetic, and synthetic polymers are discussed in detail with proper examples in subsequent sections.

2.1 Natural Biodegradable Polymers

Natural biodegradable polymers are the materials originating directly from nature, i.e., extracted from plants and animals. These polymers play a vital role in our daily life as all living beings are based on them—proteins and nucleic acid that occur in human and animal body, and polysaccharides are found in cell walls of plants and bacteria. In nature, all organisms' growth cycles leads the formation of these

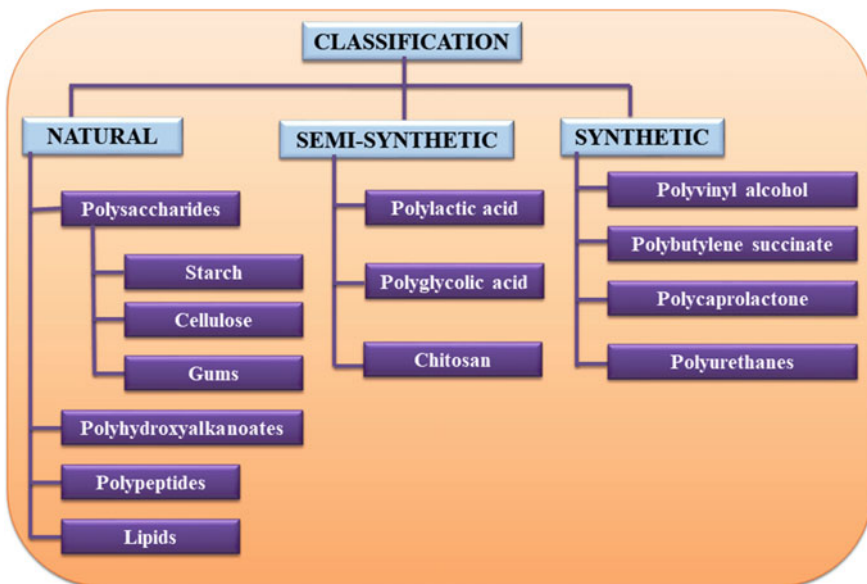


Fig. 1 Classification of biodegradable polymers. Redrawn from [35]

polymers—first, metabolic process generates different active monomers within cells, and those monomers get polymerized through enzyme catalyzed polymerization and produced natural polymers. The structure, properties, and applications of a few common natural biodegradable polymers are discussed below.

Polysaccharides

These are complex carbohydrate structures originating from bacteria or fungi. More than one unit of monosaccharides is connected via glycosidic linkages to form polysaccharides. Most of the polysaccharides are obtained from cell walls plants, crustaceans, and shrimp. Cellulose, starch, chitin, and gums are examples of polysaccharides [36].

Starch

The chemical formula of starch is $(C_6H_{10}O_5)_n$. Starch is the major component for storing sugar in plant cells during photosynthesis and hence, acts as a reservoir of food for plants [37]. Amylose and amylopectin are two units of starch which are connected via α -1,4-glycosidic linkages in branched form [chemical structure given in Table 1]. Starch contains alternating semi-crystalline growth rings which are made up of crystalline amylopectin and amorphous amylose moieties. Interestingly, the quality of starch depends on the ratio of amylose to Amylopectin. Most of the commercial starch is produced from corn, wheat, potato, and tapioca [13, 38, 39]. Because of their increased biodegradability, renewability, and superior oxygen barrier qualities, materials made from starch are the best solution for several commercial applications. However, the use of naturally occurring starch is restricted since it is highly hydrophilic in nature and presence of the intermolecular forces, and hydrogen bonds provide starch a significant impact on the polymer's processability as a thermoplastic polymer, leading to a high glass transition temperature (T_g) and low melting point (T_m). So, further processing is needed where plasticizers such as glycerol, urea, sorbitol, or glycerine are added to the starch matrix to create thermoplastic starch (TPS) which can be utilized in making compost bags, food packaging, and films for marine, meat, and vegetable sectors [40, 41]. Granular Starch [42], Gelatinized Starch [43], Thermoplastic starch [44] are some examples of modified starch that has various applications. On the other side, starch that has been blended with ester groups to provide thermal stability, control water vapor transmission rate, moisture absorption, and enhanced barrier qualities for various gases. Cassava starch, polyvinyl alcohol (which serves as an adhesive and thickening agent), glycerine (used as a plasticizer), talc powder (which acts as a lubricant), urea (which acts as a crossing link agent), and water were combined to create a biodegradable plastic packaging film [45]. The film was subsequently investigated for various physicochemical changes and their impact on the food inside during storage, and the findings revealed the comparative characteristics of the film with the traditional polymer.

Cellulose

Cellulose is also a plant-derived linear polysaccharide where monomer sugar units are connected via β -1,4-glycosidic linkage [structure given in Table 1]. Cellulose is the basic component of wood, leaves, and stalks. Other sources are algae, bacteria, and tunicates. The presence of large hydroxyl (OH) groups controls the chemical and mechanical properties of cellulose [46]. The intramolecular H-bonds between OH-groups of glucose units of the same cellulose units provide rigidity and thermo stability of the chains, whereas intermolecular H-bonds between two different cellulose chains are responsible for the development of the supramolecular structures [47]. This extensive H-bonding is responsible for poor solubility in both common organic and inorganic solvents. Cellulose is highly susceptible to acids but unreactive to strong alkalis. The human body cannot digest cellulose, so it is easy to apply cellulose material in food packaging applications. Apart from that, OH-groups can be easily modified by chemical treatment [15, 48, 49]. These cellulose derivatives (methylcellulose (MC), carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC), cellulose acetate (CA), and hydroxypropyl methylcellulose (HPMC), etc. have much more utility in the application field rather than crude cellulose.

Gums

Gums are complex carbohydrates and are hydrocolloids which are extensively used in food industries as either ingredients or food additives [50]. It has several properties like gelling, water solubility, thickening, emulsification, and stabilization. Gums are extracted from shrubs (Karaya, cashew), plant exudates (tragacanth), seed endosperm of Guar gum, algae, etc. [51]. Typically, they can create extremely viscous aqueous solutions at low concentrations. An exception is there, Gum arabic and other “low viscosity grade” gum require high concentration to form a highly viscous solution. Gums are formed by numerous sugars where complexation in structure may form due to branching. One of the most well-known and widely used gums is gum arabic, which is produced by the species *Acacia Senegal*. Gum ghatti and Karaya gum are the other two types which are extracted from the trunk of *Anogeissus latifolia* and *Sterculia urens* trees, respectively [52, 53].

Polyhydroxy Alkanoate (PHA)

PHA is an optically active biodegradable polymer which is produced by fermentation of microbes and then by microbial cell lysis. The development of microorganisms using agricultural waste as a growth medium has been studied as a potential source for bioplastics and biopolymers (polysaccharides). One such microbiologically produced plastic is polyhydroxyalkanoate, also known as PHA. It is produced by several bacterial species using inexpensive renewable resources, and it is completely degraded aerobically by microorganisms in a stimulated control environment to CO_2

and H₂O. PHA is produced utilizing various natural isolates and recombinant bacteria strains. They are produced by the fermentation of sugar or lipids to store carbon and energy via bacteria. It is generally produced from saturated and unsaturated hydroxyalkanoic acids [54]. The monomer used can be unbranched or can be a homopolymer, copolymer, or terpolymer. PHA can be produced via bacteria under balanced and unbalanced growth conditions; this controls the kind and quantity of PHA in the cell [55].

PHA are polyesters derived from (R)-3-hydroxy alkanolic acids that are biocompatible, non-toxic, and have similar thermoplastic qualities to petrochemical plastics. The length of the monomer's carbon chain influences its categorization. The final characteristics of PHA, including T_m , T_g , and their degree of crystallinity, are greatly influenced by the chemical composition of the polymer, which is affected by the source growth environment, and the method of extraction of the polymer. As a result, they are suitable for a wide range of applications. Short chain length PHA (scl PHA) often exhibits characteristics that are most similar to those of traditional polymers like polypropylene, but medium chain length PHA (mcl PHA) exhibits more elastomeric characteristics. The most extensively researched PHA polymer is poly-3-hydroxybutyrate (PHB); it is brittle and highly crystalline. PHB is produced by certain steps—The first step involves combining two molecules of acetyl CoA to form acetoacetyl-CoA via 3-ketothiolase. Then the reductase Acetoacetyl-CoA reduces the acetoacetyl-CoA via NADH to form 3-hydroxybutyryl-CoA. Lastly, polymerization of PHB-CoA occurs to generate PHB (Fig. 2). The production of PHB by bacteria is increasing significantly every year. PHB possesses distinguishable physical characteristics such that it can be processed into a transparent film with $T_m > 130$ °C and is degradable without residue [56–58].

The thermal and mechanical properties of PHA can also be tuned by co-polymerization with different monomers examples—Poly-3-hydroxybuterate-co-3-hydroxyvalerate (PHBV), Poly-3-hydroxybuterate-co-3-hydroxyhexanoate (PHBHx). With the increase in the side chain length, the degree of crystallinity decreases, hence T_m decreases and the copolymer becomes less brittle.

Polypeptides

Polypeptides are constituted of different amino acids through peptide bonds. Different proteins like—silk, wool, and collagen are all polypeptides. Collagen is an animal-based protein and consists mainly of glycine, proline, hydroxyproline, and lysine [59]. The flexibility and unique biological properties made collagen a perfect material to be used in biomedical fields. One of its denatured derivatives is gelatin which contains 19 amino acids. It is water soluble. Its physical and chemical properties highly depend on molecular weight distribution and amino acid composition. There are few plant-based polypeptides are also available—wheat gluten is one of the polypeptides derived from cereal grains. It contains two types of protein—gliadin, and glutenin [60]. Glutenin molecules are connected via disulfide bonds with gliadin chains to provide the gluten flexibility (Fig. 3). Wheat gluten is an extremely

biodegradable material and the products obtained are non-toxic. This biopolymer acts as a good film-forming agent but without a plasticizer, it became brittle. Soy protein is another type of plant-based protein which is beneficial for health [61].

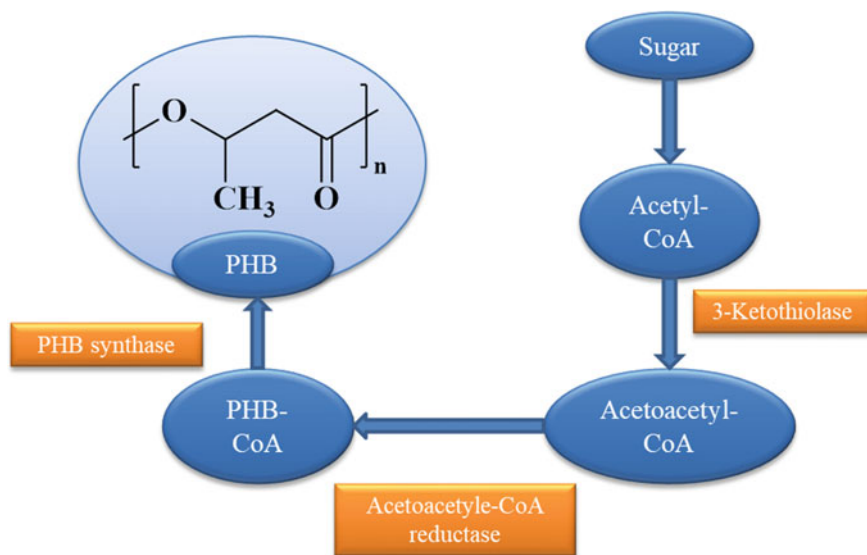


Fig. 2 Industrial production process of PHB. Redrawn from [59]

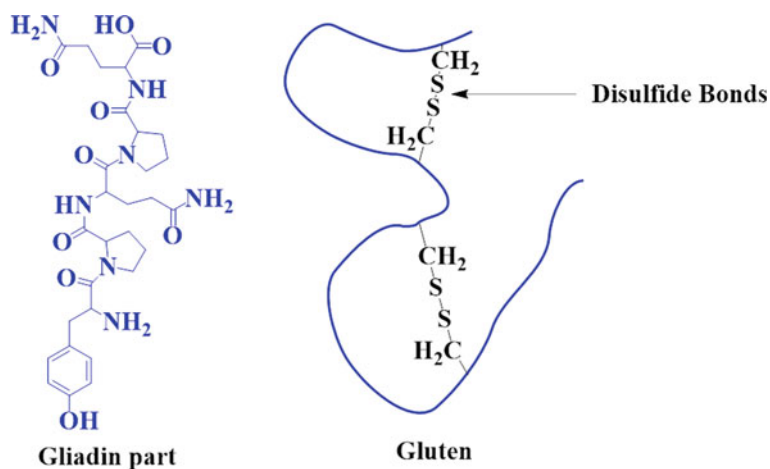


Fig. 3 Structure of gluten. Redrawn from [62]

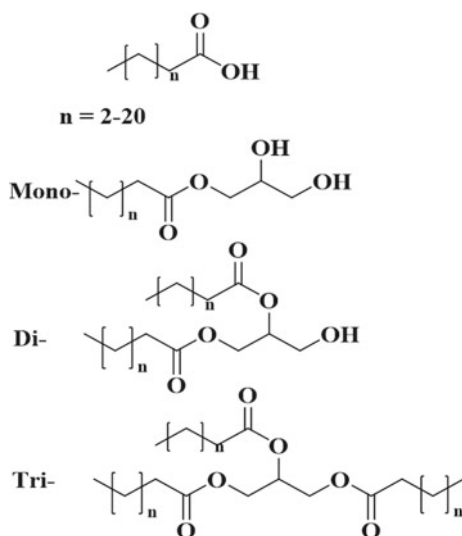
Lipids

Lipids are hydrophobic and soluble in hydrocarbons. Phospholipids, sterols, wax, saccharolipids, sphingolipids, and polyketides fall under the class of lipids. Fatty acids are extracted from oils and fats in the form of triglycerides and depending on the functional groups present over the triglycerides, lipids can be synthesized using free radical or cationic polymerization [63]. Nowadays, lipids or fatty acids become a synthetic toolbox for an industrial chemist. The functional groups of lipids can be easily modified and produce different polymers from a single feedstock. Fatty acids mainly consist of poly anhydrides, polyester, and poly (ester-anhydrides) linkages. More prominently, the structure consists of an acid group and aliphatic carbon chain (length ranges from 4 to 22 carbons) with unsaturation, monounsaturation, or polyunsaturation in their backbone (Fig. 4) having varied properties [64].

2.2 Semi-synthetic Biopolymers

Semi-synthetic polymers are also derived from nature, but they undergo chemical modifications after extraction. Monomers are derived from biomass and the extraction process and polymerization is carried out via chemical synthesis in laboratory. Some of the examples are discussed below.

Fig. 4 Structure of lipids.
Redrawn from [64]



Polylactic Acid (PLA)

PLA is an aliphatic biodegradable polyester that is frequently synthesized from hydroxyl acids. L and/or D-lactic acid (monomers) are microbial fermented and then chemically polymerized to make PLA [65]. Injection molding and extrusion are two common processing techniques that are used to transform polylactic acid (PLA). The concentration of lactic acid enantiomers within PLA chains has a significant impact on the ultimate properties of PLA, including the degree of crystallinity, T_m and T_g . PLA homopolymers (poly DL-lactic acid) containing optically pure L-lactic acid or D-lactic acid, and are semi-crystalline polyesters having T_m of about 175 °C and a T_g of around 55 °C, while PLA heteropolymers (poly DL-lactic acid) are amorphous since the polymer chains are disordered. Depending on the crystallinity, the biodegradability of PLA can be monitored. PLA shows slow degradation due to the presence of bulky CH_3 group in its polymer chain which creates a steric hindrance to resist hydrolysis.

The first approach produces PLA by using cyclic lactic acid dimer lactide, which is created during the lactic acid cycle also known as the Kori cycle [66]. The lactate is produced via an anaerobic reaction. The laboratory synthesis includes direct polymerization of lactic acid using condensation polymerization under a vacuum for the removal of a water molecule. This technique typically yields low-molecular-weight polymers with water as a by-product which leads to back biting. The alternative method includes fermentation of the lactic acid where the conversion of lactic acid into polylactic acid occurs via bacterial polyester fermentation. The bacteria such as *Bacillus megaterium* and *Alcanivoraxbor* are being employed for this process. These bacteria need sugar which is provided by corn to provide fuel for cellular activities, *Alcanivoraxbor* employed which needs sugar from plants, such as corn, to fuel their cellular functions, and the by-product of these cellular processes is the polymer, which is used to make polyesters.

The most used industrial procedure to produce PLA is represented in Fig. 5. The first step includes the fermentation of sugar sources such as corn, which provide energy for the cellular function of microorganisms, the microorganism then produces lactic acid which is further polymerized via condensation polymerization and ring opening polymerization (ROP) to produce polylactic acid. High molecular weight PLA is synthesized via ROP of lactide in the presence of catalysts is $\text{Sn}(\text{Oct})_2$ [67].

Polyglycolic Acid (PGA)

PGA is a completely linear aliphatic polyester and highly crystalline (crystallinity 45–55%). The melting point of PGA is also higher (220–225 °C) than PLA as PGA has higher crystallinity ($T_g \sim 35$ °C). But its low solubility limits biomedical applications. Higher molecular weight PGA is more soluble in organic solvent than low molecular weight PGA which is comparatively soluble in water. The degradation rate is higher for PGA as water can easily attack the carbonyl moieties leading to the formation of acids. PGA is also synthesized as the same procedure as PLA.

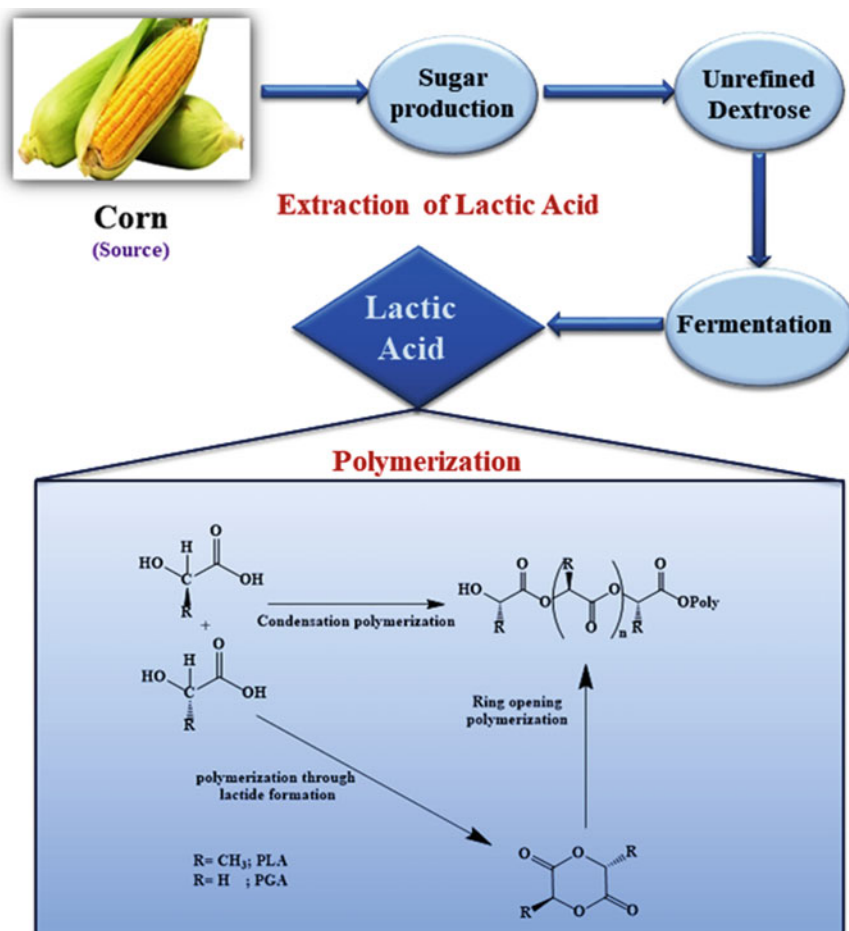


Fig. 5 Industrial process for PLA/ PGA synthesis. Redrawn from [35, 68]

Chitosan

Chitosan is an amino polysaccharide [structure given in Table 1]. It consists of copolymer N-glucosamine and N-acetyl-glucosamine units connected by β -(1,4) linkages produced by partial deacetylation of chitin [68]. Chitin is found in the exoskeleton of many crustacean animals, diatoms, algae, insects, etc. Crustacean shell waste majorly consists of protein (30–40%), calcium carbonate & calcium phosphate (30–50%), and chitin (20–30%). These ratios vary with species and with the season. Thus the preparation of chitin/chitosan also varies depending on the sources [69].

Chitin consists of polysaccharide groups connected by β -1,4-glycosidic linkages and has acetamide groups in C-2 position. It is an ordered fibrillar structure

having inter/intramolecular H-bonding, forming a highly crystalline structure which is responsible for insolubility in water, whereas chitosan with a higher degree of deacetylation contains one water molecule per polysaccharide unit and lesser crystalline part than chitin. Chitosan is soluble at acidic pH (~ 6.2 – 6.4) and less soluble above pH ~ 7.4 [69, 70].

Industrially, the shells obtained from the crustacean insects are processed through the following steps: **demineralization (DM)** [elimination of CaCO_3 in acidic treatment], **deproteinization (DP)** [alkaline treatment], **decolorization (DC)** [by hydrogen peroxide, sodium hypochlorite, or acetone], and **deacetylation (DA)** (Fig. 6). The nature and quality of the chitosan depend on the degree of deacetylation as chitosan differs from chitin by means of solubility, viscosity, and other several biological activities [36, 37].

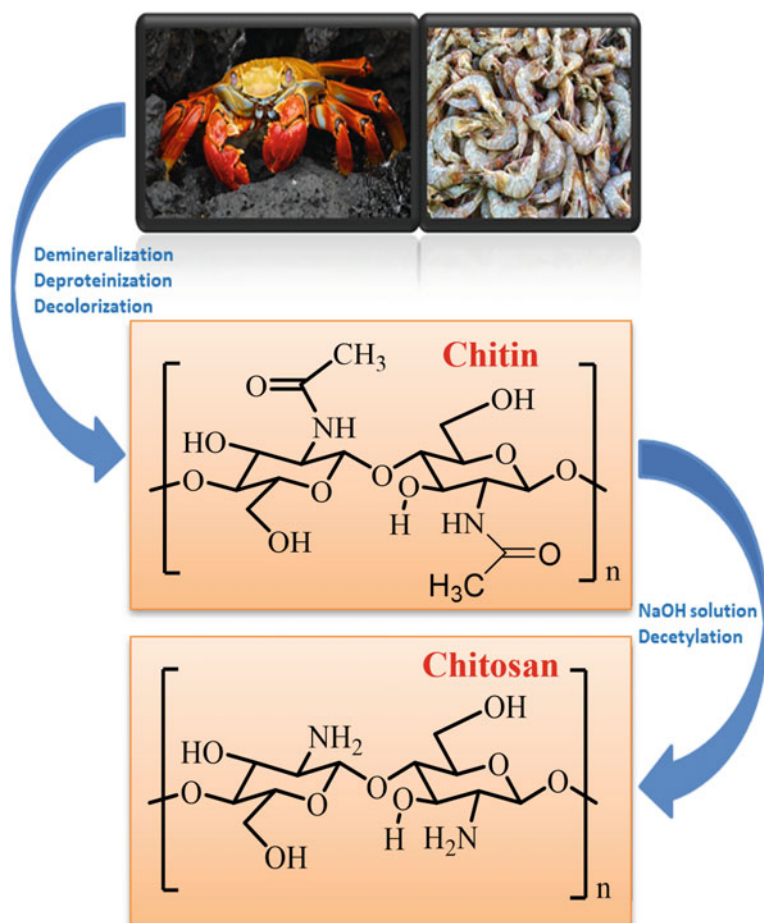


Fig. 6 Synthesis of chitosan. Redrawn from [35, 71]

2.3 Synthetic Biodegradable Polymers

These polymers are completely synthesized in laboratory, hence can be easily tuned their properties. A few common synthetic biodegradable polymers are discussed below.

Polyvinyl Alcohol (PVA)

PVA is the most common synthetic biodegradable polymer. It is highly hydrophilic, thus readily degrades in soil. It is not possible to directly synthesize PVA from vinyl alcohol due to the existence of its tautomeric form, i.e., acetaldehyde. PVA is generally synthesized from vinyl acetate through different routes. One of the most crucial methods is free radical polymerization of vinyl acetate (Fig. 7) which forms the intermediate polyvinyl acetate via emulsion polymerization in the presence of ammonium persulfate (APS) initiator at 70–80 °C [71]. PVA is obtained by hydrolysis of acetate via a strong base in the presence of methanol. Physical and chemical properties of PVA are determined by its molecular weight [72]. Generally, high molecular weight PVA shows high crystallinity and high tensile strength. PVA is an odorless, white-colored translucent granular powder. PVA is resistant to oil and grease and has flexibility that provides excellent film-forming as well as adhesive properties. PVA also possesses high moisture barrier film-forming capability as well as strong oxygen and aroma barrier properties [34, 72].

Poly (Alkylene Dicarboxylate)s (PADCs)

PADCs are the linear aliphatic polyesters. PBS is one of the family of PADCs. It is made up of 1,4-butanediol and succinic acid. PBS is synthesized by condensation process using succinic acid and 1,4 Butanediol under a vacuum. Figure 8a represents the production of PBS via the thermal polycondensation method. This produces by-products such as alcohol and water that leads to the formation of low molecular weight PBS (<30,000). This issue can be overcome by using transition metal catalysts such as Ti(IV) isopropoxide or isobutaoxide or scandium triflates. PBS obtained by ring opening polymerization of p-dioxanone (Fig. 8b) are highly degradable. PBS is thermoplastic polyester having melting temperature, $T_m \sim 113$ °C. Injection, extrusion, and blow molding are used to process this polymer for versatile

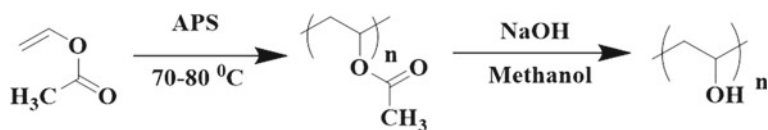


Fig. 7 Synthesis of PVA from vinyl acetate. Redrawn from [73]

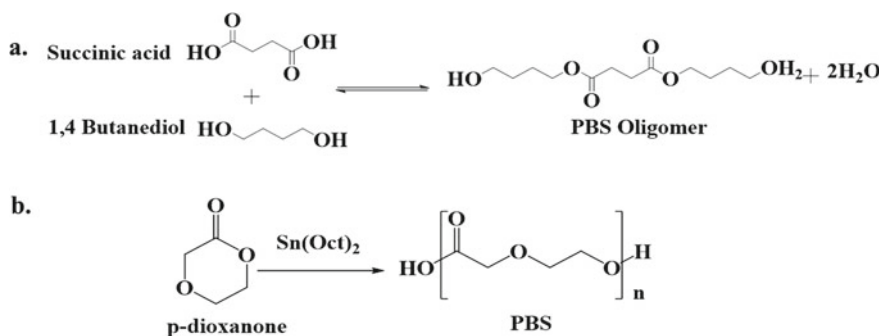


Fig. 8 Synthesis of PBS via **a** condensation reaction and **b** ring opening polymerization. Reprinted and redrawn from [82]

applications. PBS is extensively used in mulch films, containers, and plastic bags. PBS degrades slowly due to its high crystallinity. For this, different co-polymers are also synthesized. One of the superior co-polymers of PBS is polybutylene succinate adipate (PBSA) which is synthesized by butane diol, succinic acid, and adipic acid. Adipic acid is incorporated to enhance the biodegradability of PBS [26, 74, 75]. Blending and composite formation of PBS with other materials like—PLA, adipic acid, butylene terephthalic acid, butylene furandicarboxylic acid are also adopted for improving its degradability [76–79].

Polybutylene adipate (PBA) is also a part of PADCs family. It contains 1,4-butanediol and adipic acid. PBA shows polymorphism in its melt crystallized form. Wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) prove that PBA has two crystalline forms α and β which grow at temperature above 32 °C and below 27 °C [80]. Since, aliphatic portion increases in PBA, crystallinity becomes poorer than PBS, and hence biodegradation rate increases for PBA [76]. Another copolymer example is Polybutylene adipate-co-terephthalate (PBAT) (Fig. 9). It is a random co-polyester of 1, 4-butanediol, terephthalic acid, and adipic acid and synthesized by polycondensation of these monomers in presence of zinc, tin, or titanium catalyst. This biodegradable polyester is manufactured by BASF in the commercial name of Ecoflex[®]. In presence of terephthalate groups, PBAT possesses high flexibility and toughness. However, this high flexibility is the drawback for the polymer that it cannot be used in synthesizing strong materials. The degradation of PBAT was studied in compost simulation test and it was found to occur at around 60 °C. PBAT is widely used in synthesizing mulch films and is considered to be the promising materials for bio-based products [81].

Polycaprolactone (PCL)

PCL is a biodegradable aliphatic polyester. It is prepared by ring opening polymerization of ϵ -caprolactone in presence of stannous octanoate [$\text{Sn}(\text{Oct})_2$] as a catalyst

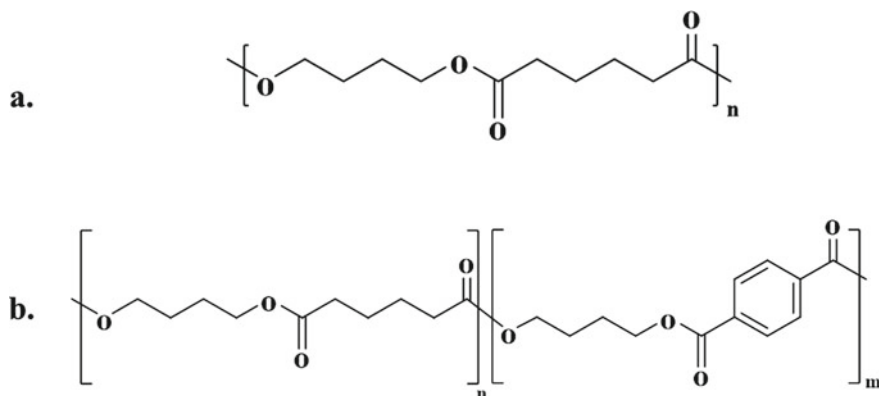


Fig. 9 **a** Structure of PBA and **b** its co-polymers PBAT . Redrawn from [82]

[82]. It is also formed as an intermediate product during the oxidation of cyclohexanol via microorganisms (Fig. 10). The by-products of this enzymatic oxidation are ϵ -caprolactone and 6-hydroxy hexanoic acid. The most effective enzyme for the production of polycaprolactone is lipase. Industrial production of ϵ -caprolactone includes oxidation of the cyclohexanone by peracetic acid. PCL is a semirigid material at room temperature. The ester bonds in PCL are easily degraded under physiological conditions. The degradation is also carried out by enzymes like lipases and esterases [83]. Its melting temperature is around 60–65 °C and Tg is about –60 °C. The number average molecular weight of the PCL are in the range of 3000–80,000 g/mol [84]. PCL has good elastic properties that are suitable for implantable biomaterial, particularly as sutures and prosthetics.

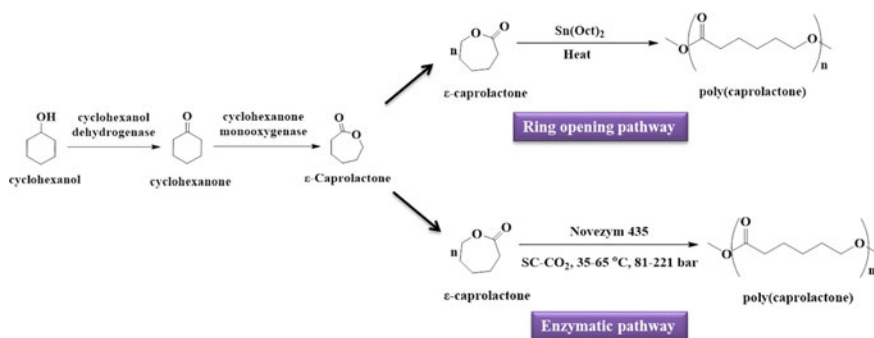
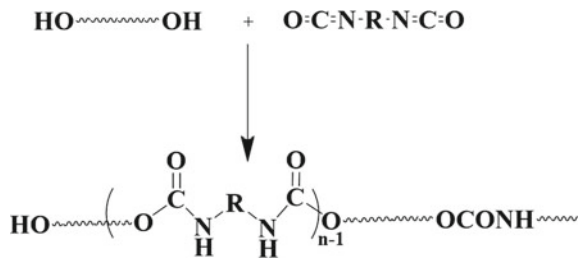


Fig. 10 Synthesis of caprolactone from cyclohexanol, and its polymerization via ring opening pathway and enzymatic pathway leads to the formation of PCL. Redrawn from [87]

Fig. 11 Synthesis of PU via step polymerization. Redrawn from [88]



Polyurethane (PU)

As we have discussed in earlier section of this chapter biodegradable polymers and their crucial application, one such important biodegradable polymer is polyurethane. PU can degrade via both abiotic and biotic pathways. PU is commonly synthesized by the reaction between isocyanates and diols in stepwise method which yield polymer with urethane bond (Fig. 11). The physico-chemical, mechanical, and degradation properties of PU can be easily tuned by the changing of building materials, i.e., isocyanates and diols. Its tunable properties have made PU very attractive for surgeons and biomedical industries. PU's one of the advanced uses in biomedical field is prosthetics.

3 Applications of Biodegradable Polymers

The biodegradable polymers are compatible with physiological conditions such that they are efficiently employed in the biomedical area. The applications are highly reliable in the case of pharmaceuticals, implants, sutures, drug delivery, tissue engineering, etc. [4]. The biomaterials are non-toxic and easily excreted or digested inside the body. Other than these, biodegradable polymers are now getting commercialized for application in the food, packaging, automobile manufacturing industries, and medical implants, etc. Details of some commercialized biodegradable products are given in next section. The constituent monomers and their ratios determine the properties of these products and their uses. Besides these, biodegradable polymers are utilized everywhere and in a wide range of products are available including kitchenware, packaging, wrapping materials, bottles, food containers, clothing, accessories, automotive parts, electronics, furniture, and many others (mentioned in Table 2). Figure 12 shows different products made up of biodegradable polymers [89].

Table 2 Commercially available biodegradable polymeric products. [85, 86]

Sl no.	Trade name	Manufacturer name	Polymer components	Applications
1.	Ecofoam [®]	American Excelsior Company (USA)	Starch	Wrapping materials
2.	Bio-D [®]	Cirad (France)	Proteins from cotton seed	Agricultural films
3.	Nodax [®]	Procter and Gamble Company (America)	Poly-3-hydroxybuterate-co-3-hydroxyhexanoate (PHBHx)	Making injection molded utensils, plastic bags, biodegradable agricultural films, etc.
4.	Bioceta [®]	Mazzucchelli (Italy)	Cellulose acetate	Making packaging films, toothbrushes, etc.
5.	Bioplast [®]	Biotech Company	Starch copolymer	Making food containers, cutlery, bags, etc.
6.	Ecoflex [®]	BASF (Germany)	Co-polyester	Making agricultural films
7.	Mater-Bi [®]	Novamont Company (Italy)	Starch and polyester	Making biodegradable trash bags, and disposable materials
8.	Biopol [®]		PHB/PHV	

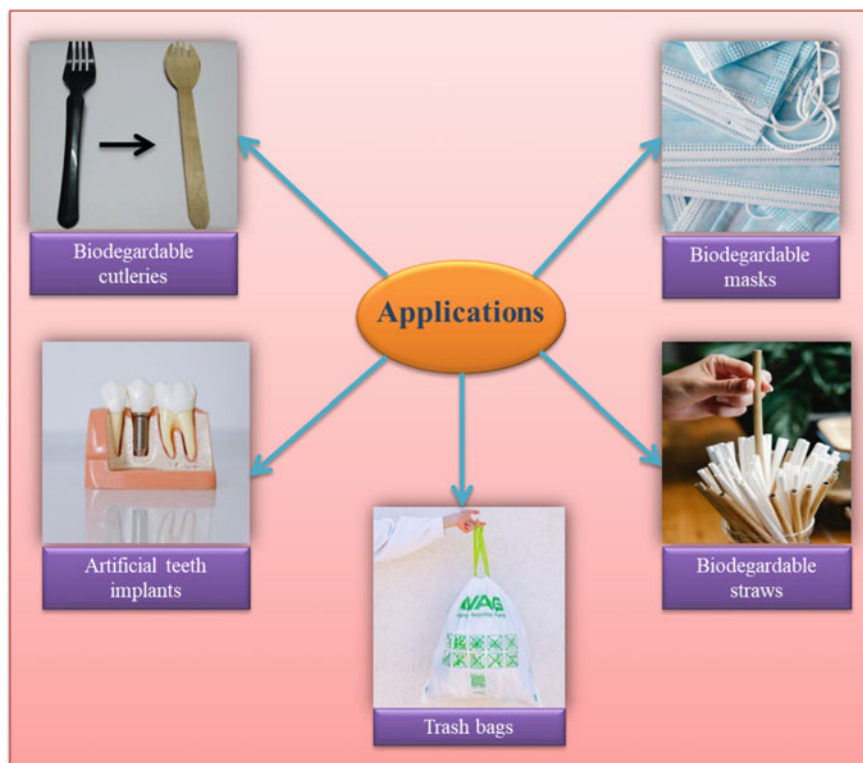


Fig. 12 Different products made up of biodegradable polymers. Reprinted with permission from [87–89]

3.1 Commercially Available Products Based on Biodegradable Polymers

4 Conclusions

Undoubtedly, biodegradable polymers have become promising materials that have potential to replace the non-degradable polymers synthesized from non-renewable sources. The petroleum-based plastics create a huge imbalance in the environment. With increase in population, people are getting habituated with the materials from cheaper sources at the expense of a compromised ecosystem. With the advancement of technology, and on growing global awareness to make a greener world, there is a dire need to commercialize the biodegradable polymers. They have introduced an appealing interest in the past few decades due to their excellent biocompatibility and biodegradability that ultimately facilitate the sustainable development of mankind. However, poor mechanical properties, molar mass, crystallinity, and toughness of

those biodegradable polymers limit their applications. Since these polymers are easily affected by natural factors, thus they are prone toward bacterial or fungal attacks, in addition to abiotic factors such as oxidation, hydrolysis, and UV light. Moreover, they face difficulty in processing them, without which no commercialized product can be made. A careful modification in processing parameters may mitigate the degradation problem, albeit with enhanced cost, thus making them not economically competitive with other commodity plastics such as polyethylene. In the present time, few groups of biodegradable polymers have market presence and their products are available for daily use. Commercialization of biodegradable products mainly relies on their price, so future work should focus on the development of industrially viable, cost-effective biodegradable products made from biodegradable polymers.

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