

Research Status and Perspectives of Plastic Degradation

Zefeng Tian *

Guanghua Qidi College Shanghai, Shanghai 200433, China

* Corresponding Author Email: 1811121209@mail.sit.edu.cn

Abstract. Contemporary society has witnessed a large variety of hazard plastic made. Plastic waste has become a major concern for individuals, governments, and organizations all over the world. The extensive use of plastics in producing consumer goods has resulted in huge amounts of plastic waste that has to be managed appropriately. Plastic waste is hazardous to the environment because it takes a long time to decompose. This article starts with a range of explanation techniques and outlines their principles and origins, for examples of common practices in today's culture include photocatalytic degradation, thermal degradation, biodegradation, etc. In the hope that they might effectively decompose these toxic compounds, many people are now pursuing study in these areas in order to offer a quick analysis of the current major explanation methods. A rise in future deteriorating methods can alleviate the negative effects on both human and animals' life, and thus a healthier ecological environment can be achieved.

Keywords: Degradation; plastic; photocatalytic.

1. Introduction

Plastic waste has become a major concern for individuals, governments, and organizations all over the world. The extensive use of plastics in producing consumer goods has resulted in huge amounts of plastic waste that has to be managed appropriately. Plastic waste is hazardous to the environment because it takes a long time to decompose.

The most significant hazard of plastic waste is environmental pollution. Plastic waste cannot be decomposed easily, resulting in large amounts of plastic clogging landfills, oceans, rivers, and other natural habitats. The accumulation of plastic waste in these areas can cause serious harm to flora and fauna. Wildlife can easily become entangled in plastics, causing injury and death. The ingestion of plastic waste also poisons animals, making them sick and, in extreme cases, dead. Plastic waste is estimated to account for a high percentage of marine pollution, disrupting the marine ecosystem and poisoning marine life.

Plastic waste can also contaminate soil, making it non-arable and denying farming communities their livelihoods. Plastic debris can remain in the soil for decades, limiting the growth of crops and leading to reduced yields and, in extreme cases, total loss of the land [1].

The hazards of plastic waste are numerous. The extensive use of plastics in consumer goods has resulted in massive amounts of plastic waste that takes years to decompose, and in some cases, never fully decomposes. Cleaning up plastic waste is a costly endeavor for governments and organizations, leading to reduced economic opportunities.

Finding techniques to breakdown plastics is therefore crucial. Plastics can decompose in a number of ways today, including photocatalysis and biodegradation (Figure 1). The aim of this article is to obtain a brief examination of the current mainstream explanation methods by beginning with a variety of explanation methods and outlining their concepts and backgrounds. In the hopes that future degrading techniques will increase and for a healthier ecological environment.

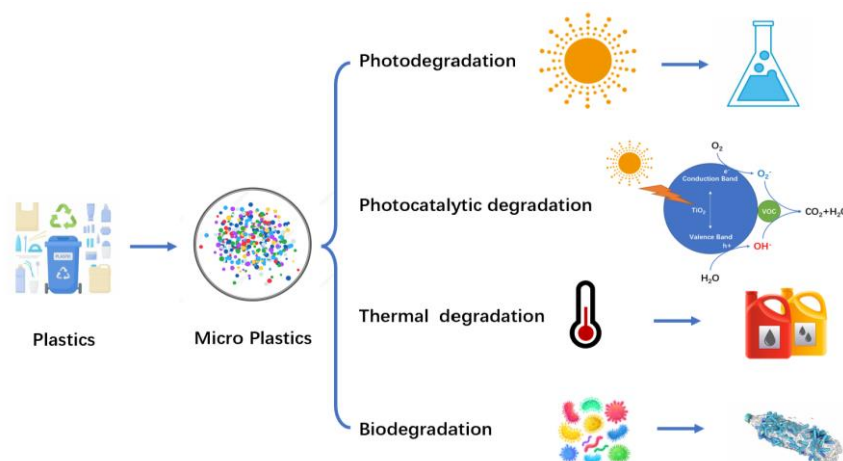


Fig 1. Degradation methods. (Picture credit: original).

2. Photodegradation

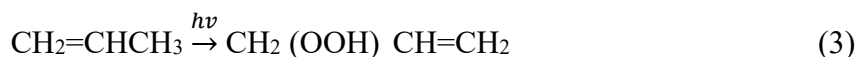
2.1. Background of photodegradation

To talk about the degradation methods, one thing that has to be mentioned is photodegradation. The sun emits energy which has a wavelength from 10 nm to 1 mm, and consists of ultraviolet, visible light and infrared. Polymers owing to their high energy know UV radiation as the most damaging source. Therefore, in polymers continuously exposed to ultraviolet radiation, structural (physical and chemical) degradation occurs, leading to photodegradation. If in an oxygen environment, more changes will occur, including chain breakage and reduced mass [1]

2.2. Mechanism of photodegradation



One mechanism of photodegradation is singlet oxygen-induced oxidation [2]. Singlet oxygen is got from a photosensitizer reacting with a triplet state of excited sensitizer, which is shown in Equation (1). It has long decay times and unpaired electrons, so they are chemically reactive. In Norrish type II reaction, a hydrogen atom and three carbon positions are removed from ketone or aldehyde (happens in carbonyl group C=O) to form a vinyl group by producing 1,4-biradical as a primary photoproduct. In the second step, excited singlet oxygen reacted with the vinyl group to break down the molecule, causing the chain to break and formed the hydroperoxide functional group (R-OOH) as shown in (2). Similarly, singlet oxygen produced peroxidation alkenes containing allyl hydrogen to form R-OOH as shown in (3) [3].



To be specific, the excited singlet states may cause chain cleavage or create saturated and unsaturated chain ends by hydrogen transfer. The resulting polymer radicals can react with molecular oxygen, forming hydroperoxide groups that undergo energy transfer and break O-O bonds. This process leads to the formation of alkoxy and hydroxyl radicals, which accelerate photodegradation by undergoing hydrogen abstraction, chain scission, and rearrangement. Double bonds can also add excited oxygen molecules to form hydroperoxide groups. Some of these polymers, however, have an oxidized surface layer that absorbs near ultraviolet and visible light and serves to stabilize them against photodegradation by blocking light from penetrating deeper layers. An auto-oxidation cycle with a number of phases is a component of the photo-oxidative degradation process.

3. Photocatalytic degradation

3.1. Background of photo-catalytic degradation

Photo-catalytic degradation is a photo-chemical process that uses photo-catalysts, typically made of semiconductors to speed up the reaction rate by absorbing light, especially sun light. This process has various applications such as killing bacteria, converting energy, and generating green hydrogen via water splitting. For a photo-catalyst to be ideal, it should be able to absorb light at room temperature and have high stability against photo corrosion while also being non-toxic.

3.2. TiO₂ as the catalyst

TiO₂ has unique physical properties and chemical properties. It has high chemical stability, high-temperature stability and is not detrimental to the environment. The energy bandgap of TiO₂ is small, so when a VB (valence band) electron absorbs energy from light in the UV spectrum, it becomes more excited and jumps to the CB (conduction band) [4]. In another words, when a UV A light shines on a material, it can cause electrons to move from the lower energy level to the higher energy level, creating new possibilities for energy transfer and utilization, forming positively and negatively charged particles (as shown in Figure 2) [5].

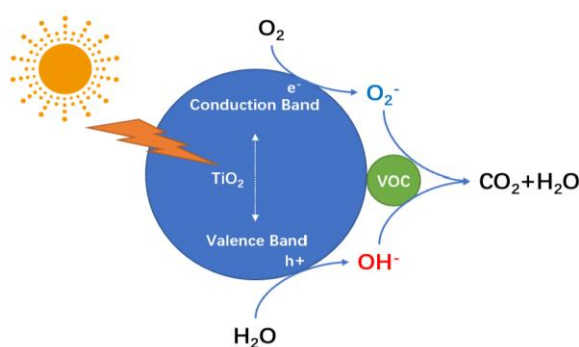


Fig. 2 Photodegradation using TiO₂ as a catalyst. (Photo credit: original).

3.3. Mechanism of photocatalytic degradation

Firstly, when light with energy greater than or equal to the bandgap of TiO₂ shines on the material, an electron from the VB gets excited and jumps to the CB. This process creates a vacancy in the VB, which we refer to as a hole (h⁺). This is the foundation of photocatalytic activity, which involves the use of light energy to promote chemical reactions. In summary, the absorption of light by TiO₂ initiates a sequence of events that generates a pair of free charge carriers (an electron and a hole), creating the potential for catalytic activity. The Equation (4) describes this process in a concise manner.



Secondly, when a water molecule comes into contact with a hole in the VB of TiO₂, it undergoes a chemical reaction that produces a highly reactive hydroxyl radical (•OH). This radical then acts as a powerful oxidizer that can attack and break down a wide range of organic contaminants that are present on or near the surface of the photocatalyst. This process, known as photo-oxidation, is driven by the energy from UV or visible light, and is particularly effective at breaking down organic pollutants. Equation (5) summarizes this process.



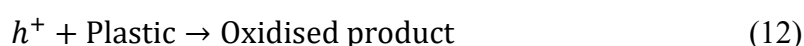
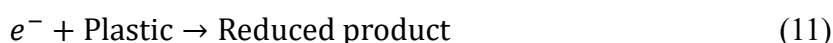
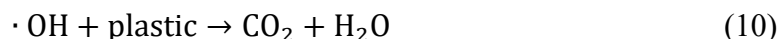
Thirdly, according to Eq. (3), a photoexcited electron in the CB interacts with an oxygen molecule to produce a superoxide radical (O₂^{-•}). This O₂^{-•} radical participates in oxidation and prevents the recombination of electron-hole pairs produced by photolysis, maintaining electron neutrality with semiconductors.



Finally, superoxide radical reacts with a proton to produce hydroperoxyl radical, which can produce hydrogen peroxide further. H₂O₂ further dissociates to produce the •OH.



To be more justified, overall reactions are listed to show the propagation clearly.



3.4. Other catalysts

Zinc oxide (ZnO) is often used instead of titanium dioxide as a photocatalyst due to its similar bandgap energy. Studies show that ZnO is capable of efficiently degrading pollutants through photocatalysis [6]. Other materials, such as Fe₂O₃, CdS, ZnS, WO₃, SnO₂, bismuth vanadate, and non-metallic carbon nitride are also commonly used as photocatalysts for the photodegradation of pollutants. However, the effectiveness of photodegradation is not only dependent on the choice of photocatalysts but is also influenced by other factors such as the structure of the polymer, the amount of photocatalyst used, and experimental conditions. These factors should also be taken into consideration when designing experiments for efficient photodegradation of pollutants.

4. Thermal degradation

4.1. Background of thermal degradation

The process of thermal degradation of polymers is a critical topic, both in terms of fundamental polymer reactions and practical applications such as heat resistance and plastic waste management. The polymers experience two distinct processes within the reactor, leading to their breakdown due to heat exposure.

4.2. Mechanism of thermal degradation

Under normal conditions, both thermal and photochemical degradations of polymers are considered oxidative degradation. However, they differ in the order of initiation stages leading to the auto-oxidation cycle. Photochemical reactions happen only on the surface of the polymer sample, while heat reactions occur throughout the majority of it. Polymers degrade thermally through random and chain degradation known as the depolymerization process caused by heat and UV radiation. Depolymerization of the macromolecule does not always start at the terminal end; instead, weak points in the chain structure can initiate the process. It can be divided into two ways, random degradation and chain-end degradation.

Random degradation can occur at any point along the polymer chain, unlike in polycondensation where the polymer breaks down into smaller molecules without releasing many monomers. Even if the polymer chain does not have any active sites, it can undergo chain scission, which can happen due to hydrolysis in polyesters or hydrogen atom movements in PE, leading to the splitting of the polymer into two pieces [7]. These types of polymers typically yield fewer monomers, and the pyrolyzed fragments are usually larger compared to the equivalent monomer unit. To initiate reactions, chain scission or chain end initiation is generally used, followed by de-propagation, which leads to the formation of monomers.

A process known as "chain end degradation" begins at the end of the polymer chain and gradually releases monomer units. Depolymerization is another term for this kind of breakdown mechanism, in which monomer units are progressively freed from the chain ends. These processes, which take place via a free radical mechanism, are the reverse of the propagation step in addition polymerization. This kind of degradation results in both the release of significant amounts of monomer and a progressive decrease in the molecular weight of the polymer. Only polymer molecules with active chain ends containing free radicals, cations, or anions, as well as when the backbone bonds are weaker than those of the side groups, often experience chain-end degradation [8].



5. Biodegradation

5.1. Background of biodegradation

Microbial consortia are more capable of breaking down complex natural and manufactured substances than individual microbial strains due to the limited metabolic capabilities of single organisms. Even though plastic breakdown by individual microbial strains has been studied more extensively, it is anticipated that microbial assemblages can more efficiently degrade plastic waste, which is a major environmental concern. Biodegradation of xenobiotics and hydrocarbons with the help of microbial consortia is a topic that has been well researched. Microbial consortia can achieve greater biodegradation efficiency than individual strains, either by directly participating in the process or by eliminating potentially harmful degradation intermediates [9].

5.2. Biodegradation synthesis

The process of microbial degradation can be divided into four phases: colonization, biofragmentation, assimilation, and mineralization.

In the colonization stage, the microbial consortium or individual species form a biofilm on the surface of the plastic polymer, causing it to deteriorate [10]. Microbial adhesion to the plastic surface occurs through the synthesis of several polysaccharides and/or proteins, which penetrate the polymer and alter its pore size and surface characteristics, according to this step leads to a physicochemical transformation that weakens the polymer's strength and resistance while increasing its surface area.

During the biofragmentation stage, specific enzymes such as hydrolases, oxidoreductases, and free radicals act on the polymeric structure, breaking it down. These enzymes have similar chemical connections to those found in natural materials such as lignocellulosic materials [11]. Thus, it is possible that enzymes used for degrading lignocellulose could also be useful in breaking down plastic waste. However, the process of breaking down the polymer substrate takes a significant amount of time as the concentration of enzymes must rise over time.

During the absorption stage, the microbial cell utilizes the generated monomers for energy and as a source of carbon. However, some compounds can be difficult for the cell to take in due to the permeability of cell membranes. In such cases, the non-assimilated monomers can still be utilized by the cell through a process known as bio-transformation. In this process, enzymes facilitate the conversion of one chemical compound into another that can be easily assimilated by the same or a different microbe. This bio-transformation process enables the utilization of a wider range of compounds, promoting microbial growth and development [12].

6. Summary

The four main explanations discussed in this paper are photodegradation, photocatalytic degradation, thermal degradation, and biological degradation. Although it did not cover every aspect,

it did explain the background and guiding ideas. There is hope for the future of plastic degradation. Many researchers and innovators are developing new technologies and materials that are designed to be more sustainable and eco-friendlier. For example, biodegradable plastics made from renewable resources such as corn starch, wheat, and soybeans have already been developed. These materials can be used in place of traditional plastics and will break down naturally over time without damaging the environment. Photocatalytic degradation is also effective without any extra hazards and is eco-friendly. Additionally, recycling and responsible waste management practices can also play a crucial role in reducing the negative impact of plastic degradation. By properly disposing of plastic waste and recycling plastics whenever possible, it can help to reduce the amount of plastic that ends up in oceans and landfills.

Overall, there is a bright future ahead for plastic degradation as continued to develop innovative solutions and focus on sustainability and environmental preservation.

References

- [1] Himani Yadav, Md Rakib Hasan Khan, Mohiuddin Quadir, Kelly A. Rusch, Partho Pritom Mondal, Megan Orr, Elvis Genbo Xu, and Syeed Md Iskander. An Overlooked Source of Microplastics in Human Food? *Environmental Science & Technology*, 2023, 57 (22), 8225-8235
- [2] Yousif, E.; Haddad, R. Photodegradation and photostabilization of polymers, especially polystyrene: Review. *SpringerPlus*, 2013, 2: 398.
- [3] Singh, B.; Sharma, N. Mechanistic implications of plastic degradation. *Polym. Degrad. Stab.* 2008, 93, 561–584.
- [4] Lee, Q.Y.; Li, H. Photocatalytic Degradation of Plastic Waste: A Mini Review. *Micromachines*, 2021, 12907.
- [5] Li L., The reaction mechanism of photoelectrocatalysis on the surface of TiO₂ nanotube array electrode, *Asia-Pac. J. Chem. Eng.*, 2020, 15: e2511.
- [6] Basavarajappa P.S., Patil S.B., Ganganagappa N., et al., Recent progress in metal-doped TiO₂, non-metal doped/codoped TiO₂ and TiO₂ nanostructured hybrids for enhanced photocatalysis, *Int. J. Hydrog. Energy*, 2020, 45 7764–7778.
- [7] Tofa, T.S.; Kunjali, K.L.; Paul, S.; Dutta, J. Visible light photocatalytic degradation of microplastic residues with zinc oxide nanorods. *Environ. Chem. Lett.*, 2019, 17, 1341–1346.
- [8] Aguado J, Serrano DP, Miguel GS. European trends in the feedstock recycling of plastic wastes. *Global NEST J*, 2007, 9-129.
- [9] Gowariker VR, Viswanathan NV, Sreedhar J. *Polymer science*. New Delhi, India: New Age International (P) Limited Publishers; 2020.
- [10] Yu, K., Yi, S., Li, B., et al. An integrated meta-omics approach reveals substrates involved in synergistic interactions in a bisphenol A (BPA)-degrading microbial community. *Microbiome* 7(1), 2019, 1–13.
- [11] Ru, J., Huo, Y.-X., Yang, Y. Microbial degradation and valorization of plastic wastes. *Front. Microbiol.* , 2020, 11, 442.
- [12] Ali, S.S., Al-Tohamy, R., Xie, R., et al., Construction of a new lipase- and xylanase-producing oleaginous yeast consortium capable of reactive azo dye degradation and detoxification. *Bioresour. Technol.*, 2020, 313, 123631.
- [13] Al-Tohamy, R., Sun, J., Fareed, M., et al. Ecofriendly biodegradation of Reactive Black 5 by newly isolated *Sterigmatomyces halophilus* SSA1575, val- ued for textile azo dye wastewater processing and detoxification. *Sci. Rep.*, 2020, 10, 12370.