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Progress in the Synthesis and Application of Biodegradable Polymers

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Abstract. With the development of science and technology, biodegradable materials have gradually emerged in people's vision. Biodegradable materials are generally high polymer materials, many of which can be artificially synthesized, and some raw materials are simple and easy to obtain, and the production process is not complicated. This material has many advantages that traditional materials cannot match, and it can be said that the current development prospects of this material are very promising. Its degradability meets the requirements of green chemistry and environmental protection, and the harm to the human body will no longer be as severe as traditional materials. This article introduces several common biodegradable materials such as PLA, PBAT, and some highly recognized synthesis methods, as well as their degradation mechanisms. It also elaborates on their applications in various fields, including biomedical, packaging, and agricultural fields, to illustrate the advantages of biodegradable materials over ordinary traditional materials and their future trends in widespread application in various fields.

Keywords: Polymer, biodegradable, synthesis, application.

1. Introduction

With the intensification of the global greenhouse effect, humans are paying more and more attention to environmental protection. Some traditional synthetic plastic materials have become essential materials for industrial products due to their excellent mechanical properties and low production costs. They play a very important role in human production and life, occupying most of the plastic market. However, while they bring various conveniences to humanity, they also bring huge environmental problems. Due to their non degradability, it usually takes decades or even hundreds of years to be completely degraded. Therefore, their high degradation elasticity and low recovery rate make them stubborn waste, which has spread all over the world and caused significant environmental damage. The current common practice for handling them is landfill, which is very ineffective for these synthetic plastics [1]. Therefore, it is necessary to develop biodegradable and environmentally friendly materials to replace traditional plastic materials.

Biodegradability is not only an environmental requirement, but the medical applications of biodegradable polymers have also attracted attention in recent years. In addition, creating soluble polymers that can replace biodegradable water for products such as detergents and cosmetics has also gained increasing value. Therefore, the development of biodegradable polymer materials and the design of methods to improve their biodegradability have become the main goals of the academic community [2].

This article mainly introduces some common biodegradable polymer materials, as well as the preparation methods and degradation mechanisms of some materials. It also elaborates on some cutting-edge applications of this material in current popular fields to illustrate the feasibility and importance of its future development. This article provides a reference for the future development of biodegradable polymer materials.

2. Biodegradable synthetic polymers

Many common biodegradable polymers can be artificially synthesized, and this article will focus on several common materials.

2.1. Poly(lactic acid) (PLA)

The polymer formed by the polymerization of L-lactic acid is called L-polylactic acid (PLLA), the polymer formed by the polymerization of D-lactic acid is called D-polylactic acid (PDLA), and the polymer formed by the polymerization of L-lactic acid and D-lactic acid in equal proportions is called (PDLLA) [3].

2.1.1. Preparation Method of PLA

There are two common synthesis methods for PLA, namely: direct condensation polymerization and lactide ring-opening polymerization (also known as the two-step method) [4].

The method of direct condensation polymerization is carried out by stepwise increasing the reaction temperature and vacuum degree in the presence of a catalyst [3]. Although the process is simple, it may be difficult to remove free substances such as water, lactic acid, and oligomers within the system, which can affect the progress of polymerization reactions and ultimately result in the failure to obtain the desired product [4].

The method of direct condensation polymerization is also known as the two-step method. The first step is to condense lactic acid into low molecular weight polylactic acid at around 130 °C, and then depolymerize to produce lactide under slightly higher temperature and low-pressure conditions; The second step is to polymerize under the action of a catalyst. According to the different reaction mechanisms, it can be divided into anionic, cationic, and coordination insertion types [3].

Anionic ring-opening polymerization is characterized by the nucleophilic anion of the initiator attacking the carbonyl group of lactide, causing the carbonyl carbon and inner epoxy bonds to break, and then forming new anions to continue attacking and causing polymerization reaction [3], as shown in Figure 1 [3].

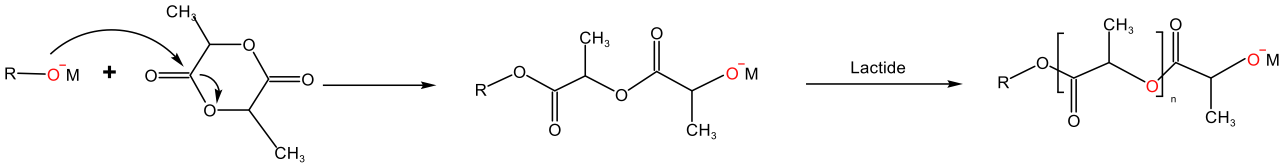

Fig. 1 Process diagram of anion ring-opening polymerization [3]

Cationic ring opening polymerization uses carbene ion donors and some strong acids as catalysts to epoxide or protonate one of the carbonyl groups of lactide, forming a positive ion and triggering polymerization [3]. The process can be represented as shown in Figure 2.

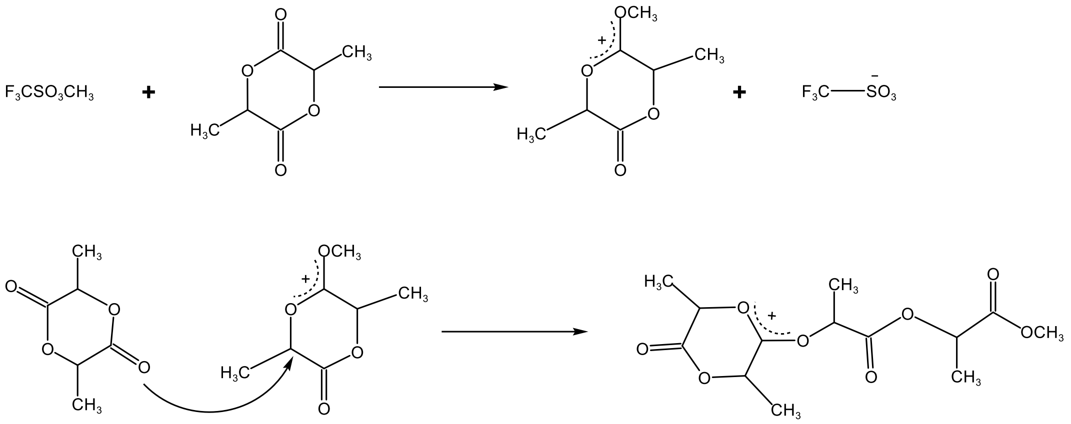

Fig. 2 Process diagram of cationic ring-opening polymerization [3]

The coordination insertion mechanism uses some metal alkoxides as catalysts to initiate polymerization reactions by inserting the metal-oxygen bonds of initiators [3].

Although the open-loop polymerization method can obtain high molecular weight PLA, the entire process is too long and time-consuming [4]. The cost of some raw materials is also high, and some catalysts have certain physiological toxicity. Therefore, these problems can be effectively avoided by improving the production route. For example, changing the catalyst to stannous octanoate that can serve as a catalyst can reduce physiological toxicity, Replacing the high-cost raw material trichloromethane with dichloromethane [5].

2.1.2. Degradation Mechanism of PLA

PLA undergoes degradation in natural environments or composting conditions. Under high temperature and high humidity active composting conditions, PLA can degrade within a few months, and its hydrolysis rate is accelerated in acidic and alkaline environments. The biodegradation of PLA is mainly divided into two stages. Firstly, PLA undergoes chain breakage, forming low molecular chains. Then, the low molecular chain PLA is metabolized by microorganisms in nature as CO_2 and H_2O [3].

2.2. Poly (butylene adipate-co-terephthalate) (PBAT)

PBAT is a copolymer of diethyl adipate and butyl terephthalate [4]. It not only has the good biodegradability and flexibility of aliphatic polyester, but also has the good mechanical properties, impact resistance, and heat resistance of aromatic polyester [6].

2.2.1. Preparation method of PBAT

There are two main ways to synthesize PBAT, one is ester exchange, and the other is direct esterification [7]. The main raw materials for synthesizing PBAT through the ester exchange method include terephthalic acid (PTA) or DMT, polybutylene glycol acetate (PBA), and 1,4-BDO [8]. This method involves obtaining PBT prepolymers through esterification or ester exchange reactions within the system under the action of catalysts, and then conducting ester exchange with PBA through melt condensation reactions. Although this method has a simple reaction setup and fewer intermediate products, resulting in a narrower relative molecular weight distribution of the products [6], the entire production process is long and may produce many by-products, which can easily lead to insufficient purity of the products and pose certain difficulties in separation and recovery [7].

The direct esterification method is the most commonly used method for synthesizing polyester. The raw materials used in this method to synthesize PBAT include AA, 1.4-BDO, and PTA or DMT. The process is divided into three steps: pre-mixing, pre-polymerization, and final polymerization. Firstly, the raw materials are mixed and esterified under the catalytic action of organic metal compounds such as zinc, tin, and titanium. Then, PBAT is synthesized through a condensation reaction under high temperature and high vacuum conditions [8], as shown in Figure 3.

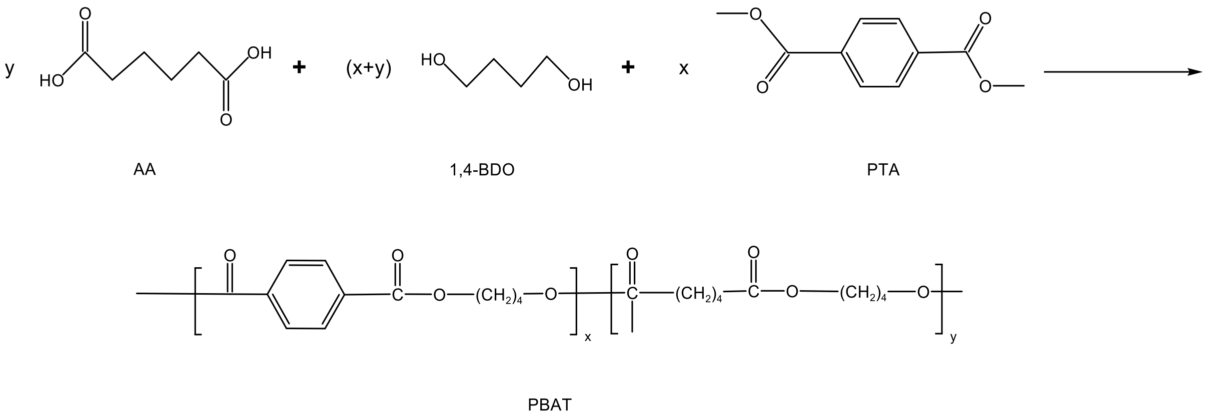

Fig. 3 Schematic diagram of the direct esterification method for synthesizing PBAT reaction [8]

2.2.2. Degradation Mechanism of PBAT

The degradation of PBAT is mainly achieved through two pathways: one is through the enzyme promotion of microorganisms in nature, and the other is through nonenzymatic reactions such as thermal hydrolysis and chemical hydrolysis. For enzyme-promoted degradation, bacteria, fungi, algae, etc. need to play a role in biodegradation; For nonenzymatic degradation, the degradation of PBAT is random and mainly occurs through ester bond cleavage. The intermediate products after cleavage are assimilated and further metabolized by microorganisms [8].

2.3. Others

2.3.1. Polycaprolactone (PCL)

PCL belongs to polymeric polyesters, which are prepared by ring-opening polymerization using organic metal compounds as catalysts and dihydroxy or trihydroxy compounds as initiators. In the soil environment, it can be completely decomposed into CO_2 and H_2O after 6 to 12 months [6].

2.3.2. Polybutylene succinate (PBS)

The raw materials for PBS preparation are aliphatic succinic acid and butanediol, which can be produced from petroleum or through microbial fermentation. PBS has excellent degradation performance, good biocompatibility, and heat resistance [6].

2.3.3. Poly (lactic-co-glycolic acid) (PLGA)

The two commonly used synthesis methods for PLGA are ring-opening polymerization and direct condensation polymerization. The main degradation method is hydrolysis degradation, which can be divided into four processes: water molecules break van der Waals forces and hydrogen bonds, the polymer main chain breaks ester bonds due to hydrolysis, and after continuous degradation, it becomes smaller fragments or monomers dissolved in the medium [9].

3. Application of biodegradable materials

3.1. Biomedicine

Biodegradable materials have a wide range of applications in the medical field. Some biodegradable polymers, such as PLA, polyglycolic acid (PGA), and their copolymers, such as poly(lactic-co-glycolic acid) (PLGA), are non-toxic to human tissues. These are biodegradable polymers approved by the US Food and Drug Administration (FDA) [10].

3.1.1. Vascular Stents and Surgical Sutures

Biodegradable materials such as PLA and PLGA are widely used in the preparation of vascular stents and sutures. These materials have good biocompatibility and mechanical properties, can provide temporary mechanical support in the human body, and can be gradually degraded and absorbed. Cyananid, an American company, has developed an absorbable surgical suture (Dexon) using PGA as a raw material; A high-strength absorbable suture (Vicryl) was developed by copolymerizing glycolic acid and lactic acid in a mass ratio of 90:10; A absorbable suture (Maxon) with higher tensile strength and nodule strength than polypropylene and nylon threads was developed through copolymerization of PGA and trimethylene carbonate, and maintained 59% of its original strength after 28 days in vivo, while the strength of PGA thread decreased by more than 50% after 14 days in tissue [11].

3.1.2. Drug delivery

Biodegradable materials are also used in drug delivery systems, such as PLA, PCL, and PLGA, which embed or encapsulate drugs in these materials. These materials can control the release rate of drugs, thereby improving their bioavailability and therapeutic efficacy. Jiang XY et al. [12] prepared a nanoparticle drug based on PTMC, which can target and deliver the drug to tumor areas rich in integrins.

3.1.3. Orthopedics

The majority of materials that are frequently used to treat bone fractures are non-biodegradable and include pure titanium and its alloys, cobalt-chromium-based alloys, and 316L stainless steel. However, these materials are metallic and belong to foreign bodies for the human body, which may cause some local inflammation and may require a second surgery. However, Biodegradable polymers are being utilized in orthopedic applications now. Bioceramics with superior biocompatibility, bioactivity, and osteoconductivity qualities include hydroxyapatite (HA). The superior mechanical qualities and osteointegration ability of the hybrid polymer products based on HA–poly (PEG-co-propylene fumarate-co-ascorbate) hybrid macromers are utilized in bone graft materials, as they facilitate albumin adsorption and osteoconduction [10].

3.1.4. Periodontal regeneration

One of the inflammatory conditions that affect the teeth, periodontal disease causes the breakdown of periodontal tissues and is quite painful. This periodontal treatment uses biodegradable polymers such as Helixician (HX) to immobilize biodegradable chitosan (CS), poly (vinyl alcohol) (PVA), and hydroxyapatite (HA)-based electrospun films and fibers. These systems were designed with extended medication release in mind. Due to their anti-inflammatory and antibacterial qualities, these biodegradable scaffolds are extensively utilized in the regeneration of periodontal tissues. PCL or PCL/CA (polylactic acid/cellulose acetate) nanofibrous scaffolds are utilized in bone regeneration with antibacterial activity as well as periodontal tissue regeneration [10]. The general application is shown in Figure 4.

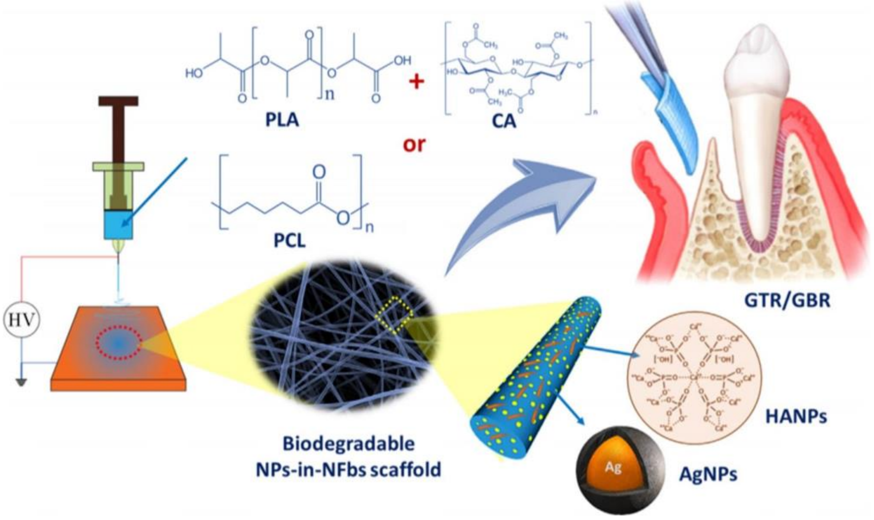

Fig. 4 Development of a new series of electrospun nanoparticles-in-nanofibrous scaffolds for GTR/GBR applications with enhanced antibacterial and bone regeneration activity [10]

3.2. Packaging materials

3.2.1. Food packing

Traditional nondegradable plastic packaging materials are mainly processed and manufactured from petroleum as raw material, and plasticizers and lubricants are also added. In the long-term food consumption process, may cause harm to the human body. Biodegradable biomaterials not only meet the performance requirements of plastics but also maintain the freshness of food for a certain period. Finally, they can degrade into non-toxic and harmless chemical components in the natural environment. Natalia et al. produced films from thermoplastic starch (TPS), PBS, PBAT, and CA using a blow-out method. It was found that these films exhibited good thermal stability with a maximum decomposition temperature close to that of pure polyester and could be used in food packaging [13].

3.2.2. Medical packaging

Biodegradable materials are a challenging field in medical packaging. The following are some traits and qualities that biodegradable polymers should possess: the substance should not be able to seep into the manufacturing process, alter the composition of medication, or react with or alter its constituent chemicals. a combination of polypropylene and poly (lactic acid) is utilized due to its antibacterial, water barrier, and contamination-reduction capabilities, it is widely used [10].

3.3. Agricultural sector

Biodegradable materials, such as polymer soil fixatives, play an indispensable role in the agricultural field by controlling soil erosion and soil and water conservation, thereby improving crop yield and quality. In addition, traditional agricultural films are made of plastic, which can cause serious environmental pollution. By using biodegradable polymer materials to prepare films, this situation will not occur and can be treated through biodegradation. Soňa et al. made the fertilizer have a slow-release effect by coating its surface with a biodegradable poly (3-hydroxybutyrate) coating. This slow-release fertilizer was found to still exhibit excellent tolerance after 76 days in water, releasing only 20% ammonium nitrate. According to pot experiment monitoring, it will gradually release nitrogen, and will not cause soil pollution, which is conducive to the growth of corn and other plants. Figure 5 illustrates the preparation process and its application in plant species [14].

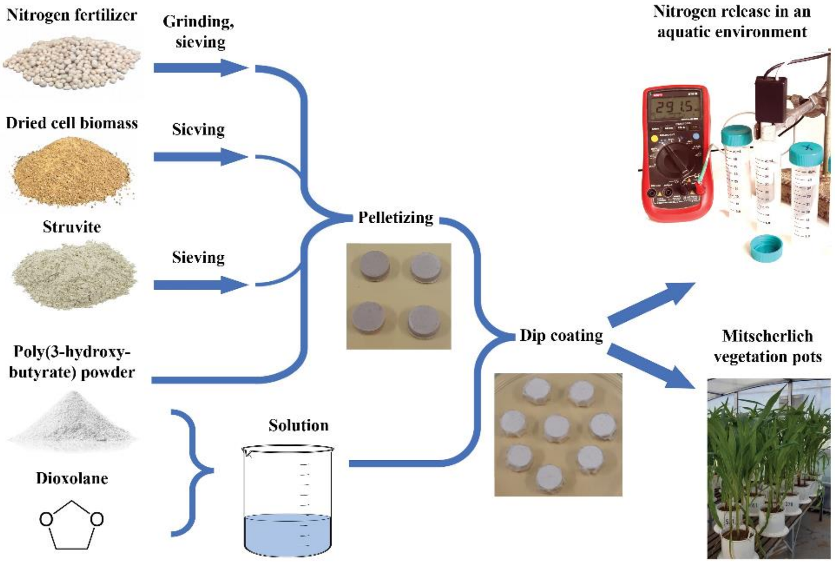

Fig. 5 Preparation and application of slow-release nitrogen fertilizer [14]

3.4. Biodegradable Synthetic Fibers

Biodegradable synthetic fibers have unique properties that traditional materials cannot match in terms of biodegradability, and they play a unique role in certain aspects. PLA fiber is currently a biodegradable synthetic fiber with good industrialization. Its raw material sources are abundant, and its production technology is relatively mature. Due to its good elasticity, antibacterial, and flame resistance, the product has a wide range of applications, such as in the textile industry such as clothing and decoration. PBAT fiber has good degradability, ductility, and toughness, and is widely used in packaging materials, home decoration products, biomedical textiles, and other fields. PHA fibers have good biodegradability, biocompatibility, and composites, but their poor stability and easy hydrolysis limit their large-scale applications. The composite fibers prepared by blending PLA into PHA exhibit excellent antibacterial properties, which can broaden the application fields of biodegradable materials [15].

4. Conclusion

This article introduces common biodegradable materials, as well as the synthesis methods and degradation mechanisms of some polymers, and elaborates on their applications in many fields, including biomedical, packaging materials, agriculture, etc.

Biodegradable materials have many advantages that traditional materials cannot match and are more harmless to the environment and human body compared to traditional plastic materials. However, there is still great room for development and improvement in biodegradable materials, and the synthesis process route has not yet fully matured. Taking PLA as an example, the two common methods used in its production are the direct condensation method. Although the process is simple, some difficult-to-remove free substances may ultimately affect the generation of products; However, the complex and high requirements of the propylene glycol ester ring-opening polymerization process, as well as the low yield, result in high production costs, which limits the popularity of PLA. Taking PBAT as an example, although this polymer has received much attention, many aspects of it still cannot compare to traditional plastic materials, such as mechanical properties, thermal properties, barrier properties, etc., which also limits its widespread application.

In the production process of biodegradable polymer materials, it is necessary to correctly add raw materials, control the feeding ratio, avoid dosage deviation, and better comply with the concept of environmental friendliness. Secondly, in the process of processing polymer materials, research should also focus on improving their performance, so that biodegradable materials can be better applied in production and daily life.

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