

A Review of Biodegradable Plastics: Chemistry, Applications, Properties, and Future Research Needs

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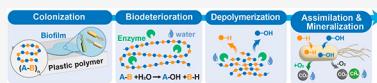
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ABSTRACT: Environmental concerns over waste plastics' effect on the environment are leading to the creation of biodegradable plastics. Biodegradable plastics may serve as a promising approach to manage the issue of environmental accumulation of plastic waste in the ocean and soil. Biodegradable plastics are the type of polymers that can be degraded by microorganisms into small molecules (e.g., H_2O , CO_2 , and CH_4). However, there are misconceptions surrounding biodegradable plastics. For example, the term "biodegradable" on product labeling can be misconstrued by the public to imply that the product will degrade under any environmental conditions. Such misleading information leads to consumer encouragement of excessive consumption of certain goods and increased littering of products labeled as "biodegradable". This review not only provides a comprehensive overview of the state-of-the-art biodegradable plastics but also clarifies the definitions and various terms associated with biodegradable plastics, including oxo-degradable plastics, enzyme-mediated plastics, and biodegradation agents. Analytical techniques and standard test methods to evaluate the biodegradability of polymeric materials in alignment with international standards are summarized. The review summarizes the properties and industrial applications of previously developed biodegradable plastics and then discusses how biomass-derived monomers can create new types of biodegradable polymers by utilizing their unique chemical properties from oxygen-containing functional groups. The terminology and methodologies covered in the paper provide a perspective on directions for the design of new biodegradable polymers that possess not only advanced performance for practical applications but also environmental benefits.



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Figure 1. Sankey diagram showing the life cycle of plastic packaging. Reproduced with permission from ref 10. Copyright 2022 Royal Society of Chemistry.

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1. INTRODUCTION: SOURCES, MAGNITUDE, AND FATE OF PLASTICS IN THE ENVIRONMENT

Plastics are ubiquitous in our lives due to their low cost, versatility, barrier properties, durability, and processing capabilities, which have made them attractive materials over metal, glass, and paper for a wide range of applications.¹ However, their durability and resistance to degradation cause end-of-life issues.² As a result, the environment faces a significant threat due to the vast amount of plastic waste and the challenges associated with its disposal.³ *Our World in Data* reported that 9,500 million tons of plastics have been cumulatively produced from 1950 to 2019.⁴ Among the plastics accumulation from 1950 to 2017, 5,300 million tons of plastics had discarded as waste, and only 600 million tons had been recycled.⁵ Yearly global plastic production was approximately 460 million tons in 2019 and is expected to continue to grow, reaching 1.2 billion tons by 2060.^{6–8} Accordingly, in the absence of comprehensive and aggressive intervention, a vast amount of plastic waste continues to enter the environment. As reported by the Ellen MacArthur Foundation in 2016, 40% of plastic packaging waste has accumulated in landfills, 27.4–30.3% has been discarded in dump sites, and 1.7–4.6% has found its way into the oceans (Figure 1).^{9,10}

Plastics that are not disposed of in a closed landfill, recycled, or combusted will often eventually be transported to the ocean through inland waterways, wastewater outflows, wind, or tides.¹¹ It is estimated that around 80% of plastic waste in the marine environment originates from land.¹² Jambeck et al. identified that the largest amount of plastic marine debris originated from regions with underdeveloped waste management infrastructures.¹³ In more developed countries, plastic can be released into the environment through environmental disasters (hurricanes, floods), leakage in waste collection, wastewater treatment plant effluent, and landfill leachate, as well as discarded fishing gear.^{14,15} Law et al. suggested that designing products and packaging with end-of-life management in mind, including explicit costs for recovery and treatment, is crucial to reduce plastic waste.¹⁶ This is because in regions

with well-developed waste management systems and high levels of per capita waste generation, such as the United States, plastic pollution can still arise due to improper disposal practices such as littering and illegal dumping. Additionally, exporting plastic wastes to regions with insufficient capacity to manage them can lead to significant plastic leakage into the environment. According to estimates, 0.15–0.99 million tons of plastic waste were released into the ocean in 2016 due to the export of recycled materials from the United States to such regions.¹⁶ Once in the ocean, plastics float at different levels in the water and cause problems such as shading of photosynthetic organisms, ingestion by and poisoning of marine animals, and contributions to ocean acidification. Over time, the plastic breaks into smaller pieces (microplastics), which eventually sink to the bottom due to biofouling and accumulate in marine sediments. Ideally, society should change from thinking about the “end-of-life” of plastics to the “beginning-of-new life” for waste plastics and focus on how we can prevent carbon from plastics from being released into the environment in order to promote and maintain a circular economy for plastics. The time scale to biodegrade conventional plastics is tremendously long (centuries).¹⁷ The cumulative mass of plastic waste in the ocean is forecasted to increase by an order of magnitude by 2025¹³ and outweigh the mass of fish by 2050¹⁸ if the current plastic production rate and trends of plastic waste management continue. In addition to establishing a reliable waste management system that can efficiently collect, sort, recycle, and dispose of plastic waste, it is also necessary to create polymeric materials that can more rapidly degrade in the environment.¹⁹ A frequently proposed option is to introduce biodegradable plastics to replace their conventional counterparts for applications where discard-after-use is still the major consumption pattern. The economic feasibility of recycling postconsumer plastics can be complicated by the inevitable presence of contaminants such as food, dyes, and additives, which can lead to contamination and make the material recycling process more challenging.^{20,21}

Plastic wastes not only contaminate the ocean but also pose a threat to terrestrial environments, especially agricultural soils.^{22–26} There is growing evidence that plastics are abundant in soils, and it is estimated that the amount of plastic in soils is larger than those in marine and freshwater environments.^{27–29} Plastic introduction to agricultural fields comes about through plastic mulching, compost, sewage sludge (biosolids), coated fertilizer, irrigation and flooding, littering, and street runoff.^{30,31} For instance, plastic mulching film which typically is made of polyethylene (PE), a nonbiodegradable polymeric material, is

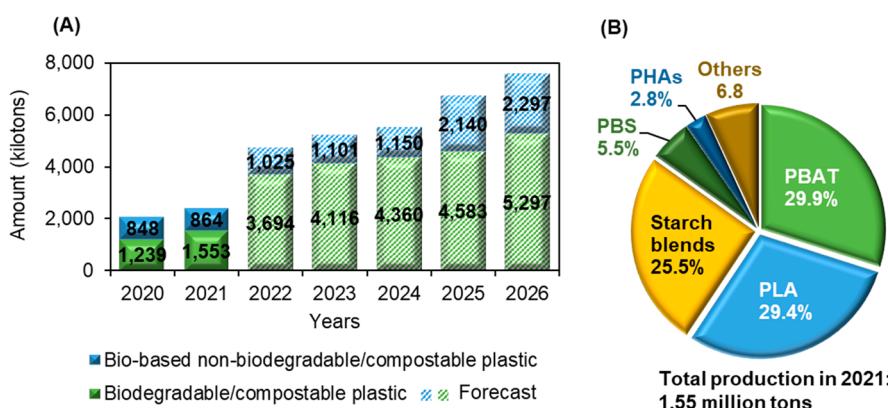


Figure 2. (A) Global production capacities of bioplastics and (B) biodegradable/compostable plastics by material type in 2021.⁴⁶

discussed as one of the sources for plastic pollution into agricultural soils.^{27,30,32} Microplastics released from mulching film consequently are expected to end up in shallow groundwater via leaching.³³ Additionally, the mulching film easily tears into small pieces due to weathering²³ and the entanglement of plastics with plant roots and stems.³⁴ Over 30 years of the mulching film use, an average of 8,885 and 2,899 particles of microplastics were accumulated in 1 kg of the topsoil (0–10 cm depth) and the subsoil (80–100 cm depth), respectively.³⁴ Moreover, it is difficult to remove plastic mulching film from the soil since it is labor-intensive and costly.²³ Recycling is also not easy because soil particles stick to plastic mulching film.²³ As a result, the mulching film residues can change the structure and composition of the soil with decreasing microbial diversity and enzymatic activity, becoming a threat to the environment and crops.^{35,36} Recent studies showed the impact of the plastic mulching film on soil structure, physical and chemical properties of soil, soil organisms, and groundwater environment.^{32,37} In 2019, the Chinese Ministry of Ecology and Environment and the National Development and Reform Commission (NDRC) proposed new regulations to address agricultural plastic issues. According to the regulations, high-quality and thicker mulch that can be reused, collected, and recycled are required. The new regulation prohibits the production and sale of traditionally used mulching films thinner than 10 μm and encourages the use of biodegradable mulching films.

Biodegradable plastic mulching films have been shown in many studies to provide advantages since they are designed to be tilled into the soil.^{38–41} According to a review by Somanathan et al., several studies have shown that the biodegradable mulching film decomposes quickly, protects the soil from both biotic and abiotic factors, increases crop yield, does not need to be disposed of separately, adds nourishment to the soil, maintains the soil microorganisms, and does not pollute the soil.⁴² The biodegradable mulching film is transformed into CO_2 and biomass by activity of microorganisms and higher-order organisms such as worms.¹⁹ There is an international standard (EN-17033) designed specifically for biodegradable agricultural plastic mulching films in soil. According to EN 17033, in order to meet the standard, more than 90% of carbon in a mulching plastic film must convert to CO_2 within 2 years. Such material can further form a mineral-related organic matter or be encapsulated in soil aggregates, thereby becoming persistent soil organic carbon.³⁸ Thus, plastic-derived carbon can be converted into stable soil

organic carbon, which potentially stores that carbon for a long time. Therefore, long-term use of biodegradable mulching films could increase the amount of soil carbon, which would help soil health.³⁸ In this respect, mulching films including polybutylene adipate terephthalate (PBAT), poly(lactic acid) (PLA), and polyhydroxyalkanoates (PHAs) have been developed, and the films can be left on the field after use for biodegradation.^{43–45}

According to the European Plastic Report, approximately 1.5 million tons of biodegradable/compostable plastics were produced in 2021 which represent 0.66% of the total plastic market.⁴⁶ Biodegradable/compostable plastic production is expected to reach 5.3 million tons/year in 2026, as shown in Figure 2A.⁴⁶ Several types of biodegradable/compostable plastics are on the market today in the following order of decreasing volume, as shown in Figure 2B: PBAT, PLA, starch blends, polybutylene succinate (PBS), PHAs, and others, including polycaprolactone (PCL) and regenerated cellulose. The different plastics have a different degree of biodegradability, as will be discussed here. For the purpose of clarity and to avoid confusion, the definitions of biodegradable and compostable plastics along with other degradable plastics will be addressed in Section 2.

The objective of this review is to discuss the properties of biodegradable plastics and the mechanisms of biodegradation and review the various standard tests to measure the biodegradability of plastics. Relevant definitions and several myths about biodegradable plastics are discussed. We also present current biodegradable plastics that are on the market today and their properties compared with petroleum-based commodity plastics. Finally, we propose how new biodegradable plastics with improved properties can be designed by introducing biomass-derived monomers.

2. DEFINITIONS OF BIODEGRADABLE PLASTICS AND PLASTIC BIODEGRADATION PROCESS

2.1. Definitions and Diverse Terms for Biodegradable Plastics and Plastic Biodegradation Agents

Polymers include water-soluble polymers, plastics (thermoplastics and thermosets), proteins, DNA, and cellulose. Among these, plastics are a subset of polymers that can be molded or shaped typically by heating and then hardened through cooling. It is worth noting that this paper employs the term “polymer” when discussing the fundamental properties of the polymer chain. Conversely, when referring to macro properties or applications, the term “plastic” will be used to ensure

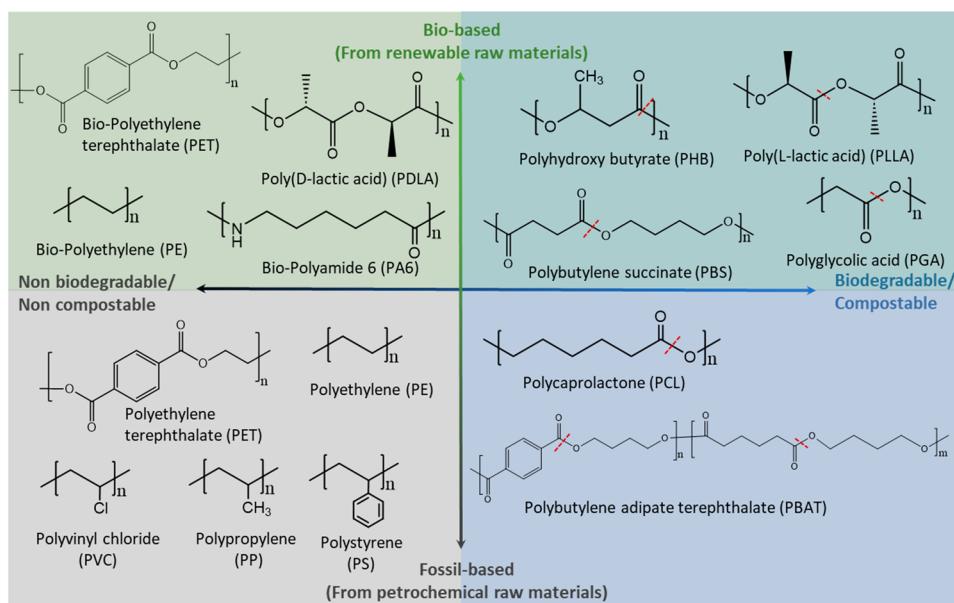


Figure 3. Classification and examples of plastics based on biodegradability and their monomer sources. Biodegradable/compostable plastics commonly harbor an ester bond formed during polymerization and can be broken down by enzymes such as esterase, lipase, and cutinase where the cleavage site is marked as red dashed lines. All plastics presented in this figure can be (entirely or partly) produced from either renewable or petrochemical raw materials.

precision and clarity. Definitions of biodegradable plastic can vary among colloquial uses, industry standards, different countries, fields of research, and even the setting of organism carrying out the biodegradation activity. For instance, the UK government has opted for the following definitions: Biobased plastics are plastics that are made using polymers derived from plant-based sources, such as starch, cellulose, or lignin. Biodegradable plastics are the plastics that can be broken down into water, biomass, and small gases such as CO_2 and CH_4 . Compostable plastics are a subset of biodegradable plastics that biodegrade under composting conditions, such as high humidity and oxygen at $55 \pm 2^\circ\text{C}$ (industrial composting conditions) and $28 \pm 2^\circ\text{C}$ (home composting conditions).^{1,47}

In general, it can be concluded that all biodegradable plastics degrade under industrial composting conditions. A smaller subset of these plastics decomposes in soil and under home composting conditions. An even smaller group of biodegradable plastics exhibit the ability to break down in freshwater and marine environments, as well as in anaerobic conditions such as those employed in wastewater treatment plants and anaerobic digestors in agricultural systems.⁴⁸ The term “biodegradable plastic” is frequently and incorrectly used interchangeably with the terms “biobased plastic”, “compostable plastic”, “oxo-degradable plastic”, and “enzyme-mediated degradable plastic”. Figure 3 shows classifications and examples of plastics, biobased plastics, and biodegradable/compostable plastics.⁴⁹ Biobased polymers are polymers (including plastics but other polymer categories as well) that are produced from biological material such as fruits, sugars, and waste biomass. Some consumer plastics, currently produced from petroleum or natural gas, are being produced from various biomass feedstocks. For example, producing biomass-derived terephthalic acid, a monomer precursor for polyethylene terephthalate (PET) and polybutylene adipate terephthalate (PBAT), has been attracting much research effort, but industrial scale processes are rare.^{50–55} Companies such as Anellotech and Suntory have been able to produce PET from wood.^{56,57}

Braskem commercially produces high-density polyethylene (HDPE) from bioethanol.^{58,59} Biobased versions of PET, polypropylene (PP), and HDPE have the same properties as PET, PP, and HDPE produced from petroleum and are not biodegradable. Also, many polyamides on the market are (partly) biobased. By contrast, a biodegradable plastic is a degradable plastic where the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi, and algae.¹⁹ The biodegradability of plastics is dependent on the polymer structure rather than on the raw material or feedstock source. Thus, biodegradable plastics and polymers can be produced from both petroleum and biomass feedstocks.

2.1.1. Compostable Plastics. The term “compostable plastics” is also often used interchangeably with “biodegradable plastics” since the mechanism of compost is biodegradation. However, it is necessary to state the conditions under which biodegradation occurs. Compostable plastics are defined as those that biodegrade under controlled conditions, characterized primarily by forced aeration and natural heat production from biological activity that degrades the material. For instance, poly(lactic acid) (PLA) degrades under industrial composting conditions (aerobic digestion at $58 \pm 2^\circ\text{C}$).⁶⁰ In the United States, if a polymer is biodegradable in only a composting system, it can be labeled as compostable, not biodegradable.⁶¹ According to 16 CFR part 260—guides for the use of environmental marketing claims (often known as the Federal Trade Commission’s “Green Guides”), it is deceptive to misrepresent, directly or by implication, that a product or package is degradable, biodegradable, oxo-degradable, oxo-biodegradable, or photodegradable, unless competent and reliable scientific evidence that the entire item will completely break down and return to nature (i.e., decompose into elements found in nature) within one year after customary disposal.⁶² An in-depth summary is available from the Biodegradable Products Institute.⁶³

Although the Green Guides do not supersede state law, some states in the United States have adopted laws that cover certain types of claims with respect to certain types of products and specific claims for those products.⁶⁴ California, Maryland, and Washington have criminalized the use of misleading terms such as “biodegradable”.⁶⁴ For the clear certification of industrially compostable products, the products are required to meet the specifications established in ASTM D6400 which is one of the well-developed standard specifications for compostable products. Note that ASTM D6400 applies only to municipal or industrial composting. An ASTM method for home composting (specification for the home composting of biodegradable plastics) is under development. Specific methods for evaluating the biodegradability of plastics are summarized in Section 2.4.

2.1.2. Oxo-degradable Plastics. Oxo-degradable plastics are produced by mixing pro-degradants or pro-oxidants with conventional plastics like polyethylene terephthalate (PET), poly(vinyl chloride) (PVC), and polypropylene (PP). The pro-oxidants help the polymer decompose faster abiotically as the additive results in polymer molecular weight loss which can lead to embrittlement and fragmentation of the article.⁶⁵ Specifically, the pro-oxidants promote chain scission via an oxidation mechanism. There is an ongoing debate whether fragmentation generates microplastics or if once molecular weight is sufficiently low, assimilation by microorganisms can occur. These additives, usually produced from manganese, cobalt, or iron compounds, serve to accelerate oxidative depolymerization via Fenton chemistry.⁶⁶ Oxo-degradable plastics are primarily used in low and middle income countries so that plastic bags and other films do not clog sewage systems since plastic bags/films that enter the environment as litter frequently find their way into sewers. Some have incorrectly claimed that oxo-degradable plastic undergoes biodegradation.⁶⁷ However, this is a controversial statement, as there is not good evidence that biodegradability is associated with oxo-degradability additives. The degradation of oxo-degradable plastics produces biologically recalcitrant microplastics and low molecular weight organic molecules, which can end up in leachates and potentially contaminate the environment. The introduction of the pro-oxidants into the plastics can also increase the polymer's level of ecotoxicological risk.⁶⁵ For these reasons, oxo-degradable plastic products have been banned in some areas like the EU and the United Arab Emirates.^{67,68}

2.1.3. Enzymes-Mediated Degradable Plastics. Another emerging class of more ecofriendly degraded polymers includes enzyme-mediated degradable plastic where enzymes and organic additives are added into conventional plastics. Enzymes or organic additives in the enzyme-mediated plastic can play a role as a catalyst to improve the biodegradability of conventional polymers. The organic additive is consumed by microorganisms, and they excrete enzymes and acids that make polymers degrade more easily. Advanced Enzyme Science Ltd., which produces Enzymoplast, claimed that PE with 4–10% of Enzymoplast can be 100% biodegradable and compostable.⁶⁹ ENSO Plastics manufactures an organic additive, referred ENSO Restore, and the company claims that incorporation into conventional plastics achieves 90% biodegradation faster than without ENSO Restore.⁷⁰ Organic Waste Systems (OWS),⁷¹ an independent testing laboratory, reviewed available information on enzyme-mediated degradable plastics manufactured by the following producers: Advanced Enzyme Science Ltd. (Enzymoplast),⁶⁹ Biosphere Plastic LLC,⁷² Bio-

Tec Environmental LLC (EcoPure),⁷³ Earth Nurture (ENA),⁷⁴ and ENSO Plastics (ENSO Restore).⁷⁰ OWS concluded that there was no evidence for complete degradation of enzyme-mediated degradable plastics, and the companies' claimed biodegradation tests were not conducted according to international standards.⁷⁵ Specifically, three companies claimed that a microbial additive created water plastic bottles that were advertised as “100% biodegradable and recyclable.” In 2011, however, the office of the California Attorney General filed a lawsuit against those three companies for misleading claims on additive-based bottles in violation of the Bioplastic labeling law. As a result, the companies were required to change all labels to remove the false claims.⁷⁶ Some of the additives are not enzymes but increase the hydrophilicity of the polymer matrix in which they are incorporated. These additives are designed to cause the polymer to adsorb water and swell. This supposedly supports the growth of bacteria that feed on the polymer and reduce its molecular weight. The use of a single enzyme can limit the biodegradability when the plastic consists of various functionalities (comonomers); thus, additional research work involved improving the efficiency of enzyme-mediated plastic degradation by blending different enzymes. In this circumstance, Carbios, a French industrial biotech company, along with their partners in Toulouse, have developed a novel hyper-thermostable biocatalyst that can remain active when integrated into PLA at high extrusion temperatures of up to 170 °C.^{77,78} As a result, this approach can significantly increase the biodegradability of the polymer under ambient conditions, thus enabling the development of more suitable applications for this innovative bioplastic such as mulching films or packaging. While modifying PLA through advanced techniques appears to be technically promising, its current implementation may be prohibitively expensive. As such, further research and development are needed to optimize the manufacturing process and reduce costs.

2.1.4. Development of Enzyme Cocktails for Plastic Degradation. To improve the stability of enzymes for plastic degradation and to develop enzymes capable of degrading more types of plastic, extensive research on enzyme-mediated degradation, especially PET, is ongoing. This work is sometimes confused with the additive route described above. In this case, enzymes are being developed to have specific chemistries and geometries to promote scission of conventionally produced plastics such that enzymatic treatment could be done in a waste collection facility. This would be similar to how enzyme cocktails are currently used in wastewater treatment plants, in biomass hydrolysis, and even in agriculture as plant fertilizer. In isolating a PET degradation enzyme (PETase) from soil samples taken near a PET recycling facility, Yoshida et al. found that *Ideonella sakaiensis* was able to metabolize PET scission products as its only carbon source. Genome sequencing showed that the bacterium comprised gene sequence signatures that were characteristic of esterase enzymes. These enzymes were shown to be responsible for the depolymerization via hydrolysis of PET into MHET (mono(2-hydroxyethyl) terephthalate), which is the ester produced by the reaction of terephthalic acid (TPA) and ethylene glycol (EG). Following absorption of MHET by the bacterium, another enzyme, MHETase, cleaved MHET into TPA and EG, which were then further metabolized. From a practical standpoint, the depolymerization rate offered by the *Ideonella sakaiensis* derived enzymes was slow (6 weeks to completely degrade a thin PET film).⁷⁹ Rate improvement was difficult as

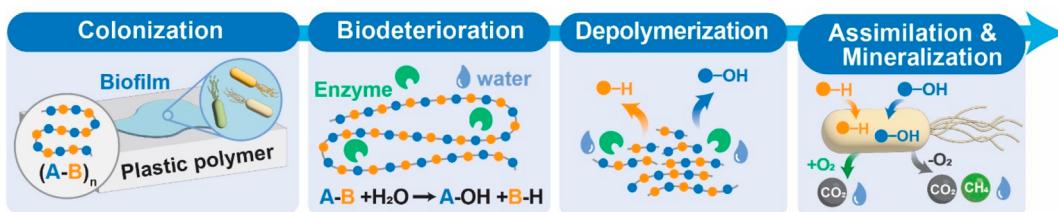


Figure 4. General process of plastic degradation under aerobic or anaerobic conditions.

chain mobility was found to be beneficial for positioning the polymer chain onto the enzyme's active site, which resided in a "trench", "groove", "cleft", or "canyon" in the surrounding protein. Since crystalline regions are much less mobile, the best success was found with predominantly amorphous PET. Elevating the temperature above PET's glass transition temperature (T_g) benefited mobility but hindered the thermal stability and activity of the enzyme. Additionally, elevated temperature caused PET crystallization over the relevant time frame of the degradation cycle.⁸⁰ Austin et al. further explored the structure and proposed mutant enzymes that would improve the degradation capacity.⁸¹ Recently, a new PET hydrolase, called FAST-PETase (functional, active, stable, and tolerant PETase), was designed by using a structure-based machine learning algorithm. FAST-PETase showed superior PET-hydrolytic activity at a wide range of temperatures and pH levels and was demonstrated by degrading different postconsumer-PET almost completely in 1 week.⁸²

Discoveries and commercial development of carboxylic ester hydrolases⁸³ that promote the hydrolytic scission of PET have inspired broader exploration of enzymatic pathways for recovery of plastic waste. A vast majority of the plastic-degrading enzymes reported to date act on hydrolyzable plastics such as polyesters, polyamides, and polyurethanes. These enzymes primarily belong to the CEH (carboxylic ester hydrolase) family, such as cutinases (EC 3.1.1.74), lipases (EC 3.1.1.3), and carboxylesterases (EC 3.1.1.1). Nonhydrolyzable plastics like PE, PP, PVC, and polystyrene (PS) are extremely resistant to biological cleavage, and thus only limited enzymes have been reported to degrade them.^{84,85} Allpress et al. noted that one of the most challenging reactions in chemistry and biology is the selective oxidative cleavage of aliphatic carbon–carbon bonds.⁸⁶ For successful enzymatic attack of PE, PP, etc., their highly stable carbon–carbon (C–C) bonds have to be oxidized first prior to depolymerization.⁸⁷ One approach to C–C bond oxidation is to add oxo-degradable additives (Section 2.1.1). By coupling oxo-degradation with a suitable enzyme, it might be possible to improve the hydrolysis outcome obtained when oxo-degradables are used alone. Because enzyme activity and turnover number depend on geometric (like the active site "canyon" in the PETase enzyme produced by *Ideonella sakaiensis*) as well as chemical factors, substrate specificity challenges might arise. For example, a hypothetical enzyme that cleaves a predominantly linear, highly crystalline polymer like HDPE may not have activity with a branched polymer like LDPE, even though their chemical make-ups are similar.⁸⁸ Given the challenge of C–C bond oxidation and cleavage, initial research for plastic biodegradation enzymes targeting C–C bonds will likely focus on materials with low crystallinity, such as LDPE, and having high glass transition temperature, like atactic PS.

2.2. Processes of Abiotic and Biotic Plastic Biodegradation in the Environment

Plastics undergo biodegradation in different environments including landfills, waterways, wastewater treatment plants, biosolids, oceans, and marine sediments. Plastic degradation can be divided into two categories: biological degradation (biotic) and nonbiological degradation (abiotic).⁸⁹ Abiotic degradation typically occurs prior to biodegradation in the natural environment. Abiotic degradation, which includes processes such as hydrolysis, thermal degradation, and photodegradation,^{90,91} produces smaller plastic fragments (higher surface area) with lower molecular weight (MW) that are more susceptible to microbial activity.⁹² In photo-induced processes, absorption of UV light produces radicals that promote polymer chain scission leading to photodegradation.^{93–95} Radicals also cause photo-oxidation which creates oxygen functionality on the plastic surface and an increase in the polymer's hydrophilicity.⁹⁰ Thermal degradation initiates oxidative reactions throughout the entire polymer matrix, whereas photodegradation occurs primarily on the polymer surface.⁹⁶ Thermal degradation typically occurs over 100 °C and thus is not a major contributor to abiotic degradation of plastics in the environment.⁹⁰ Abiotic degradation of plastics serves to enhance biotic degradation.

Biotic degradation takes place through microbial enzymatic actions, which results principally in the production of CO₂, CH₄, and H₂O under aerobic or anaerobic conditions.⁹⁷ The process of plastic biodegradation by microbial mechanisms has been recently reviewed.^{98–100} The exact process and chemical and biochemical reactions of plastic biodegradation vary based on the size and type of plastic, polymer, environment, and microorganisms present, but can be broadly described in five main stages shown in Figure 4. The five stages are (1) surface colonization: microorganisms first adhere to the surface of the polymer; (2) biodeterioration: excreted enzymes prefer to attack amorphous regions (easier permeation of moisture and enzymes) of plastics to form large pores and cracks increasing the surface area; (3) additive metabolism and depolymerization: in this stage, extracellular enzymes continue to hydrolyze chemical bonds (e.g., ester, ether, amide) to break down the polymers, including plastics, into increasingly water-soluble intermediates such as oligomers, dimers, and monomers; (4) assimilation: because polymer molecules are too large to passively diffuse across cellular membranes or cell walls, the depolymerized smaller molecules can enter into the cells through protein transporters that span the cellular membrane; (5) mineralization: those smaller molecules are processed via intracellular metabolism to produce energy, cellular biomass, and their end products. It is unclear if the water-soluble fragments and monomers that escape the cellular uptake and get into the surrounding medium are eventually broken down by other bacteria. Under aerobic conditions, the ultimate end products are CO₂ and H₂O, while under anaerobic conditions,

the end products are CO_2 , H_2O , and CH_4 , depending on the type of organism involved. Deciphering the detailed biochemical mechanisms of plastic biodegradation will help improve development of degradation strategies for existing plastic waste and the design of improved biodegradable plastics.

2.3. Factors Affecting Biodegradation

While the exact mechanism of plastic biodegradation is not yet determined, advancements in our understanding of the factors that affect biodegradation also help the design of degradation methods and new types of biodegradable plastics. Biodegradation of plastic depends on three main factors: polymer characteristics, environmental conditions, and nearby microorganisms.¹⁰¹ The chemical properties of a polymer determine how susceptible it is to degradation. Parameters such as the surface properties (surface area and hydrophilic and hydrophobic properties), the first-order structure (chemical structure, molecular weight, and molecular weight distribution), and the high-order structure (glass transition temperature, melting temperature, modulus of elasticity, crystallinity, and crystal structure) of polymers including plastics play important roles in the biodegradation processes.^{102,103} The crystallinity can have a significant effect on the biodegradation of plastic. For example, the microstructures in plastics and related polymer, such as chain orientation and stretchiness of amorphous and crystalline regions, provide different diffusion rates of reacting species (e.g., solvents, enzymes, and oxygen) that can affect the degree of swelling and biodegradability of plastics.^{104,105} In addition, the higher surface area of plastic samples may help accelerate the hydrolysis process by exposing more enzyme binding sites. The surface area can be affected by parameters such as the plastic sample sizes.

Environmental conditions, such as moisture, oxygen content, temperature, and carbon-to-nitrogen ratios (C/N), are deterministic factors in rates and extent of plastic biodegradation because the conditions influence the activity and membership of the microbial community. In marine sediments and soil environments, the degradation rates of plastic wastes are determined by the total action of abiotic and biotic processes, including swelling, cracking, creep, hydrolysis, leaching, and biodegradation.¹⁰⁷ In general, polymers (including plastics) have a lower degradation rate in marine environments, including sediments⁵⁰ and simulated natural seawater⁵¹ columns, compared to landfills. This is attributed to lower ambient temperatures ($<4\text{ }^\circ\text{C}$) and low dissolved oxygen concentrations in the marine environment.¹⁰⁶ Industrial compost offers environmental conditions that can accelerate degradation rates provided sufficient oxygen is available.¹⁰⁷ In addition, both acidic and basic environments can enhance the hydrolysis of ester bonds. Soil environments can provide a wider range of local pH than deep water marine environments, which have a circumneutral pH of 8.2.¹⁰⁸ It should also be noted that solar UV radiation is an efficient mechanism for plastic degradation when the polymer is exposed in air to sunlight; whereas landfill/soil/compost conditions experience little solar UV radiation, hindering photodegradation.^{17,109}

Another important factor that affects plastic degradation rates in soil or marine environments is the quantity and identity of microorganisms' present. Since microorganisms typically prefer natural carbon sources over non-natural polymers, biodegradation of plastic is affected by the presence of competing substrates.¹¹⁰ Many bacteria and fungi species

have reported biodegradation capabilities. These microorganisms can act by breaking the crystalline structure of polymers, depolymerizing polymers to oligomers, and assimilating oligomers and monomers through their metabolism. Comprehensive reviews on recent advances in plastic degradation organisms and enzymes, including genomic and molecular characterization, have been recently published^{91,111,112} and point to the diverse organisms and chemistries involved. A number of microorganisms capable of degrading plastics have been isolated from the soil of plastic-dumping sites, soil contaminated by crude oil, sewage sludge, and landfills.¹¹³ These soil environments have sufficient nutrients, oxygen, and proper temperature to support microbial growth and adaptive evolution of strains to utilize plastics as a carbon source. To date, more than 90 genera of plastic-degrading microorganisms have been discovered from soil,¹¹⁴ whereas 4 genera have been found in seawater.^{115,116} Although a large diversity of microorganisms has been reported in the marine environment, the percentage of functional microorganisms that degrade plastic is less than 0.1 % of marine microbial diversity.¹¹⁷ The main reason is that biopolymeric plastics like poly(hydroxy alkanoates) (PHAs) already naturally occur in these environments. Members of microbial communities that can live on polymers are rare in seawater. A "seed bank" theory suggests that these microorganisms appear as opportunists that stay in a dormant state for long periods but can quickly become active when encountering a suitable polymer substrate. Increasingly, research efforts focus on microorganisms isolated from cold marine environments to study their unique characteristics in the role of eliminating plastic waste from ecosystems.¹⁰⁶ Taken together, the presence of polymer biodegradation activity in diverse environments suggests an opportunity to improve polymeric materials to prevent accumulation in the environment.

2.4. Standardized Methods for Testing Plastic Biodegradability

To quantify the biodegradability of different materials, biodegradation tests have been developed by regulatory agencies to determine the performance of polymer materials in the environment. Typically, these tests focus on evaluating the properties of the plastics themselves rather than examining the effects of incorporating additives into the final product, along with the plastic. Accepted tests and standards vary among governments and industries, contributing to issues with terminology and the development of internationally accepted or ideal biodegradable plastics. There have been a number of issues related to labeling certain plastics as biodegradable without scientific evidence. Policies and public perceptions around biodegradable plastics are beyond the scope of this review but have been reviewed elsewhere.^{1,108,118,119} There are also various test methods used for polymers (including plastics) in different geographic areas, and polymer suppliers must comply with the relevant standards and regulations in each region.

It is difficult to objectively evaluate the biodegradation rate of different plastics in real environmental conditions, as mentioned in Section 2.3. Moreover, establishing a laboratory setting that mimics a natural environment is hardly possible.¹²⁰ Thus, standard tests have been developed by both ASTM International (ASTM) and the International Organization for Standardization (ISO) to determine whether certain polymeric materials are biodegradable by measuring the evolved CO_2 or

Table 1. Standards Describing Test Methods for Biodegradation

Category	Standard	Medium	Temperature	Time
Aerobic atmosphere	ASTM D6400-21 "Standard specification for labeling of plastics designed to be aerobically composted in municipal or industrial facilities"	Compost	58 ± 2 °C	180 days
	ASTM D5338 "Standard test method for determining aerobic biodegradation of plastic materials under controlled composting conditions incorporating thermophilic temperatures"	Compost	58 ± 2 °C	45 days
	ISO 14855-1 "Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions – Method by analysis of evolved carbon dioxide - Part 1: General method"	Compost	58 ± 2 °C	180 days
	ASTM D5988 "Standard test method for determining aerobic biodegradation of plastic materials in soil"	Soil	25 ± 2 °C	180 days
	ISO 17556 "Plastics-determination of the ultimate aerobic biodegradability in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved"	Soil	25 ± 2 °C	180 days
	ASTM D6691 "Standard test method for determining aerobic biodegradation of plastic materials in the marine environment by a defined microbial consortium or natural sea water inoculum"	Seawater	30 ± 2 °C	28 days
	ISO 14851 "Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium-Method by measuring the oxygen demand in a closed respirometer"	Aqueous	25 ± 1 °C	28 days
	ISO 14852 "Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium-Method by analysis of evolved carbon dioxide"	Aqueous	25 ± 1 °C	100 days
Anaerobic atmosphere	ISO 14853 "Determination of the ultimate anaerobic biodegradation of plastic materials in an aqueous system-Method by measurement of biogas production"	Aqueous	35 ± 2 °C	90 days
	ASTM D5511 "Standard test method for determining anaerobic biodegradation of plastic materials under high-soils anaerobic-digestion conditions"	Household waste	52 ± 2 °C	28 days
	ASTM D5526 "Standard test method for determining anaerobic biodegradation of plastic materials under accelerated landfill conditions"	Household waste	35 ± 2 °C	30 days
	ISO 15985 "Plastics-Determination of the ultimate anaerobic biodegradation and disintegration under high-solids anaerobic-digestion conditions-Method by analysis of released biogas"	Household waste	52 ± 2 °C	15 days

biogas production from the tested materials. The measurement of CO₂ is one of the clear methods to identify that a polymer has been consumed by microorganisms, assuming polymer is the only carbon source in the environment.^{108,120} Table 1 summarizes different methods for the biodegradation testing of biodegradable plastics. The standard tests for the biodegradability of plastics are mainly conducted in aerobic conditions while some tests are under anaerobic conditions. The required time of the standardized tests can be flexible according to the biodegradation degree of the test substance, except ASTM D6400 because it is a standard specification, not a test method. A standard specification is a set of requirements that a product or material must meet. It typically includes the physical, chemical, and mechanical characteristics of the product, as well as the quality standards that it must meet. A test method is a procedure or protocol used to evaluate a particular property. Test methods are developed to ensure that the requirements outlined in the standard specification are satisfied, and they are often standardized themselves to ensure consistency and comparability of results across different laboratories or testing facilities. ASTM D6400 will be specifically discussed in the last paragraph in Section 2.

In this review, we mainly describe the standard specification (ASTM D6400) and focus on the standard test in soil (ASTM D5988). Figure 5 shows the schematic view of a biodegradation test in soil according to ASTM D5988.¹²¹ The CO₂ is evolved during the biodegradation in soil, and KOH captures the CO₂ in an airtight desiccator. The amount of absorbed CO₂ by KOH is determined by titrating the remaining KOH with HCl to a phenolphthalein end point as an indicator or by an automatic titrator. This test determines the biodegradation rate by comparing the amount of CO₂ evolved during its degradation (CO₂ test) with the theoretical amount of CO₂ that can be ideally produced from the tested material (CO₂ theoretical), as shown in eq 1. The CO₂ blank is the amount of CO₂ evolved from only soil without the tested polymer material.

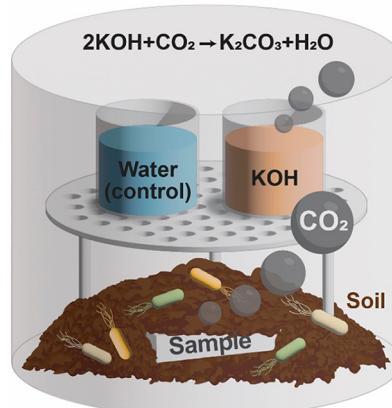


Figure 5. Schematic view of the biodegradation test setup according to ASTM D5988.¹²¹

$$\text{biodegradation (\%)} = \frac{\text{CO}_2 \text{ test} - \text{CO}_2 \text{ blank}}{\text{CO}_2 \text{ theoretical}} \times 100 \quad (1)$$

As mentioned in Section 2.3, biodegradation rates are affected by many factors. Thus, this review investigated characteristics of the tested materials and soil mediums and compared the biodegradation rates. Figure 6 shows an illustrative example of biodegradation rates of cellulose and PBAT according to ASTM D5988 from four different studies.^{71,122–124} The different degradation rates may be attributed to different temperatures, molecular weight (MW) of PBAT, sample dimensions, and ratios of carbon content in samples to soil. Table 2 summarizes the conditions of samples and soil used in the 4 studies as well as the required conditions to follow ASTM D5988. Cellulose was used as the reference plastic. Ninety percent of cellulose degraded after 200 days according to Saadi et al.¹²² This study had the highest cellulose degradation rate among all four studies. Saadi et al. used the highest temperature and added compost into the soil. PBAT

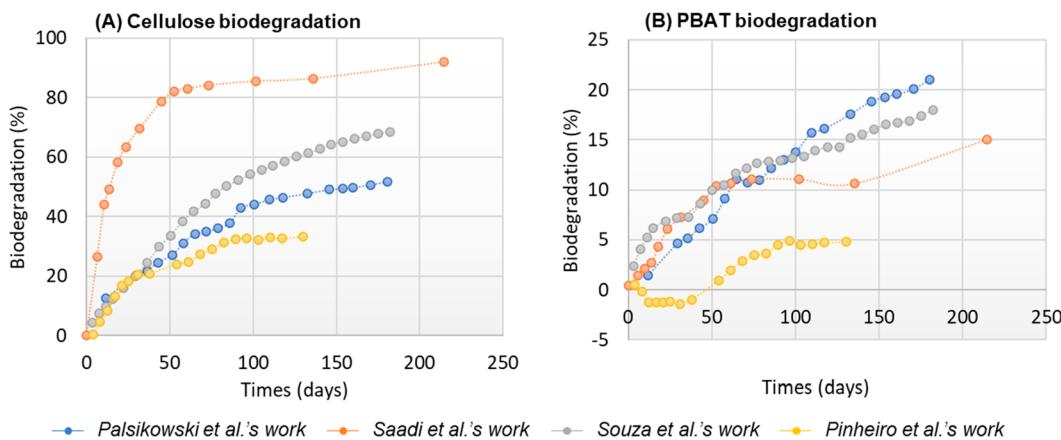


Figure 6. Comparison of (A) cellulose degradation and (B) PBAT biodegradation in soil according to ASTM D5988. (Data extracted from refs 71 and 122–124).

Table 2. Required Experimental Conditions for ASTM D5988-18 and Conditions of Samples Including Soil, PBAT, and Cellulose

	ASTM D5988-18	Palsikowski et al. ⁷¹	Saadi et al. ¹²²	Souza et al. ¹²³	Pinheiro et al. ¹²⁴
Soil conditions					
pH	6.0–8.0	6.3	N/A	N/A	N/A
Initial moisture content (%)	4.7	N/A	N/A	N/A	N/A
C:N ratio	10:1–20:1	16.7	N/A	110:1	N/A
Water holding capacity (%)	36	N/A	33.5	N/A	N/A
Adjusted moisture content (% of water holding capacity)	50–70	60	80	60	N/A
Soil size	2 mm particle size	N/A	N/A	N/A	N/A
Amount of soil	100–500 g of soil	200 g of soil	25 g of soil + 3 g of compost	200 g of soil	N/A
Temperature	20 ± 2 °C to 28 ± 2 °C	25 ± 2 °C	30 °C	28 °C	28 °C
PBAT					
Weight-average molecular weight (Mw)	N/A	44,000 g/mol	140,000 g/mol	31,000 g/mol	105,000 g/mol
Number-average molecular weight (Mn)	N/A	19,000 g/mol	67,140 g/mol	6,000 g/mol	47,000 g/mol
Sample size		3 cm × 3 cm × 0.003 cm	1 cm × 2 cm × 0.01 cm	N/A	N/A
Glass transition temperature (T_g)	N/A	−32 °C	−29 °C	N/A	−32 °C
Melting temperature	N/A	130 °C	121 °C	N/A	120 °C
Sample amount	200 mg to 1,000 mg carbon for 500 g of soil	N/A	50 mg of carbon in sample	240 mg of carbon in sample	N/A
Carbon in PBAT: Soil ratio (mg/g)	0.4–2	N/A	1.78	1.2	N/A
Cellulose					
Sample size	N/A	N/A	From Sigma-Aldrich	Microcrystalline powder	N/A
Sample amount	200 mg to 1,000 mg carbon for 500 g of soil	N/A	50 mg of carbon in sample	168 mg of sample in sample	N/A
Carbon in Cellulose: Soil ratio (mg/g)	0.4–2	N/A	1.78	0.84	N/A

degradation reported in the Saadi paper¹²² showed slower degradation than in the papers from Palsikowski et al.⁷¹ and Souza et al.¹²³ This can be explained by a relatively thick sample (0.01 cm) and high MW of PBAT (140,000 g/mol) used in Saadi et al.¹²² compared to the other papers (Palsikowski et al.⁷¹ thickness, 0.003 cm; MW, 44,000 g/mol; Souza et al.¹²³ thickness, N/A; MW, 31,000 g/mol). Plastics with high MW are less susceptible to microbial actions.¹²⁵ Thicker plastics also need a longer time to degrade.⁴⁸ According to ASTM D5988, soil samples should

be obtained from at least three diverse locations to maximize biodiversity. Each soil has different microbial species. Even if tests are conducted in the same soil conditions, for instance, PBATs with different MWs might yield different results. Therefore, it is difficult to compare the soil biodegradability of PBAT from one manufacturer with PBAT from another manufacturer because of differences in the MW, sample preparation, and even the soil activity.

ASTM D6400, shown in Figure 7, covers the requirements for labeling biodegradable plastics as compostable in industrial

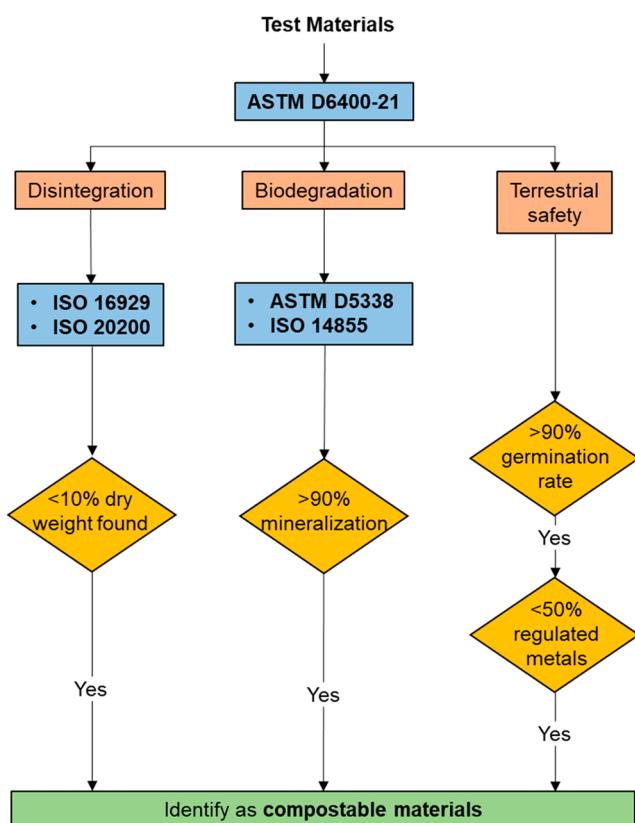


Figure 7. Compostable material identification flowchart with ASTM D6400-21. Figure adapted from ref 125.

composting systems. This test has three main components: (1) disintegration, (2) biodegradation, and (3) terrestrial safety. A product can be labeled as compostable if it meets the suitability requirements established by those tests. First, the disintegration test is carried out in accordance with ISO 16929 (or ISO 20200). The test samples are cut with dimensions of 25×25 mm. Within 84 days, the fragments with a size greater than 2 mm should not be more than 10% of the dry original plastic weight in the final compost. Second, the cumulative percentage of organic carbon converted into CO_2 gas compared to the theoretical value for the test plastic must be at least 90% of a cellulose positive control in 180 days according to ASTM D5338 (or ISO 14855). Finally, the terrestrial safety requirement specifies the allowable concentration of regulated metals, which must be lower than 50% of those prescribed for sludges for composts as listed in 40 CFR Part 503.13 in the United States Code of Federal Regulations. This list is dependent on the country where the product is sold. The terrestrial safety criterion also measures the plant growth rate for two different species following the Organization for Economic Co-operation and Development (OECD) Guideline 208. The growth rate from the compost containing the test materials must be greater than 90% compared with the corresponding blank composts. Even though ASTM D6400 is a well-organized standard specification, it could be improved to specify the types of compost media and the minimum thickness for the test material. For example, if a material is claimed to be “compostable” based on passing certain tests, it typically means that a film of a specific thickness has been tested and shown to biodegrade within a certain time frame. However, in many cases, injection-molded parts are made from

the same material but are much thicker than the tested film, leading to claims of biodegradability that may be inaccurate. Thus, the use of these standardized methods is crucial to quantify and assess the biodegradability of plastics, and the experiments must be rigorously performed to obtain reliable results.

Furthermore, when evaluating the biodegradability of plastics, it is essential to assess their potential toxicity, particularly when new biodegradable materials are introduced alongside traditional biowaste.^{126,127} Toxicity assessments can be species-specific, with single-species tests, such as the earthworm acute toxicity test (OECD Guideline 207) and the terrestrial plant growth test (OECD Guideline 208) being commonly used. However, these tests have limitations, and multispecies tests with model ecosystems provide more comprehensive information on the real fate of compounds.¹²⁸ Ecotoxicity tests use model organisms under controlled laboratory conditions to ensure that no harmful degradation products are released into the environment.¹²⁹ The choice of test species depends on the ecosystem under investigation, and test systems vary in duration and evaluated effects, including lethal and sublethal effects, growth, reproduction, and specific responses.¹²⁸

3. CURRENT BIODEGRADABLE/COMPOSTABLE PLASTICS: PROPERTIES, BIODEGRADABILITY, AND APPLICATIONS

The properties, production costs, and applications of biodegradable/compostable and common plastics are summarized in Table 3. Polymeric properties include thermal properties, such as the glass transition temperature and melting temperature, mechanical properties, (e.g., tensile modulus, tensile strength, and elongation at break), and gas permeability. Properties of biodegradable/compostable plastics can be changed by adding natural fillers or blending in other plastics to achieve the desired properties for applications. Blending of different biodegradable/compostable plastics can improve the mechanical and biodegradability properties of the final material. Degradation rates of common plastics in various environments such as landfill, compost, soil, and marine were summarized by Chamas et al.¹⁷ Chamas et al. measured the specific surface degradation rates of common plastics (PET, HDPE, PVC, LDPE, PP, and PS) and extrapolated the rates to estimate half-lives for plastic degradation. The estimated half-lives for PET (water bottle), HDPE (pipe), PVC (pipe), and PS (insulating packaging) are $>2,500$ years in buried land. In the marine environment, the estimated half-lives for HDPE (pipe), LDPE (plastic bags), and PP (food container) are 1200, 3, and 53 years, respectively.

Figure 8 shows an overall scheme for the fate of a range of biodegradable plastics in various environments (marine, freshwater, soil, home composting, industrial composting, landfills, and anaerobic digestion). PHB, cellulose, starch, and other natural polymers are considered biodegradable under selected environments. The biodegradability of the plastics was evaluated using test methods suggested by a certifying company, TÜV Austria. Table 4 tabulates quantitative biodegradation rates of biodegradable plastics in different environments and specific conditions, but the biodegradability will be affected depending on the geometry of the samples and different conditions.

Table 3. Properties of Biodegradable and Common Commodity Plastics

	Biodegradable plastics						Common commodity plastics				
	PBS	PCL	PBAT	PLA	PHB	PET	LDPE	HDPE	PP	PVC	PS
Glass transition temperature, T_g (°C)	-33 ¹³¹	-60 ¹³⁶	-30 ¹⁸⁴	50–80 ¹⁶²	2 ¹⁴²	70–80 ¹⁸⁵	-125 ¹⁸⁶	-135 ¹⁸⁶	-18 ¹⁸⁶	85 ¹⁸⁷	116 ¹⁸⁸
Melting temperature, T_m (°C)	112–128 ¹³¹	60 ¹³⁶	110–115 ¹⁸⁴	130–180 ¹⁶²	160–175 ¹⁴²	250–265 ¹⁸⁵	110 ¹⁸⁹ –125 ¹⁹⁰	135 ¹⁹¹	164–168 ¹⁹²	115–230 ¹⁹³	200–230 ¹⁹⁴
Tensile modulus (MPa)	500 ¹⁸⁴	390–470 ¹⁸⁴	65–90 ¹⁸⁴	2800–3500 ⁸⁴	1000–2000 ¹⁴²	5451 ¹⁹⁵	301 ¹⁸⁹	1,095 ¹⁹⁶	1,491 ¹⁹⁵	3,500 ¹⁹⁷	1400 ¹⁹⁸
Tensile strength (MPa)	40–60 ¹⁸⁴	4–28 ¹⁸⁴	25–40 ¹⁸⁴	44–65 ¹⁸⁴	15–40 ¹⁴²	460 ¹⁹⁵	15–22 ¹⁹⁹	106 ¹⁹⁶	29 ¹⁹⁵	8 ²⁰⁰	43 ¹⁹⁸
Elongation at break (%)	170–500 ¹⁸⁴	700–1000 ¹⁸⁴	500–800 ¹⁸⁴	10–240 ¹⁸⁴	6–8 ¹⁸⁴	49 ¹⁹⁵	290–570 ¹⁹⁹	863 ¹⁹⁶	>100 ¹⁹⁵	130 ²⁰⁰	7 ¹⁹⁸
Water vapor permeability ^a						16–20 ²⁰¹	15–25 ²⁰¹	5–12 ²⁰¹	3–7 ²⁰¹	20–60 ²⁰¹	70–160 ²⁰¹
Oxygen permeability ^b						60–120 ²⁰¹	7,000–8,000 ²⁰¹	1,500–2,000 ²⁰¹	1,800–2,500 ²⁰¹	50–80 ²⁰¹	4,000–6,000 ²⁰¹
Production cost (\$/ton) ^c	2,300 ¹⁸⁴	3400 ¹⁸⁴	1700 ¹⁸⁴	2500–3000 ¹⁸⁴	4300–7200 ¹⁸⁴						
Applications	Packaging, coating film	Long-term items, agricultural film	Bag, Mulching film	Food container, Compost bag	Bottle, bag, wrapping film	Bottles, Film, Fiber	Soft packaging, Film, Wrapping	Rigid packaging, Bottle, Screw caps	Film, Thin wall containers, Bottles, Closure	Film, Thin wall containers, Bottles	Insulator, Thin wall containers, Bottles

^aMoisture vapor transmission rate for 25 μm film at 38 °C, 90% relative humidity. ^bOxygen transmission rate for 25 μm film at 25 °C, 50% relative humidity, 1 atm. ^c2022 USD.

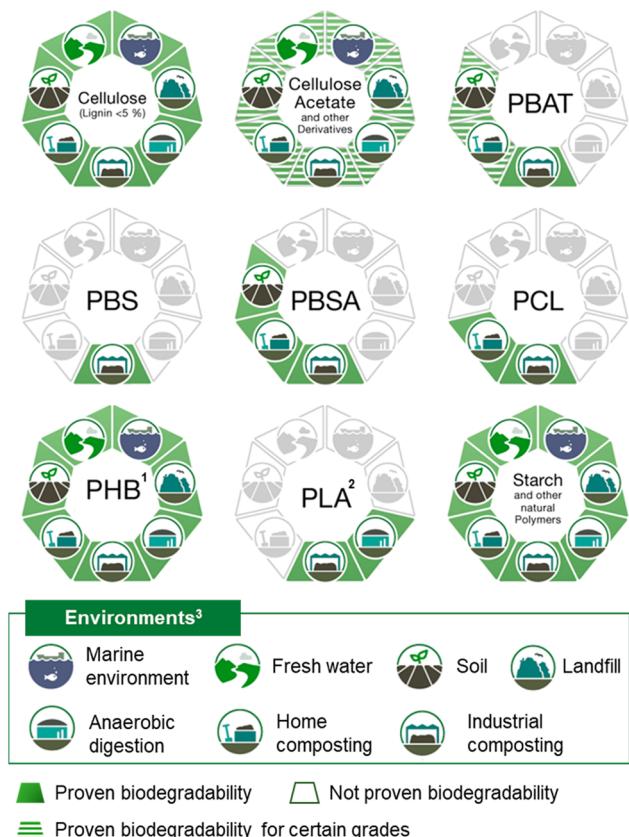


Figure 8. Biodegradable plastics in various environments are based on established standards and certification schemes. ¹PHB includes its copolymers. ²PLA is not biodegradable in mesophilic digestion. ³For more details of the environmental conditions, refer to the original documents. Reproduced with permission from ref 130. Copyright 2021 nova-Institute.

3.1. Poly(butylene succinate) (PBS)

1,4-Butanediol and succinic acid are used to synthesize the biodegradable aliphatic polyester, PBS. It is a white semicrystalline thermoplastic polyester with a melting point of 112–128 °C and a glass transition temperature of –33 °C.¹³¹ The stiffness of PBS is between LDPE and HDPE.¹³² Thus, PBS is a soft, strong, biodegradable material that can replace

polyethylene in some applications. However, PBS is comprised of a large spherulite structure with high crystallinity, which results in a brittle physical property.¹³³ Copolymerization has been used to overcome the weak impact resistance property of PBS.¹³⁴ For example, ethylene glycol is substituted for some of the 1,4-butanediol. PBS can produce a copolymer with poly(ethylene succinate) (PBS-*co*-ES). The biodegradability of the copolymer depends on its crystallinity with biodegradability increasing with decreasing crystallinity.¹³⁵ When the ethylene succinate content is 53 mol %, the PBS-*co*-ES copolymer has a minimum symmetric crystallinity and minimum melting point, which exhibits a maximum enzymatic degradation by measuring the formation of water-soluble total organic carbon.¹³⁵ The degree of crystallinity is determined by the ratio of butylene succinate and ethylene succinate in the copolymer. Enzymes selectively degrade the amorphous region of PBS because they can diffuse into the amorphous region more easily. Similarly, the properties of PBS can be varied by copolymerization with adipic acid to produce poly(butylene succinate-*co*-adipate) (PBSA). Commercial biodegradable plastics that are composed of PBS or PBSA are BIONOLLE by Showa Denko and BioPBS by PTT MCC Biochem.

3.2. Poly(ϵ -caprolactone) (PCL)

PCL can be prepared by ring-opening polymerization of the cyclic ester, ϵ -caprolactone. PCL is a moderately rigid plastic at room temperature. The glass transition temperature, crystallization, and melting points of PCL are –60 °C, 28 °C, and around 60 °C, respectively.¹³⁶ The low melting point, slow rate of biodegradability, and compatibility with other plastics promote the application of PCL in the biomedical field, such as tissue engineering, sutures, wound dressing, and drug delivery.¹³⁷ For instance, PCL can be used in long-term drug-delivery devices due to its slower biodegradation rate. Furthermore, the kinetics of degradation and mechanical properties of PCL can be tailored by blending with other plastics. Blending starch with PCL not only improves the biodegradability of PCL but also reduces the production cost of the plastics.¹³⁸

3.3. Poly(hydroxy alcanoates) (PHAs)

PHAs are a type of Bioplastic that can be categorized into three main subsets based on their chain length. The first subset has a short chain length of 3–5 carbon atoms, the second subset has

Table 4. Biodegradability of Biodegradable Plastic According to the Literature^a

	PBS	PCL	PBAT	PLA	PHB
Biodegradation in soil ^b	85.1% after 150 days ²⁰²	99% after 136 days ¹⁸³	21% after 180 days ²¹	16% after 180 days ⁷¹	99% after 136 days ¹⁸³
Biodegradation in industrial compost ^c	90% after 207 days ¹⁸³	90% after 45 days ¹⁸³	92% after 90 days ²⁰³	90% after 70 days ¹⁸³	90% after 45 days ¹⁸³
Biodegradation in home compost ^d	N/A	90% after 88 days ¹⁸³	N/A	N/A	N/A
Biodegradation in seawater ^e	1% after 28 days ¹⁸⁴	50% after 56 days ¹⁸³	7% after 42 days ^{h 204}	1% after 28 days ¹⁸⁴	65% after 35 days ^{h 205}
Biodegradation in aqueous (Aerobic) ^f	2% after 117 days ¹⁶¹	77.6% after 117 days ¹⁶¹	2% after 117 days ¹⁶¹	2% after 117 days ¹⁶¹	83.0% after 117 days ¹⁶¹
Biodegradation in aqueous (Anaerobic) ^g	3.1% after 77 days ¹⁶¹	4.5% after 77 days ¹⁶¹	2% after 77 days ¹⁶¹	4.6% after 77 days ¹⁶¹	83.9% after 77 days ¹⁶¹
Applications	Packaging, coating film	Long-term items, agricultural film	Bags, mulching film	Food container, compost bag	Bottle, bag, wrapping film

^aThe geometry of the samples used in these studies differed which will influence the biodegradability rate. ^bISO 17556 (Aerobic degradation in soil at 25 °C). ^cISO 14855 (Aerobic degradation in industrial composting conditions at 58 °C). ^dISO 14855 (Aerobic degradation in home composting conditions at 28 °C). ^eASTM D6691 (Aerobic degradation in seawater at 30 °C). ^fISO 14852 (Aerobic degradation in aqueous at 28 °C) after 117 days. ^gISO 14853 (Anaerobic degradation in aqueous at 35 °C) after 77 days. ^hWeight loss.

a medium chain length of 6–14 carbon atoms, and the third subset has a long chain length of 15 or more carbon atoms.¹³⁹ Poly(hydroxybutyrate) (PHB or Poly(3-HB)) and poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBH) are two of the most well-known PHAs. Both plastics are considered short-chain PHAs and represent the most basic forms commercially available from many manufacturers. For instance, PHB is produced by Danimer Scientific, and PHBH is supplied by 6 companies, including Kaneka.^{60,140} In addition to PHB and PHBH, there are several other types of PHAs, such as poly(3-hydroxybutyrate-*co*-3-hydroxyoctanoate) (PHBO), poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHx), poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHBV), and poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (PH4B). Tianan Biologic Material is the only supplier for PHBV, containing ~1% of 3-hydroxyvalerate, and there are other companies that work on the commercialization of PHBV production. Similarly, PH4B is currently supplied by two manufacturers.

It can be of critical importance to review the properties and synthesis of PHB because advanced PHAs utilize PHB as a platform to improve thermal and mechanical properties by copolymerization or additives. PHB is a semicrystalline, isotactic polymer, which can be produced through various methods, such as bacterial fermentation, direct copolymerization of propylene oxide and carbon monoxide, and ring-opening polymerization of β -butyrolactone.¹⁴¹ Generally, PHB has been synthesized by the bacterial fermentation process since it can yield high molecular weight PHB. This requires polymer separation from the bacterial culture after cell lysis. The molecular weight of PHB depends on the sort of microorganism, cultivation conditions, and method of extraction. After polymer extraction, PHB becomes more brittle because of recrystallization by aging at room temperature.¹⁴² Therefore, plasticizers and nucleating agents that can affect the rate of crystallization have been studied to improve the flexibility and elongation of PHB-derived products.^{143,144} Coates et al. developed an alternative approach for high molecular weight PHB via one-pot tandem catalytic transformation in which β -butyrolactone was synthesized from propylene oxide and carbon monoxide and thereafter polymerized *in situ*.¹⁴⁵ Coates et al. achieved PHB with number-average molecular weight (M_n) of 52,000 Da and removed the need to separate toxic β -butyrolactone intermediate.¹⁴⁵ PHB is a nontoxic, thermoplastic polymer that is insoluble in water and resistant to hydrolysis but has poor resistance to acids and bases. Barrier properties of PHB, such as oxygen transmission rate and water vapor transmission rate, are higher than those of other compostable plastics, such as PLA.¹⁴² Biodegradability, better barrier properties, and nontoxicity of PHB suggest that it can be used in the packaging industry¹⁴⁶ and biomedical fields.¹⁴⁷ An issue with PHB is that it has a restricted processability window, namely, a small difference between the melting point and the decomposition temperature. As a result, PHB is sensitive to thermal deterioration. To modify processability, copolymers of 3-hydroxy butyrate (3HB) and 4-hydroxy butyrate (4HB) or 3-hydroxyhexanoate (3HHx) have been developed.¹⁴⁸

Poly(3-hydroxypropionate) (poly-3HP) is another member of the group of PHAs. Poly-3HP can be synthetically produced by anionic ring-opening polymerization of β -propiolactone that was synthesized from ethylene oxide over a bimetallic catalyst.¹⁴⁹ The thermolysis of the poly-3HP can be used to provide highly pure acrylic acid for the production of

superabsorbent polymers (SAPs).¹⁵⁰ The melting point, glass transition temperature, Young's modulus, and tensile strength of poly-3HP are 77 °C, -20 °C, 0.3 GPa, and 27 MPa, respectively.^{151,152} In contrast to PHB, poly-3HP is not brittle, so it can be used as a plasticizer in blends to improve their properties.¹⁵³ Poly 3HP from lactone monomers has been produced by Novomer.¹⁵⁴ According to the company, their poly 3HP (Rinnovo 3HP H1000 XP) can be used for packaging films, agricultural films, and waste collection, which can be an alternative to conventional plastics including PE, PP, and PET. In 2021, Danimer Scientific acquired Novomer to commercialize this technology.¹⁵⁵ In recent decades, there have been several trials to develop plastics in the natural PHAs category that have superior material properties for practical application with biodegradability. One example is a copolymer, poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate), with the acronym of PHBH. Recent advances in bioengineering enabled the genetic modification of microorganisms and the synthesis of PHBH with various composition of 3HH from 0.07 to 62 mol % from natural resources, such as palm oil, sucrose, fructose, and soybean oil.¹⁵⁶ The adjustable mechanical properties, classical processing behavior, enhanced barrier properties, and biodegradability of PHBH allow the application of PHBH in the manufacturing of packaging, disposable items, and agricultural items.¹⁵⁶ These engineered PHAs can have improved properties, such as flexibility, thermal stability, and biodegradability, and broaden the processing window, making them attractive for different applications and becoming possible alternatives for conventional plastics in environmental settings.⁶⁰

3.4. Poly(butylene adipate-*co*-terephthalate) (PBAT)

PBAT is a flexible aromatic–aliphatic polyester. PBAT is synthesized using 1,4-butanediol, terephthalic acid, and adipic acid by esterification and transesterification reactions. The synthesis of PBAT involves several steps in sequential reactors with increasing temperature and vacuum levels that suppress side reactions, such as hydrolysis.¹⁵⁷ By introducing chain extenders and branching agents, PBAT molecular weight, melting point, and mechanical properties are modified. The composition of terephthalate in PBAT affects the mechanical properties and biodegradability. A maximum 20 mol % composition of terephthalate can improve mechanical properties of PBAT without sacrificing biodegradability.¹⁵⁸ Due to the combination of mechanical properties and biodegradability, PBAT and its related products have been commercialized by several companies, including BASF, Kingfa, and Eastman, who later sold their business to Novamont. PBAT has been applied in the packaging industry as an alternative to LDPE. Commercial PBAT has a melting point between 110 and 120 °C, tensile strength of 35–44 MPa, elastic modulus of 95–80 MPa, and elongation at break of 560–710%. We note that mechanical properties are highly dependent upon crystallinity and orientation, which depends on the fabrication process. The thermal properties of PBAT depend on its composition. The melting point increases from 79 to 137 °C as the terephthalic acid component increases from 31 to 48 wt %.¹⁵⁹ PBAT is a compostable plastic as studies indicate that PBAT (BASF Ecoflex) can be totally depolymerized by *Thermomonospora fusca*, a thermophilic bacteria strain isolated from compost.¹⁶⁰ PBAT degrades in the soil and composting conditions, but its degradation in marine, fresh water, aerobic digestion, and landfill settings has not been proven.¹⁶¹ Further

research is needed to better understand the environmental fate of PBAT and its potential as a sustainable material.

3.5. Poly(lactic acid) (PLA)

PLA is produced from the ring-opening polymerization of a cyclic lactide dimer, which has three stereoisomers including (−,−)-lactide, (+,+)-lactide, and (±)-lactide.¹⁶² The composition of the lactide isomers can change the properties of PLA. Bulk and melt polymerization with nontoxic catalysts, based on tin, zinc, iron, and aluminum, are used for commercial-scale production of PLA. Temperature and time of polymerization affect the molecular weight of the plastics and the reaction kinetics. Plastic additives can function as chain transfer agents, and the molecular weight of PLA is affected by the additives, containing functionalities such as hydroxyl groups.¹⁶² The composition of stereoisomers determines the crystallinity of PLA. For example, >93% of (−)-lactic acid unit yields a semicrystalline structure, whereas 50–93% of (−)-lactic acid unit results in an amorphous structure. Addition of (+,+)-lactide and (±)-lactide decreases the degree and rate of crystallization.¹⁶²

The rate of crystallization decreases as the polymeric structure is more disordered and the quenching time increases. The glass transition temperature and melting point of PLA have been reported to be 50–80 °C and 130–180 °C, respectively.¹⁶² The PLA complexes with stereoisomers (i.e., (−) and (+)-lactic acid) have a 230 °C melting point, and this stereocomplex PLA can provide better melting and mechanical properties for fiber and textile application than pure PLA. Annealing conditions can affect thermal and mechanical properties of PLA.¹⁶³ PLA is soluble in many organic solvents, such as chloroform, dioxane, dioxolane, furan, acetone, pyridine, ethyl lactate, tetrahydrofuran, xylene, ethyl acetate, dimethylformamide, and methyl ethyl ketone, while it is insoluble in water, alcohols, and alkanes.¹⁶⁴ CO₂ permeability coefficient of PLA is lower than that of polystyrene but higher than that of PET. Higher degree of crystallization decreases vapor permeability because the gas diffusion occurs predominantly through the amorphous region of a polymer. Similar to typical plastics, O₂ permeability coefficient of PLA film, containing 98% (−,−)-lactide unit, is improved by increasing the temperature. The modulus and elongation at break of commercial PLA, consisting of 92% of (−,−)-lactide and 8% of (±)-lactide, were reported to be 2.1 GPa and 9%, respectively. Addition of plasticizer can decrease the modulus to 0.7 MPa and increase the elongation at break to 200%. Thus, the mechanical properties of PLA are significantly tunable by material formulation.¹⁶⁵

PLA can be thermally, biologically, and chemo-catalytically degraded. Thermal decomposition of PLA produces cyclic oligomers, lactides, acetaldehyde, acrylic acid, CO₂, and CO at 230–260 °C.¹⁶⁶ Biotic degradation of PLA in the presence of enzymes, such as proteinase K and Pronase, as well as pH, contributes to enzymatic hydrolysis.¹⁶⁷ Acids or bases decompose PLA to oligomers, and microorganisms convert the oligomers to CO₂ and H₂O. Biodegradability of PLA has led it to be used in several biomedical applications. For example, PLA is used to produce fracture fixation materials such as screws, plates, and sutures. PLA fracture fixation materials are biologically decomposed and resorbed in the human body. Mechanical properties of PLA can be used to produce environmental packaging, such as containers, drinking cups, wrappings, lamination films, and water bottles.

3.6. Poly(glycolic acid) (PGA)

PGA is the simplest aliphatic polyester and can be produced by polycondensation of glycolic acid or the Sn-catalyzed ring-opening polymerization of glycolide, a cyclic dimer of glycolic acid.¹⁶⁸ Multifunctional comonomers, such as trimethylolpropane and pentaerythritol, have been introduced to decrease melting point and viscosity to benefit coextrusion and coinjection molding applications.¹⁶⁹ PGA has a melting point of crystalline at 220 °C and a glass transition temperature of 40 °C. PGA has been shown to completely biodegrade in 30 days when tested according to ASTM D6400 because it is susceptible to hydrolysis.¹⁷⁰ The biodegradability of PGA enables its application in the commercial production of fabricated articles, which can be used in downhole drilling and synthetic absorbable sutures.^{170,171} Among aliphatic polyesters, PGA and its copolymers have sufficiently low oxygen transmission rates to be useful in some food packaging applications.¹⁷² The minimization of acidic end groups in PGA and addition of a catalyst deactivator can suppress the rate of hydrolytic degradation and improve the hydrolysis resistance of PGA.¹⁷³

3.7. Blended Biodegradable Plastics

Biodegradable polymers blended with additives or different types of biodegradable/compostable plastic can improve not only polymeric properties, such as mechanical and thermal properties, but also biodegradability. Addition of other biodegradable/compostable plastic or fillers, such as montmorillonites,¹⁷⁴ cellulose nanocrystals,¹⁷⁵ and coffee grounds,¹⁷⁶ improves the tensile strength and modulus of biodegradable plastic. In Table 3, PBAT has relatively lower tensile modulus (65–90 MPa) and higher elongation at break (500–800%) than other commodity plastics, which have desired properties for soft materials such as films and bags. Blending of PLA (40 wt %) with PBAT (60 wt %) improves tensile modulus of PBAT from 73 to 1,320 MPa and the elongation at break from 3.7 to 183%.¹⁷⁷

The addition of natural fillers also increases the biodegradability of PBAT. 3 wt % addition of cellulose nanocrystals into a PBAT matrix enhances the rate of biodegradability in soil.¹⁷⁸ The control of filler dispersion in a PBAT matrix by modifying the surface of the fillers can lead to the production of green materials.¹⁷⁹ Addition of natural polymers (e.g., starch) can reduce the production costs of biodegradable plastics and improve the sustainability of the production processes. The increased hydrophilicity can improve the degradation rate of hydrophobic plastics when starch is blended with the plastics. However, the blending of starch and plastics can cause a phase separation due to the limited adhesion between the interfaces, which lead to poor polymeric properties.¹⁸⁰ To overcome this issue, organic substances such as potassium sorbate, ascorbic acid, chitosan, and cinnamaldehyde have been used to increase interfacial adhesion. As an example, a bilayer film comprising a layer of PCL and a layer of starch blended with 5 wt % PCL showed good mechanical performance when potassium sorbate was added at the layer interface.¹⁸¹ These adhesive agents also have antimicrobial and antioxidant properties. Sousa et al. confirmed that the biodegradable films made from PBAT, rice flour, and glycerol containing potassium sorbate enhanced the microbiological safety of fresh lasagna.¹⁸² The blending of semicrystalline natural PHAs with amorphous PHAs, such as PH4B (50/50 = 3-HB/4-HB) or PHBH (30% of 3-hydroxyhexanoate), yielded materials with higher elongation

	Controlled environments			Uncontrolled environments			
	Standard	ISO 14855	ISO 15985	ISO 14855	ASTM D6691	ISO 14851	ISO 14853
Medium	Industrial composting	Anaerobic digestion	Home composting	Marine	Fresh water	Anaerobic aqueous digestion	Soil
PLA/PCL (80/20)	Pass	Pass	Pass	Fail	Fail	Fail	Fail
PLA/PBS (80/20)	Pass	Pass	Pass	Pass	Pass	Pass	Pass
PLA/PHB (80/20)	Pass	Pass	Pass	Pass	Pass	Pass	Pass
PLA/PHO (85/15)	Pass	Pass	Pass	Pass	Pass	Pass	Pass
PHB/PHO (85/15)	Pass	Pass	Pass	Pass	Pass	Pass	Pass
PHB/PCL (60/40)	Pass	Pass	Pass	Pass	Pass	Pass	Pass
PHB/PBS (50/50)	Pass	Pass	Pass	Pass	Pass	Pass	Pass
PCL/PHO (85/15)	Pass	Pass	Pass	Pass	Pass	Pass	Pass
PCL/TPS (70/30)	Pass	Pass	Pass	Pass	Pass	Pass	Pass
PLA (Polylactic acid)	Pass	Pass	Pass	Pass	Pass	Pass	Pass
PCL (polycaprolactone)	Pass	Pass	Pass	Pass	Pass	Pass	Pass
PBS (polybutylene succinate)	Pass	Pass	Pass	Pass	Pass	Pass	Pass
PHO (polyhydroxy octanoate)	Pass	Pass	Pass	Pass	Pass	Pass	Pass
PHB (Polyhydroxy butylate)	Pass	Pass	Pass	Pass	Pass	Pass	Pass
TPS (thermoplastic starch)	Pass	Pass	Pass	Pass	Pass	Pass	Pass

Pass Fail

Figure 9. Biodegradation capacity of several plastics in controlled and uncontrolled environments tested following international biodegradation standards.¹⁸³ “Pass” represents that plastic passed the appropriate test.

and lower modulus than natural PHAs, and these blended PHAs enable the 3D printing technology to mold the plastics.

Narancic et al. investigated the effect of blending biodegradable and compostable plastics on the biodegradation in different mediums.¹⁸³ Figure 9 shows the biodegradability of PLA, PHB, PHO (polyhydroxyoctanoate), PBS, TPS (thermoplastic starch), and PCL with standardized biodegradation tests (ISO and ASTM; see Table 1).¹⁸³ Narancic et al. conducted the standardized biodegradation tests for biodegradable plastics, compostable plastics, and their blends in controlled (industrial composting, anaerobic digestion, and home composting) and uncontrolled environments (seawater, fresh water, aquatic anaerobic digestion, and soil).¹⁸³ Narancic et al. reported a binary result (either pass or fail) for the different test methods, based on the validity criteria, which were 90% relative biodegradation of the reference material (cellulose) for each plastic within the specific durations. All tested plastics and blends were biodegradable in the controlled industrial composting facility but exhibited poor biodegradability in soil and aquatic environments. Interestingly, Narancic et al. observed that, although PLA is generally not home-compostable, blends with PCL can be biodegradable under home-composting conditions. At the same time, blends of PLA and PHB were not home compostable.

4. CONSIDERATIONS FOR FUTURE BIODEGRADABLE PLASTICS

4.1. Synthesis of Monomers from Lignocellulosic Biomass

Biomass-based monomers have a high composition of oxygen and nitrogen atoms in their molecular structures. The intermolecular bonds (e.g., ether, ester, amide), containing oxygen and nitrogen atoms, are favorable bonds to be digested by the metabolism of microorganisms, but the bonds are difficult to obtain from petrochemicals. Thus, even though the use of biomass-derived monomers does not guarantee the production of biodegradable plastics, one option to create new types of sustainable plastics is to use monomers from biomass-based sources, which can possess higher biodegradability and provide unique properties. During the last several decades, approaches to produce a wide variety of new biomass-based monomers have been developed. Table 5 shows several monomers that can be produced from biomass. 5-Hydroxymethylfurfural (HMF) can be produced from the dehydration of fructose.²⁰⁶ Selective hydrogenation of HMF produces furandimethanol (FDM) and tetrahydrofurandimethanol (THFDM) as diols.²⁰⁷ Oxidation of HMF yields furandicarboxylic acid (FDCA) as a diacid.²⁰⁸ Cellulose can be dehydrated to levoglucosanone (LGO). LGO can be converted to 1,2,5,6-hexanetetrol by hydrogenation and

Table 5. Monomers from Biomass-Derived Platform Chemicals^{207,210,212–218}

Product	Chemical structure	Feed	Reaction conditions	Catalyst	Yield (%)
1,5-pentanediol ²¹⁰		Furfural	Multi-steps ^a	Ni/SiO2, Ru/C, γ -Al2O3, NaOH	97.5
HMF-Acetone-HMF dimer (HAH) ²¹²		HMF	50°C in water for 1 hours		86.3
Partially hydrogenated HAH ²¹³		HAH	120°C in IPA/water under 30 bar H2	Cu/Al2O3	84
Fully hydrogenated HAH ²¹⁴		HAH	120°C in IPA under 30 bar H2	Ru/C	93
Tetrahydrofuran-2,5-dimethanol ²⁰⁷		HMF	100°C in MeOH under 82 bar H2 for 16 hours	Ru/MnCo2O4	97.3
2,5-Furandimethanol ²⁰⁷		HMF	100°C in MeOH under 82 bar H2 for 4 hours	Ru/MnCo2O4	98.5
1,2,5,6-Hexanetetrol ²¹⁵		Levoglucosanone	150°C in water under 35.5 bar H2 for 6 hours	Pt/SiO2-Al2O3	91
2,5-furandicarboxylic acid ²¹²		HMF	110°C in GVL/water under 40 bar O2	Pt/C	93
Tetrahydrofuran-2,5-dicarboxylic acid ²¹⁶		HMF	110°C in water under 30 bar air for 7 hours	Au/hydrotalcite	91
Levulinic acid ²¹⁷		HMF	120°C in water-MIBK biphasic system for 35 minutes	HCl with ScCl3	95.6
1,6-hexanediol ²¹⁸		HMF	Multi-steps ^b	Raney-Ni, Rh-Re/SiO2 with Nafion SAC-13	86
Caprolactone ²¹⁸		1,6-hexanediol	Reflux in MIBK for 30 minutes	[Ru(cymene)Cl2]2 with 1,1'-bis(diphenylphosphino)ferrocene	>99

^aFurfural is converted into tetrahydrofurfuryl alcohol (140 °C under 1 bar H₂ over Ni/SiO₂ for 3600 s with 94.3% yield), tetrahydrofurfuryl alcohol is converted into dihydropyran (375 °C under 1 bar H₂ over γ -Al₂O₃ for 22 s with 86.8% yield), dihydropyran is converted into 2-hydroxytetrahydropyran (130 °C under 16 bar H₂ for 7200 s with 94.3% yield), and 2-hydroxytetrahydropyran is converted into 1,5-pentanediol (120 °C under 66 bar H₂ over Ru/C for 645 s with 97.5% yield).²¹⁰ ^bHMF is converted into tetrahydrofuran-2,5-dicarboxylic acid in ethanol (100 °C under 90 bar H₂ over Raney-Ni (10 wt % Ni loading) for 14 h with 100% yield), and tetrahydrofuran-2,5-dicarboxylic acid is converted into 1,6-hexanediol in ethanol (80 °C under 80 bar H₂ over Rh-Re/SiO₂ with Nafion SAC-13 for 20 h with 86% yield).²¹⁸

hydrolysis.²⁰⁹ The tetrol can play a role of cross-linker, and the control of tetrol and diadic acid ratio can produce polyesters that have unique morphologies. Furfural from hemicellulose fraction is converted to 1,5-pentanediol (PDO) by hydrogenolysis, and the technology is being commercialized by Pyran.^{210,211}

4.2. Effect of Biomass-Derived Monomers on Polymeric Properties

4.2.1. Effect of 2,5-Furandicarboxylic Acid (FDCA) on Polymeric Properties. The furan moiety is a common functional group in these biomass monomers which creates new functionality in the polymer. 2,5-Furandicarboxylic acid (FDCA) has been used to synthesize polyamides²¹⁹ and polyesters²²⁰ for the production of performance-advanced plastics.²²¹ One example is poly(ethylene 2,5-furandicarboxylate) (PEF), produced from FDCA and ethylene glycol. The PEF has been reported as a promising substitute for PET. PEF has unique or enhanced properties, involving mechanical and barrier properties, due to the furan functionality. The lone electron pairs in the oxygen atom of the furan ring are involved in a resonance with π bonds in diene and *p*-orbital; thereby, the furan ring has 0.70 D of dipolar moment from the ring to oxygen atom.²²² The molecular structure of FDCA (angle between dicarboxylic acid: 129 °) is less linear compared to terephthalic acid (angle between dicarboxylic acid: 180 °).²²³

Nonlinear structure and lower aromaticity result in lower covalent strength in PEF chain axis than PET and contributes 16% shorter interatomic distance (4.83 Å) between the two carboxylic acid groups than terephthalic acid (5.73 Å).²²⁴ The energetically favorable conformation of PEF is the combination of anti FDCA (carbonyl oxygen is away from the furanic oxygen) and gauche ethylene glycol (60 ° dihedral angle), which forms a coiled-helix conformation.²²⁵ The absence of linearity and the coiled-helix conformation reduces the chain packing efficiency.²²⁶ The lower chain packing in PEF gives the improved Young's modulus of PEF (2.0 GPa) compared to PET (1.3 GPa).^{227,228} The coiled-helix conformation restricts mobility of the repeating units in amorphous PEF and contributes to the glass transition temperature of PEF being higher than that of PET.²²⁹ Even though the dipole moment of the furan ring increases CO₂ absorption compared to PET, the mobility constraint in the PEF chain significantly decreases the permeability of CO₂, O₂, and H₂O by 19, 11, and 2.2 times versus PET.²³⁰ Accordingly, PEF has superior mechanical and barrier properties compared to PET for bottle applications. PEF is also more biodegradable than PET. As reported by Avantium,²³¹ the degradation rate of weathered PEF and unweathered PEF reached 90% in the industrial composting system (58 °C) after 240 days and 385 days, respectively, while the biodegradation rate of PET was below 5% after 240 days.

Weinberger et al. studied the enzymatic hydrolysis rate for both PEF and PET with *Humicola insolens* cutinase.²³² PEF films were degraded 1.7 times faster than PET films. This also suggests that the use of furan functionality in other polyesters can provide improved biodegradability.

Lotti et al. synthesized furan-based polyesters using FDCA as a diacid, such as poly(butylene 2,5-furanoate) (2,5-PBF), poly(butylene 2,4-furanonate) (2,4-PBF), poly(hexamethylene 2,5-furanoate) (PHF), poly(propylene 2,5-furanoate) (PPF), and poly(pentamethylene 2,5-furanoate) (PPeF).^{233–235} PPF and 2,5-PBF were found to be acceptable for rigid packaging with superior CO₂ barrier properties compared to PET. PHF could be used in rigid packaging that can maintain an atmosphere rich in O₂ and poor in CO₂. Thus, these polyesters could be suitable for use in food packaging films. Ethylene vinyl alcohol (EVOH) is one of the most commonly used gas barrier materials in multilayer food packages, but it is a petroleum-based material having a relatively low degradability.²³⁶ Other than FDCA, furan-based monomers, vegetable oils, and polysaccharides have been used for the production of polyesters.²³⁷

4.2.2. Effect of 1,5-Pentandediol (PDO) on Polymeric Properties. Biomass-derived 1,5-pentanediol (PDO)-based polymers, including thermoplastics, have drawn increasing attention from both academia and industry to replace petroleum-derived diols.^{210,238–240} PDO-based aliphatic polyesters have been synthesized using various aliphatic dicarboxylic acids with different chain lengths (carbon number: 4, 5, 6, 7, 9, 10, 12).²⁴¹ The crystallinity and melting point increased with the chain length of the diacid unit. The melting point increased overall with carbon number in dicarboxylic acids (from 24 to 62 °C) except for poly(pentylene glutarate) that exhibited a lower melting point. The tensile modulus increased from 254 to 344 MPa when carbon number of diacids increased from 9 to 12, which is attributed to higher crystallinity as measured by wide-angle X-ray diffraction.²⁴¹ These aliphatic polyesters have tensile properties comparable to those of linear low-density polyethylene. However, the ease of hydrolysis and low melting point may limit their applications. Previous studies showed that terephthalate esters exhibited decreasing melting temperatures and glass transition temperatures with increasing diol carbon length (carbon number: 2, 4, 5, 6, 10), while poly(pentylene terephthalate) (PPT) had a lower melting temperature than terephthalate esters synthesized from 1,4-butanediol and 1,6-hexanediol.^{242,243}

PPT crystallizes slowly from the melting state under both nonisothermal and isothermal crystallization conditions. The crystallinity is higher at lower cooling rates while undergoing nonisothermal crystallization. For instance, the values of crystallinity increased from 0.7 to 17.3% by decreasing the cooling rate from 15 to 5 °C/min. The crystallization half-time ($t_{1/2}$) became longer at higher crystallization temperatures. The values of $t_{1/2}$ were measured to be 3.9 min (at 60 °C) and 17.4 min (at 100 °C) when the values of crystallinity were 21% and 22%, respectively.²⁴⁴

Aliphatic-aromatic polyesters are important copolymers due to the combination of superior thermomechanical properties and biodegradability. PDO-based polyesters, such as poly(pentylene adipate-*co*-terephthalate) (PPAT), poly(pentylene succinate-*co*-terephthalate) (PPST), and poly(ethylene furandicarboxylate-*co*-pentylene furandicarboxylate) (PEPF), have been synthesized and investigated. The crystallinity of

PPAT and PPST increased when fractions of pentylene terephthalate¹⁵⁷ units were greater than 45 mol % and increased Young's modulus and tensile strength.^{245,246} PDO was used to modify the mechanical properties of PEF as the homopolymer has an inherently poor toughness. This PDO-containing PEPF showed the enhanced mechanical properties, such as tensile strength (83 MPa), O₂ barrier property (0.01–0.07 barrer), and elongation at break (115%), and can be compared with bottle-grade PET.²⁴⁷

5. CONCLUSIONS AND PERSPECTIVES

Biodegradable plastics are one of the solutions to improving the environmental sustainability of plastics. In contrast to commodity plastics, biodegradable plastics can be degraded where the degradation results from the action of naturally occurring microorganisms, such as bacteria, fungi, and algae. Biodegradation of plastics involves five main stages. Microorganisms physically adhere to the plastic polymer surface by forming a biofilm. After colonization, excreted enzymes by microorganisms can break down the intermolecular bonds, such as hydrogen bonds and van der Waals bonds, between polymer chains to produce small fractions. After deterioration of polymers, excreted enzymes continue to hydrolyze intramolecular bonds, such as covalent bonds (e.g., ester, ether, and amide) in the fractionated polymers into oligomers, dimers, or monomers, which can be transported across cellular membranes. After depolymerization, the plastic monomers, which are organic compounds composed of C, H, N, and O atoms, can be assimilated by the cells and catabolized through their metabolisms. Finally, the polymer's monomers are converted into CH₄, CO₂, and H₂O under anaerobic or aerobic conditions, respectively. The findings underscore that the molecular mechanisms and enzymes involved in plastic degradation are still being elucidated and that new types of plastics continue to be produced due to industrial and consumer use. In this context, it is important to deepen our understanding of the current biodegradation capabilities of microorganisms while also considering that microorganisms are evolving their degradation abilities to cope with new types of plastics. Therefore, more extensive and systematic research is needed, which can help us understand microbial–polymer interactions and devise strategies for a more sustainable future.

Biodegradability is complex and depends on the external conditions, especially different mediums (soil, compost, water, and marine) and part structure and geometry. Therefore, the development and design of plastics biodegradable in soil and ocean must be encouraged. Moreover, PHB, several of its copolymers, and TPS are degradable in not only compost but also soil and marine environments. However, some of them have poor mechanical properties compared to commodity plastics and even other biodegradable plastics. Thus, blended polymeric materials with biodegradable plastics or other additives are being developed, which have improved mechanical properties.

Finally, this review addresses recent research works on biomass-derived plastics that are chemically synthesized from green feedstocks and produce unique properties for supplying performance-advantaged materials. Biomass-derived monomers can effectively provide a range of oxygen-containing chemical functionalities, including furan rings, polyols, and multifunctional monomers. This functionality can be used to create new types of plastics with distinct properties. To achieve the ultimate goal, which is the substitution of petrochemical

plastics with renewable carbon-based biodegradable plastics, the development of biodegradable polymers using renewable carbon-based monomers should be continued. The improved biodegradation tests of the biomass-based biodegradable plastics are needed since there is a lack of understanding about the biodegradability of biomass-based polymers. Lastly, relying solely on biodegradable plastics is not sufficient to prevent environmental leakage. In the end, it is important to focus on changing people's behavior, specifically by reducing plastic usage and properly disposing of used plastics instead of littering. Simultaneously, it is also crucial to provide the necessary tools and facilities to encourage these desired behaviors, such as clear labeling on products and the availability of separate collection bins in close proximity.

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John Klier, Ph.D., serves as Dean of the Gallogly College of Engineering at the University of Oklahoma and professor in the School of Chemical, Biological and Materials Engineering. He joined OU from UMass Amherst where he served as professor and department head of Chemical Engineering for 5 years. Previously he spent 25 years at The Dow Chemical Company in technology and technical management roles. Responsibilities included leading Core R&D materials organization, Dow Coating Materials research and development organization, and the Performance Materials and Chemicals divisional research, development and technical service organizations. In 2014 he was named Distinguished Fellow, the highest technical position at Dow. Klier is a member of the National Academy of Engineering, National Academy of Inventors, and several professional organizations. Students and postdoctoral associates in the Klier group combine surfactant and functional polymer assembly and association phenomena with state-of-the-art processing technologies to produce new structured polymer, hybrid, and colloidal materials. They are applying these materials to address applications in collaboration with industrial, agency, and governmental partners.

Kevin Nelson is a Senior Fellow in Amcor's Global Core R&D Group. He received a B.S. degree in Chemical Engineering from the University of Wisconsin—Madison in 1979 and joined The Bemis Company immediately thereafter. Throughout his career, he has worked in areas related to polymer processing as well as the materials science aspects of food packaging design. His current focus relates to process/material and product/package interrelationships. Kevin has been awarded four Bemis President's Awards for Outstanding Technical Achievement and is an inventor on 25 U.S. patents.

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