

Preparation and degradation mechanisms of biodegradable polymer: a review

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Abstract. Polymers are difficult to degrade completely in Nature, and their catabolites may pollute the environment. In recent years, biodegradable polymers have become the hot topic in people's daily life with increasing interest, and a controllable polymer biodegradation is one of the most important directions for future polymer science. This article presents the main preparation methods for biodegradable polymers and discusses their degradation mechanisms, the biodegradable factors, recent researches and their applications. The future researches of biodegradable polymers are also put forward.

1. Introduction

Synthesized polymeric materials with low density, high specific strength, good wear and corrosion resistance, etc., which are being widely used in industry, agriculture, national defense, transportation, are difficult to be broken down naturally and completely in the natural environment [1]. If not recycled properly, they would do harm to the environment. The conventional treatment methods for waste polymeric materials include landfilling, incineration, blending with new materials after granulation, chemical degradation, recycling, etc. [2]. However, some of these methods are not cost-efficient, others can cause serious environmental pollution. Therefore, in recent years, the research and development of new biodegradable polymeric materials have become a hot topic in science and industry.

Biodegradable polymeric materials can be resistant to degradation during usage period and have a biodegradable property at the end of their useful life [3]. The biggest advantages of biodegradable polymeric materials are preserving fossil resources on one hand, and on the other hand reducing the environmental pollution in a sustainable development context [4]. Biodegradable polymers can be degraded by microorganisms under either aerobic or anaerobic conditions and ultimately converted to the bio-decomposed products including CH₄, H₂O and some inorganic compounds[5]. The processes can be promoted by abiotic chemical reactions such as hydrolysis, photodegradation, oxidation, etc. [6].

The field of biodegradable polymers has developed rapidly since 1980s. According to the statistics from European Plastic, the worldwide production capacity for bioplastics will increase from around 1.4 million tons in 2011 to approximately 6.0 million tons in 2017. Even though the speed-up rate is obvious, the output of bioplastics only account for about 1.7% of the whole polymer industry, which indicates that biodegradable polymers have a great and promising future. There are three kinds of biodegradable polymers: natural polymers, microbiologically synthesized polymers, and chemically synthesized biodegradable polymers [7]. According to their origins, biodegradable polymeric materials



can be further classified into two species, the petroleum resources and biological resources respectively (renewable resources). The biodegradable polymers have been mainly applied now into agriculture, medicine, tissue engineering, industry, etc. [8].

This review mainly focuses on recent progress in biodegradable polymeric materials including preparation methods, biodegradation mechanisms, and influencing factors. It provides a general overview of the theme in the last five years. Finally, the applications and the future trends of biodegradable polymers are also briefly summarized.

2. Preparation of biodegradable polymeric materials

2.1. Traditional methods

2.1.1. Modified natural polymers. The polysaccharide polymers that are readily biodegradable in Nature such as starch, cellulose, chitosan and chitin can be transformed into new biodegradable polymers by co-blending modification. The biodegradable films have demonstrated an improved mechanical properties, low water vapor permeability and solubility [9]. For example, biodegradable blend films were developed by casting rice starch-chitosan solution on levelled trays [10]. However, the performances of thermal and mechanical properties of these products are quite poor. Many efforts have been made to obtain the desired functions through various modification methods [11].

2.1.2. Chemically synthesized polymers. These polymers are chemically synthesized with the chemical structures similar to natural polymers. These polymeric chains containing ester, amide and peptide bonds can be readily biodegradable. Luo et al. [12] have reported using L-lactic acid and glycerol as starting materials to synthesize a biodegradable material (poly(lactic acid-co-glycerol)) under the optimal synthetic conditions. However, the required synthesis condition was harsh and bad and led to many by-products, therefore this chemical synthesis method is not cost-efficient for biodegradable polymers [13].

2.1.3. Microbiologically synthesized polymers. Microorganism can fabricate a series of complex polymeric materials using some organic matters (like glucose or starch) as food sources. These polymers contain the various types of silk, polysaccharides, polyesters, etc. The separation of these products is difficult due to their similar chemical properties. Bacterially synthesized polyhydroxyalkanoates (PHAs) as highly biocompatible and biodegradable plastics have attracted wide attention and can be prepared through many renewable resources [14].

2.2. Enzymatic synthesis

Enzymatic synthesis is a new method for the preparation of biodegradable polymeric materials. Some enzymes show different properties and can catalyze some special polymerization reactions. This kind of polymerization process may not produce any by-products due to the high specificity of the enzymes, which makes the product separation easy to perform. Furthermore, the enzyme can be recycled, and the mild catalytic reaction conditions (generally at room temperature and atmospheric pressure) reduce the process cost significantly [15]. Using the stereospecificities of the enzymes, some special products, which cannot be produced with traditional methods, can also be made [16].

One example is the aliphatic polyesters synthesized by lipase-catalyzed polymerization, which has become an important synthetic method for polymeric materials [17]. By enzymatic synthesis, fully biodegradable polymers such as polyester, polysaccharide, polyamide, etc., can also be produced [18].

2.3. Chemo-enzymatic synthesis

Enzymatic synthesis can not only endow the polymer with both high specificity and stereoselectivity, but also adjust the polymer molecular weight [19]. The chemo-enzymatic synthetic method combines the conventional polymerization with the highly efficient and regioselective enzymatic approach, and

is therefore a very attractive strategy for the preparation of high molecular weight biodegradable polymers [20]. Cai et al. [21] have used an efficient chemo-enzymatic route to fabricate some optically active polymeric prodrugs for non-steroidal anti-inflammatory drugs with high molecular weight.

3. Biodegradation mechanism

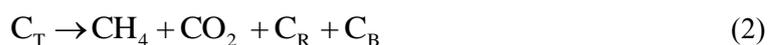
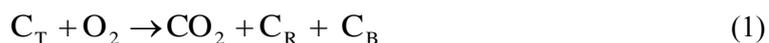
3.1. Abiotic involvement

The phenomenon of “biodegradation” can be explained by biological activity as the predominant factor. However, the organic matter is decomposed due to the synergism of biotic and abiotic factors in Nature [22]. Biodegradable polymers exposed to outdoor conditions (e.g., weather, aging or burying) can undergo more or less transformations such as in mechanical, chemical, light, thermal forms, etc. [23]. This exposure reduces the performance of the biodegradable polymers. In most cases, abiotic involvement contributes to weakening the macromolecular structure of biodegradable polymers, and in this way favor the degradation. Moreover, these abiotic parameters may be useful to initiate the biodegradation process [24]. Consequently, the involvement of the abiotic conditions should not be neglected.

3.2. Biotic involvement

So far, several biodegradable mechanisms of biodegradable polymers have been reported, three main biodegradable mechanisms are, (1) physical biodegradation: polymers are eroded by microorganisms and then destroyed due to cell growth; (2) Chemical biodegradation: with the direct action of biological enzymes, microorganisms erode the polymer chain which results in the depolymerization. Usually, biochemical degradation can be divided into two steps. The first step, extra-cellular enzymes (exo-enzymes) acting on the surface of materials break the polymer chains and generate small molecule compounds (acids, esters, etc.) with the molecular weight of less than 500 daltons. The second step, the small molecule compounds are assimilated by the microorganisms through metabolic routes, and then transformed into biomass and bioenergy, until final products of CO₂ or CH₄ and water can be obtained [4]. In general, the second step is often concomitant with the first one; (3) The interaction between microorganisms and polymers form new macromolecules. Polymers are usually not degraded by a single mechanism, but by a complex combination of biophysical, biochemical and physicochemical mechanisms [25].

Since microorganisms play an important role in the biodegradable process, proper humidity is always necessary for the polymer to achieve a biodegradable property [26]. Polymers can be further biodegraded under either aerobic or anaerobic conditions or the combination of both [27]. In the presence of oxygen, aerobic microorganisms contribute to the degradation of polymeric materials, with CO₂, water and microbial biomass as the final products. Equation (1) shows the mass balance equation for aerobic biodegradation. In contrast, anaerobic microorganisms can degrade the biodegradable polymers under the anaerobic environment. The final products will be CO₂, water, CH₄ or other hydrocarbons, or microbial biomass. Equation (2) shows the total carbon equation for anaerobic biodegradation. When the primary metabolites are some inorganic species, e.g., N₂, CO₂, H₂O, salts, etc., the degradation is called mineralization [28].



Where, C_T is the total carbon content of biodegradable polymers, C_R is any residual products of polymers left or any by-products produced during the degradation process, gaseous CO₂ is a measurable product, and C_B is the microbial biomass from the reproduction and growth of microorganisms.

In addition, the effect of enzymes occupies a key position. When the active enzymes from microorganisms are secreted and permeated into the active sites of polymer chains, hydrolysis reactions occur on the macromolecular chains, which may break into short chains or smaller molecules, even dis-

appear, and polymers undergo complete degradation [29]. Results have been found that microbial enzymes tend to decompose the polymer structures, such as amide, enamine, ester, urea, urethane linkages, etc.[30].

4. Effect factors of biodegradation

Based on in-depth researches, some scientists have found that the polymer biodegradation depends not only on the polymers characteristics including chemical structure, morphology, molecular weight but also on some environmental conditions, e.g., temperature, humidity, pH value, radiation, etc.

4.1. Polymeric configuration

4.1.1. Chemical structure. Biodegradability is ultimately controlled by the chemical structures which directly affects the ability of degradation. Functional groups' biodegradation ability may be descendant in such order: Aliphatic ester, Peptide bond > Carbamate > Aliphatic ether > Methylene.

The polymers with hydrophilic groups (amino, hydroxyl, carboxyl and amide groups) are easily biodegradable under certain humidity, and those amphiphilic diblock copolymers are more biodegradable than polymers are with only one hydrophobic block [31]. Linear polymers are more easily biodegradable than branched and cross-linked polymers [32].

4.1.2. Aggregation structure. Polymers with flexible chains are easily biodegradable, and the amorphous areas are easier to degrade than crystallization areas. Unsaturated compounds are hard to biodegrade [33], while aliphatic polyester are easier to biodegrade [34]. Moreover, rigid aromatic polyesters such as polyethylene terephthalate (PET) are bioinert [35]. Blend-modification usually can help to achieve biodegradation [36]. Recently, some special plasticizers and additives which can play important roles in polymer degradation have attracted wide attention in this field [37].

4.1.3. Polymerization degree. Typically, the molecular weight of polymers has an important effect on its biodegradation. When polymers have a higher molecular weight, the rate of biodegradation may be slower [38]. If the molecular weight reaches an upper limit or goes beyond the scope that microbial cells can take, the biodegradation will not occur in polymers [39]. The synthetic plastics are usually too large to allow the cells to enter, but natural polymers do not have these problems. In most cases, alkane-based polymers with the molecular weight of exceeding 400–500 daltons must be degraded into smaller molecules by biological or chemical means or photodegradation before biodegradation [40].

4.2. Environmental conditions

Water is necessary for the growth of microorganisms. Polymeric materials can be biodegraded only under certain humidity.

Temperature has a dual effect on biodegradation. In a certain range, high temperature speeds up microbial metabolic processes and causes the vigorous growth, which is helpful to degradation on one hand. On the other hand the temperature has a greater effect on the biological activities of proteins and enzymes. Therefore, each kind of microorganisms has its own optimal temperature for growth and reproduction [41].

The pH value also has a great influence on the growth of microorganisms [42]. Optimal pH can accelerate microbial metabolism, eventually speed up the degradation rate. For example, the biodegradation of poly(lactic-co-glycolic acid) (PLGA) and polyglycolic acid (PGA) mainly depends on bacteria, actinomyces, fungi and other microbes under pH 5–9 [43].

Moreover, biodegradable materials produce free radicals or ions after γ -ray radiation, which can also speed up the degradation [44].

5. Applications

5.1. Industry

With high heat resistance, waterproof, chemical erosion resistance, dirty resistance and strong coloring power, biodegradable polymers can be widely used in making leather, fiber, and packaging film, especially the biodegradable packaging films attracting increasing attention [45]. Compared with other biodegradable polyesters, poly- ϵ -caprolactones (PCL) enjoys easy availability and lower price, which can be widely applied as an environment-friendly material. Some polysaccharide-based biopolymers, e.g., pullulan, starch, chitosan, etc., have been investigated and used as packaging films [46]. Another biodegradable polymer, poly-3-hydroxybutyrate (PHB) can be used to fabricate the packing materials or disposable products [14].

5.2. Agriculture

Biodegradable polymers can be used as agricultural mulches, the planting support, gradual releasing agents of the agricultural pesticide, ropes and fishing nets in fish culture [47]. Under appropriate conditions, biodegradable materials especially chitin and chitosan materials can degrade into compost or organic muck, which is beneficial to plant growth and the soil environment [48]. Some natural polymers, e.g., starch, lignin, cellulose, chitin, etc., are being applied in the releasing agent system, and the PCL is being used as a support material for agricultural planting [49].

5.3. Medicine and pharmacy

As a biomaterial, biodegradable polymers have three important characteristics: mechanical resistance, biological absorbability, and biocompatibility [50]. Biodegradable polymers are mainly being used as the releasing agents of drugs, absorbable sutures, and also in orthopedic surgery and tissue engineering [51].

In drug releasing delivery systems, biodegradable polymers, such as proteins, gelatin, chitin and their derivatives, polylactic acid (PLA), PHB, etc., have been extensively used as drug carriers due to their biological absorbability. PGA, PLA, and their copolymers are used to prepare absorbable sutures, which can automatically degrade and be absorbed by organisms in wound healing. Polybutylene succinate can be used as a promising substance to repair bone and cartilage [52]. Biodegradable fixing materials can also avoid osteoporosis and secondary operation caused by using stainless steel [53]. Moreover, antibiotic drugs, bone growth factors, and regulatory proteins can be implanted into the biodegradable materials to prevent infection and promote bone healing during the treatment period [54]. Poly(propylene fumarate) (PPF) is the best biodegradable scaffold for the bone tissue regeneration so far [55]. PLGA with a good cell adhesion has been applied in the bone tissue engineering [56].

5.4. Other fields

Biodegradable polymers can be used in other specific fields such as electronics[57], automotive sectors, sports and leisure [58], construction sectors [59], etc., even with some unusual applications [60]. A huge and promising market in the future will be expected.

6. Conclusions

The development of biodegradable polymers is still in the early stage yet with a promising prospect in the future. The researches of biodegradable polymer will help to alleviate the environmental pollution and also have a critical significance in relieving the shortage of oil resources. Compared with traditional plastics, biodegradable polymers are still expensive and have relatively lower mechanical properties. Therefore, at present, only limited biodegradable polymer materials are being used. With the development of smart design, more and more new preparation methods will be explored, and better biodegradable materials will be developed.

Future researches of biodegradable polymeric materials should be anticipated in the following aspects, (1) To control the degradation rates of biodegradable polymers and balance the properties between the material performance and the shelf life; (2) To explore new methods to make existing polymers biodegradable and synthesize biodegradable polymers with novel structures; (3) To further improve biodegradability of biodegradable polymers and reduce the cost to broaden their applications; (4) To develop biodegradable composites based on natural polymers.

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