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A Unified Research on Advanced Biodegradable Copolymers Based on Their Biodegradable Properties

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Abstract. Recently, biodegradable materials can effectively reduce the environmental hazards. However, they still have limitations in terms of degradation rate and stability. This paper systematically reviews the progress of various biodegradable materials, such as polylactic acid, polyhydroxy-fatty acid ester, polybutylene succinate, and carbon dioxide copolymer. This study found that the degradation rate of polylactic acid can be enhanced through composite methods involving biomaterials. Polyhydroxyl fatty acid esters were synthesized using copolymer preparation, solution pouring, and hot pressing techniques in order to improve their degradation rate. Furthermore, the degradation rate of polybutanediol succinate was improved through composites with biomaterials as well as organic and inorganic materials. Lastly, the degradation rate of carbon dioxide copolymers can be enhanced by utilizing copolymers formed from carbon dioxide monomers along with other polymers or monomers in composite materials. Polylactic acid prepared by the composite method of biological materials can improve the utilization rate of biological resources. The mass preparation of polyhydroxy-fatty acid esters in industry can be enhanced by solution pouring and hot pressing. The composite of polybutanediol succinate and biomaterials improved the mechanical properties. The preparation of carbon dioxide copolymers can improve the utilization of carbon dioxide and reduce greenhouse gases. Most importantly, this research can effectively enhance the degradation performance of biodegradable materials then reducing their impact on the environment.

Keywords: Biodegradable Materials; PLA; PHA; PBS; Carbon Dioxide Copolymers.

1. Introduction

Nowadays, the demands of daily lives and biomedicine have contributed to an increase in environmental pollution. However, traditional biodegradable materials are often resistant to degradation and can cause serious harm to the environment. Therefore, alternative degradable materials have emerged.

Biodegradable materials [1] can suffer the chemical, biological, physical degradation, or enzymatic hydrolysis, under the action of microorganisms existing in nature such as bacteria, fungi, and algae in the natural environment. They are usually made from natural resources, such as plant fibers, starch. Biodegradable materials can be degraded into harmless substances by the natural environment in a short time, reducing pollution to the environment, and its wide application can reduce the impact of plastic pollution on the environment and biodiversity, and promote sustainable development. However, the decomposition rate of traditional biodegradable materials such as polylactic acid is not stable, and the degradation time is relatively long. Therefore, it is particularly important to modify these traditional biodegradable materials to improve their degradation performance.

In this paper, biodegradable materials, such as polylactic acid, polyhydroxyl fatty acid ester, poly-butanediol succinate, and carbon dioxide copolymers are reviewed and summarized. The study shows that the degradation of polylactic acid can be accelerated by combining with biological materials. At the same time, polyhydroxy-fatty acid esters can also be prepared by copolymer, solution pouring method, or hot pressing technology combined with biological materials, which can improve the degradation rate. In addition, polybutanediol succinate combined with biological materials, and organic or inorganic substances can also form high degradation rate composite materials. The copolymer produced by carbon dioxide as a monomer also has a good degradation rate by combined with other polymers or monomers. The utilization rate of biological resources can be improved by the preparation of polylactic acid by the composite method of biological materials. Industrial production of large quantities of polyhydroxyfatty acid esters can be improved by solution pouring and hot pressing. The composite of polybutanediol succinate and biomaterial improves the material's mechanical properties. The preparation of CO_2 copolymer can improve the utilization rate of carbon dioxide and reduce the emission of greenhouse gases. Therefore, the properties of biodegradable materials can be effectively improved via solution pouring, hot-pressing methods, and so on, thereby reducing its pollution to the environment.

2. Polylactic Acid

Polylactic acid (PLA) as a serious of non-toxic and harmless, and strong plasticity degradable materials, can be used in a variety of plastic products [2]. It can be obtained from plant resources and normally has excellent renewability, reducing the use of non-renewable resources. However, there also have some shortcomings such as poor heat resistance and weak mechanical properties, which need to be further improved to promote its application.

Azadeh Sadeghi et al. [3] used polycaprolactone (PCL) and PLA as degradation raw materials and green tea extract (GTE) as natural antioxidants respectively, to prepare PLA/PCL film by the casting method. The structure of this film is shown in Figure 1(a). It is relatively compact. The higher content of PLA, the lower the hydrophilicity, water solubility, water vapor permeability and oxygen conversion rate of film. The degradation of this film is related to its hydrophilicity, and the hydrophilic component can make it more easily degraded. The GTE molecules can promote the formation of cracks on the surface of the film and be decomposed, improving its degradation rate. Finally, the biodegradable properties of this film were maximized, as the GTE was 30%.Wang Ling et al. [4] used polylactic acid as raw material and electrospinning technology to prepare PLA nanofibers with multi-scale structures. This PLA nanofiber has the structure of small holes and high porosity distribution, and has excellent degradability, mechanical properties and hydrophobic properties. The results showed that the PLA nanofiber film was completely decomposed at a temperature of 60°C for about 16 hours, and the structure of the film could also become thin after prolonged exposure, as shown in Figure 1(b). The PLA nanofiber has a large specific surface area and can be in better contact with microorganisms in soil and air, which is conducive to its own degradation.

Zou Dongfang et al. [5] used PLA and bamboo charcoal (BC) as raw materials, to prepare biodegradable bamboo charcoal/polylactic acid composite materials by the melt blending and hot pressing methods. It has degradability, high thermal properties fire resistance, and good mechanical strength, as is shown in Figure 1(c). BC is normally unevenly distributed in the composite, easy to agglomerate, and difficult to effectively interact with the PLA molecular chain. Finally, the pores become denser and larger, reducing the mutual "penetration" between the BC and PLA molecular chains, allowing water molecules to enter well and promote the degradation of the material.Gabriel Murilo-Morale et al. [6] prepared PLA/TPU thermoplastic blend by the melting deposition method, using laccase-modified lignin as a nucleus agent (EL) and adding thermoplastic polyurethane (TPU) to polylactic acid (PLA). The prepared PLA/TPU thermoplastic blend has excellent mechanical properties, chemical compatibility and degradability. The modified lignin also makes it have good low crystallinity. The PLA/TPU with EL mass fraction of 5.00% at 6 months showed good degradability through soil burial test, as shown in Figure 1(d). The chemical changes in EL during thermoplastic extrusion can led to a relatively low reduction in molar mass. It means that molecular structure of PLA/TPU are cracked to a limited extent, thus triggering the phenomenon of biodegradation under hypoxic conditions.

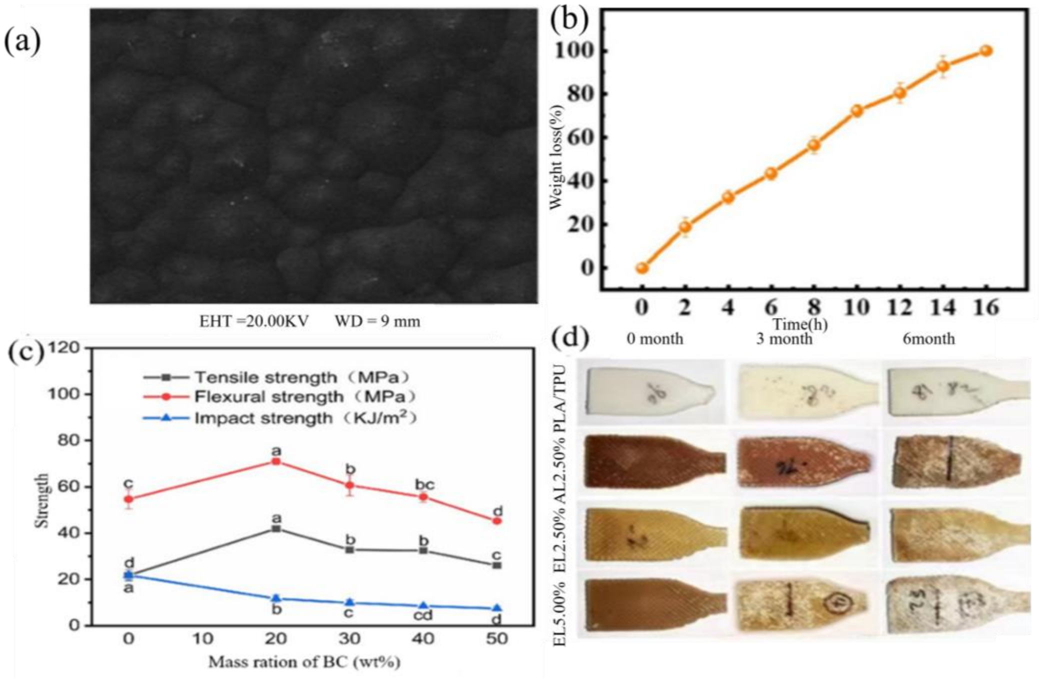

Figure 1. (a) Structure of PLA/PCL films containing green tea extract from Azadeh Sadeghi; (b) Degradation of PLA nanofibers by Wang Ling; (c) Mechanical properties of PLA/TPU thermoplastic blends by Zou Dongfang; (d) Degradation of PLA/TPU thermoplastic blends by Gabriel Murillo-Morale [6]

In conclusion, the combination of PLA and biological materials can promote its degradability, and its degradation performance is different with different content. The degradation rate of PLA biodegradable materials prepared by the electrospinning process and melt blending method is higher. But , methods, such as the molten deposition method, still needs to consume a lot of energy , and the renewable resources can be used to reduce the consumption of non-renewable resources. The structure of PLA can be changed by electrospinning method and melt blending method d to improve the degradation rate.

3. Polyhydroxy-fatty Acid Esters

Polyhydroxyfatty acid ester (PHA) is a kind of biodegradable material with good heat resistance and high strength, and it can meet the advantages of certain engineering plastics, and is non-toxic and safer for human body and the environment [7]. However, PHA has limitations in engineering application and high cost.

Natsumi Hyodo et al. [8] Preparation of PHA microbeads by melting homogenization. The pha microbeads prepared by this method have good degradation efficiency in the deep sea, and surface holes and irregular shapes appear after 5 months in the deep sea environment. Among them, the degradation rate of P(3HB) microsphere is the highest 85%. Preeyaporn Injorhor et al. [9] prepared biodegradable PLA-PHA using PHA and nano-hydroxyapatite (nHAp) as materials by the solution pouring method. It has better mechanical properties and electrostatic textile properties, and the thermal stability tensile strength can be-improved by adding nHAP. It also has good degradability, and the degradation effect is shown in Figure 2(a). Due to the dissolution of nHAp and its hydrophilicity, the degradation amount increases with the increase of nHAp content. Therefore, the addition of PHA led to the increase of surface roughness and degradation of this nanocomposite. Nor Azillah Fatimah Othman et al. [10] prepared a double-layer degradable film based on PHA and polycaprolactone (PCL) by the hot-pressing technology as is shown in Figure 2(c). This film has high degradability and good thermal stability. Moreover, this film also has a more dense, smooth, dense and uniform surface structure, as shown in Figure 2(b). Through soil burial test, the degradation degree of mulch film with 100% PHA and PCL content was the highest, about 48.43%. The double-layer PHA/PCL achieved nearly 50% degradation in just 5 weeks, highlighting the strong biodegradability of the prepared material. Finally, this film has a low polymer crosslinking density and is conducive to better biodegradation.

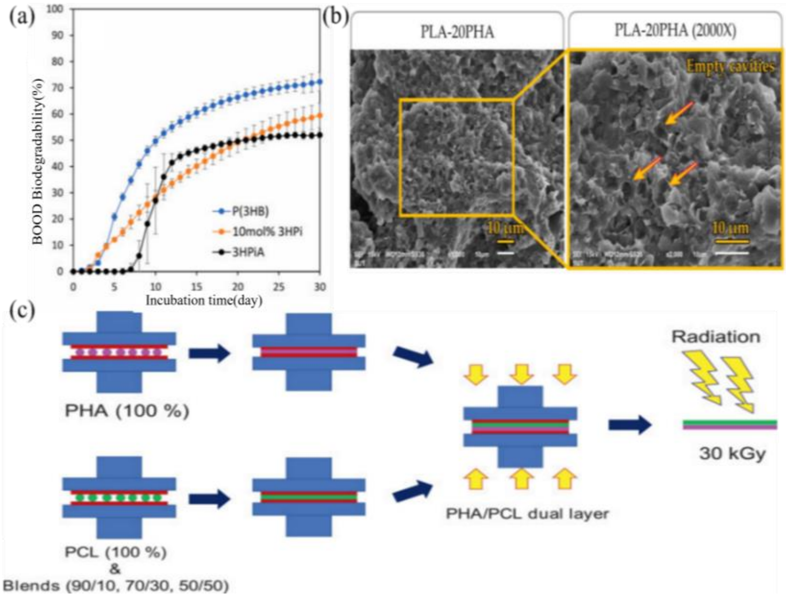

Figure 2. (a) P (3HB-co-3HPi) degradation of M. mierzati; (b) Structure of biodegradable of Preeyaporn Injorhor; (c) Preparation of double-layer degradable mulch by Nor Azillah Fatimah Othman [10]

In summary, PHA-based biodegradable materials prepared by the copolymer preparation, solution pouring method, hot pressing technology, and other ways can improve their degradation rate, and they can be used in biodegradable packaging materials, instead of traditional plastic packaging materials they also has certain heat resistance and mechanical properties, and it can meet the packaging materials, agriculture, and other fields. The structure of PHA can be changed by copolymer preparation, solution casting and hot pressing, and the degradation rate of PHA biodegradable materials can be increased.

4. Polybutylene Succinate

Polybutanediol succinate (PBS), as an environmentally friendly degradation material that can be degraded by microorganisms, has the advantage of good heat resistance [11]. However, their degradation rate is affected by environmental conditions, microbial species, and mechanical properties.

Mario Ivan Penas et al. [12] prepared self-degrading PBS films by embedding alginate particles filled with lipase. The surface of this biofilm is smooth. The porous form can be displayed in some locations, and the biofilm is biodegradable. Increasing the amount of lipase embedded in algembli and its content in PBS films can increase the self-degradation degree of PBS films, as shown in Figure 3(a). The film shows good degradability and plays an important role in the development of degradability in biomedical, agricultural, or food industry fields. Ding Yue et al. [13] used succinic acid (SA), butanediol (BDO), and glycolic acid (GA) chain segments to form PBSGA copolymer by melting condensation. PBSGA copolymer has good thermal stability, excellent mechanical properties, and degradability. The degradation test showed that the PBSGA copolymer was completely decomposed in an alkaline solution in 21 days, and the degradation effect was shown in Figure 3(b). The increase of GA content in acidic and neutral solutions increases the degradation rate of the copolymer. The ester bond can be quickly hydrolyzed, and seawater degradable plastics can be obtained. Lovisa Rova et al. [14] prepared PBS-BF plates with PBS-and basalt fiber (BF) via by hot pressing under uniaxial pressure. This plate has good degradability and stable mechanical properties, and its degradation effect is shown in Figure 3(c). The degradation is caused by the action of hydrolysis and hydrolase, which occurs through the ester bond of the polymer chain cleaved by water, and the bacterial solution passes through the BF/PBS interface that is physically contacted but not chemically bonded at a faster rate, accelerating the biodegradation.

Nara Shin et al. [15] prepared PBS films containing bioplastics by the solvent casting process. Through the combination of Bacillus NR4 and Bacillus JY35, a consortium can be formed to degrade PBS. The degradation effect of the film is shown in Figure 3(d). Bacillus JY35 and Bacillus NR4 showed low degradability in PBS respectively, but the combination of the two strains significantly increased the PBS degradation yield and promoted the degradation of plastics. The surface of PBS films is smooth before degradation, but cracks begin to form on the third day of degradation. Degradation can be caused by the break of high molecular weight chains into smaller fragments.

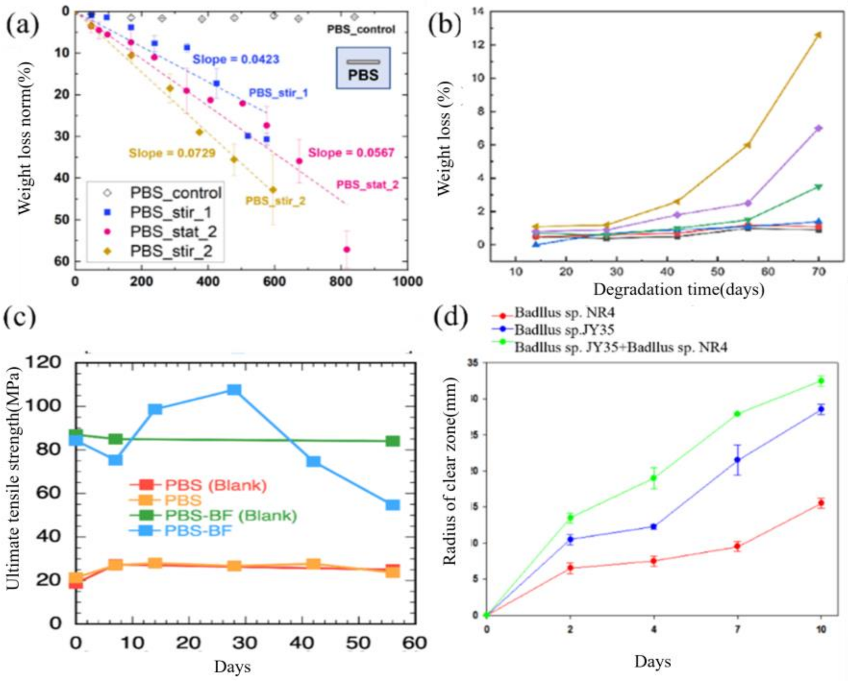

Figure 3. (a) Degradation of self-degrading PBS films by Mario Ivan Penas; (b) Degradation of Ding Yue's PBSGA copolymer [14]; (c) Degradation of Lovisa Rova's PBS (PBS-BF) composite panels; (d) Degradation of Nara Shin's PBS films [15]

In summary, the combination of PBS with other biological materials as biodegradable plastics can improve the degradation rate, help reduce the negative impact on the environment, and reduce the degree of pollution of plastics to the environment. The structure of PBS can be changed to improve the degradation rate of PHA biodegradable materials, by combining with other biological materials,

5. Carbon Dioxide Copolymer

Carbon dioxide copolymers can be used to enhance the utilization of carbon dioxide to reduce greenhouse gases. Carbon dioxide is a cheap gas resource, and the carbon dioxide copolymer also has good thermal stability and certain mechanical properties [16], and the prepared carbon dioxide also has certain degradability. But it also has the disadvantage of low technical cost.

Wang Wen et al. [17] adopted a general polymerization method, using norbornene dianhydride (EA) as a monomer, and its molecule contains active groups, such as double bonds and anhydride groups, to synthesize the binuclear complex salen [Co (III) TFA]$_2$ as a terpolymer catalyst to prepare the terpolymer of CO_2, propylene oxide (PO) and EA. The obtained PPCEAS terpolymer has good thermal properties, mechanical properties and degradability, and its mechanical properties are shown in Figure 4(a). polypropylene carbonate (PPC) has ester bonds and thus produces degradation, which can be divided into hydrolytic degradation. The ester bonds in the backbone are hydrolyzed to produce carboxyl groups and transfer the pH in the environment to acidic, to promote the hydrolysis of ester bonds. Wang Zi et al. [18] prepared the terpolymer of CO_2, 1,3-butadiene (BD), and epoxide using BD and epoxide as raw materials by cationic open-ring copolymerization, as shown in Figure 4(b). The terpolymer was chemically reacted in an alkaline methanol solution containing 1mol/L NaOH, indicating that it could be degraded, and no polymer was observed after the reaction. The prepared terpolymer has randomness and degradability and has additional functions for CO_2. Tang Shuo et al. [19] used binary Schiff base cobalt system to catalyze the copolymerization of 1, 2-epoxide butane (BO) with CO_2 and the tripolymerization reaction with other epoxides to prepare high molecular weight PBC. It has hydrophilic properties, thermal stability, and good biodegradability, and the degradation effect is shown in Figure 4(c). Its contact Angle increased with the increase of PBC content, and the hydrophilicity promoted the degradation of enzymes, thus promoting the degradation. Chen Kaihao et al. [20] used CO_2 and 1, 3-butadiene to prepare 3-vinylidene-6-vinyltetrahydro-2H-pyranyl-2-one (EVL) and mint ε-caprolactone (CL) to produce thermostable, non-cytotoxic and degradable polyester elastomer P (Cl-Co-EVL) by copolymerization. The crosslinking of the separated C=C double bonds of the material is limited, thus proving that it is degradable. The degradation effect is shown in Figure 4(d), and it expands the application range of CO_2-based polymer materials.

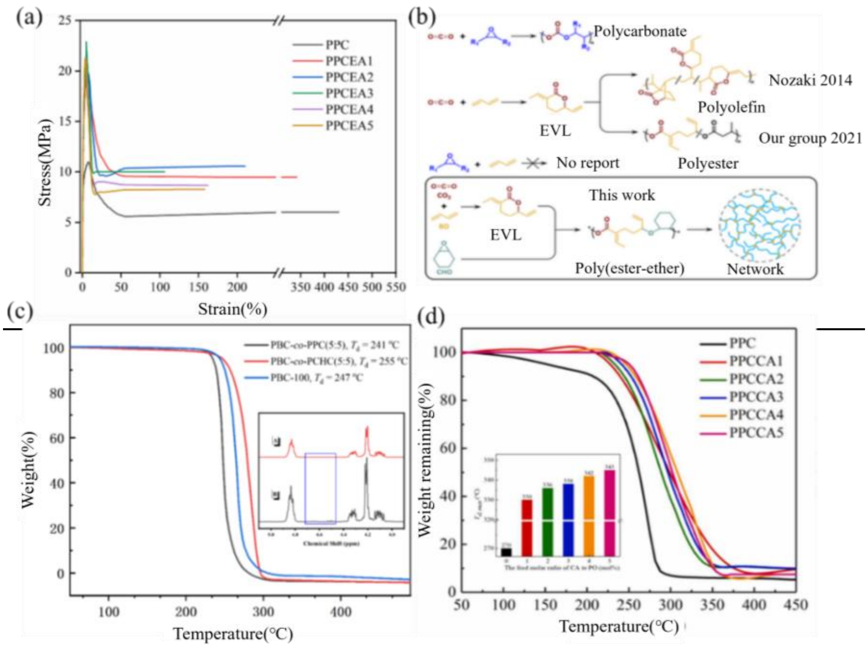

Figure 4. (a) Mechanical properties of Wang Wen's binuclear complex salen [Co (III) TFA] 2; (b) Preparation of CO_2, BD and epoxide terpolymer of Wang Zi; (c) Degradation of high molecular weight poly (butene carbonate) (PBC) of Tang Shuo; (d) Degradation of Chen Kaihao's polyester elastomer P (CL-co-EVL) [20]

In summary, carbon dioxide copolymer materials synthesized through the triple polymerization reaction, general polymerization process methods and copolymerization methods can improve its degradation performance and rate and have certain advantages for environmental protection. They also have hydrophilic properties, mechanical properties, and certain heat resistance properties, which can promote the application of degradation in packaging materials, agriculture, medical, and other fields, thus reducing environmental pollution. The structure and degradation rate of CO_2 copolymer can be improved by triple polymerization, general polymerization process and copolymerization.

6. Conclusion

Nowadays, residents and medicine needs lead to various non-degradable waste, and this causes environment pollution. It is found that the degradation rate of biodegradable materials can be improved by the composite method of multiple materials. The degradation rate of polylactic acid can be iproved by combining with biomaterials. Polyhydroxy-fatty acid esters can be synthesized by copolymer preparation, solution pouring and hot pressing technology to improve the degradation rate of materials. The degradation rate of polybutanediol succinate can also be improved by the composite of polybutanediol succinate with biological materials and organic and inorganic substances. CO_2 copolymers can also increase their degradation rate by forming composites with other polymers or monomers. Using biological materials to prepare polylactic acid is helpful to improve the utilization efficiency of biological resources. The industrial production level of polyhydroxy fatty acid ester can be improved by solution pouring and hot pressing process. The mechanical properties of polybutanediol succinate were significantly enhanced by the composite of polybutanediol succinate and biomaterials. In addition, the preparation of CO_2 copolymers helps to improve the utilization of carbon dioxide, thereby reducing greenhouse gas emissions. In this study, the methods to improve the performance of biodegradable materials such as PLA, PHA, PBS and carbon dioxide copolymers were studied from the aspects of synthesis and material composition, which can also effectively improve the degradation rate of biodegradable materials, and can be applied to environmental pollution problems in the future, and promote industrialization and commercial applications to solve the production cost and scale challenges.

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