The 3rd International Conference on Materials Chemistry and Environmental Engineering
DOI: 10.54254/2755-2721/3/20230345

Degradation of Polymers and the Improvements of Polybutylene Terephthalate /Polyethylene Glycol Terephthalate Composite-material

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Abstract. Polybutylene terephthalate and polyethylene glycol terephthalate are subjected to thermal-oxidative degradation and thermomechanical degradation during the process of melt blending, which affect the polymer structure and properties. The effect of feed properties of polyethylene glycol terephthalate and the addition of modified nanoparticles on blends are a question worthy of discussion. This paper introduced the latest development of biodegradable plastics industry as well as the applications of biodegradable plastics in fibers, daily expenses of membranes and bags, agricultural products and automobile industrial products. These biodegradable plastics included poly (lactic acid), polyhydroxyalknoates, poly (butyl**-** enes adipate**-**co**-**terephthalate), and poly (propylene carbonate). In addition to biochemical effects, degradation also has biophysical effects, that is, after microorganisms erode the polymer, the polymer material is mechanically damaged due to the increase of cells. Therefore, biodegradation is not a single mechanism, but a compomise biophysical and biochemical synergy and mutual promotion of physical and chemical processes. So far, the mechanism of biodegradation has not been fully elucidated. This paper focuses on explaining the currently clear polymer degradation mechanism and the improvement in composition and structure, so as to offer some references for future studies.

Key words: polymers, plastic, polybutylene terephthalate, polyethylene glycol terephthalate, production, degradation.

1. Introduction

Polymer materials are used extensively in human life and production. Due to the widespread usage of polymer materials, which cannot be decomposed automatically, there are typically two techniques for disposing of the materials: burial and incineration. However, neither of these two types of treatment can completely prevent the pollution of polymer materials. Therefore, the study and development of biodegradable polymer materials is highly valued in the field of scientific research nowadays. The use of this substance is a crucial strategy for cleaning up the environment. biodegradable polymer materials theories Materials made of biodegradable polymers are crucial to human life and economic activity. Biodegradable polymer materials refer to some polymer materials that can produce chemical reactions, biological reactions and physical reactions with the help of microorganisms, and then have a decomposition effect, and microorganisms mainly include bacteria, algae and other naturally occurring organisms. These microorganisms can secrete biological enzymes. Under the action of enzymes,

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biodegradable polymer materials can decompose macromolecules into small molecules. It is precisely because of this material property that they have been widely used. For some wastes that cannot be decomposed naturally, the effect of this material is obvious, and the material can be decomposed freely in the body, so it is also used in medical instruments and medicines. The types of biodegradable polymer materials are explained below [1].

Biodegradable plastics can be categorized into two groups based on the source of their raw materials: bio-based plastics and petrochemical-based biodegradable plastics. Bio-based biodegradable plastics can be mainly divided into four categories: the first category is plastics directly processed from natural materials; the second category is polymers obtained by microbial fermentation and chemical synthesis; the third category is polymers directly synthesized by microorganisms; the fourth category is the biodegradable plastics obtained by blending these materials or these materials and other chemically synthesized biodegradable plastics. Petrochemical-based biodegradable plastics refer to plastics obtained by polymerizing petrochemical monomers by chemical synthesis, for example, poly (butyleneadipate-co-terephthalate), poly (butylene succinate), Poly propylene carbonate etc. [2]. This paper introduced the latest development of biodegradable plastics industry as well as the applications of biodegradable plastics in fibers, daily expenses of membranes and bags, agricultural products and automobile industrial products. These biodegradable plastics included poly (lactic acid), polyhydroxyalknoates, poly (butyl-enes adipate-co-terephthalate), and poly (propylene carbonate), This paper collects some of the latest researches of recycled plastics and its improvements for later researches [3].

2. Degradation mechanisms of polymers

Polymers can degrade in both physical and chemical ways. The chemical alterations brought on by the environment can be used to explain the physical deterioration of polymers. The degration processes driven by chemical and physical events is covered in the next section. Depending on the properties of the polymer, while taking into account biological interactions, the degradation rate can be tuned in the desired way [4].

2.1. Physical degradation

Basically, two parallel processes—deterioration and erosion—are involved in the physical degradation of polymers in biological environments, as shown in Figure 1.

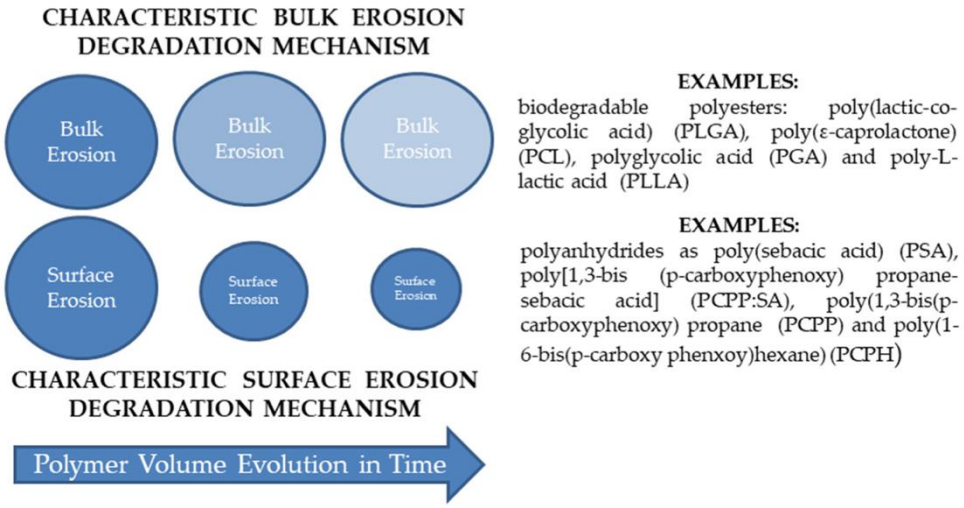

Figure 1. Schematic representation of evolution in time of surface erosion versus bulk erosion [5].

Bulk degradation is the process by which the interior of a polymer deteriorates more quickly than the exterior. In a perfect scenario for bulk erosion, the rate is determined by the total mass concurrently lost

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from the entire volume of the polymer as a result of water permeating the bulk, while retaining a constant size during degradation. Many hydrophilic polymers, including biodegradable polyesters, polylactic-glycolic acid (PLGA), polycaprolactone, polyglycolic acid, and poly-l-lactic acid (PLLA), exhibit this distinctive bulk erosion breakdown mechanism. Depending on the monomers utilized and their molecular weights, the degradation durations of these polymers, which are frequently used in drug delivery applications, can range from months to years. Surface erosion occurs when the rate and surface area are proportionate. Specifically, the erosion of the polymer surface becomes less, while maintaining its original geometry during degradation (biomaterial is only lost from the surface of the polymer matrix). Some typical examples of polymers that exhibit a typical surface erosion degradation mechanism are polyanhydrides such as prostate specific antigen, poly [1,3-bis(p-carboxyphenoxypropane)] (PCPP), poly [1,3-bis(p-carboxybenzene) oxy] propane sebacic acid (PCPP:SA), and poly [1-6-bis(p-carboxyphenoxy)hexane] (PCPH). Such polymers generally exhibit hydrophobic behavior where water is not readily penetrate into the body.

In this case, the erosion time may be different from a few days to several years. The disintegration process is related to the breaking of the granules to an acceptable size. Another discussion interferes with the clarification of the dissolution term, which is attributed to the dissolution of macromolecules that make up polymeric biomaterials in liquid media [6].

2.2. Chemical degradation

Chemical degradation is the most advantageous method of degradation for polymers utilized in biomedical applications. The kind of degradation is determined by the kind of bonds in the polymer, which are typically found in the backbone. Enzymatic hydrolysis can start molecular chain scission either passively or actively, and oxidation can also happen. The interference with regularly ordered chains and crystallinity caused by chemical degradation by random breakage of covalent bonds, depolymerization, or cross-linking of linear polymers causes significant degradation of polymer chains and ultimately a loss in mechanical characteristics.

While hydrolytic degradation refers to breakdown brought on by the hydrolytic cleavage of macromolecules, enzymatic degradation refers to the catalysis of enzymes under abiotic circumstances. Although hydrolytically unstable and capable of altering bonds are present in enzymatically degradable polymers, these bonds are too stable under physiological conditions and also require enzymatic catalysts for disintegration. However, numerous bonds, including anhydrides, orthoesters, esters, ureas, polyurethanes, carbonates, and amides, experience passive hydrolytic breakdown in a physiological setting. Changes in chemical structure and a reduction in molar mass (as with vinyl polymers and polyamides) may occur in conjunction with the degradation process (e.g.polymers with aromatic rings in the backbone). Cross-linking may also be present throughout this process.

Since the resulting polymers are typically mechanically robust and resistant to abrasion, heat, or solvent attack, crosslinking is a crucial component. The proportion of interconnected polymer chains in the network determines how much cross-linking takes place [7].

Numerous studies have demonstrated that under stress, polymer nanocarriers can deform reversibly while preserving structural integrity or transmembrane diffusivity. Cross-linking occasionally results in negative outcomes, including diminished mechanical characteristics and service durability. The mechanical characteristics of collagen fibers that have been mineralized and non-mineralized have both been shown to be significantly impacted by the cross-linking process. The composition and molecular structure of the polymer, polydispersity, hydrophilic or hydrophobic properties, surface area, or crystallinity are other factors that affect the degradation process [5].

3. PBT/PET composite material

Polybutylene terephthalate (PBT) is an engineering plastic first developed in the United States in the 1970s. It is a polyester obtained by condensation polymerization of terephthalic acid and 1,4-butanediol. The molecular structure is shown in Figure 2. The benzene ring in the molecular structure of Polybutylene terephthalate increases the rigidity of the molecular chain, the four CH_2 main chains on

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the main chain increase the mobility of the segments, and the carbonyl group also makes the molecular arrangement tighter, so the PBT molecular chain also has higher rigidity. Polybutylene terephthalate (PBT) has excellent comprehensive properties, such as fast crystallization rate, high crystallinity, excellent processing performance and good wear resistance, so it is widely used in electrical and electronic, automotive parts and other fields. However, its notched impact strength is low, and its thermal deformation temperature is also low. Although glass fiber-reinforced plastic parts can increase its thermal deformation temperature and mechanical properties, the plastic parts are prone to warpage. PBT can be blended with many plastics. Therefore, there are many possibilities for Polybutylene terephthalate research. In order to enhance the toughness of polybutylene terephthalate (PBT) materials, some scholars have carried out toughening research on it [8].

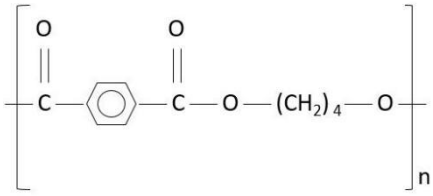

Figure 2. Structure formula of PBT molecules.

Polybutylene terephthalate (PBT) is a linear saturated crystalline resin with a high melting point that can reach 225°C. Due to the fast crystallization speed and good fluidity of Polybutylene terephthalate, it has good processing properties and can be processed by ordinary extruders and injection molding machines. Polybutylene terephthalate (PBT) has a fast-cooling rate. During the injection molding process, it can quickly cool and mold, and it only takes a few seconds to process small and thin parts, and it can be completed within one minute for larger parts. When pure Polybutylene terephthalate encounters water, the ester group in the chain is easily broken. In water below 50°C, the performance will not change significantly, but it is easily degraded in water at high temperature, and all properties will be affected. At the same time, the defects such as the low molding rate of Polybutylene terephthalate (PBT) can be improved by modification.

With the advent of the era of automation, the automotive industry, mechanical appliances, electrical and electronic industries have developed rapidly, and the application of Polybutylene terephthalate (PBT) as an engineering plastic has become more and more extensive. People's performance requirements for PBT are also constantly improving. Reduce costs while meeting requirements. It is still difficult for PBT to be more stable while still recyclable, a combination of several materials is possible, for example, polybutylene terephthalate (PBT) / polyethylene glycol terephthalate (PET) /nano-barium sulfate powder can strength the structure while it still can be recycled.

Table 1. Experiment samples of Nano-barium sulfate filled PBT/PET alloy [9].

Sample	$BaSO_4$ (%)	PBT/PET (%)	PTW (%)	Polycarbodiimide (%)	Antioxidant (%)
CB-1	1	90/10	2	2	0.5
CB-2	2	90/10	2	2	0.5
CB-3	3	90/10	2	2	0.5
CB-4	4	90/10	2	2	0.5
CB-5	5	90/10	2	2	0.5

Table 2. Temperature of deformation of PBT/PET/$BaSO_4$ complex material [9].

Sample	CB-1	CB-2	CB-3	CB-4	CB-5	PBT/PET	Pure PBT
Temperature of deformation / ℃	168.1	170.4	173.2	174.4	150.2	142.3	151.0

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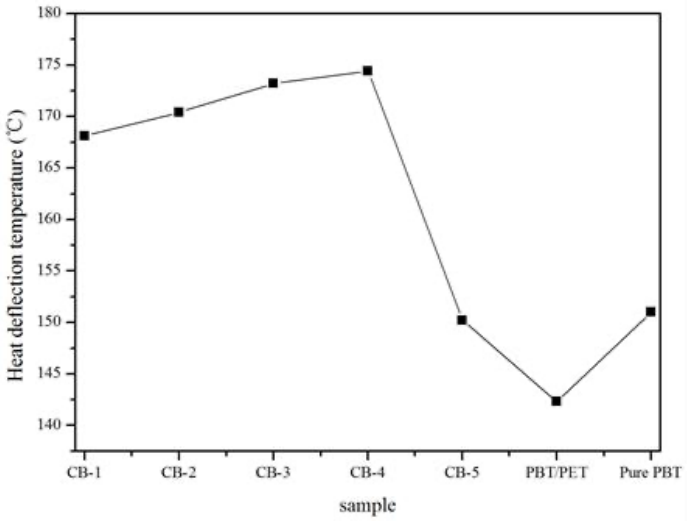

Figure 3. Temperature of deformation of PBT/PET/$BaSO_4$ complex material with different $BaSO_4$ content [9].

Figure 3 is drawn using the data in Table 2, it shwos the change of deformation temperature between these different samples.

According to Table 1 and Figure 3, with the increase of nano barium sulfate content, the thermal deformation temperature of PBT/PET/$BaSO_4$ composite material also increases. When the barium sulfate content is 4%, the thermal deformation temperature of the system reaches the maximum value, which is 174.4 °C, which is higher than that of polybutylene terephthalate (PBT) / polyethylene glycol terephthalate (PET) system about 21.8%. When the content of barium sulfate was 5%, the heat distortion temperature of the system was the lowest, which was 150.2 °C. This is because the surface of the nano-barium sulfate is very polar, and it can be adsorbed on the macromolecular chain of the matrix to increase the physical cross-linking point of the system, so that the macromolecular chain is not easy to move when heated, and the deformation of the composite material is small when heated. Thereby increasing the heat distortion temperature of the system [10, 11].

4. Conclusion

In conclusion, an appropriate amount of nano-barium sulfate can increase the heat distortion temperature of the polybutylene terephthalate (PBT) / polyethylene glycol terephthalate (PET) system. With the increase of nano barium sulfate content, the thermal deformation temperature of the system increases first and then decreases. When the nano barium sulfate content is 4%, the thermal deformation temperature of the system is the highest, which is 22.6% higher than that of polybutylene terephthalate (PBT) / polyethylene glycol terephthalate (PET) system, and the heat resistance is the best. Nano barium sulfate can significantly improve the comprehensive mechanical properties of the polybutylene terephthalate (PBT) / polyethylene glycol terephthalate (PET) system. When the nano $BaSO_4$ content is 2%, the comprehensive mechanical properties of the system are the best. Nano barium sulfate has no significant effect on the thermal stability of polybutylene terephthalate (PBT) / polyethylene glycol terephthalate (PET) system. In addition, $BaSO_4$ has no significant effect on the structure of polybutylene terephthalate (PBT) / polyethylene glycol terephthalate (PET) alloy.

With the advent of the era of automation, the automotive industry, mechanical and electrical appliances, electrical and electronic industries are developing rapidly. Polybutylene terephthalate and polyethylene glycol terephthalate, as engineering plastics, are also more and more widely used. People are also constantly improving the performance requirements of Polybutylene terephthalate and

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polyethylene glycol terephthalate. It is hoped that materials can meet the requirements of material performance and reduce costs at the same time.

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