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A Comprehensive Review on Polymer and Plastic Decomposition: Mechanism, Environmental Impact and Sustainable Approaches

Manisha Yadav[1] | **Dr. Manisha Sheoran**[2*]

[1]Research Scholar, Department of Chemistry, Dr. K. N. Modi University, Newai, Tonk, Rajasthan, India.
[2]Assistant Professor, Department of Chemistry, Dr. K. N. Modi University, Newai, Tonk, Rajasthan, India.

[*]Corresponding Author: Manishasheoran480@gmail.com

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ABSTRACT

Plastic waste is very harmful burdens on the environment. Chemical recycling do not decrease quality repeated regeneration, but it is requires harsh reaction conditions, this is environmentally unfriendly. Under the mild conditions recycling is possible for enzymatic catalyst, but it faces inherent limitations like poor stability, high cost, and narrow substrate applicability. Biomimetic catalysis may provide a new avenue by combining high enzyme-like activity with the stability of inorganic materials. Biomimetic catalysis has demonstrated great potential in biomass conversion and has recently shown promising progress in plastic degradation. plastic degradation from biomimetic perspectives: the imitation of active centers and substrate-binding clefts. Similarity between biomass and plastics, relevant work is discussion to draw inspiration. The conclusion is highlighting the challenges and opportunities in achieving sustainable plastic recycling via a biomimetic approach recycling technologies are, chemical depolymerization a route to virgin quality of recycled plastics, especially when valorizing complex, waste streams poorly clean by mechanical methods.

***Keywords**: Ezymatic Catalysis, Plasticdegradation, Polymer, Sustainable, PVC.*

Introduction

Polymer–this is a large molecule, it is made up combine of small units.

First Synthetic polymer – Bakelite (1907)

These materials have become an integral part of modern life due to their unique properties are such as light weight, flexibility strength and resistance to corrosion.

The large scale of growth of plastic production and mismanagement of plastic waste in the past few decades have caused escalating concerns across the globe.1–3 To mitigate the environmental impact of plastic waste, it is imperative to develop plastic recycling approaches beyond landfill and incineration. While mechanical recycling has been used for recovery of thermoplastics, the regenerated raw materials often suffer from deterioration.[1]Chemical recycling has attracted increasing research interest in recent years.4,6–9 Breaking the C–C, C–O, or C-Nbondsinpolymer backbones enable esthens transformation of post-consumer plastics into building blocks for new materials. For example, hydrolysis of polythenes produces valuable products such as liquid fuels, waxes, and lubricants;10–12 solvolysis of polyesters yields corresponding monomers or value-added derivatives; 4,13–16 and polyamides can be catalytically converted to either 3-caprolactam by a chain-end back biting process or alcohols and amines by hydrogenolysis. 17,18 Despite the progress, the depolymerization of waste plastics often requires harsh conditions to achieve bond cleavage, undermining the economic viability of these processes. There

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fore, developing cost-effective and energy-efficient chemical recycling processes plays a significant role in achieving a more sustainable future.[2]

In 1950, the global production of plastics (excluding fiber) was 1.3 million tons, and by 2018, it reached an alarming level of 359 million tons (excluding f iber), resulting in widespread environmental contamination [2]. It is estimated that only 10% of plastic waste is recycled, 14% is incinerated, and the rest is dumped into landfills, ultimately entering the natural environment [3]. Plastics are transported through air and water currents, therefore, they not only affect the natural environment but also pose adverse ecological impacts in the deep-sea sediments and polar regions [4]. In fact, plastics and microplastics (MPs, size 5 mm) have been commonly found in freshwater, the atmosphere, and soil environments across the world. A class of high molecular weight polymers is referred to as plastics in general. The formation of “white pollution” has caused serious environmental pollution and ecological damage around the world. Polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS), and polyvinyl Microorganisms 2023, 11, 1661. https://doi.org/10.3390/microorganisms11071661 https://www.mdpi.com/journal/ microorganisms Microorganisms 2023, 11, 1661 2 of 17 chloride (PVC) are the most widely utilized plastics, with PE and PP making up more than half of global output [5]. Plastic waste is persistent when released into the environment, high polymers may take a much longer time for plastics to degrade in the environment, and even complete degradation of plastics may take centuries [6]. Therefore, it is necessary to investigate the pathways of plastic degradation and their efficiency in the environment.

Methodology

Plastic is considered as one of the threat full elements in the environment because of its slow degradation in the environment which seriously takes some decades, so it’s considered a non-degrading material. These non-degradable plastics accumulated considered as solid waste on the earth’s surface which is assumed as food by terres- trial animals, such as cows, buffaloes, and consuming it which causes the death of animals.[9] These plastics which form particulate matter by UV irradiation Correspondence: Department of Biotechnology, College of Science and Technology, Andhra University, Visakhapatnam 530003, India Full list of author information is available at the end of the article and weathering increase surface area and mobility and, therefore, easily incorporate into the food chain causing serious effects to all the living organisms.[10] Disposing of the plastic waste in oceans leads accumulation of toxic chemicals, such as polychlorinated biphenyl (PCB’s), nonpoylphenol (NP), dichlorodiphenyltrichloroethane (DDT), polycyclic aromatic hydrocarbons (PAH), poly brominated diphenyl esters (PBDE), and bisphenol A (BPA) [11], which have been found as a serious problem of indigestion, gastrointestinal blockages and reproductive problems in marine organisms. Due to this plastic pollution in the marine environment minimum of 267 species are being affected which includes sea turtles (86%) and seabirds (44%) [3]. The worldwide annual The Author(s) 2022. Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. They are various forms of plastics, i.e., nylon, polycarbonate, polyethylene terephthalate, polyethylene, polypropylene, polystyrene, polytetrafluoroethylene, polyurethane, and polyvinyl chloride.[12] To degrade these plastics, there are different methods, such as photo degradation, thermos oxidative degradation, hydrolytic degradation, and bio degradation.

Therefore, the present study aims to explore the degradation of major synthetic polymers through both **chemical and biological processes**. The paper emphasizes the mechanisms, reaction pathways, and environmental significance of these degradation methods. Special attention is given to the role of **microorganisms and catalytic agents** that enhance the degradation efficiency and promote sustainable management of plastic waste.[11]

In addition to highlighting the chemical and biological routes for plastic degradation, this study also discusses the factors influencing degradation efficiency such as temperature, pH, microbial activity, and catalyst type. The integration of green chemistry principles in polymer breakdown has been emphasized to minimize secondary pollution. Ultimately, the research aims to provide a scientific foundation for developing **eco-friendly, energy-efficient, and sustainable plastic waste management strategies** that can be adopted at both industrial and environmental levels.

Types of Polymers

Polymers can be classified in different ways — based on **origin, composition, structure,** and **mode of polymerization.**

On the Basis of Origin

- **Natural Polymers**

  These polymers occur naturally in plants and animals.

  Examples
  - **Proteins** – silk, wool, collagen
  - **Polysaccharides** – cellulose, starch
  - **Natural rubber** – obtained from latex
- **Synthetic Polymers:**

  These are man-made polymers prepared by chemical reactions.

  Examples:
  - Polyethylene (PE)
  - Polyvinyl chloride (PVC)
  - Polystyrene (PS)
  - Bakelite, Nylon, Teflon
- **Semi-synthetic Polymers:**

  These are chemically modified natural polymers.

  Examples:
  - **Cellulose acetate** – used in photographic films
  - **Vulcanized rubber** – modified form of natural rubber

Based on Composition

- Homopolymers:

  Formed from only one type of monomer unit.

  Examples:
  - Polyethylene → from ethene
  - Polystyrene → from styrene

  Representation:
  $A + A + A \rightarrow (A)n$
- **Copolymers:**

  Formed from two or more different monomer units.

  Examples:
  - Buna-S → Butadiene + Styrene
  - Nylon-6,6 → Adipic acid + Hexamethylenediamine
  - PET → Terephthalic acid + Ethylene glycol

  Representation:
  $A + B + A + B \rightarrow (AB)n$

Based on Intermolecular Forces

- **Elastomers**

  These polymers can stretch and return to their original shape.

  Examples: Natural rubber, Neoprene, Buna-S
- **Fibres**

  These polymers have strong intermolecular hydrogen bonding and high tensile strength.

  Examples: Nylon-6,6, Terylene, Silk, Cotton

- **Thermoplastics**

  These soften on heating and harden on cooling — reversible process.

  Examples: Polyethylene, PVC, Polystyrene

- **Thermosetting Polymers:**

  Once hardened, these cannot be softened again — irreversible process.

  Examples: Bakelite, Urea-formaldehyde resin, Melamine

Based on Polymerization Process

- **Addition Polymers**

  Formed by the repeated addition of unsaturated monomers (like alkenes) without eliminating any small molecule.

  Examples:
  - Polyethylene from ethene
  - Polystyrene from styrene
  - PVC from vinyl chloride

  Reaction:
  $n\ CH_2{=}CH_2 \rightarrow (–CH_2–CH_2–)_n$

- **Condensation Polymers**

  Formed by the combination of two different monomers with the elimination of a small molecule (like H_2O, HCl, etc.).

  Examples:
  - Nylon 6,6 (from adipic acid and hexamethylenediamine)
  - Terylene (from terephthalic acid and ethylene glycol)
  - Bakelite (from phenol and formaldehyde)

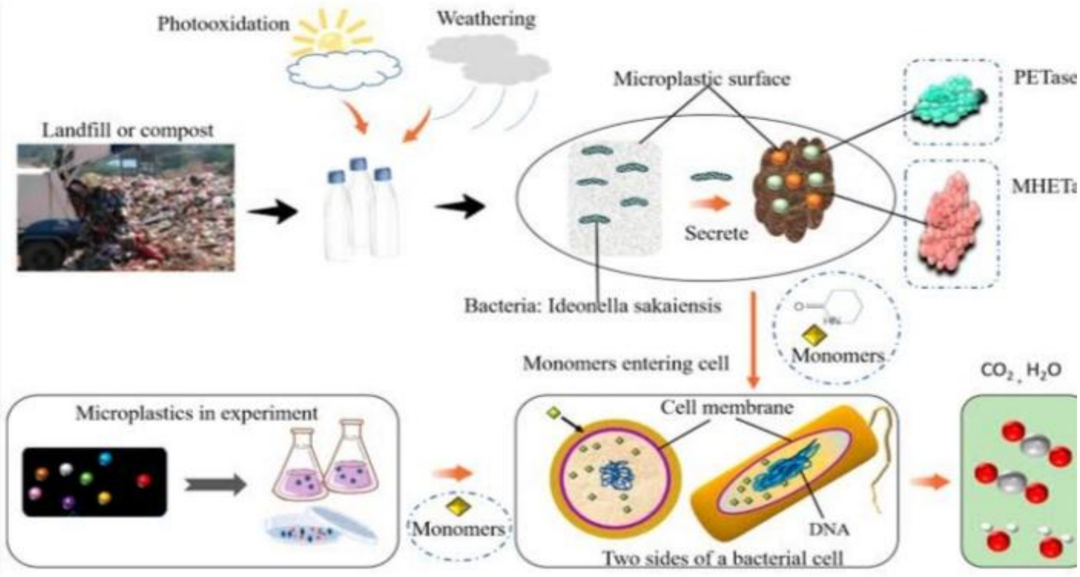
  Reaction:
  Monomer + Monomer → Polymer + H_2O

Decomposition Mechensm

The decomposition of polymers involves the breaking of long-chain macromolecules into smaller fragments through physical, chemical, or biological processes. Biodegradation, on the other hand, is facilitated by microorganisms that secrete enzymes to convert polymers into carbon dioxide, water, and biomass. In thermal degradation, high temperature causes chain scission and the release of volatile compounds. Chemical degradation occurs mainly via hydrolysis, oxidation, or photo degradation, depending on environmental conditions. The overall decomposition rate depends on polymer structure, crystallinity, temperature, moisture, and the presence of catalysts or microbes.

- **Biodegradation and Microbial Decomposition**

Plastics are not part of rich functional groups and hydrolyzable bonds, they are not a suitable substrate for microbial attachment and enzymatic reaction due to their intrinsic composition and properties, such as durability and resistance to degradation. The recalcitrant polymers do not completely degrade, making these polymers difficult to assimilate in the environment. The recalcitrant polymers with less flexibility and long chains effectively biodegrade into small monomers, which require more enzymatic activities for a longer period of time to cause specific sensitive bonds with the chemical groups on the polymer side chain or polymer chain and enhance their fracture. In a biodegradation process, the problem of conventional petroleum-based plastics involves not being completely decomposed and assimilated by microorganisms when they fragmented Microorganisms under abiotic factors over a long time, such as UV radiation, temperature, and physical stress . Because plastic is a long-chain molecule or macromolecule with a single functional group, high molecular weight (MW), hydrophobicity, and crystallinity, the ability of microbes to break it down has been significantly reduced as a result of its manufacturing performance.



This diagram clearly illustrates the biodegradation sequence of PET, beginning with abiotic fragmentation followed by enzymatic hydrolysis by Ideonellasakaiensis. The enzymes PETase and MHETase break PET into monomers, which are transported into microbial cells and metabolized into CO_2 and H_2O. However, due to the high crystallinity, hydrophobicity, and limited functional groups in plastics, the biodegradation rate is extremely slow, supporting the recalcitrant nature described above.

- **Thermal and Photodegradation**

In photo catalysis, a catalyst—typically a semiconductor material—is used to accelerate a chemical reaction in the presence of light. During MP degradation, the photo catalyst frequently produces reactive oxygen species (ROS) whenever it inter act switch light. Certain ROS, such as hydroxyl radicals (OH•), are very reactive and have the ability to harm

- $TiO_2hv \rightarrow h+VB+ e\ CB$
- $H + VB + H_2O \rightarrow •OH + H+$
- $O_2+e\ CB \rightarrow O_2•$
- $O_2• + H+ \rightarrow HOO•$
- $2HOO• \rightarrow O_2 + H_2O_2$
- $H_2O_2 \rightarrow 2OH•$

The photo catalyst produces hydroxyl radicals (•OH) that react with adsorbed pollutants that are adhered to or in close vicinity to the photo catalyst's surface without showing any preference. The pollutants miner alize as are sult of thisreaction.TiO2 is especially good at photo degrading or ganic contaminants when exposed to both UV and visible light. Eq.(3)describes the reaction between the photo excited electron in the CB and an oxygen molecule, which produces super oxide radicals (O2•).In addition to actively taking part in oxidation reactions, these O2• radicals stop photo generated electron-hole pairs from recombining. This procedure aids in preserving the semiconductor's electron neutrality. Eq. (4) illustrate show the produced O2• radical is protonated to create the hydro per oxy radical (HO2•). Eq. (5) there for estates that hydrogen per oxide (H2O2) is produce by there action of the hydro per oxy radical(HO2•).Eq.(6)illustrates how H2O2dissociatestoproduce•OHradicalsasaresult.

The following Eqs. (7)–(9)provide an illustration of the general response to plastic degradation in order to aid understanding.

- $H + VB+ MPs \rightarrow$ oxidize products
- $•OH+MPs \rightarrow CO2+H2O$
- $e +MPs \rightarrow$ reduced products

Additionally, MPs are some what directly degraded by TiO_2 under visible light. When visible light photons enter this mechanism, MPs are excited from their ground state to an excited state. In this excited state, the polymers inject electrons into the catalyst's CB, producing semi oxidized cation radicals. Subsequently, the trapped electrons combine with the dissolved oxygen to createO_2• . The target pollutants decompose because of the production on •OH radicals by these O_2• radicals. Demonstrating that the indirect method of plastic deterioration prevails over the direct mechanism, plastic breakdown is more prevalent than the reaction triggered by visible light. Furthermore, reactions to visible light are initiated at far slower rates than those to UV radiation. Furthermore, the generation of OH• and O_2• radicals causes the lengthy chains of polymers of low-density polyethylene (LDPE) to break down in susceptible locations. Small molecular weight polyethylene alkyl radicals (-CH_2-CH•-n) are produced as are ult. Moreover, it has been demonstrated that organic compounds can react to produce organic free radicals with the photo generated hole (H^+) .However, in the absence of a catalyst, photo degradation plays a major role in the decomposition of polymers. Long-term exposure to sunlight, particularly UV light, can disruptor link chemical chains related to micro plastics (MPs), add oxygen, extract hydrogen, and create environmentally hazardous free radicals .Additionally, morphological alterations like flaking and cracking may arise from this process, with UV radiation being found to be the main contributing element. Controlling MPs' natural photo degradation is challenging, though. During laboratory-accelerated photo degradation of MPs, Tanetal. have reported the development to oxygen-containing groups and fissures on their surfaces. However, since reactive oxygen species (ROS) are found in relatively low concentrations in aquatic environments, little is known about how they affect MP aging. Furthermore, MPs photo degrade slowly in the wild, particularly in watery environments. Examined the aging process of PS as a mode line an aquatic setting with artificial sunshine for a maximum of 150 days. They found that the PS suspension included ROS as a result of light exposure. The work clarified the process by which ROS a recreated and MPs photo degrade in the presence of artificial sunshine. The amount of photo aging and the kinds of intermediate products in this photo chemical system, however, were not investigated in this study. Furthermore, prolonged exposure to artificial light radiation may result in energy waste or even light pollution.

Chemically Degradation

- **Hydrolysis:** Hydrolysis is the cleavage of PET by water, yielding terephthalic acid and ethylene glycol. Hydrolysis is the primary environmental degradation pathway of PET released into wet environments, taking hundreds of days to even partially degrade PET.91 Purposeful hydrolysis can be done in the absence of a catalyst, neutral hydrolysis, with forcing conditions like high temperature (up to 420 °C) and/or pressure needed as water is a weak nucleophile. Most catalytic hydrolyses use acids, bases, or enzymes Each of these methods is discussed here in. 2.2.1. Neutral Hydrolysis. Neutral hydrolysis reactions are done at neutral pH, often without a catalyst, at high temperature and/or pressure to achieve depolymerization. Pereiraetal. Investigated the effect of temperature, pressure, and water phase(e.g., saturated, supercritical)on the neutral hydrolysis of PET.93 By rapidly heating($5-10°Cs^{-1}$) their reactor to ward 500°C, 78%TPA yield was obtained in 1min. The process had an impressively lo environmental energy metric compared with similar works. By removing catalysts, neutral hydrolyses benefit from reducing the amount of product purification and waste generation.
    - **Acidic Hydrolysis** :-.Acidic hydrolysis uses protons as the primary catalyst for hydrolysis. Protonation of the PET carbonyl activates it for nucleophilic attack by water. The adduct formed by nucleophilic attack then fragments, and these steps are repeated until TPA and EGareyielded. 98Due to PET's hydrophobicity, there action is usually heterogeneous with shrinking-core model kinetics reported.

Sulfonic acid catalysts have been investigated for the hydrolysis of PET. Yang et al. used p-toluene sulfonic acid (PTSA) and achieve da 96.2% TPA yield after 90min at 150°C, while maintaining this performance across 5 cycles. 102An in-depth probing into aryl sulfonic acid catalysts by A be desoltanetal. Was revealing. 103U sing PTSA, 2-naphthalene sulfonic acid (2-NSA), and 1,5-naphthalene di sulfonic acid (1,5-NDSA) Scheme 5. Four Hydrolysis Approaches, Differentiated by Catalyst Type and Conditions Use da a Adapted with permission from Chemical PTSA, 2-NSA, and 1,5-NDSA respectively. Interestingly the bi functional 1,5-NDSA was a slower and less active catalyst than PTSA. This decreased speed and activity was ascribed to a difference in affinity of the catalyst for the PET surface.

- **Basic Hydrolysis:-** Basic hydrolysis uses a strong base (e.g., OH) to perform nucleophilic attack on the PET carbonyl. The initial product is a terephthalate/metal salt, which requires acidic workup to yield the desired TPA monomer. The additional workup and stoichiometric waste are drawbacks of basic hydrolysis. Efforts to design catalysts that lower the amount of base (NaOH, KOH) are needed. 105 96 A further challenge faced is poor water solubility of PET. Ügdüler et al. overcame this solubility issue by including an ethanol cosolvent. Under optimized conditions (60:40 EtOH:H 2 O, 5 wt % NaOH and 80 °C), a 95% TPA yield was observed after only 20 min. The system was tested on postconsumer PET waste of differing types and a decreased product yield of 60% was observed. This difference between pure and postconsumer waste highlights the importance of designing robust systems able to meet the demands of industrial application.
- **Enzymatic Hydrolysis:-** Enzymatic hydrolysis is a promising method to selectively produce monomers under mild conditions while avoiding chemical waste (e.g., organic solvents). For more detailed discussion, see the extensive reviews on the topic. Enzymatic hydrolysis of PET was pushed to the fore by the 2016 discovery of a bacteria (Ideonella Sakaiensis) which produced a PET-degrading enzyme known as Is-PETase. Mechanistically, the action of the Is-PETase enzyme was proposed to be similar to chemical depolymerization; nucleophilic attack of a serine linked O anion on the carbonyl carbon. Work by Jerves et al. elaborated on this mechanism by probing with DFT. Several Asp residues were identified in the active site for mutation that could improve activity.

- **Oxidative Degradation**

Oxidative degradation is one of the most common chemical degradation pathway for plastic such as polyethylene(PE) and polypropylene(PP). It occurs in the presence of oxygen, often acceleration by heat, UV radiation, or metal catalysts. The process involve free radical formation, peroxide generation and subsequent chain scission reaction.

The degradation mechanism typically includes initiation, propagation, and termination steps, leading to the formation of oxygen containing functional group such as carbonyls, alcohols, and acid.

- **Glycolysis :-** Glycolysis is a transesterification reaction between PET and a glycol. Ethylene glycol (EG) is the most reported glycol and its use forms BHET, which is repolymerizable to PET by polycondensation (Scheme 3). 66 Various glycolysis catalysts have been explored and often catalyze reaction via dual activation of the PET carbonyl and EG alcohol. An inherent challenge of glycolysis is the poor solubility of PET in ethylene glycol at room temperature. High glycolysis temperatures (160−300 °C) not only overcome the activation energy barrier but also enhance PET swelling in EG and encourage dissolution. Inclusion of cosolvents like dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone, and nitrobenzene alongside EG can facilitate complete depolymerization in as little as 5 min. 67 68 Addition of an anisole cosolvent also enabled lower glycolysis temperatures of 153 °C with similar BHET yield (>80%). Density functional theory (DFT) (a computa tional technique for probing reaction mechanisms) and 1 H/ 13 C NMR spectroscopic evidence suggested that anisole stabilized glycolysis transition state(s) and reduced activation energy requirements. Specifically, π−π interactions between anisole and PET and electron donation from the anisole methoxy group were vital. The solubility of PET in EG decreases with increasing PET molecular weight, making this a key parameter for comparison of glycolysis results.

Environmental Impact

Plastic degradation's environmental impact is severe, creating persistent microplastics that harm wildlife through ingestion and entanglement, contaminating ecosystems, and releasing greenhouse gases as they break down, disrupting food chains, soil health, and potentially human health as these tiny particles enter water, air, and food. While plastics don't fully biodegrade quickly, they fragment into microplastics, which become pervasive carriers for toxins, impacting everything from marine birds and terrestrial insects to humans.

- **Microplastic Pollution** Larger plastics break down (often via sunlight/heat) into microplastics (<5mm), entering soil, water, and air, and getting ingested by organisms.

- **Wildlife Harm:** Animals mistake plastics for food or get entangled, causing injury, starvation, or death; ingestion blocks digestive tracts and affects reproduction.
- **Ecosystem Disruption:** Plastic debris smothers habitats like coral reefs, altering natural processes and reducing ecosystem resilience to climate change.
- **Chemical Release:** As plastics degrade, they leach harmful chemicals (additives, adsorbed pollutants) into the environment, making them toxic carriers in ecosystems.
- **Climate Change Contribution:** Plastic production (from fossil fuels) and incineration release significant greenhouse gases (CO2, dioxins).
- **Food Chain Contamination:** Microplastics and associated toxins accumulate up the food chain, from plankton to humans, with unknown long-term health effects.
- **Soil Degradation:** Accumulation in soil reduces fertility and harms soil organisms like earthworms and microbes, impacting plant growth.

Future Prospects

Polymer decomposition involves physical, chemical (photo, thermo-oxidative, hydrolytic), and biological breakdown, leading to harmful microplastics and toxic substances that contaminate ecosystems, harming wildlife and human health. Sustainable solutions focus on biodegradable alternatives, advanced recycling (chemical/mechanical), enzyme-based biodegradation, and waste management to reduce pollution, while future prospects involve integrated circular economy models and policy.

- **Biodegradable polymers** :Developing plastics from bio-resources (e.g., PLA, PHA) with controlled degradation.
- **Advanced Recycling:** Chemical recycling to break polymers into monomers for virgin-quality materials.
- **Enzymatic Degradation:** Using specific enzymes (like PETase) for targeted breakdown.
- **Waste Management:** Improved collection, reduction (lifestyle changes), and reuse.
- **Circular Economy:** Designing for reuse, repair, and recycling to minimize waste.
- **Policy & Regulation:** Implementing frameworks to manage plastic production and disposal.

In essence, understanding degradation is key to mitigating pollution, with future success relying on integrated strategies that blend material innovation, better waste management, and circular economic models.

Conclusion

Plastic degradation has emerged as a crucial strategy for addressing the global plastic waste crisis and moving toward a sustainable circular economy. Conventional mechanical recycling, although widely used, is limited by quality loss, contamination issues, and inefficiency in handling mixed plastic waste. Chemical degradation methods offer the advantage of converting polymers back into valuable monomers or chemicals, but their reliance on harsh reaction conditions, high energy input, and toxic reagents raises concerns regarding environmental and economic sustainability.

Enzymatic degradation provides a greener alternative by operating under mild conditions; however, its large-scale application remains constrained due to enzyme instability, slow reaction rates, and high production costs. In this context, biomimetic catalysis has emerged as a promising and innovative approach that bridges the gap between chemical and biological methods. By mimicking enzyme active sites and substrate-binding environments, biomimetic catalysts can achieve high catalytic efficiency while maintaining structural robustness and recyclability.

Overall, no single degradation method alone can provide a complete solution to the plastic waste problem. A synergistic integration of mechanical, chemical, enzymatic, and biomimetic strategies is essential for efficient, scalable, and environmentally responsible plastic recycling. Future research should focus on developing cost-effective, durable, and scalable catalytic systems capable of degrading complex and mixed plastic waste under mild conditions. With continued advancements, plastic degradation technologies have the potential to significantly reduce environmental pollution, conserve resources, and contribute to a truly sustainable materials economy.

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