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High-value recycling and biodegradation of polyolefin materials

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Abstract. The pollution of plastic materials has seriously affected global environmental problems. Polyolefin materials are widely used as raw materials for plastics. This is due to their practical physical properties and low cost. However, there are major challenges in the disposal of waste polyolefin materials. Recycling and degradation have emerged as the two main approaches for the treatment of plastic waste today. Through a comprehensive literature analysis and review of methods, this paper provides an in-depth study of recycling and biodegradation of polyolefin materials. The study is based on a detailed search of several papers through Google Scholar in order to provide valuable insights into the different methods that are used for the recycling and biodegradation of polyolefins. The review summarizes the most effective technologies for recycling and biodegradation, while highlighting recent advances and future directions in the field. In particular, the research has focused on two main approaches: closed-loop recycling and chemical recovery. The latter technology is aimed at non-polluting biodegradation, which has become an increasingly important topic of interest for the scientific community. Given the urgency of the environmental challenges posed by polyolefins, the development of efficient and sustainable recycling and degradation methods is essential to create a circular economy and ensure a sustainable future.

Keywords: polyolefins, closed-loop recycling, chemical recycling, biodegradation.

1. Introduction

Plastic pollution is becoming more and more of a serious problem these days. The Earth's environment has been plagued by plastic pollution ever since humans invented and began using plastic. Oceans and soils around the world have been exposed to varying degrees of plastic pollution. Studies show that plastic pollution in the world's oceans has reached "unprecedented levels," with approximately 170 trillion pieces of plastic currently floating in the ocean, weighing an estimated 2.3 million metric tons [1]. If humans don't take action now, the rate of plastic entering the ocean could accelerate many times over in the coming decades. This is why it is particularly important to develop degradation technologies for plastic recycling. They can help people reduce the amount of plastic pollution, increase the value of plastic waste, and make an important contribution to sustainability.

This paper focuses on recycling methods and biodegradation in a summarized and organized manner. There are four methods of recycling plastics: closed-loop recycling, mechanical recycling, chemical recycling, and energy recycling [2]. Recycling of plastic waste remains an important strategy for reducing plastic waste and protecting the environment because of the process and the material itself.

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Biodegradation is a different way of thinking about how to deal with plastic waste. In the biodegradation process, microorganisms such as bacteria and fungi consume organic materials and break them down into smaller compounds by means of enzymatic reactions [3]. The resulting compounds are then used as a source of energy for the microorganisms or released into the environment as harmless by-products. However, not all materials are biodegradable, and some may take many years or even centuries to biodegrade. As a result, this area of biodegradation continues to be of great interest to researchers.

Polyolefins are thermoplastic polymers made from olefin monomers, including ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, alpha-olefins such as 4-methyl-1-pentene, and certain cyclic olefins. The most common of these are polyethylene (PE), polypropylene (PP), and copolymers based on these two. Due to the abundance of raw materials, low cost and excellent overall performance, they are a class of polymeric materials with huge production and wide application [4]. They are used in a variety of industries, including packaging, automotive, construction and agricultural products. These waste materials can cause plastic pollution. In order to protect the environment and reduce plastic pollution, it is necessary to study the disposal methods of these materials. This paper mainly explores new advances and breakthroughs in recycling and biodegrading polyolefin materials. It is a source of new thoughts and ideas for solving the plastic pollution problem.

2. Recycling methods for polyolefin materials

At present, there are four main methods for the recycling of plastics. They are "primary recycling", "secondary recycling", "tertiary recycling" and "energy recovery" [2].

Secondary recycling is also known as the mechanical recycling process. This recycling process includes the sorting, washing, grinding, shredding, melting, and reshaping of plastics [4]. Because the value of the product resulting from mechanical recycling is lower, mechanical recycling is also referred to as "downcycling" [2]. Mechanical recycling has limitations in terms of the process and the materials to be recycled.

The energy recovery process is the combustion of the plastic and the release of heat, part of which can be recovered. A portion of the heat energy is recovered for use in the process. Therefore, another name for energy recovery is incineration. Incineration is the most "wasteful" method of recycling than the previous three methods, and the recovery rate and product are far less than the previous three recycling methods. However, it is one of the oldest and most widely used methods. The incineration process produces toxic gases. These gases can cause environmental pollution. The dioxins produced are extremely biotoxic and cannot be emitted directly into the atmosphere [4].

2.1. Closed-loop recycling of polyolefin materials

Primary recycling is also known as closed-loop recycling. It is the processing of post-consumer plastics into products with similar properties and uses to the original plastic [2]. Primary recycling is primarily used for uncontaminated plastics or plastics that do not contain additives. Therefore, there are limitations to the use of this recycling method. Contamination is inevitable during the use and recycling of plastics. Therefore, pre-treatment is the most common solution for the removal of contaminants. Pretreatment is also a necessary step in primary recycling.

According to Mecking S, et al, polyethylene-18,18 (PE-18,18) and polycarbonate-18 (PC-18) polyethylene polymers produced by refining vegetable oils have properties similar to those of high-density polyethylene (HDPE) [5]. PC-18 and PE-18,18 materials can be used as raw materials for 3D printing. PC-18 depolymerizes in alkaline solutions to form long-chain 1,18-octadecanediols and small amounts of diethyl carbonate, and PC-18 completely depolymerizes in methanol at 150 °C for 24 hours without catalyst. 1,18-octadecanediols can be prepared in 98% yield and 99% purity. The purified 1,18-octadecanediol was polymerized with diethyl carbonate to recover PE-18 with a recovery of 96%. PE-18,18 was depolymerized in alkaline solution to form a mixture of two non-volatile long chain monomers, diesters and diols. PE-18,18 can be completely depolymerized in 12 hours at 150 °C without catalyst drop. Although this mixture is difficult to separate, it can be repolymerized directly to PE-18,18

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after purification. This excellent closed-loop recycled material can be used to replace conventional HDPE in some aspects [5].

2.2. Chemical recycling of polyolefin materials

Secondary recycling is also known as chemical recycling. Chemical recycling can reduce plastics to some monomers or some new raw materials [2]. These monomers and new feedstocks have a high potential for use and development. For example, polyolefin materials can be chemically recycled under certain catalytic conditions to produce fuel oil. The oil produced by chemical recycling can be used as a substitute for fossil fuels [4]. As a result, chemical recycling has been the focus of more and more attention and success in the chemical industry. Depending on the physical and chemical properties of different polymers, different methods of chemical recovery are used. Chemical recovery includes gasification, methanolysis, glycolysis, hydrolysis, pyrolysis, hydrogenation and ammonolysis [4]. For each of these processes, different equipment, conditions, and catalyst steps have the potential to be used. However, chemical recovery is still insufficient for industrial applications.

Liquid oil can be obtained from the pyrolysis of polyolefin-based personal protective equipment (PPE) and has excellent commercial value, according to Govindarajan et al. [6]. Due to the global pandemic of COVID-19, there has been a dramatic increase in the production and disposal of PPE. Disposable surgical masks and N95 respirators are the most common PPE. Govindarajan et al. studied the pyrolysis of 500-2000 g of masks without any pretreatment and quantified the amount of oil produced. In the experiment, they found that the oil yield reached a maximum of 59.3% and a minimum of 26.4%. The highest oil yield of 59.3%-53.35% was obtained at 510 °C. The catalyst used was 5% zeolite (ZSM-5). When the reaction temperature was lowered to 450 °C, the oil yield decreased to 40%. After changing the catalyst to 5% montmorillonite, the oil production rate was 39.4% at an operating temperature of 510 °C. The oil yield drops significantly to a minimum of 26.4% when the catalyst loading is reduced by half [6]. According to the analysis, the oil obtained at 450 ° contains about 51% C11-C20 and about 42% C5-C10, and at 520 °C it is about 74% C11-C20 and about 15% C5-C10, and the density, kinematic viscosity and sulfur content of these oils are in accordance with commercial diesel standards [6]. Although this technology has a promising application, the industrialization of this technology remains a challenge. This is the drawback of many chemical recycling methods. The process from laboratory success to real industrial production is arduous and long.

3. Biodegradation of polyolefin materials

The recycling of plastic waste is limited by a number of factors, including environmental and cost considerations. Biodegradation offers a new idea for the degradation of polyolefin materials. Biodegradation can be defined as the process by which microorganisms in nature, such as bacteria and fungi, produce biological enzymes that, under the right conditions, can convert the complex chemical structure of a polymer into a simple chemical structure [2]. This process converts environmentally harmful polymers into substances such as carbon dioxide, water and biomass in the geochemical cycle. Microbial degradation of plastics is non-polluting and does not require large amounts of energy [7]. This makes it a safe and ecological method of degradation. Microorganisms, suitable conditions and readily degradable polymers are the key factors influencing biodegradation.

3.1. Effect of microorganisms on biodegradable polyolefin materials

Polyolefin materials are often defined as materials that are difficult to biodegrade. This is because polyolefin materials are chemically stable, consisting mainly of -C-C- and -C-H-covalent bonds, and have no groups susceptible to oxidation and hydrolysis. They are prevented from directly entering microbial cells and being degraded by intracellular enzymes by the spatial barrier created by their long-chain, high molecular weight structure. The high degree of hydrophobicity makes it difficult for cells and enzymes to come into contact and react. As a result, the biodegradation of these materials is very slow.

Although biodegradation is not sensitive to polyolefin materials, researchers have had more positive results on microorganisms that can degrade polyolefin materials. Sarker et al. found that Enterobacter cloacae (AKS7), enriched from rural soils, could efficiently degrade LDPE [8]. AKS7 was found to be efficient in degrading low density polyethylene (LDPE). The efficiency of the degradation of PE reached 9% within 45 days. AKS7 has a high hydrophobicity on the cell surface. Therefore, it interacts with PE, which is also hydrophobic, and binds to the PE surface. According to Nag et al., a new marine strain of Alcaligenes faecalis LNDR-1 isolated from seawater showed enhanced degradation of PE. Without any pretreatment, the degradation of LDPE reached 15.25%-21.72% in 70 days [9].

Polypropylene plastic has a chemical structure that is similar to that of polyethylene plastic and is a typical representative of plastics with a carbon-carbon skeleton. The difference in chemical structure from polyethylene plastic is that polypropylene plastic has methyl groups in the side chains. With too high molecular weight, too strong hydrophobicity, too high chemical bonding energy and too low bioaccessibility, these properties make these plastics difficult to be degraded by microorganisms in the environment. As a result, the bottleneck in the microbial degradation of PP has been difficult to overcome. Yang et al. provided a new idea for the degradation of PP. They fed feed containing PP to yellow mealworms (Tenebrio molitor) and superworms (Zophobas atratus) [10]. T. molitor larvae appeared to be superior to Z. atratus larvae in terms of PP biodegradation. Although it is known that both larvae have the ability to preferentially degrade low molecular weight PP polymers, the enzymes, genes, and larvae that are involved in the degradation process have not been clearly identified [10]. Thus, there is still a large gap and great potential for research in this area.

3.2. Environmental conditions for biodegradable polyolefin materials

Suitable conditions are necessary for the survival of organisms. Various physical and chemical conditions are important for biodegradation. These conditions have an effect not only on the degradation efficiency but also on the survival of the test organisms. Such conditions include lighting, humidity, temperature, pH and oxygen levels [7].

Humidity not only affects the growth of microorganisms, but high humidity facilitates the hydrolysis of polymers by increasing the number of chain breakage reactions [7]. pH is important for the growth and reproduction of microorganisms, the rate of hydrolysis reactions and the activity of enzymes. In addition, the products of polymer degradation also have an effect on the pH. Selecting and adjusting the appropriate pH is key to successful experiments [7].

The microorganisms that react with the polymer also change under different oxygen conditions. Under conditions of sufficient oxygen, anaerobic microbial growth is inhibited and aerobic microbial growth is rapid. In this case, polymer degradation is primarily by aerobic microorganisms. Aerobic microorganisms degrade the polymer to biomass, carbon dioxide and water. Under anaerobic conditions, aerobic microbial growth is inhibited and anaerobic microbial growth is rapid. The degradation of polymers is mainly dependent on the anaerobic microorganisms. The polymer decomposes into carbon dioxide, water and methane in the presence of methanogenic bacteria. The polymer decomposes to carbon dioxide, water and hydrogen sulfide in the presence of sulfur-producing bacteria [7].

3.3. Easily degradable polymers

Polyolefin materials are defined as difficult to biodegrade due to their stable chemical structure and high hydrophobicity. In order to seek a breakthrough in the materials, the most promising approach in front of the addition of additives to polyolefin materials. Polymer matrices are modified by introducing additives that have a disruptive effect on the polymer backbone structure. One of the most widely used methods is the incorporation of oxidatively degradable additives based on transition metal salts of cobalt, nickel or iron into polyolefin materials [7]. Another approach that is emerging is the production of composite materials based on blends of polymers with natural or synthetic biodegradable additives. Composites of soy protein and polyethylene can be effectively degraded. Under the right conditions, the percentage weight loss of this material can reach 76% within 4 months [7]. This material is undoubtedly easier to degrade. However, the lack of mechanical properties and the high cost are issues that need to

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be addressed. According to the experiments of Varyan et al., the composites of polyethylene and natural rubber are not only more degradable but also have good pull-up properties [7].

4. Conclusion

The purpose of this thesis is to study the methods of recycling and biodegradation of polyolefin materials. Closed-loop recycling and chemical recycling are the main means of high-value recycling of polyolefin materials and have great application potential. However, there are still challenges in the practice and application of their technologies. Biodegradation offers unique environmental benefits, but the degradation process is slow. This paper focuses on presenting new research results without analyzing the mechanisms involved. For the problems of recycling methods and degradation, it is difficult for the authors to provide substantive suggestions and solutions. It is not enough to focus on material and technological improvements when dealing with the pollution of polyolefin wastes, even plastic wastes. There should be coordination between governments, companies and individuals. It is also essential to have sound policies, standardized systems for enterprises, and proper publicity and guidance. The problem of plastic waste pollution will achieve great success with the combined efforts of various parties.

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