



Degradation of Plastics - A Brief Review

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ABSTRACT:

Plastics have been indispensable to humans because of their widespread applications due to their favorable mechanical and physical properties. Hence, the increasing demand for their production, coupled with their non-biodegradability, has drawn public attention for their significant accumulation as wastes that could lead to environmental problems. Globally, this has encouraged to modify existing products considering the different aspects of their degradation. This article delves into various types of degradation in plastics, providing an exploration of these processes. Additionally, this article also details insights and strategies for controlling and preventing these types of degradation.

INTRODUCTION

Plastics are polymers characterized by their lengthy chain molecules [1]. They comprise carbon, hydrogen, oxygen, nitrogen, silicon, and chloride [2,3]. For a long time, they have played an essential role in our daily lives due to their various usability not only because of their mechanical and thermal characteristics but also to their stability and durability [4]. Over time, there has been significant enhancement in their stability and durability, showcasing increased resistance to various environmental factors [5].

For instance, synthetic plastics find extensive use in packaging applications due to their superior strength, lightweight nature, and resistance to water and waterborne microorganisms. Some of these plastics are polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyurethane and polyethylene terephthalate (PET) [6].

Although beneficial, synthetic or commercial plastics, in the long run, could pose drawbacks in degradation due to their mechanical and physical properties. Hence, the rising demand for their production and their non-biodegradable nature have drawn public concern regarding the significant accumulation of wastes, potentially resulting in environmental pollution persisting for centuries [7]. This has also prompted

global apprehension, driving efforts to encourage the modification of existing products to prioritize degradability. This has also spurred the development of new alternatives in alignment with the different mechanisms in degradation [8].

In this present review, the different types of degradation that could happen in plastics are discussed. These are namely, photo-oxidative, thermal, mechanochemical, catalytic, ozone-induced and biodegradation. Previous reviews primarily focused on factors and mechanisms of plastic degradation [9-18]. However, in this article, the prevention methods associated with various degradation types are also incorporated in details.

TYPES OF DEGRADATION

Degradation in polymers, such as plastics, is known as the alteration in the properties which occurs due to chemical, physical, or biological reactions, leading to bond breakages and subsequent chemical transformations [19]. Polymers undergo degradation at various stages throughout their life cycle, spanning from their initial processing, use, disposal into the environment, and recycling processes [20]. The degradation of polymers can be categorized based on the nature of the inducing agents, such as photo-oxidative, thermal, mechanochemical, catalytic, ozone-induced, and biodegradation [18, 21].



Photo-oxidative Degradation

Photo-oxidation occurs through the combined effects of UV-light and oxygen, primarily contributing to the weathering of plastics [22]. Polymers may exhibit varying degrees of UV-light absorption, but they often contain impurities like hydroperoxide and carbonyl groups, introduced during their thermal processing stages [23]. These impurities can serve as photoinitiators [24] and are able to absorb UV-light above 290 nm [25]. As a result, they contribute to complex free radical chain reactions, enabling the combined processes of autooxidation and photodegradation [23].

Synthetic polymers used in outdoor applications commonly undergo this form of degradation. Typically, their longevity when exposed outdoors is dictated by the near-UV radiations (290-400nm) present in sunlight [26-28].

Thermal Degradation

Thermal degradation occurs at high temperatures and involves detrimental chemical alterations, even in the absence of oxygen [29-30]. When exposed to high temperatures without air, polymers initiate degradation. This differs from thermal oxidation, which typically occurs at lower elevated temperatures [31].

This type of degradation commences with chain scission, producing free radicals that participate in disproportionation and crosslinking reactions [32]. The reactions involved in degradation are influenced by various factors including heating rate, pressure, reaction medium, and reactor geometry. High viscosity is a significant factor that complicates the reaction by obstructing heat and mass transfer [33-34]. At temperatures exceeding 200°C, degradation progresses towards chain scission and is significantly influenced by impurities such as unsaturation sites, head-to-head units, and similar factors [35].

Among the common polymers, polyvinyl chloride (PVC) stands out as one of the most thermally sensitive, typically undergoing degradation at temperatures starting around 250°C (480°F) and beyond [32]. Other polymers are known to degrade at elevated temperatures [36].

Mechanochemical Degradation

Mechanochemical degradation occurs when polymers undergo degradation due to mechanical stress and intense

ultrasonic irradiation [37]. Here, molecular chains experience breakdown due to shear or mechanical force, often assisted by a chemical reaction [38].

Under high stress, molecular chains can break into free radicals, which can participate in subsequent reactions. In the presence of oxygen, the initial reaction leads to the formation of peroxy radicals. These radicals stem from the cleavage of the main backbone segments of polymer chains within the stressed amorphous regions that connect crystallites [39].

At high-intensity ultrasound, this degradation process is also facilitated. The polymer undergoes very high vibrations, acting as mechanical forces. When ultrasonic waves pass through the solution, the localized shear gradient causes the tearing off of molecules, leading to chain scission and a reduction in molecular weight [40].

Catalytic Degradation

The catalytic degradation of waste plastics into hydrocarbons that hold commercial value is highly advantageous. Polyolefins found in both industrial and domestic waste can be thermally or catalytically degraded into gases and oils. Adding catalysts enhances the quality of products obtained from the pyrolysis of plastic waste, reduces the decomposition temperature, and even allows for specific product selectivity [41].

In this form of degradation, when polymers are heated above 380°C, they undergo depolymerization and degradation through a free radical chain reaction [42]. In the case of propylene, the degradation mechanism involves a free radical process where Fe/activated carbon can be utilized as a catalyst [43]. Other catalysts employed in polymer degradation also include zirconium hydride [39], Pt-Co and Pt-Mo supported over SiO₂ [44], zeolite and non-zeolite catalysts [45], transition metal catalysts such as Cr, Ni, Mo, Co and Fe on the support (Al₂O₃, SiO₂) [46], among others.

Ozone-induced Degradation

Ozone in the atmosphere can induce polymeric degradation. When oxidative processes are inactive, polymers can maintain their integrity for a longer duration [47]. Despite being present in small quantities in the atmosphere, ozone can significantly impact polymers. It degrades the polymers by generating reactive oxygen species (ROS) [48]. The formation of



reactive oxygen species (ROS) is linked to the reduction in the molecular weight of polymers and alterations in their electrical and mechanical properties [49].

Ozone degradation leads to the rapid and consistent production of carbonyl and unsaturated carbonyl products derived from aliphatic esters, ketones, and lactones. Additionally, it involves aromatic carbonyl products associated with the styrene phase. Subsequently, there is a more gradual formation of ether, hydroxyl, and terminal vinyl groups with time and concentration [50].

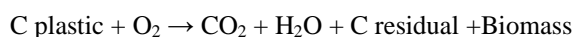
Furthermore, this degradation occurs within main chains containing C = C bonds, aromatic rings, or saturated hydrocarbon links. The process unfolds through unstable intermediates like the bipolar or peroxy radicals, which have the capacity to isomerize or degrade, consequently leading to the decomposition of macromolecules [51].

Biodegradation

Biodegradation refers to any physical and chemical transformation induced by microorganisms. Plastics undergo degradation due to the influence of microorganisms, which include bacteria, actinomycetes, and fungi [52-53]. They undergo aerobic biodegradation in nature, anaerobic degradation in sediments and landfills, and a partly aerobic breakdown in compost and soil. In aerobic biodegradation, the primary products are carbon dioxide and water. Conversely, in anaerobic degradation, the byproducts consist of carbon dioxide, water, and methane [52].

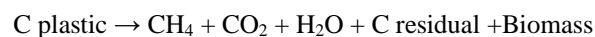
Biodegradation is influenced by multiple factors, including polymer characteristics (such as mobility, tacticity, crystallinity, molecular weight, and types of functional groups and structural substituents), the specific organism involved, and the nature of any pre-treatment undergone by the material [54-55].

In aerobic degradation or aerobic respiration, microorganisms utilize oxygen as an electron acceptor to break down large organic compounds into smaller compounds [56]. The by-products of this process are carbon dioxide and water, as illustrated in the reaction below [52, 56]:



Anaerobic degradation is the process by which microorganisms break down compounds in the absence of oxygen. Instead of oxygen, certain microorganisms

utilize alternative electron acceptors such as nitrate, sulfate, iron, manganese, and carbon dioxide to decompose organic chemicals into smaller compounds [57]. The by-products of the entire anaerobic degradation process include carbon dioxide, water, and methane, as represented in the reaction below [52, 57]:



Polymers, due to their large size and being water-soluble, are not directly transported into the cells of microorganisms through their cell walls. Instead, microorganisms use polymers as an energy source by secreting extracellular enzymes. These enzymes depolymerize the polymers outside the bacterial cells. Enzymes are central to the biodegradation process, operating either within the cell (intracellularly) or outside the cell (extracellularly). Depolymerization and mineralization are the two key processes involved in biodegradation [57].

PREVENTION OF DEGRADATION

Polymer stabilizers are chemical substances that can be incorporated into polymeric materials, such as plastics, to hinder or delay degradation. These stabilizers are applied at various stages throughout the polymer life cycle to preserve the material's integrity [58]. Examples are antioxidants, light stabilizers, acid scavengers, metal deactivators, heat stabilizers, flame retardants, among others.

Antioxidants

Antioxidants function to impede the process of autoxidation in polymers, which involves their reaction with atmospheric oxygen [59]. Autoxidation refers to the process of oxidation that occurs at regular temperatures, involving reactions with oxygen without the aid of a flame or an electric spark [60]. Antioxidants can be primary, secondary or antiozonants.

Primary Antioxidants

Primary antioxidants function as radical scavengers, eliminating peroxy radicals, alkoxy radicals, hydroxyl radicals, and alkyl radicals. The oxidation process initiates with the creation of alkyl radicals, which form under high temperatures and high shear stress during processing. These alkyl radicals rapidly react with molecular oxygen, resulting in the generation of peroxy radicals [61].



Secondary Antioxidants

Secondary antioxidants work to eliminate organic hydroperoxides that are created due to the actions of primary antioxidants. While hydroperoxides are less reactive than radical species, they still have the potential to trigger new radical reactions [62]. Given their lower chemical reactivity, hydroperoxides necessitate a more reactive antioxidant. Among the commonly used classes of antioxidants for this purpose are phosphite esters, often derived from hindered phenols [63]. These antioxidants serve to transform polymer hydroperoxides into alcohols, undergoing oxidation themselves and being converted into organophosphates [64-65].

Antiozonants

Antiozonants are substances that hinder or decelerate ozone-induced degradation. Ozone, naturally present in the air at very low concentrations, is highly reactive, especially towards unsaturated polymers leading to ozone cracking. Ozonolysis necessitates a distinct class of antioxidant stabilizers, which are typically based on *p*-phenylenediamine. These antiozonants react with ozone more rapidly than ozone can react with vulnerable functional groups in the polymer, typically alkene groups. They achieve this by having a low ionization energy, which enables them to engage with ozone via electron transfer. This transformation results in the creation of radical cations that are stabilized through aromaticity. These species remain reactive and continue to react, yielding products such as 1,4-benzoquinone, phenylenediamine dimers, and aminoxyl radicals [66-67].

Light Stabilizers

Light stabilizers function to impede polymer photo-oxidation, a process resulting from the interaction of light and oxygen. Similar to autoxidation, this constitutes a free radical process, where the antioxidants mentioned earlier are effective inhibiting agents. However, other classes of additives also prove beneficial, including UV absorbers, quenchers of excited states, and hindered amine light stabilizers (HALS) [68].

UV Absorbers

The susceptibility of polymers to UV rays varies; materials like polycarbonates, polyesters, and polyurethanes are notably prone to UV degradation. UV stabilizers function by absorbing and dissipating the energy from UV rays as heat, typically through reversible intramolecular proton transfer. This process lessens the

absorption of UV rays by the polymer matrix, thereby reducing the rate of weathering. Different types of UV stabilizers are utilized for various polymers: phenolic benzotriazoles and hydroxyphenyl-triazines are employed to stabilize polycarbonates and acrylics; oxanilides are used for polyamides and polyurethanes, while benzophenones are favored for PVC [69].

Quenchers

Photo-oxidation can commence with the absorption of light by a chromophore present within the polymer, causing it to enter into an excited state. This can then interact with ambient oxygen, transforming it into highly reactive singlet oxygen. Quenchers have the capability to absorb energy from these excited molecules through a Förster mechanism and then dissipate it harmlessly as either heat or lower frequency fluorescent light. Singlet oxygen can be quenched by metal chelates, with nickel phenolates standing as a common example [70].

Hindered Amine Light Stabilizers (HALS)

The efficacy of hindered aminelight stabilizers (HALS) in scavenging radicals generated by weathering can be elucidated through the Denisov Cycle, where aminoxyl radicals are formed. Aminoxyl radicals combine with free radicals within the polymers. HALS exhibit remarkable effectiveness in polyolefins like polyethylene and polyurethane. While recognized as light stabilizers, they are also capable of stabilizing thermal degradation [71].

Other Classes

Polymers are vulnerable to degradation through various pathways beyond oxygen and light exposure. There have been reported preventive strategies in the literature to address the diverse types of degradation that may affect polymers.

Acid Scavengers

Acid scavengers play a critical role in neutralizing acidic impurities, especially those that release hydrochloric acid (HCl). PVC is particularly susceptible to acid-catalyzed degradation, often due to the release of HCl from the polymer itself. Halogenated flame retardants could also serve sources of acids along the process. Various acid scavengers are employed for this purpose, such as metallic soaps including calcium stearate and zinc stearate, mineral agents like hydrotalcite and hydrocalumite, as well as basic metal oxides including calcium oxide, zinc oxide, or magnesium oxide. These



scavengers work to counteract the acidic compounds, mitigating their adverse effects on the polymer material [72].

Metal Deactivators

Metal ions, like those from titanium (Ti), aluminum (Al), and copper (Cu), can hasten degradation, particularly when polymers directly contact metal surfaces, as seen in wiring and cable applications. Additionally, metal catalysts employed during polymer formation might become enclosed within the material during production. This encapsulation often occurs with Ziegler-Natta catalysts used in polypropylene production. To enhance stability, metal deactivators are introduced. Deactivators function through chelation, forming inactive coordination complexes with the metal ions, thus preventing their deleterious effects on the polymer [73].

Heat Stabilizers

Heat stabilizers are commonly applied to PVC since unstabilized PVC is highly susceptible to thermal degradation. These agents serve to minimize the loss of hydrochloric acid (HCl), a degradation process that initiates at temperatures above 70°C. Once dehydrochlorination begins, it becomes autocatalytic, accelerating the degradation. Various agents have historically been utilized, including derivatives of heavy metals like lead and cadmium. However, increasingly, metallic soaps are favored, species such as calcium stearate, due to their effectiveness as heat stabilizers [74].

Flame Retardants

Flame retardants are diverse range of compounds utilized to enhance the fire resistance of polymers. Examples include brominated compounds, along with aluminum hydroxide, antimony trioxide, and various organophosphates, all of which contribute to reducing flammability in polymers [59, 75].

Biocides

Biodegradation is a process driven by microorganisms and, as a result, necessitates the use of biocides. Isothiazolinones are compounds known for their antimicrobial properties and are used to manage bacteria, fungi, and algae. They serve as effective antifouling agents, inhibiting the unwanted accumulation of microorganisms on various surfaces [76-77].

CONCLUSION

Plastics, regardless of their form, are susceptible to various types of degradation, including photo-oxidative, thermal, mechanochemical, catalytic, ozone-induced, and biodegradation. Various polymer stabilizers have been introduced to combat the degradation of plastic materials. These stabilizers play a crucial role in preserving the integrity and performance of plastic products. The ongoing increase in the demand for plastic production will drive more persistent efforts in the manufacturing process to develop more new innovations aimed at controlling and mitigating the effects of various degradation mechanisms.

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