REVIEW PAPER



Biodegradable Polymers—a Review on Properties, Processing, and Degradation Mechanism

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Abstract

Pollutants in the environment are growing as a result of the use of plastic. Our environment and food chain contain plastic particles and other pollutants made of plastic, threatening human health. From this point of view, biodegradable plastic material focuses on building a more sustainable, greener world with a lower impact on the environment. This evaluation should be kept in view of the objectives and priorities for producing a wide variety of biodegradable plastics throughout their entire life cycle. The properties of biodegradable plastics are similar to traditional plastics. Additionally, the greatest benefits of biodegradable polymeric materials are the preservation of fossil fuel resources and the reduction of environmental pollution in the environment of sustainable development. This review summarizes the main synthesis methods and the most common type of biodegradable polymers. Lastly, the biodegradation mechanism of biodegradable polymers is also discussed.

Keywords Biodegradable polymers · Biobased plastics · Synthesis methods · Biodegradation mechanism · Application areas

Introduction

A major environmental issue today is plastic pollution. Plastic is present in the atmosphere, soils, sediments, rivers, lakes, oceans, and animal biomass [1]. The development of a "disposable" lifestyle, rising consumption, and the usage of disposable packaging have all contributed to this problem [2]. Recently, the advancement of eco-friendly materials has received a lot of attention, due to the virtue of biodegradability which may completely resolve the problem of "white pollution" [3]. In the perspective of sustainability, the primary benefits of biodegradable polymeric materials are the preservation of fossil resources and the reduction of environmental pollution [4]. In the near future, petrochemical plastics will likely be replaced with biobased and biodegradable plastic as one of the solutions to the plastic industry's sustainable growth [5]. Despite the terms "biobased" and "biodegradable" are commonly used interchangeably, they do not mean the same thing. Biobased plastics are produced by using non-petroleum biological resources [6]. Plastics that are biodegradable, whether they

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are petroleum- or biobased, decompose when they are exposed to naturally occurring bacteria [7]. Even though some biobased plastics are biodegradable, not all of them are biodegradable [8]. The phrase "biobased" primarily refers to the method used to manufacture the material. It does not indicate what could happen to it at the end of its existence [4].

In order to achieve this sustainable expansion of the plastic sector and provide a viable alternative to petrochemical plastics in the near future, biobased and biodegradable plastics can be considered one of the options. In contrast to ordinary plastics, which have a lifespan of between 100 and 1000 years, biodegradable plastic may degrade into carbon dioxide (CO₂) and water (H₂O) in 20 to 45 days if there is sufficient humidity, oxygen, and a sufficient quantity of microorganisms [9, 10]. Therefore, biodegradable polymers can be utilized in place of conventional plastics.

Biodegradable polymers already have a big influence across a variety of areas [11]. However, their low mechanical strength, relatively high cost, and thermomechanical properties compared to conventional plastics limit the application. These restrictions can be solved by producing biodegradable polymer blends with desirable characteristics by incorporating a suitable compatibilizing agent during the blend preparation [12]. Usually, synthetic fibers such as carbon and glass fibers are used to reinforce bioplastics, but they are not biodegradable. Therefore, they can be replaced by more abundant, affordable, and environmentally friendly materials: natural fillers such as nano-/micro-sized particles of layered alumino-silicate: halloysite, bentonite and montmorillonite, hydroxyapatite, calcium carbonate, and natural fibers (lignin, lignocellulosic fibers, wood, and vegetable fibers etc.) exert reinforcement and protection actions. Furthermore, they enhance considerably the system rigidity, thermal-resistance, and, in some cases, the durability [13-16]. For instance, the addition of fillers and fibers can greatly increase the elastic modulus and tensile strength of polymer and biopolymer-based systems, while the number of fillers added and their aspect ratio have a major impact on the reduction of elongation at break [17]. The literature indicates that the aspect ratio of fillers and fibers is an important factor for their dispersion and distribution into the organic matrices. It is obvious that the morphology of the generated fillers and/or fibers has a significant impact on the final properties and performance of the polymer and biopolymer-based complex systems, expanding their application fields [18, 19]. Moreover, natural fillers that are hydrophilic and more biodegradable enhance the adhesion of microorganisms to the composite material and enable degradation [20]. As an example, a 40-µm thick polybutylene succinate (PBS) polymer film degrades at a rate of 50% every month in garden soil [21]. Furthermore, mold temperature rise, dehydrothermal treatment, and ultrasound application are different approaches for physical strengthening methods. Applying heat treatment, dehydrothermal treatment, and ultrasounds resulted in a structure with fewer holes in soy protein-based bioplastics while also improving their mechanical characteristics and superabsorbent capacity. As a consequence, biobased plastics which have been processed can be used for a wide range of applications [14].

This review mainly focuses on biodegradable polymeric materials consisting of types of biodegradable polymers, preparation techniques, and biodegradation mechanisms.

Biodegradable Polymers

The word "biobased" refers to a polymer produced entirely or partly from biomass, which comprises any sort of renewable organic material of biological origin, as well as organic waste [8]. The degradation of plastic materials is significantly reliant on the particular exposed environmental factors. Degradable plastics are those that demonstrate

considerable loss in features due to environmental influences such as light, heat, and moisture over time [22]. The word compostability refers to biodegradable polymeric substances that are digested by naturally occurring microorganisms. Biodegradation can take place in a variety of environments, including marine, soil, and composting ecosystems. Compostable plastics, according to the ASTM D6400 standard, should degrade under composting circumstances to generate H2O, CO2, biomass, and inorganic compounds at a consistent rate of recognized compostable materials while leaving no obvious distinctive or harmful residue [23]. Compostable materials can be considered to be biodegradable materials. Under particular climatic circumstances, biodegradability and compostability can be evaluated by the quantity of carbon dioxide evolved or the amount of oxygen demand during the degradation process [8]. Several parameters (such as sample size, sample composition, and crystallinity) influence the rate of degradation of biodegradable materials under composting conditions [24].

In practice, biodegradable (compostable) plastic materials have a more positive impact on the environment than non-biodegradable plastics. As a result, environmental regulations, prohibitions on non-biodegradable plastic bags, and global warming are all driving up demand for biodegradable plastic materials. Biodegradable plastics have the potential to eliminate the disposal problem while also encouraging long-term sustainable development.

Biobased Biodegradable Polymers

The monomer sources of biodegradable polymers can be used to classify them. Now, there are various commercially available biodegradable polymers on the market. Polymers which are generated from 100% renewable resource-based monomers are called biobased biodegradable polymers. For instance, polylactic acid (PLA), polyhydroxyalkanoates (PHAs), and starch are most commonly used biobased biodegradable polymers [25].

Polylactic Acid (PLA)

PLA is a biodegradable thermoplastic aliphatic polyester synthesized by condensation polymerization of lactic acid, which is obtained from renewable sources, like corn, sugarcane, starch, roots, chips, and tapioca [26, 27]. PLA is primarily utilized in the food market to manufacture disposable tableware items including drinking cups, cutlery, trays, food plates, food containers, and packaging for delicate food goods [28]. Nevertheless, PLA bioplastics are too brittle to be employed in other package manufacturing methods. As a result, PLA requires additives to increase its durability [29]. Remarkably, PLA is the most biodegradable polymer, degrading mostly by hydrolysis (Fig. 1) [30, 31].

Some commercial types of PLA are particularly engineered for processes like thermoforming and extrusion/injection molding [32]. Furthermore, it can be used for soil retention sheathings, agricultural films, garbage shopping bags, and packaging materials. PLA can also be converted to fibers and used to make woven, disposable, and biodegradable fabric items such as disposable clothes, feminine hygiene products, and diapers [30, 31].

Polyhydroxyalkanoates (PHA)

PHAs belong to the polyhydroxester family of 3-, 4-, 5-, and 6-hydroxy alkanoic acids [33]. The general chemical structure of PHA is demonstrated in Fig. 2 [31]. PHAs are

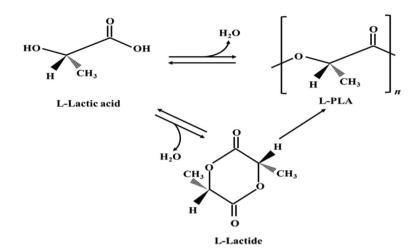
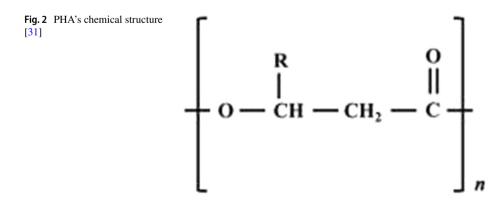


Fig. 1 Hydrolysis of polylactic acid (PLA) [31]

biocompatible, biodegradable, and non-toxic polyesters produced by certain bacteria and plants from renewable sources [32, 34]. Currently, only a few types of PHA structures are marketed, particularly medium chain length PHA (mcl PHA), polyhydroxy butyrate (PHB), and poly (hydroxy butyrate-co-valerate) (PHBV) [35]. PHB is one of the most researched short-chain lengths PHA polymers. The restrictions of the PHB consist of brittleness, slow crystallization, poor thermal stability, and poor melt processability. PHB functionalities can be adjusted by copolymerizing with hydroxyvalerate (HV). The resulting copolymerized PHB with HV is known as PHBV. The PHBV polymer with high HV content illustrated much better ductility and toughness than PHB [25, 29]. Shopping bags, disposable products (razors, cutlery, cups, compostable bags, and packaging), food and cosmetic containers, thermoformed articles, medical surgical garments, and medical implants are the most common applications for PHAs [36, 37]. Many researchers, notably Choi et al. [38] Kumar et al. [39], and Li et al. [40], have exhaustively investigated the preparation, characteristics, uses, and future advancements of PHAs.



Starch is a low-cost, renewable, and easily adjustable biopolymer derived from plant resources such as tubers of plants, seeds of cereal grains, and tapioca palm [41]. Starch-based bioplastics are utilized for packaging products and for generating food utensils such as cups, bowls, bottles, cutlery, egg cartons, and straws [31]. It comprises of a significant number of glucose units linked together by glycosidic bonds, with linear amylose homopolymer units and helical/branched amylopectin homopolymer units (see Fig. 3) of 20–25% and 75–80%, respectively [25]. Amylose is a linear polysaccharide formed of -D- glucose monomers joined by -1,4-glycosidic linkages, whereas amylopectin is comprised of the same monomers but is highly branched by a different type of network, the -1.6-glycosidic linkage [42]. Starch properties vary considerably between species depending on crystallinity, glass transition temperature (Tg), and ratio of amylose and amylopectin [43]. The high Tg (240 °C), strong inter- and intra-hydrogen bonding, susceptibility to the water, and weak flowability of virgin starch granules restrict the starch processability and applications [44, 45]. Therefore, starch can be chemically modified and blended with other biopolymers to improve its properties. The intrinsic characteristics of starch, involving its digestibility, solubility, thickening power, pasting properties, and shear stability, can be enhanced by the chemical modification starch, which includes introducing functional groups at the molecular level to change the bulk properties [46]. The properties obtained via the chemical modification of starch are affected by several parameters, for instance the botanical source, reaction conditions (reactant concentration, reaction time, pH, and the presence of a catalyst), the type of substituent, degree of substitution, and substituent distribution in starch molecules [47]. Chemical modification of starches is usually achieved by derivatization such as acetylation, cationization, acid hydrolysis, oxidation, and cross-linking [48, 49]. However, these methods are restricted because of environmental and consumer safety concerns. Combining multiple chemical methods has become a growing trend as a way to produce new sorts of modification. Similar to this, several physical modification techniques, like extrusion, radiation, and microwave, have been combined with various chemical modification techniques to yield a starch with certain functional characteristics [50, 51]. Table 1 lists several of the latest chemical modification techniques.

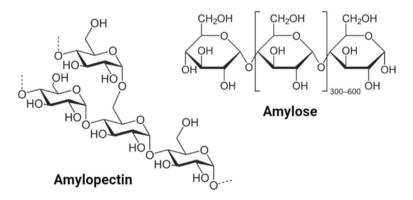


Fig. 3 Chemical structure of amylose and amylopectin

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Chemical modificationSources of starAcetylationCassava starch			
	of starches	Observation	References
	starch	Acetylated cassava starches with low and medium degrees of substitution (DS) were produced. Acetylated [52] starch pastes exhibited lighter transparency than native starch paste when the DS was low	[52]
Commercia	cial corn starch	Starch performance in textile applications was enhanced. Surface tension, impregnation, wetting, and diffu- [53] sion of starch in textile fibers were reduced	[53]
Cationization Waxy maize	aize starch	Fragmentation and starch granule size were reduced. Esterification reaction is formed on the granule surface	[54]
Acid hydrolysis Corn starch	rch	Study demonstrated that consecutive treatment of mild acid hydrolysis and freeze thawing treatment allowed more amylose to aggregate and therefore improve the possibility of retrogradation	[55]
Arrowroot starch	ot starch	A combination of acid hydrolysis and three cycles of autoclaving-cooling in arrowroot starch was described. According to research, this can enhance resistant starch output by up to four times	[56]
Oxidation Potato starch	arch	The properties of potato starches are affected differentially by oxidation at various active chlorine concen- trations. The intensity of the potato starches' oxidation was increased by the rise in active chlorine content	[57]
Cross-linking Canna starch	arch	The stability of starch viscosity was increased by cross-linking modification method. Starch cross-linking [58] made starch granules stronger, so they were less likely to gelatinize	[58]

Petroleum-Based Biodegradable Polymers

Synthetic polymers are often synthesized from crude oil, although they can also be derived from natural gas and coal. Because these polymers do not exist naturally, the majority of them are not biodegradable or compostable. However, petroleum-based non-biodegradable polymers can be rendered degradable through integrating unstable (amide, ether, or ester) bonds that can undergo hydrolysis under particular circumstances [59, 60]. Poly (butylene succinate) (PBS), polycaprolactone (PCL), polyvinyl alcohol (PVA), and poly (butylene adipate terephthalate) (PBAT) are the most well-known polymers in this class, and their chemical formulas are illustrated in Fig. 4 [61]. They can be synthesized by using biomass or fossil fuels and they are biodegradable polymers which are evaluated in anaerobic environments. Anaerobic degradation is a biological procedure that alters organic materials in an atmosphere devoid of oxygen. It can follow two paths: a process known as anaerobic fermentation in which organic materials can serve as an electron donor or receptor, or anaerobic respiration, which needs acceptors such as CO_2 , SO_4^{2-} , and NO_3^{-} . The process is enhanced in four stages—hydrolysis, acidogenesis, acetogenesis, and methanogenesis-which cause the production of a mixture of CH_4 and CO_2 , known as biogas. Two thirds of CH_4 produced in an anaerobic process is due to fermentation and one third by respiration [37, 62, 63]. The existence of volatile fatty acids, sulfate, ammonia, and heavy metals influences how effectively anaerobic biodegradation takes place [64]. The efficiency of anaerobic biodegradation is also affected by pH, temperature [63], redox potential, and hydrogen concentration [65, 66]. Additionally, it relies on the concentration and type of microorganisms that exist in the media [67], presence of nutrients [68], and the characteristics of the substrate [69].

Poly (Butylene Succinate) (PBS)

PBS is semicrystalline thermoplastic polyester generated by polycondensation of succinic acid and 1–4-butanediol [70]. PBS can be synthesized from renewable or non-renewable

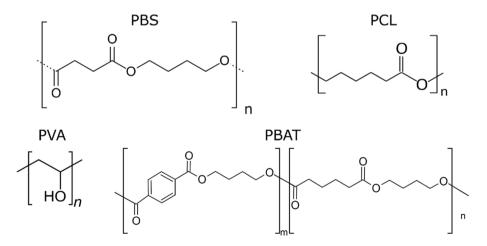


Fig. 4 Chemical formula of poly (butylene succinate) (PBS), polycaprolactone (PCL), polyvinyl alcohol (PVA), and poly (butylene adipate terephthalate) (PBAT) [61]

monomers; however, the large percentage of commercially accessible PBS is generated from fossil-based resources.

PBS is a semicrystalline thermoplastic polymer. Because of the high crystallinity degree, it demonstrates a relatively slow biodegradation rate. PBS is utilized in a wide range of applications, including food packaging films, shopping bags, agricultural mulch film, plant pots, and hygiene goods. However, it is not widely used in the biomedical area, due to its limited biocompatibility and bioactivity. PBS is also applied as a filler in blends and composites to enhance thermal conductivity, mechanical performance, gas-barrier characteristics, and flame resistance [71, 72].

Polycaprolactone (PCL)

PCL is a slow-degrading aliphatic polyester that is commonly used in biomaterials and sustainable packaging. PCL is a semicrystalline polymer with great toughness and flexibility, with a glass transition temperature of -60 °C and a melting point of around 60 °C [73]. It is a hydrophobic, biocompatible, and relatively slow-degrading polymer that has been widely employed in medical applications such as some sutures, drug delivery systems, and tissue engineering scaffolds [74, 75]. PCL, like other petrochemical-derived biodegradable plastics, is applied in blends with biobased biodegradable plastics including such starch-based polymers, PLA, PHAs, and PBS [61, 76].

Polyvinyl Alcohol (PVA)

PVA is derived primarily from polyvinyl acetate by hydrolysis. Its features are determined by the degree of hydrolysis, which can be complete or partial and normally ranges between 80 and more than 99% [77]. Its degradability is improved by hydrolysis due to the presence of hydroxyl groups on the carbon atoms [78]. Furthermore, it is water-soluble and hydrophilic, so it is commonly employed by blending with other polymer compounds for using in a variety of industrial applications to improve the mechanical properties of films [77, 79].

PVA is utilized in biomedical applications, because of its compatibility [46]. PVA composites, for instance PVA gels, are used in different biomedical fields, like in the manufacturing of contact lenses, artificial heart surgery, drug delivery systems, and wound dressings. In medical devices, PVA is used as a biomaterial due to its highly desirable properties, such as biocompatibility, nontoxicity, non-carcinogenic, swelling properties, and bioadhesive characteristics [77–80].

Poly (Butylene Adipate Terephthalate) (PBAT)

PBAT is an aliphatic–aromatic random copolyester, synthesized from a polycondensation reaction of adipic acid, terephthalic acid, and 1,4-butanediol [81]. PBAT has good mechanical properties because of the aromatic unit in the molecule chain [82].

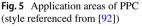
Pure PBAT features are insufficient for consumer adoption because of higher manufacturing costs or inferior mechanical properties as compared to traditional polymers. As a result, the improvement of a PBAT market will be achievable if production costs are reduced or its features are enhanced. The use of inexpensive components (such as starch) and strengthening substances (such as PLA) is an efficient strategy to reduce the final price and enhance the characteristics while keeping the composites' biodegradability. PBAT-based composites such as packaging, mulch film, and cutlery have been commercialized in the last 10 years [82, 83].

Biodegradable Polymers Derived from Renewable and Petroleum-Based Resources

In this group, at least one renewable resource-based monomer is utilized to synthesize biodegradable polymers. For example, polypropylene carbonate (PPC) is an aliphatic polyester which is generated from CO_2 and propylene carbonate by copolymerization [25, 84]. CO_2 -based polymers are attractive because of their advantages of synthesizing biodegradable polymers by utilization of the abundant greenhouse gas— CO_2 [85]. Poly (cyclohexene carbonate) (PCHC) and poly (propylene carbonate) (PPC) are the most researched CO_2 -based polycarbonates [85, 86]. Compared to PCHC which is usually produced through the copolymerization of CO_2 and cyclohexene oxide, PPC has advantages such as cheaper price to produce and better mechanical properties. PCHC is too fragile for applications [87].

PPC films have good tensile and barrier (O_2 and H_2O vapor) properties [88], but the amorphous PPC shows various restrictions such as poor thermal stability, high shrinkage, low glass transition temperature (25–45 °C), and performance variability based on the type of catalyst employed to produce the PPC [89]. Various attempts have been taken to address the restrictions of PPC through blending PPC with various biodegradable polymers [89–91]. The application areas of PPC are demonstrated in Fig. 5 [92].





Synthesis Methods of Biodegradable Polymers

Modification of Natural Polymers

Polysaccharide polymeric materials, for example chitosan, chitin, starch, and cellulose, are readily biodegradable in nature and can be modified into new biodegradable polymer materials by coblending [93].

Natural polymers can be modified chemically in a variety of ways, including nitration, hydroxylation, sulfonation, acylation, alkylation, phosphorylation, thiolation, xanthation, quaternization, and graft copolymerization, which is the most promising approach that leads to a broad range of molecular designs [93, 94]. Graft copolymerization is a popular method for improving chitosan's antibacterial, chelating, and complexation properties. The grafting of chitin and chitosan through covalently binding a molecule onto the backbone allows for the synthesis of functional derivatives [95].

Chemically Synthesized Biodegradable Polymers

Polymeric materials are chemically produced with chemical structures similar to natural polymers. The chains of ester, amide, and peptide bonds found in polymeric materials are readily biodegradable. Polymerization is the term used to describe the process by which a large number of little molecules, referred to as monomers or repeating units, combine to make a covalently bonded chain or network. Each monomer can lose a few chemical groups as the process progresses [96]. Ring-opening polymerization (ROP) is the most flexible method for the synthesis of major groups of biopolymers to obtain product in large quantities. PLA is generated through the polycondensation of lactic acid or the chain growth ROP of lactide. The ROP of lactide can be carried out with the help of a variety of catalysts and initiators. Sn(Oct)2 is a frequently employed catalyst/initiator [97]. High-molecular-weight PLGA is produced by the ROP of lactide and glycolide and the cyclic diesters of lactic acid and glycolic acid, respectively, under catalyst Sn(Oct)2 (see Fig. 6) [93, 98, 99].

Microbiologically Synthesized Biodegradable Polymers

Microorganisms can produce a variety of complicated polymeric materials by utilizing certain organic materials as food sources such as glucose or starch. These polymeric

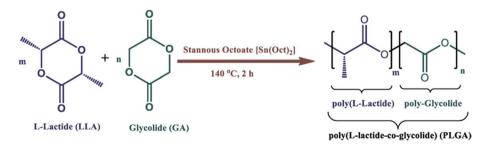


Fig. 6 Synthesis of poly(lactide-co-glycolide) by using ROP process (PLGA: m=number of lactide units, and n=number of glycolide units) [99]

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materials include PCL, various types of silk, polysaccharides, and polyesters like poly (hydroxybutyrate) (PHB) and poly (hydroxybutyrate-hydroxyvalerate) (PHBV), and poly (hydroxyalkanoates) (PHAs). The separation of these products is difficult because of their similar chemical properties [6, 100, 101]. PHAs are a group of intracellular biopolymers generated by bacteria through the fermentation of lipids or sugars to store carbon and energy. Furthermore, PHAs, which can be made from a variety of renewable resources, have received a lot of attention because of their putative high biodegradability in different environments, biocompatibility, chemical diversity, their manufacture from renewable carbon resources, and release of non-polluting and non-toxic products after degradation [102, 103]. Many prokaryotic bacteria produce and accumulate PHAs as energy and carbon storage compounds when a primary non-carbonaceous nutrient (such as nitrogen or phosphorus) is limited [104]. The accumulation of these polymers enables better survival under unfavorable environmental circumstances [105].

Degradation of polymers by microbial (Fig. 7) is a promising method to depolymerize waste polymers into monomers for recycling, or mineralize them into carbon dioxide, water, and new biomass, with concomitant production of higher value bioproducts [102]. Polymers are biodegraded by microorganisms by the release of extracellular enzymes, attachment of the enzyme to the polymer's surface, and hydrolysis to short polymer intermediates, which are then assimilated by microbial cells as a carbon source to emit CO_2 [102, 106].

Enzymatic Synthesis of Biodegradable Polymers

Enzymatic polymerization's kinetics has been researched in innovative works and is typically explained as a monomer-activated process. Some enzymes exhibit various characteristics by catalyzing particular polymerizations. Because of the high specificity of enzymes, these reactions do not yield any by-products, making the products easy to separate [107].

Biodegradable polymers such as polyamide, polyaaccharide, and polyester can be produced through enzyme-mediated synthesis. Enzymes may also be recycled. Enzymes can be used to catalyze reactions under fairly mild conditions (typically at room temperature and atmospheric pressure), which can dramatically lower processing costs [108].

Cheng et al.[109]. reported that the bulk lipase-catalyzed polymerization (LCP) of diamines and diesters (see Fig. 8), which resulted in aliphatic polyamides, roughly have a 3000–15,000 g/mol molecular weight.

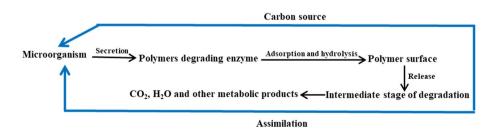


Fig. 7 The main process that causes polymers to degrade microbiologically

$$\begin{array}{c} O \\ R_{1} \\ O \\ H_{1} \\ O \\ H_{1} \\ O \\ H_{1} \\ O \\ H_{1} \\ O \\ H_{2} \\ H_{2} \\ H_{2} \\ H_{3} \\ R_{4} \\ H_{2} \\$$

R1 and R2 = methyl, ethyl, or other convenient leaving groups R, R3 and R4 = alkyl groups that may contain olefinic bonds or heteroatoms X = O, CH2, NH or S

Fig. 8 LCP for aliphatic polyamides [93, 109]

Chemoenzymatic Synthesis of Biodegradable Polymers

Chemoenzymatic methods demonstrate both high stereoselectivity and economic efficiency when compared to chemical and enzymatic approaches [110]. The chemoenzymatic synthesis methodology incorporates traditional polymerization with an extremely effective enzymatic strategy. As a result, it can be described as a desirable method for producing high-molecular-weight biodegradable polymers.

Using an effective chemoenzymatic method, researchers were able to synthesize some optically active polymeric prodrugs as nonsteroidal anti-inflammatory substrates with high molecular weights. Cai et al. [96] have utilized an efficient chemoenzymatic method to synthesize some optically active polymeric prodrugs for nonsteroidal anti-inflammatory drugs with high molecular weight. Gutman et al. [97] reported the lipase-catalyzed ROP of ε -caprolactone (ε -CL) in n-hexane to successfully produce PCL which has up to a 4400 g/mol molecular weight.

Biopolymer Processing Techniques

The functioning of the biopolymer is dependent on a number of parameters in addition to its structure and composition, including the type, quality, and quantity of the solvent employed and the processing method utilized to form the final structure that will identify the interaction of the materials [111, 112]. The main processing methods for biobased polymers from renewable sources are mentioned as follows.

Compression Molding Method

In the compression molding process, sometimes referred to as press molding, the appropriate biopolymer is inserted between two molds that have been heated to a high temperature. In this process, after applying pressure to the molds, the material takes on its final shape, and after curing, its final matrix is cooled and removed [113, 114]. Figure 9 demonstrates the compression molding technique.

The advantages of the compression molding process include the ability to produce complex shapes and excellent reproducibility of the components produced by this process. Additionally, the molding technique results in minimal material loss and high production rate as the mold cycle time needs only a few minutes; therefore, it can be used

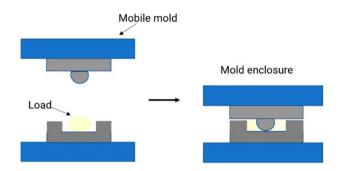


Fig. 9 Scheme of the compression molding process [112]

on an industrial scale [115]. However, compared to other equipment used in other processes, compression molds are more costly [113, 116, 117].

In accordance with the current literature, the most common natural polymers are those comprised of proteins and polysaccharides. These polymers exhibit numerous interactions between their intermolecular bonds, which widen the range of their functional properties [118]. The primary application of this method is in the production of films. Citric acid was used to produce chitosan films [119]. Additionally, this method was used to generate active films made of chitosan and cassava starch. The shelf life of pork slices kept in the refrigerator was increased by these films [116].

Injection Molding Method

One of the most common techniques to manufacture items made of biopolymers is injection molding. Figure 10 illustrates the injection molding technique. The injection molding technique involves injecting a paste into a mold, with many control variables, for instance powder granulation, paste temperature, filling rate, and mold temperature [120, 121]. It is desirable to employ the PLA biopolyester in this method because, in comparison to other biopolymers, it has good mechanical characteristics. Different mold temperatures were used to produce stereocomplex PLA compositions by injection molding. Biocomposites were made by combining PCL with crayfish meal. With PCL present, an improvement in the mechanical properties of the systems was seen [122]. Furthermore,

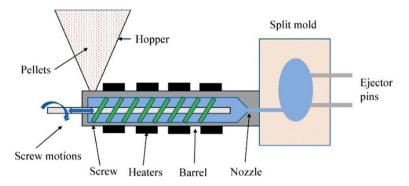


Fig. 10 Schematic diagram of the injection molding method [112]

this process is employed for the enhancement of PLA/PHA nanocomposites. PHA cannot be processed even if the chemical composition and flow temperature are similar to those of PLA. However, when incorporated with PLA, it functions as a nucleating agent, which enhances the material's mechanical characteristics and barrier behavior [112, 123].

Film Blowing Technique

The film blowing technique is the most utilized for synthesizing plastic films [124]. The advantages of this method are simple production equipment, low-cost, adjustable film size, and continuous production. Additionally, this method is adaptable; it can be used for manufacturing single-layer or multilayer films with a range of film thicknesses and widths [121].

Film blowing methods are manufactured through the extrusion process using a circle-shaped extrusion die. Air pressure is then applied to the film to further expand it. The film is chilled to encourage the material's solidification after expanding it to the desired size [125]. Starch is one of the most widely utilized materials in this technique. A mixture of chitosan and thermoplastic corn starch was employed to build the films. The investigation revealed homogenous films without the presence of starch or chitosan granules. In spite of losing some of their mechanical features, the films gained more extensibility and thermal stability [126].

Three-Dimensional (3D) Printing Technique

Three-dimensional (3D) printing, which is an advanced additive manufacturing process by accumulating 3D parts with complex shapes layer by layer, is in high demand globally and will continue to grow over the coming decades [127]. The innovative method offers a distinct advantage for the quick prototyping of complicated products, such as parts with particular functions and multi-material with complicated geometric structures [115, 128].

Significant applications of this method have the potential to revolutionize fields like medicine. The use of 3D printing technology allows for the replacement or repair of wornout bone and cartilage tissues. For the repair of these, biopolymers for instance alginate are commonly used [129]. A collagen-alginate blend was evaluated as a bioink for cartilage synthesis. This cartilage has suitable biological functionality and mechanical strength [130]. Chitosan is another biopolymer that is frequently employed in this method. Through the use of 3D printing, a chitosan hydrogel scaffold was enhanced [131]. A biopolymer-based scaffold was built with exceptional human fibroblast adhesion and proliferation capacity. Furthermore, starch contains heat- and pressure-sensitive molecules, which makes the depolymerization process used in 3D printing easier. The biopolymer's structure, as well as its physical and chemical characteristics, is altered during this depolymerization, making it attractive for applications such as functional foods [132].

Biodegradation Mechanism

Biodegradation of a polymer is described as the deterioration of its physical and chemical characteristics as well as a reduction in its molecular mass to the production of CO2, H2O, and CH4 and other low-molecular-weight products under the influence of microorganisms in both aerobic and anaerobic environments with the assistance of abiotic chemical reactions such as photodegradation, oxidation, and hydrolysis [101]. According to ASTM D

6400–99 [99], biodegradable plastic is determined as degradable plastic that is degraded through the action of naturally occurring microorganisms like bacteria, fungi, and algae.

Figure 11 summarizes the biodegradation stages [133]. Abiotic deterioration is the initial stage at the end of the polymer's usable lifetime where the polymer starts to lose its physical and structural properties. The rate of the initial breakdown depends on many factors, for example, atmospheric pollutants or agrochemicals; thermooxidative; UV radiation from the sun or artificial light source; the polymer chain length; crystallinity; molecular weight distribution; the size, shape, and geometry of particle; the surface porosity; pore size and distribution; pore geometry; and water diffusivity in the polymer matrix—all of which are functions of the polymer's manufacturing process [134, 135]. Lastly, physical forces such as compression, tension, and shear forces like air and water turbulence, snow pressure, and animal tearing also affect the initial degradation mechanism [136].

The second stage is biofragmentation. Polymer is more susceptible to enzymatic (i.e., biological) "attack" once it breaks up into shorter chains (oligomers) [137]. The substance is more physically and chemically accessible to the action of microorganisms and the enzymes they release, which results in a rise in the material's bioavailability [138]. The rate of breakdown is linked with the nature of the polymers. In comparison to polymers with several functional groups that provide a handle for the enzymes to act on, linear non-reactive segments will be more difficult for the enzymes to reach and disrupt [139].

Microbial assimilation and mineralization are the last stage which can be thought of as the microorganism eating and digesting the polymers for its own development and energy requirements [107]. The assimilation of the monomers into microorganisms, which produce cellular biomass and either carbon dioxide or methane that depends on the availability of oxygen (effectively air), is the final stage of biodegradation [140]. Conditions with excess amount of oxygen are demonstrated as aerobic, limited oxygen as anoxic and no oxygen as anaerobic. When a reaction is carried out in a bioreactor, increases in the biomass of the selected microbe can be used to quantify the rate of this stage [141]. Other environmental parameters, including pH, temperature, and moisture content, will influence fragmentation and microbial degradation rate in addition to oxygen 148]. Table 2 illustrates a list of environmental factors that influence how quickly plastics are assimilated by microorganisms.

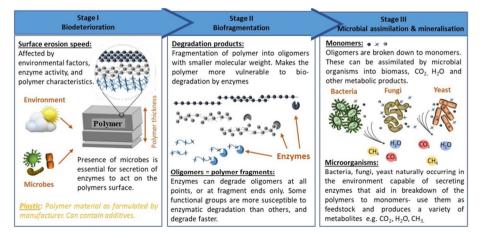


Fig. 11 Summary of biodegradation [133]

Environment	Degradation
Fresh water or salt water	Moderate temperatures, UV rays, and atmospheric oxygen are all factors that can affect plastic that is floating on the surface [142]. This may accelerate their abiotic degradation Because of limited UV, oxygen availability, and low temperatures in deep waters, photodegradation and thermooxidative degradation decreased [143] The hydrolysis rate of polymers in saltwater is influenced by lower microorganisms'
	concentrations [144] and based on the ability of the organisms to adhere to the polymer surface
Soil	The UV rays of the sun, which are required for photodegradation to start, are not exposed to plastic that is buried in the soil. According to certain research, photodegradation is a chain process that can continue in ground-level polymers following UV light exposure [145]
	Thermooxidative degradation is restricted in deeper soil areas by anaerobic conditions [146]
Landfill	The rate of photodegradation and thermooxidation reduces in a dark and anaerobic environment. The production of methane and carbon dioxide will be favored by anaerobic conditions [147]
Composting facilities	The fundamental components that are required for bacterial metabolism, such as nitrogen, potassium, and phosphorus, are lacking in plastics. This creates a necessity to add fertilizers in order to facilitate the degradation process [148]

Table 2 Environmental factors influencing the rate of microbial assimilation of plastics are listed briefly

In deep waters, photodegradation and thermooxidative degradation are reduced due to UV availability and oxygen supply limitations and relatively low temperatures.

Discussions Regarding the Complicated Process of Biodegradation

Not all polymers degraded in the environment are biodegradable. There are three primary categories of ecologically friendly polymers, as defined by ASTM and ISO [149]. The first one is degradable polymer. Important modifications in the polymer's chemical structure cause a loss of some of its properties. Without considering the naturally occurring microorganisms' specific environmental conditions trigger decomposition that happens [150]. The second one is compostable polymers. Compostable polymer degrades biologically during composting to produce CO₂, water, inorganic compounds, and biomass at a rate comparable to other compostable materials and leaves no discernible, toxic, or visible residue [77]. Decomposition is the consequence of biological processes employing specialized microorganism combinations. The last one is biodegradable polymer. Microorganisms including bacteria, fungus, and algae that are present in nature perform the decomposition process. There should be no remains of the material in the environment after it has been entirely assimilated [151]. The various degrading paths need to be distinguished clearly in order to make it clear which waste route is appropriate. Since the incomplete degradation process results in a buildup of highly mobile micro-polymers in the environment, it is clear that polymers degraded into micro-polymers should not be allowed to enter landfills or rivers [152].

In a review, Singh et al. [153] discussed various polymeric degradation processes and their underlying mechanisms, such as thermal degradation, photo-oxidative degradation, catalytic degradation, biodegradation, mechanic-chemical degradation, and ozone-induced degradation. They also highlighted how various polymers can behave in a variety of ways

depending on the specific degradation environment and the underlying mechanisms. This was further supported by Ramasubramanian's research [154] in his report of polymer degradation mechanisms, which also provided some potential parameters affecting the degradation process and stated that the degradation process is influenced by the nature and mechanism of the degradation process in addition to molecular weight, chemical structure, and bond type.

More research on the degradation of particular systems is provided in the paragraphs that follow, based on the biodegradable polymers used.

Fukushima et al. [155] reported the biodegradation of neat poly (DL-lactide) (PDLLA), PCL, and a partially miscible PDLLA/PCL blend in compost, over a 12-week period. According to their findings, the PDLLA degraded very quickly due to its amorphous structure, whereas the PCL showed to be resistant against abiotic hydrolysis due to its semicrystalline structure and hydrophobicity, in agreement with the previously reported discussion on the degradation mechanisms of PCL. A fascinating finding was observed about the blend: the continuous PDLLA phase sped up the PCL phase's hydrolysis. The rate of degradation in compost seemed to be usually faster.

Tsutsumi et al. [156] investigated the actual degradability, both enzymatic (induced by lipases) and chemical (in NaOH solution) of several biodegradable polyesters, such as poly (butylene succinate adipate) (PBSA), poly (butylene succinate) (PBS), poly (ethylene succinate) (PES), poly (butylene succinate)/poly(caprolactone) blend, and PBAT. Because of its aromatic ring, PBAT was not considerably degraded by several kinds of the lipases, but PBSA was illustrated to be significantly degradable. PES degraded in NaOH solution much more quickly than in the other polyesters, and under these circumstances, PBSA degraded at a slower rate than in enzymatic degradation.

Mofokeng et al. [157] utilized thermogravimetric analysis (TGA) and Fourier-transform infrared (FT-IR) spectroscopy to investigate the thermal stability of PLA/PCL mix nanocomposites including TiO₂. While pure PLA displayed a higher activation energy of degradation, pure PCL demonstrated better thermal stability. It means that the rate of degradation is more temperature-dependent, most likely as a result of a mechanism for degradation based on chain scission and re-formation. Although the TiO₂ nanoparticles enabled enhance it, the PLA/PCL mixture still displayed a decreased thermal stability.

Regarding the functions of other biodegradable polymers, Muller et al. [158] studied how three different types of shopping bag polymers including standard, biodegradable, and degradable plastic decompose in the digestive juices of sea turtles. A standard bag was built on HDPE, and a degradable bag was attributed to a proprietary material comprised of either PE or PP with additives, whereas a biodegradable bag was built on Mater-Bi. Only negligible degradation rates (dependent on mass loss) were observed for the standard and the degradable plastic over a 49-day notice period, as anticipated. The degradation rate for the biodegradable bag, on the contrary was found to be as low as 9%, which is lower than what is generally anticipated under industrial composting environments.

Applications

The usage of biodegradable polymers is expanding quickly, and the global market for them is worth many billions of dollars per year. Applications for biodegradable polymers include food packaging, computer keyboards, auto interior components, and medical uses such as implanted big devices and medical delivery [159–161]. Figure 12 illustrates the numerous

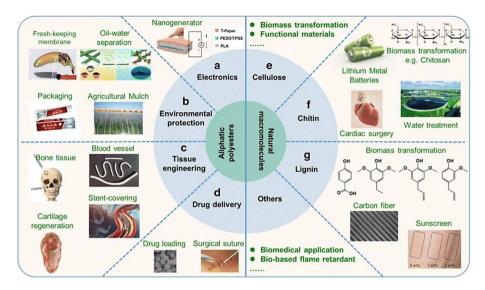


Fig. 12 Application of biodegradable materials [159]

uses for biopolymer materials [159]. Furthermore, biodegradable polymers are employed in certain applications in which plastics cannot be utilized, for instance making artificial tissue. These applications can demand biomaterial properties like biocompatibility, environmental responsiveness, and biodegradable candidates with sensitivity to variations in pH and physicochemical and thermal variations [162]. In comparison to synthetic polymers, biopolymers typically exhibit inferior thermal and mechanical properties (tensile strength and brittleness), chemical resistance, and processability. As mentioned in the "Introduction" section, they can be strengthened with fillers and fibers that significantly improve these properties in order to make them suitable for particular uses.

Conclusion

In a variety of fields, including surgery, pharmacology, agriculture, and the environment, biodegradable polymers for short-time applications have received a great deal of attention all over the world. The incompatibility of plastic waste with the environment where it is disposed of after use is the cause of this increasing interest. The recent technological advances into biodegradable polymers enable to reduce environmental pollution and greenhouse emissions and also have a critical significance in the lack of supply of oil resources. The high production costs and poor performance of some biodegradable plastics are the main issues that must be effectively resolved, which need further research to avoid competing with other environmental effects.

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Data Availability Not applicable.

Declarations

Ethics Approval and Consent to Participate Not applicable.

Consent for Publication Not applicable.

Competing Interests The author declares no competing interests.

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