Synthesis Approaches of Bio-Degradable Polymer Materials

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Abstract. Numerous polymer materials are used in various fields of human's life. However, for traditional petro-based polymer materials, because of the pollutants produced during the process of fabrication, as well as their difficulty in degradation and recycle, they contribute to major environmental issues such resource waste, global warming, and white pollution. In order to address those problems, an important way is to produce and apply more biodegradable polymer materials, which can be easily cycled in nature. Biodegradable polymers can be produced using a variety of synthetic approaches, including directly chemical synthesis, natural polymer modification, microbial synthesis, and enzymatic synthesis. These approaches offer biodegrable polymer materials both better mechanical or thermal properties as well as biodegradability, which make them desirable and appropriate for the application in diverse fields. The basic concept and mechanism of biodegradation of biodegradable polymers are discussed in this review, along with a presentation of various synthesis approaches and their related studies recently.

Keywords: Biodegradable polymers; synthesis; modification.

1. Introduction

Polymer materials are widely used in people's daily life since most of the traditional polymer materials have a series of excellent properties, such as low density, flexible structure, good processibility or hydrophobicity. However, during the production of traditional petro-base polymer materials, reactions including polyaddition or polycondensation occur which produce chemicals such as carbon dioxide. Besides, the products made from these materials are difficult to be disposed of after use due to the characteristics of toxicity and non-biodegradability, thus resulting in the problems of global warming, resource waste and environmental pollution [1]. The interest of research into biodegradable polymers is raised due to the urgency of eliminating the negative effects to the environment. Those bio-degradable polymers not only have good physicochemical properties and mechanical properties, but also have good biodegradability so that the materials can be better recycled and used. Biodegradable polymers are high molecular weight molecules that can degrade into low molecular weight compounds by enzymatic reactions in organisms [2].

Biodegradation is a process of decomposing organic materials under the catalysis of enzymes, which provides microorganisms with energy and carbon sources. The large biopolymers are firstly broken down into oligomers or some monomeric units by enzymes in microorganisms. Then, through the metabolism of microorganisms, the remanent segments of polymer degrade into small compounds like water, carbon dioxide and methane, the final product of biodegradation depends on whether oxygen participates in the reactions.

2. Synthesis Approaches of Biodegradable Polymers

There are several commonly used methods of producing biodegradable polymers: Directly chemical synthesis, natural polymer modification, microbial synthesis and enzymatic synthesis.

2.1. Directly Chemical Synthesis of Biodegradable Polymers

The artificial use of chemical processes to create polymeric materials with biodegradable constituents, such as ester, ether, or anhydride groups, is referred to as the directly chemical synthesis of biodegradable polymers. Chemical synthesis approaches such as ring-opening polymerization

(ROP), condensation polymerization as well as radical polymerization have been utilized to produce biodegradable polymers with desired properties.

ROP is one of the key methods used in macromolecular nanotechnology to produce biodegradable polymers. In order to create linear polymers, cyclic monomers like lactide, glycolide, and -caprolactone must open up [3,4]. A wide range of initiator and catalyst systems start the reaction, typically a metal alkoxide, to generate the active species that opens the monomer ring [5]. By altering the reaction circumstances, such as the monomer content, catalyst type, and reaction temperature, one may adjust the attributes of the intended polymer, such as molecular weight, stereochemistry, and thermal properties. Jiang et al., for instance, proposed the fabrication of biodegradable nanoparticles without the adding of degassing, heating, catalysts, or chain transfer agents as a one-pot open-to-air Method of NCA-induced self-assembly (NCA-PISA). By varying ratio between initiator and monomer as well as solid content, shape of the nanoparticles may be altered. Polymer vesicles are generated at a ratio of 1:20 and a solid concentration of 20%.This method provides a simple pathway to produce biodegradable nanoparticles in the air [5].

In addition, condensation polymerization is another popular technique for the synthesis of biodegradable polymers. This method involves reaction of two or more monomers with the elimination of small molecules, such as water or alcohol, to form a polymer. Common biodegradable polymers synthesized via condensation polymerization include PLA, polyethylene glycol (PEG), polyesters, polycarbonates and so forth. Generally, PLA can be synthesized via ring-opening polymerization with a higher molecular weight [6]. Despite the fact that direct condensation polymerization is a more affordable and straightforward technique for producing PLA, it creates PLA with a considerably lower molecular weight because of the formation of undesirable byproducts like water which cannot be effectively removed [7].

Furthermore, radical polymerization is a widely used method for synthesizing biodegradable polymers, which involves the initiation of free radicals that react with monomers to form a polymer chain. For example, Ullah et al. discussed the fabrication of chemical crosslinking hydrogels using carboxymethyl chitosan and polyvinyl alcohol through free radical polymerization. The potential for carefully regulated oxaliplatin administration and targeting in cancer therapy was demonstrated by the synthesized hydrogels, which displayed excellent performance in drug loading and release [8].

2.2. Modification of Natural Polymers

Natural polymers are substances that can be extracted from plants, animals, or other organisms in nature, they have characteristics of abundant resources, non-toxic, low good biocompatibility and degradability [9]. However, natural polymer such as starch and chitosan have poor mechanical properties and thermal plasticity which make them difficult to be processed into products. Therefore, these natural polymers are usually modified by synthetic polymers that have better mechanical or thermal properties [10]. Because of its excellent mechanical qualities and biocompatibility, polymers like polyvinyl alcohol (PVA) are frequently employed to alter those natural polymers. Blending starch and other natural polymers with PVA. is a simple approach to realize modification, producing the material that have both excellent mechanical properties and biodegradability [9]. Yu Chen et al. modified the starch by blending with PVA in solution, nitric acid modified starch and PVA with a mass ratio of 4:6 was put into a hot bath heated to 80 °C and stirred to blend until completely dissolved. Finally, the liquid product was formed into the membrane by method of flow casting on a Teflon plate. The biodegradable starch-PVA composite membrane shows good mechanical properties and transmittance [10]. Jiayu Zheng et al. produced biodegradable plastic using the solution casting process with PVA, octenyl succinic anhydride (OSA), potato starch, and gliadin. At the beginning, starch emulsion and gliadin solution were combined and swirled. Then PVA solution and glycerin solution were added and stirred together under the conditions of 90 °C, 800 rad/min for an hour. Finally, the composite plastic was formed by pouring the liquid product into the film scraper and dried. The composite plastic showed better plastic properties and degradability than pure PVA which is desirable for food packaging materials. Both mechanical strength and thermal performances

improved as the proportion of PVA and OSA starch increased, and the rate of degradation increased with the increasing proportion of starch and glycerin [11]. Wei Liang et al, prepared a hybrid plastic by the casting of chitosan, soy protein isolate (SPI) and PVA, where SPI was added to further improve the biocompatibility and degradability, compensating the defect of binary plastics. The film-forming emulsion was obtained by firstly mixing the 2% chitosan solution and 10% SPI solution in different ratios, then 7.5%PVA and glycerol were added and stirred under the conditions of 90 °C, 800 rad/min for an hour. The composite plastic was formed by pouring mixed emulsion to a scraper, heating to crosslink and finally cooling down. Results showed that compared to pure chitosan and pure PVA, the ternary composite plastic have continuous microstructure which indicated a good compatibility of three materials. Better thermal performance was shown due to an obvious rise in the values of Tc, Tm, ΔHc and ΔHm and better degradability was also shown due to the lower surface integrity in the soil burial test [12].

2.3. Microbial Synthesis of Biodegradable Polymers

Microbial synthesis means that some biopolymers such as Polyhydroxyalkanoates (PHAs) can be synthesized and accumulated in various microbial cells. PHAs bioplastics are regarded as one of the potential alternatives for traditional plastics due to their similarity to some polyolefin, but improved processability, biocompatibility, and biodegradability due to ester groups on the main chain [13].

At the begining, PHAs were produced using pure bacterial culture. However due to the strict production conditions, the approach was costly, which made it difficult to achieve mass production. Nowadays, mixed microbial cultures are used to produce PHAs, which is a more effective and low-cost approach because of the undemanding production conditions [14]. There are generally three steps in the production process. The first step is fermentation of carbon sources, producing the precursors of PHA. Then suitable cultures and microorganisms are selected. Finally, raw materials needed to produce PHA are added to cultures, and PHA will accumulate after a period of time [15]. Besides, to obtain the final products, extraction and purification of PHA from microorganisms are also considered necessary. Jianing Li et al. synthesized PHA successfully in activated sludge containing rubberwood hydrolysate and xylose, where the activated sludge composes of sufficient microbial cells. Then, the activity and accumulation with or without xylose and with different ratios of rubberwood hydrolysate and xylose were investigated. The findings demonstrated that xylose addition boosted PHA synthesis, and in a certain range, rubber wood hydrolysate had a synergistic impact with xylose that resulted in an increase in PHA yield [16]. Bianca Colombo et al. suggested combining diverse microbial cultures with fermented cheese whey as a carbon source. The outcomes demonstrated that certain organic acids, which are the precursors of PHA, were first created during the manufacture when employing fermented cheese whey, followed by PHA [17].

2.4. Enzymatic Synthesis of Biodegradable Polymer

As a kind of catalyst with high catalytic activity, enzyme can also be used in polymer polymerization process [18]. Enzyme polymerization refers to the synthesis of macromolecules using isolated enzymes in vitro. In the past decades, enzymatic polymerization has been proved efficient in the fabrication of natural polymers such as cellulose and chitin, as well as artificial polymers such as polyester and polycarbonate. As natural catalysts, enzymes are advantageous of being able to react under mild conditions and being renewable and environmentally friendly compared to conventional catalysts. Due to the excellent stability in organic solvents and compatibility with most substrates, lipases have been reported as a type of enzyme that can be used in various polymerization of polymers. Lipase-catalyzed copolymerization of macrolides and methyl 12HS was conducted by Takuma Kobayashi et al. The produced copolymer presented properties of elastomer as well as good biodegradability, which is the desired green material [19]. Using enzyme-catalyzed ring-opening polymerization, Chunyang Bao' team created a biodegradable protein-PCL conjugates by employing lipase B (CALB)-poly (N-hydroxyethyl acrylamide) conjugates as both an initiator and catalyst in

the polymerization step. According to reports, the created copolymer has strong biodegradability and amphipathicity, making it a useful medication carrier for organisms [19].

3. Conclusion

During the lifecycle of traditional polymer materials, the fabrication and disposal of them have negative impacts on the environment. Finding environmentally friendly alternatives is proposed urgently to alleviate the effects, among which synthetic biodegradable polymers are the most effective solutions. Various synthetic methods including directly chemical synthesis, natural polymer modification, microbial synthesis and enzymatic synthesis have already been investigated and even applied to the fabrication of biodegradable polymers, which present the desirable combination of mechanical, thermal performance and better biodegradability. Hence, biodegradable polymer materials have found use in a number of industries, including packaging, tissue engineering, and medicine delivery.

References

[1] Kalidas V K, R P, K S, et al. Study of synthesis and analysis of bio-inspired polymers-review [J]. Materials Today: Proceedings, 2021, 44: 3856-3860.

[2] Yin G, Yang X. Biodegradable polymers: a cure for the planet, but a long way to go [J]. J. Polym. Res., 2020, 27(2): 38.

[3] Kamber N E, Jeong W, Waymouth R M, et al. Organocatalytic ring-opening polymerization [J]. Chemical reviews, 2007, 107(12): 5813.

[4] Coulembier O, Degée P, Hedrick J L, et al. From controlled ring-opening polymerization to biodegradable aliphatic polyester: Especially poly (β-malic acid) derivatives [J]. Prog. Polym. Sci., 2006, 31(8): 723-747.

[5] Jiang J, Zhang X, Fan Z, et al. https://pubs.acs.org/doi/abs/10.1021/acsmacrolett.9b00606. accessed 16 Mar 2023.

[6] Nampoothiri K, Nair N R, John R P. An overview of the recent developments in polylactide (PLA) research [J]. Bioresource Technology, 2010, 101 8493.

[7] Sin L T, Rahmat A R, Rahman W A. Synthesis and production of poly (lactic acid) [J]. Polylactic Acid, 2013: 71-107.

[8] Ullah K, Sohail M, Murtaza G, et al. Natural and synthetic materials based CMCh/PVA hydrogels for oxaliplatin delivery: Fabrication, characterization, In-Vitro and In-Vivo safety profiling [J]. Int. J. Bio. Macromol. 2019, 122: 538.

[9] Gao X P, Wang X, Du L Y, et al. Research progress of polysaccharide-based natural polymers/PVA biodegradable blended films [J]. Packaging Engineering, 2016, 37(09): 74-79+88.

[10] Chen Y, Chen S. Preparation and properties of nitrate modified starch/polyvinyl alcohol composite film [J]. Guangzhou Chemical Industry, 2022, 50(16): 39.

[11] Zheng J, Hu Y, Su C, et al. Structural, physicochemical and biodegradable properties of composite plastics prepared with polyvinyl alcohol (PVA), OSA potato starch and gliadin [J]. J. Food Eng., 2023, 339: 111278.

[12] Liang W, Liu X, Zheng J, et al. Insight into crosslinked chitosan/soy protein isolate /PVA plastics by revealing its structure, physicochemical properties, and biodegradability [J]. Indust. Crops Prod., 2022, 187: 115548.

[13] Behera S, et al. Polyhydroxyalkanoates, the bioplastics of microbial origin: Properties, biochemical synthesis, and their applications [J]. Chemosphere, 2022, 294: 133723.

[14] LI J, LI D, et al. https://www.sciencedirect.com/science/article/abs/pii/S0260877422003326. accessed 16 Mar 2023.

[15] Tu W, Zhang D, Wang H, et al. Polyhydroxyalkanoates (PHA) production from fermented thermal-hydrolyzed sludge by PHA-storing denitrifiers integrating PHA accumulation with nitrate removal [J]. Bioresource Technology, 2019, 292: 121895.

[16] Zou Y, Yang M, Tao Q, et al. Recovery of polyhydroxyalkanoates (PHAs) polymers from a mixed microbial culture through combined ultrasonic disruption and alkaline digestion [J]. J. Environ. Manage., 2023, 326: 116786.

[17] Colombo B, et al. Polyhydroxyalkanoates (PHAs) production from fermented cheese whey by using a mixed microbial culture [J]. Bioresource Technology, 2016, 218: 692-699.

[18] Kobayashi T, Matsumura S. Enzymatic synthesis and properties of novel biodegradable and biobased thermoplastic elastomers [J]. Polym. Degrad. Stability, 2011, 96(12): 2071.

[19] Bao C, Xu X, Chen J, et al. Synthesis of biodegradable protein–poly(ε-caprolactone) conjugates via enzymatic ring opening polymerization [J]. Polymer Chemistry, 2020, 11(3): 682-686.