

# Degradation Rates of Plastics in the Environment

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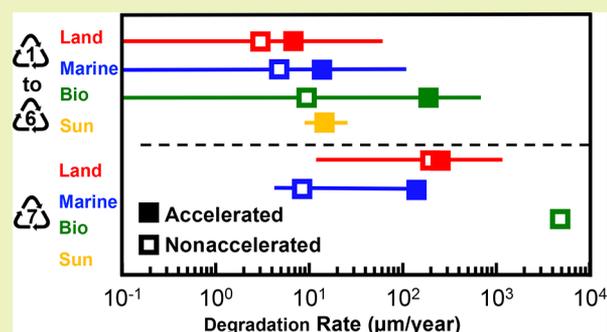
**ABSTRACT:** Plastic waste is currently generated at a rate approaching 400 Mt year<sup>-1</sup>. The amount of plastics accumulating in the environment is growing rapidly, yet our understanding of its persistence is very limited. This Perspective summarizes the existing literature on environmental degradation rates and pathways for the major types of thermoplastic polymers. A metric to harmonize disparate types of measurements, the specific surface degradation rate (SSDR), is implemented and used to extrapolate half-lives. SSDR values cover a very wide range, with some of the variability arising due to degradation studies conducted in different natural environments. SSDRs for high density polyethylene (HDPE) in the marine environment range from practically 0 to approximately 11  $\mu\text{m year}^{-1}$ . This approach yields a number of interesting insights. Using a mean SSDR for HDPE in the marine environment, linear extrapolation leads to estimated half-lives ranging from 58 years (bottles) to 1200 years (pipes). For example, SSDRs for HDPE and polylactic acid (PLA) are surprisingly similar in the marine environment, although PLA degrades approximately 20 times faster than HDPE on land. Our study highlights the need for better experimental studies under well-defined reaction conditions, standardized reporting of rates, and methods to simulate polymer degradation using.

**KEYWORDS:** Plastic waste, Polymer degradation rate, Commodity plastic, Biodegradable plastic, Environmental influences, Shape dependence

## INTRODUCTION

Synthetic polymers are made by linking together hundreds or thousands of organic subunits (“monomers”) via strong covalent chemical bonds. The first fully synthetic polymer, Bakelite (made by a condensation reaction of phenol with formaldehyde) dates to the early 20th century, but true mass production of polymers began only in the 1950s. Since then, global manufacturing has grown exponentially, reaching 380 Mt year<sup>-1</sup> in 2015.<sup>1</sup> Today, thousands of polymer grades are produced on commercial scales.<sup>2</sup> The largest market shares belong to low-cost, commodity thermoplastic polymers, henceforth referred to as “plastics.” They include polyethylene terephthalate (PET), high, low, and linear-low density polyethylene (HDPE, LDPE, and LLDPE), polyvinyl chloride (PVC), polypropylene (PP), and polystyrene (PS).

The vast majority of plastics produced today, including all of the aforementioned commodity polymers, are made from nonrenewable petrochemicals, so named because they are derived from fossil oil, natural gas, and coal. Although these plastics are inexpensive, each is a highly engineered material with precise physical properties. They can be molded into virtually any desired shape through rotation, injection, extrusion, compression, blowing, or thermoforming. Their material properties are adjusted during and/or after synthesis



to achieve the desired strength, permeability, porosity, opacity, and color. Polyolefins are particularly durable, due to their chemical and biological inertness, which is a result of their high molecular weight and hydrophobicity, and the absence of functional groups that are susceptible to attack by microbial enzymes, light, water, etc.<sup>3,4</sup> The recalcitrance and impermeability of these plastics make them ideal for applications such as food packaging, sterile medical uses, and construction, among others, but also make them particularly long-lived when they are discarded. Various antioxidants and stabilizers, which are used to prolong the working life of plastics, slow environmental degradation of plastics waste even further.<sup>1,5,6</sup>

Consequently, the very properties that make plastics so versatile for humans has also created an emerging threat to the environment.<sup>7</sup> Globally, only 18% of plastics waste are recycled, and 24% are incinerated. The remaining 58% are

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either landfilled or enter the natural environment, where plastics accumulate and persist for a long period of time.<sup>1</sup> In the United States, where the landfill rate for discarded plastics exceeds 75%, such polymers are now responsible for a significant fraction (19%) of all municipal solid waste.<sup>8</sup> At current growth rates, the accumulation of plastics waste in landfills and/or in the natural environment is projected to reach nearly 12,000 Mt globally by 2050.<sup>1,9</sup>

The amount of plastic waste entering the oceans has emerged as a major concern. Large-scale concentrated accumulations of plastics have been found in the South Pacific subtropical gyre and the Eastern Pacific Ocean gyre.<sup>10–12</sup> Even in a medium waste-to-debris conversion rate scenario, the total amount of plastics waste in the ocean is expected to grow from 50 Mt in 2015 to 150 Mt by 2025.<sup>13</sup> The sources of this material are highly correlated with the absence of effective waste management infrastructures. It has been estimated that nearly 90% of the plastics entering the ocean comes from just 10 rivers, all located in Asia or Africa.<sup>14</sup> Ocean plastic debris is associated with persistent organic pollutants (POPs), including polychlorinated biphenyls (PCB), pesticides, and polycyclic aromatic hydrocarbons (PAHs), due to the higher affinity of these hydrophobic molecules for plastics compared to their affinities for sediments or water.<sup>15,16</sup> Finally, nearly 700 marine species have been observed to interact directly with plastics marine debris through ingestion, entanglement, and/or smothering.<sup>17</sup>

There are often vast differences between plastics degradation rates reported in the peer-reviewed literature and those reported by the popular press. A few media reports acknowledge the deficit of knowledge about the degradation rates of plastics,<sup>18,19</sup> but more often, they present degradation times as known, despite the paucity of scientific evidence. Media estimates of degradation times for plastic bags tend to fall into one of two ranges: 10–20 years<sup>20</sup> or 500–1000 years,<sup>21</sup> while that for “plastic” bottles is reported as over 70 up to 450 years.<sup>21</sup> Some media have reported that “plastics” do not degrade at all.<sup>22</sup> In these claims, however, the type of plastics is often unclear, and the environmental conditions are not specified. Also, the extrapolation method is unknown. Each of these factors has a large impact on degradation times. Furthermore, scientific studies of plastics degradation times are evolving, and estimated lifetimes can change dramatically based on new evidence. For example, a recent study found that polystyrene exposed to sunlight degrades on much shorter time scales than the thousands of years in previous estimates.<sup>23</sup>

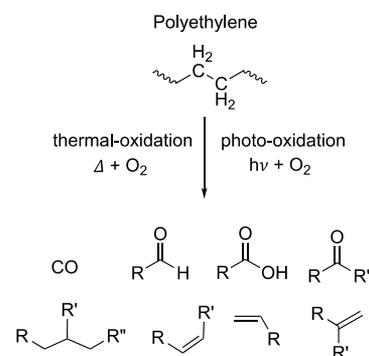
This study aims to present an overview of plastics degradation pathways in the environment and to summarize current knowledge about degradation rates for different types of commodity plastics under various environmental conditions. The results should help researchers and policymakers to more accurately describe the times needed for various plastics to degrade in the environment.

## ■ ABIOTIC DEGRADATION PATHWAYS

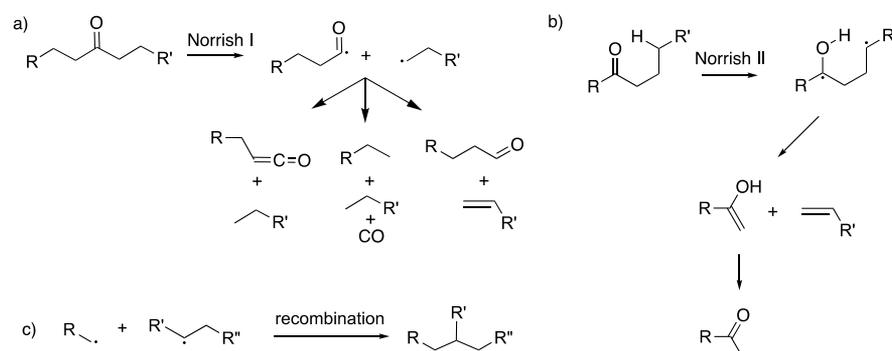
The environmental degradation mechanisms for plastics can be classified as either (i) physical, referring to changes in the bulk structure, such as cracking, embrittlement, and flaking, or (ii) chemical, referring to changes at the molecular level such as bond cleavage or oxidation of long polymer chains to create new molecules, usually with significantly shorter chain lengths. The potential environmental hazards associated with the soluble chemical byproducts of plastics degradation must be

considered,<sup>24</sup> as well as with the leaching of small molecules added during product formulation. Typically, chemical degradation at near-ambient temperatures in the environment involves either hydrolysis (requiring H<sub>2</sub>O) or oxidation (requiring O<sub>2</sub>), both of which can be accelerated by microbial action, heat, light, or combinations thereof.<sup>25,26</sup> In the sections below, we focus on natural abiotic processes that lead to the chemical degradation of polyethylene (PE), polyethylene terephthalate (PET), and polylactic acid (PLA). Although biotic degradation pathways are also undoubtedly important,<sup>27</sup> degradation is typically initiated abiotically (light, heat, acids, etc.).<sup>28,29</sup> Abiotic and biotic processes often work in tandem, with abiotic degradation leading to smaller molecules that are subsequently mineralized by microbes.<sup>30</sup> In this section, we focus on degradation pathways for PE, PET, and PLA due to the high relative number of studies of these plastics described later in this Perspective. Degradation mechanisms for other commodity plastics (including polyvinyl chloride (PVC),<sup>31,32</sup> polypropylene (PP),<sup>33–35</sup> and polystyrene (PS)<sup>36,37</sup>) have been reviewed elsewhere.<sup>38</sup>

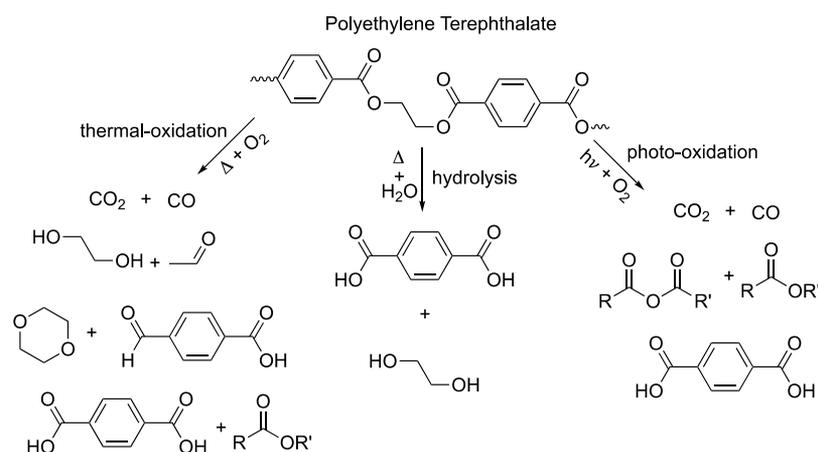
**Polyethylene (PE).** Although PE is the most inert of the polyolefins, it does degrade slowly in the natural environment. The backbone chains of PE are constructed exclusively from C–C single bonds which do not readily undergo hydrolysis and which resist photo-oxidative degradation due to the lack of UV–visible chromophores. Adventitious impurities or structural defects that form in PE during its manufacturing, or during subsequent weathering,<sup>38</sup> can act as chromophores.<sup>39</sup> PE may also contain a small number of unsaturated (C=C) bonds in the main chain or at the chain ends (typically, vinyl groups in HDPE and vinylidenes in LDPE). These sites are readily oxidized by O<sub>3</sub>, NO<sub>x</sub>, or other tropospheric radicals, often to highly unstable hydroperoxides, which are then converted to more stable UV-absorbing carbonyl groups.<sup>40</sup> An increased rate of photo-oxidation was reported for LDPE, relative to HDPE, due to the higher frequency of reactive branch points in the low density polymer.<sup>41</sup> In the absence of sunlight, thermal oxidative degradation of PE does not occur at appreciable rates at temperatures below 100 °C.<sup>42</sup> Since the role of light in photo-oxidative degradation is only to initiate chain reactions,<sup>42</sup> similar product distributions are generated in both photochemical and thermal processes (Figure 1). In environments lacking both sunlight and oxygen (e.g., landfills), anaerobic thermal degradation is unlikely to proceed naturally due to the high temperatures required (≥350 °C).<sup>43,44</sup>



**Figure 1.** Common products in the thermal- and photo-oxidative degradation pathways for polyethylene (R, R', and R'' are polymer chains of variable length).



**Figure 2.** Photo-oxidative degradation of PE containing carbonyl impurities, via (a) a Norrish type I mechanism or (b) a Norrish type II mechanism. (c) Radical recombination to form cross-linked chains.<sup>38</sup> R, R', and R'' are polymer chains of variable length.



**Figure 3.** Small molecule products of the three common degradation routes in the environmental degradation of polyethylene terephthalate. R and R' are polymer chains of variable length.

The mechanism of photo-oxidative degradation begins when an excited state (localized at a carbonyl or other structural defect) in PE abstracts a hydrogen atom from the polymer backbone, generating a reactive carbon-based alkyl radical. The first step in the subsequent radical chain mechanism is the reaction of the alkyl radical with  $O_2$  to form a peroxy radical, which abstracts a hydrogen atom from another polymer chain (or from a distant site on the same polymer chain) to form a hydroperoxide and a new alkyl radical. Subsequent O–O bond scission in the hydroperoxide leads to alkoxy and hydroxyl radicals, each of which can abstract another hydrogen atom and generate a new alkyl radical. Finally, termination occurs through bimolecular radical recombination.<sup>24</sup>

Carbonyl defects introduced into polyethylene via oxidative reactions can also lead to Norrish Type I reactions (Figure 2a), in which photochemically induced homolytic cleavage leads to free radical intermediates, or Norrish type II reactions, in which intramolecular  $\gamma$ -H abstraction generates ketones and vinylidenes (Figure 2b).<sup>45,46</sup> Although HDPE, LDPE, and LLDPE all have nominally the same chemical compositions, they have very different degrees of crystallinity. The rate of degradation depends strongly on the amorphous fraction of the polymer. Thus, degradation is far slower for crystalline HDPE, whose lower chain mobility promotes radical recombination at the expense of radical propagation reactions.<sup>47</sup>

**Polyethylene Terephthalate (PET).** The chemical structure of polyethylene terephthalate (PET) consists of alternating ethylene glycolate and terephthalate subunits, linked via ester bonds. It therefore belongs to the class of

polymers known as polyesters. In the natural environment, PET can degrade by thermal oxidation, but hydrolytic cleavage and photo-oxidation initiated by UV light are more common under ambient conditions.<sup>48</sup> In particular, the low temperatures typical of the marine environment mean that floating plastics degrade primarily by slow, photo-oxidative degradation. When PET is landfilled, or sinks below the upper regions of the ocean penetrated by sunlight, the buried polymer obviously cannot undergo photodegradation. Under these conditions, slow thermal oxidative degradation and hydrolysis may occur together, or sequentially. If PET is landfilled in an oxygen-poor environment, anaerobic degradation is unlikely to occur naturally due to the high temperatures required ( $\geq 200$  °C).<sup>36</sup> The chemical products resulting from each of these processes are compared in Figure 3.

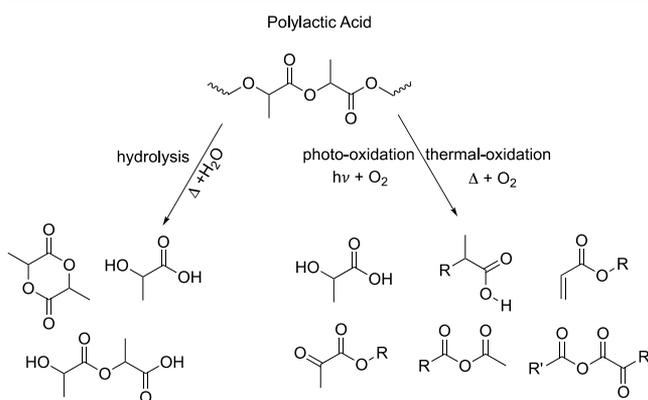
Hydrolysis of PET forms shorter carboxylic acid-terminated and alcohol-terminated chains, leading ultimately to terephthalic acid and ethylene glycol. In the near-neutral pH of the marine environment, hydrolytic cleavage of PET is very slow,<sup>49,50</sup> but the rate is strongly enhanced under acidic conditions.<sup>51</sup> In landfills, ester hydrolysis can induce a local drop in pH if the amount of moisture is insufficient to dilute the carboxylic acid products, resulting in autocatalytic acceleration.<sup>24</sup>

In the presence of  $O_2$ , thermal degradation may proceed via a free-radical mechanism, initiated when the  $\alpha$ -H of the ester is abstracted by an excited carbonyl group. The resulting carbon-centered radical reacts rapidly with  $O_2$  to give a peroxy radical which abstracts another  $\alpha$ -H to form a new hydroperoxide and

perpetuate the chain reaction. The final products are mostly small molecule carboxylic acids, aldehydes, and other oxygenates.<sup>52</sup> In the absence of O<sub>2</sub>,  $\alpha$ -H abstraction can also trigger the cleavage of ester linkages, resulting in carboxylic acid-terminated and vinyl-terminated chains. Subsequent anaerobic reactions generate small molecule oxygenates with higher overall aldehyde contents relative to the carboxylic acids.<sup>36,49</sup>

Degradation of PET initiated by photolytic cleavage of an ester bond results in the release of CO, CO<sub>2</sub>, terephthalic acid, anhydrides, carboxylic acids, and esters (Figure 3). As expected, higher yields of CO<sub>2</sub> are observed in aerobic environments.<sup>53</sup> Both aerobic and anaerobic photodegradations follow a Norrish type II mechanism (similar to that shown in Figure 2b), in which an excited state carbonyl abstracts an  $\alpha$ -H to yield carboxylic acid and vinyl chain ends. In the presence of O<sub>2</sub>, hydroxyl radicals formed by hydroperoxide O–O bond cleavage can react with the aromatic rings in the polymer backbone to form hydroxyterephthalate groups. Radical intermediates and products can recombine to form cross-links and new chromophores, which can lead to polymer embrittlement and discoloration (but not necessarily mineralization).<sup>24,49</sup>

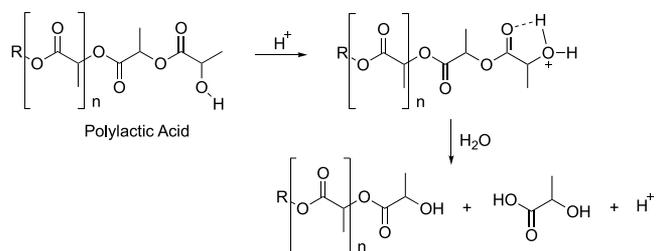
**Poly(lactic Acid) (PLA).** Bioderived polyesters such as PLA are interesting alternatives to petrochemical-based polyesters, due in part to their appreciable rates of degradation under industrial composting conditions (>60 °C, in the presence of O<sub>2</sub> and moisture).<sup>54</sup> Analogous to PET, PLA degradation typically proceeds through either hydrolysis or thermal-oxidative or photo-oxidative degradation (Figure 4). Degradation can also occur under anaerobic thermal conditions but only at temperatures much higher than those normally found in the natural environment ( $\geq 230$  °C).<sup>36,55</sup>



**Figure 4.** Common products in the hydrolytic and photo-oxidative degradation pathways of poly(lactic acid) (R and R' are polymer chains of variable length).

Slow hydrolysis of the PLA ester linkages occurs during exposure to moisture at temperatures of at least 30 °C, leading to the release of smaller oligomers and monomers.<sup>56</sup> The hydrolysis reactions initially take place in amorphous regions within the polymer,<sup>57</sup> where they lead to an increased concentration of carboxylic acid chain ends. PLA exposed to the resulting lower pH conditions experiences accelerated degradation due to autocatalysis<sup>58</sup> but ultimately yields the same lactic acid monomer (Figure 5).

PLA is unlikely to hydrolyze in marine environments, where the temperature rarely reaches 30 °C. Consequently, the predominant degradation pathway in marine environments is



**Figure 5.** Mechanism of PLA degradation by chain-end scission in acidic environments. Adapted from de Jong et al., 2001.<sup>58</sup>

photo-oxidative. The carbonyl group of PLA absorbs UV radiation below 280 nm, making the polymer susceptible to photodegradation.<sup>59</sup> The Norrish type II mechanism results in C–O bond dissociation, similar to PET and PE (Figure 2b).<sup>60</sup> Random chain scission nevertheless occurs more readily in amorphous regions, which experience less radical recombination than rigid crystalline regions.<sup>56,60</sup> In addition to the Norrish type II products, hydroperoxide intermediates arise from activation of the methine group of the PLA backbone and insertion of O<sub>2</sub>. They subsequently degrade to carboxylic acids, anhydrides, and diketones.<sup>61</sup> Analogous to PET, on land and in the presence of O<sub>2</sub>, thermal-oxidative degradation occurs through a free-radical mechanism and results in the similar product distribution to photo-oxidative degradation.<sup>56,62</sup>

## METHODS FOR ASSESSING PLASTICS DEGRADATION

The approaches reported for the analysis of plastics degradation can be grouped into methods associated with assessing the elimination of small molecules, methods which assess chemical changes (hydrophobicity, functional groups) in the polymer structure, and methods which record physical changes in materials properties (tensile strength, surface morphology, crystallinity, etc.).

**Assessing Bond Cleavage. Mass Loss.** The simplest and most direct way to quantify the extent of degradation of polymers involves measuring changes in their mass. Quantification of mass loss has been used to assess degradation in soil,<sup>63–66</sup> in compost,<sup>67,68</sup> and in microbially enriched lab settings.<sup>28,69–71</sup> Because degradation takes place at the surface, the rate of mass loss is closely related to (and is typically proportional to) the surface area of the plastic piece.<sup>72,73</sup> Partial conversion to small molecules (including but not limited to CO<sub>2</sub> and H<sub>2</sub>O) and their resulting volatilization or solubilization leads to a reduction in the mass of nonvolatile or insoluble polymeric material.<sup>74</sup> However, the overall mass loss convolutes the liberation of small molecules with the flaking of larger, insoluble pieces, including microplastics (0.5–5 mm) and mesoplastics (5–200 mm).<sup>25,75</sup> Our understanding of how plastics fragment and the generation of microplastics is far from complete. However, recent reports suggest that the shape of the plastic piece influences its fragmentation behavior in the ocean and that small pieces with low aspect ratios fragment faster because their isotropic motion inhibits biofilm development.<sup>76</sup>

Little or no mass loss may be observed in the initial phases of degradation.<sup>77</sup> Instead, the mass may actually increase at short exposure times due to oxygen incorporation and/or the attachment of microorganisms.<sup>78,79</sup> Clinging biomass and other debris can also accumulate in surface cracks and pits that develop during degradation. Thus, extremely long

experimental times are usually necessary to obtain meaningful results. Since mass loss measurements alone are not easy to interpret or extrapolate, it is desirable to combine this method with some of the other analytical techniques described below.<sup>80</sup>

**CO<sub>2</sub> Evolution.** CO<sub>2</sub> is the ultimate fate of carbon under aerobic polymer degradation conditions<sup>81–84</sup> (although polyesters can produce some CO<sub>2</sub> under anaerobic conditions).<sup>85,86</sup> Its formation is frequently used as an indicator of biological degradation. In anaerobic conditions, soluble carbon compounds are metabolized by methanogens or sulfate reducers, producing CH<sub>4</sub> and CO<sub>2</sub>, respectively.<sup>3,4</sup> The polymer degradation rate is inferred by measuring the CO<sub>2</sub> liberated during abiotic or biotic mineralization in a controlled environment.<sup>87–89</sup> CO<sub>2</sub> can be quantified by trapping and titration methods<sup>90</sup> or by analytical techniques such as gas chromatography with thermal conductivity detection (GC-TCD)<sup>84</sup> and IR spectroscopy.<sup>91</sup> The CO<sub>2</sub> yield is defined as in eq 1:

$$\text{CO}_2(\%) = \frac{n_{\text{CO}_2,\text{test}} - n_{\text{CO}_2,\text{control}}}{n_{\text{CO}_2,\text{theoretical}}} \times 100\% \quad (1)$$

where  $n_{\text{CO}_2,\text{test}}$  is the total accumulated amount of CO<sub>2</sub> product from polymer degradation,  $n_{\text{CO}_2,\text{control}}$  is the amount of CO<sub>2</sub> released in a blank experiment, and  $n_{\text{CO}_2,\text{theoretical}}$  is the total amount of CO<sub>2</sub> that would be liberated by complete mineralization of the polymer sample.<sup>92</sup> However, at short time scales, it is unlikely that polymer carbon is fully oxidized to CO<sub>2</sub>. Therefore, the use of CO<sub>2</sub> evolution as a probe to measure the kinetics of polymer degradation must be applied with caution.

**Gel Permeation Chromatography (GPC).** This method reveals changes in the molecular weight, an important parameter in polymer degradation, by size exclusion.<sup>89,93,94</sup> Reduction in the molecular weight of partially degraded polymers has been observed during both biotic and abiotic degradation processes, which increase the concentration of chain ends and can lead to mineralization of the smaller polymer chains.<sup>27</sup> GPC requires the polymer to be dissolved in a carrier solvent, which for polyolefins requires high temperatures. Care must be taken to ensure that dissolution of the polymer or the high-temperature measurement conditions do not cause further degradation.<sup>95</sup>

**Assessing Changes in Chemical Functionality.** *Chemical Analysis.* Nuclear magnetic resonance (NMR) and infrared (IR) spectroscopies can readily detect the presence and concentration of certain functional groups in polymers, even at low concentrations.<sup>96–99</sup> For example, <sup>13</sup>C CP/MAS NMR reveals the formation of cross-linked polymer chains (via a peak at 39.7 ppm) upon  $\gamma$ -irradiation of HDPE.<sup>100</sup> IR is particularly valuable for detecting polar functional groups, such as ketones and ester carbonyls (intense peaks at ca. 1715 and 1735 cm<sup>-1</sup>, respectively), which are typical of oxidative degradation pathways.<sup>101–104</sup> The extent of oxidation during degradation can be quantified from the change in absorbance for the carbonyl stretch relative to the C–H stretching modes,<sup>105,106</sup> although a recent study suggests that this Carbonyl Index may be less accurate than other modes, such as methyl deformation in the case of PP, to quantify the extent of oxidation.<sup>107</sup>

**Contact Angle.** Changes in the surface density of polar functional groups, for example, those formed during oxidative

degradation, cause changes in the surface energy, which are reflected in the contact angle with liquids.<sup>108,109</sup> Hydrophilic surfaces, with their high wettability, have higher surface energies and give lower contact angles with water. Thus, formation of polar functional groups in polymers due to environmental weathering effects (e.g., UV exposure) results in a decrease in contact angle. Increased hydrophilicity promotes the attachment of microorganisms to the polymer surface, further accelerating the degradation rate.<sup>110</sup>

**Assessing Changes in Materials Properties.** *Dynamic Mechanical Analysis (DMA).* This technique is typically used to characterize polymer strength. Changes in the tensile strength and elongation at break are also indicators of physical deterioration during polymer degradation.<sup>111,112</sup> Changes in these mechanical properties are associated with the formation of cracks and pores at the surface, as well as a reduction in molecular weight.<sup>113</sup>

*Thermal Analysis.* This method generally involves heating or cooling a sample at a controlled rate while monitoring its physical characteristics.<sup>114–116</sup> Differential scanning calorimetry (DSC) measures heat capacity ( $C_p$ ), melting temperature ( $T_m$ ), and glass transition temperature ( $T_g$ ).<sup>117</sup> A decrease in  $T_g$  during polymer degradation results from a decrease in the average chain length, due to the higher motility of shorter chains.<sup>118</sup> Thermal gravimetric analysis (TGA) records mass changes that occur upon heating. When coupled with product analysis, this method can provide information on the nature of the decomposition, such as oxidation or loss of volatiles, during thermal degradation.<sup>119</sup>

*Surface Analysis.* Surface modification of polymers during degradation can be detected with scanning electron microscopy (SEM) and atomic force microscopy (AFM).<sup>120–122</sup> These methods can directly image topographical changes at the polymer surface, such as the formation of holes and cracks, increases in roughness, or even attachment of microbes to the surface.<sup>123</sup> Typical changes in polymer morphology are visible as cracks and cavities; surface degradation and deterioration of HDPE films can be seen after 6 months in the marine environment.<sup>124</sup>

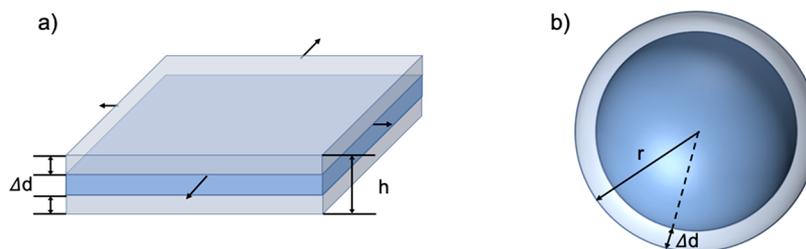
## ■ RATES OF PLASTICS DEGRADATION AND EXTRAPOLATED LIFETIMES

**Describing Degradation Rates.** In the literature, the term degradation may include depolymerization, chemical modification, alteration of physical properties, overall mass loss by any and all mechanisms, or complete mineralization to CO<sub>2</sub> and H<sub>2</sub>O. For the purposes of this study, we limit the definition of degradation to overall mass loss from the initial polymer piece. However, it must be noted that this definition is most appropriate for large plastic pieces. Recent studies suggest that surface ablation may be important for small plastic pieces in the marine environment.<sup>125</sup> Loss of microplastic or nanoplastic fragments reduces the initial mass, without changing the total amount of plastic present.

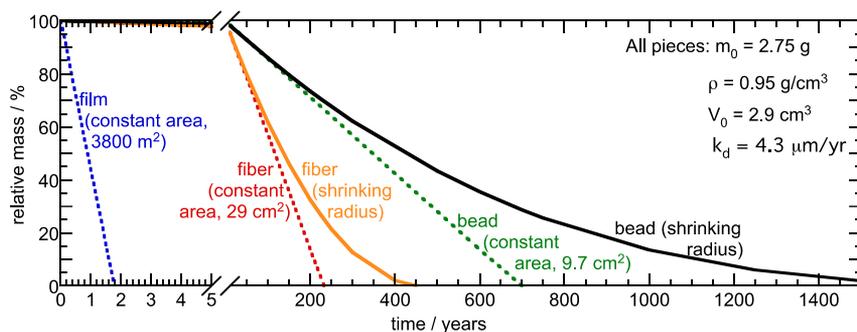
The polymer degradation rate,  $r_d$ , is the differential mass loss per unit time

$$r_d = -\frac{dm}{dt} = k \cdot SA \quad (2)$$

Since degradation occurs principally at exposed surfaces, we assume the degradation rate to be proportional to the surface area SA and the rate constant  $k$  to have dimensions kg s<sup>-1</sup> m<sup>-2</sup>. Therefore, the rate of degradation depends not only on the



**Figure 6.** Representative structures for (a) a section of a flat produce bag with total thickness  $h$  and (b) a sphere of radius  $r$ . The specific surface degradation rate (SSDR) is defined as the volume of material lost by removal of a layer of thickness  $\Delta d$  in a specified time.



**Figure 7.** Comparison of predicted degradation profiles for HDPE pieces with the same mass, density, and SSDR but different shapes (thin film, fiber, and bead). The dashed lines correspond to extrapolations assuming constant surface area; the solid lines correspond to a model which assumes the radius, and therefore the surface area, decrease over time.

intrinsic properties of the plastics (polymer type, molecular weight, fillers, etc.) and environmental conditions such as the temperature, presence of moisture and air, etc. but also on the extrinsic properties such as the size and shape of the material.

Samples with the same composition and mass but different surface areas can show very different rates. For example, a common HDPE produce bag has a thickness of 0.015 mm and dimensions of 25 cm  $\times$  38 cm, corresponding to a total (interior and exterior) surface area (SA) of ca. 3800 cm<sup>2</sup> and a volume ( $V$ ) of 2.9 cm<sup>3</sup> (Figure 6a). A spherical HDPE resin bead with a radius of 8.8 mm (Figure 6b) represents the same polymer volume but with a SA of only 9.7 cm<sup>2</sup>. If degradation takes place only at the polymer surface, with a rate that is linearly proportional to the SA,<sup>72</sup> the initial degradation rate for the bead will be nearly 400 times slower than that of the bag.

We define a surface degradation speed  $k_d$  with dimensions  $\text{m s}^{-1}$ , obtained by dividing  $k$  by the density  $\rho$  in  $\text{kg m}^{-3}$ . The rate law becomes

$$-\frac{dm}{dt} = k_d \rho SA \quad (3)$$

The constant  $k_d$  is the specific surface degradation rate (SSDR), and it resembles the linear growth rate in crystallography.<sup>126</sup> In contrast to a conventional reaction rate (i.e., the rate at which reactants are converted to products), the SSDR is a linear rate representing the perpendicular depth of plastic ( $\Delta d$ , Figure 6) degraded per unit time. For the thin film described above, the surface area (and the rate) may be considered essentially constant for most of the degradation time. If we also assume constant density, then integration and rearrangement yield simple algebraic solutions for the mass as a function of time and the time for complete degradation  $t_d$  (eqs 4 and 5)

$$m_t = m_0 - k_d \rho SA t \quad (4)$$

$$t_d = \frac{m_0}{k_d \rho SA} = \frac{V_0}{k_d SA} \quad (5)$$

Using a value of  $k_d = 4.3 \mu\text{m year}^{-1}$  (median estimated degradation rate for HDPE in the marine environment, *vide infra*) leads to a predicted time for complete degradation of the HDPE film  $t_d$  of just 1.8 years.

The assumption of constant surface area is not appropriate for the HDPE bead. The decreases in radius  $r$  and SA with time are incorporated into eq 6, which is formulated in terms of the bead's mass  $m$ :

$$-\frac{dm}{dt} = k_d \rho SA = k_d (4\pi r)^{1/3} (3m)^{2/3} \quad (6)$$

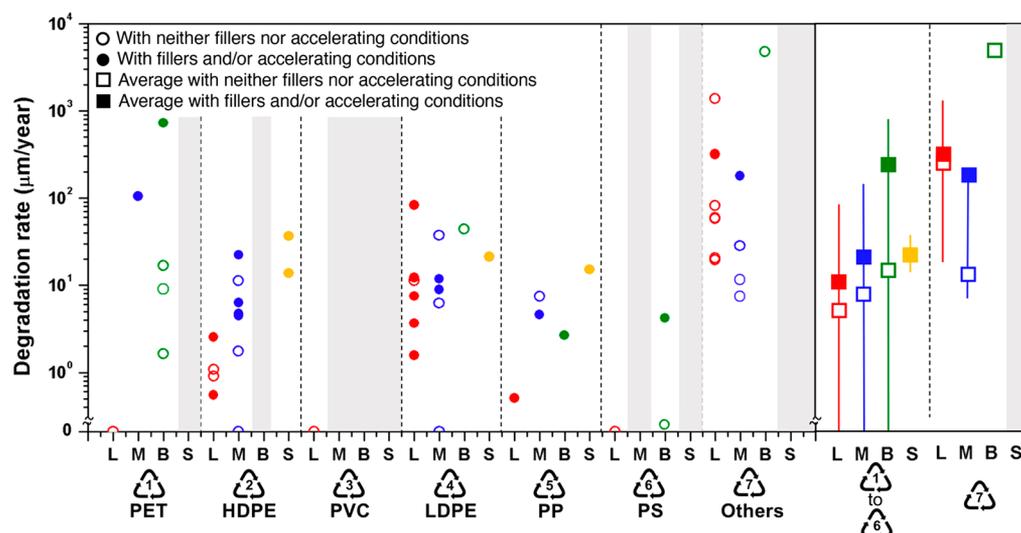
Integration and rearrangement (also assuming constant density) give the algebraic solutions in eqs 7 and 8 for the mass as a function of time and the complete degradation time

$$m_t = \left[ (m_0)^{1/3} - \frac{6^{2/3}}{3} k_d (\pi \rho)^{1/3} t \right]^3 \quad (7)$$

$$t_d = \frac{3}{6^{2/3} k_d} \sqrt[3]{\frac{V_0}{\pi}} \quad (8)$$

Using eq 8 and the same value for  $k_d$ , 4.3  $\mu\text{m year}^{-1}$ , the time required for complete degradation of the shrinking HDPE bead is estimated to be 2000 years. Of course, such values do not account for spontaneous fragmentation, resulting in a discontinuity where the surface area, and degradation rate, abruptly increase.

For plastic fibers, a cylinder is a better approximation of the shape. If the aspect ratio is large (i.e., radius  $r \ll$  height  $h$ ), we can assume  $SA \approx 2\pi rh$ . If we further assume that  $h$  is



**Figure 8.** Specific surface degradation rates for various plastics, in  $\mu\text{m year}^{-1}$ . Vertical columns represent different environmental conditions (L, landfill/compost/soil; M, marine; B, biological; S, sunlight) and plastics types (represented by their resin identification codes). Plastics type 7, “others”, corresponds to various nominally biodegradable plastics. The range and average value for plastics types 1–6 are shown on the right as lines and squares, respectively, as well as for biodegradable “others”. Data points representing degradation rates that were unmeasurably slow are shown on the  $x$ -axis. Gray columns represent combinations for which no data were found.

essentially invariant with time, we obtain the corresponding equations for mass loss and estimated complete degradation time shown in eqs 9 and 10

$$m_t = [(m_0)^{1/2} - k_d(\pi\rho h)^{1/2}t]^2 \quad (9)$$

$$t_d = \frac{1}{k_d} \left( \frac{m}{\pi\rho h} \right)^{1/2} \quad (10)$$

A cylindrical HDPE fiber of volume  $2.9 \text{ cm}^3$  ( $r = 2 \text{ mm}$ ,  $h = 23 \text{ cm}$ ,  $SA = 29 \text{ cm}^2$ ) would require an estimated 465 years for complete degradation.

Thus, an HDPE film should degrade completely 260 times faster than a fiber of the same mass and crystallinity, and 1100 times faster than a comparable bead, in the absence of significant fragmentation, crystallization, or shape dependence of the SSDR. The ratios of the initial degradation rates (based on surface area ratios) are 390:3:1 for the film, fiber, and bead, respectively. However, the degradation rates of the fiber and the bead decrease as their radii shrink, so their “average” degradation rates are even lower. In addition, the exceedingly long extrapolations for the fiber and the bead result in errors with a far greater magnitude, in years, than the short extrapolation for the film. Thus, if the relative error in  $k_d$  is 20%, the film will degrade in  $1.8 \pm 0.4$  years, while the fiber will degrade in  $465 \pm 100$  years and the bead in  $2000 \pm 400$  years. We can also reasonably assume that  $k_d$  will vary far more in the course of two millennia than it will during the first decade, making the actual error for the bead even larger. The shape-dependent degradation profiles are compared in Figure 7.

Some additional points are worth mentioning. First, the surface roughness is unlikely to remain constant over time. Polymers that are melt processed may have initially smooth surfaces. However, as degradation proceeds, the surface will become pitted, and cracks will appear, increasing the surface area and hence the degradation rate. Such cracks can also lead to surface ablation and mass loss due to the release of microplastic fragments. Second, an amorphous polymer

(whose surface abundance may or may not be the same as the bulk) will undergo faster degradation than a crystalline polymer, requiring the addition of a scaling factor to eqs 3 and 6 to represent the amorphous surface area fraction ( $aSA$ ,  $0 \leq a \leq 1$ ). Once the amorphous polymer is eliminated, degradation in the remaining crystalline regions may be much slower. Furthermore, partial polymer degradation can lead to cross-linking and/or crystallization in the amorphous regions adjacent to crystallites,<sup>107</sup> thereby slowing degradation, although this effect cannot be quantified or modeled at this time.

Clearly, polymer degradation times in the environment should be tremendously sensitive to the shape and size of the material, in addition to its intrinsic chemical reactivity. Nevertheless, for plastics pieces of different sizes and compositions but with similar aspect ratios, it is possible to compare initial degradation rates via the SSDR, which is inversely proportional to the degradation time for a material whose surface area remains approximately constant. This assumption is discussed further below.

**Analysis of Reported Degradation Rates.** Of the hundreds of published papers screened for this Perspective, only 25 reported all of the information needed to calculate an SSDR (mass loss, sample dimensions, experiment duration).<sup>71,79,127–149</sup> The resulting 54 data points are organized in Figure 8. The data are arranged according to plastics type and degradation environment (Landfill/soil/compost, Marine, Biological, or Sunlight). While these categories are not completely orthogonal, they are useful to represent the four major categories of polymer degradation experiments that have been conducted: on land (without exposure to sunlight), in water (in freshwater or seawater with exposure to sunlight), in a lab using enzymes or microbes, or with exposure exclusively to sunlight and air. Data for plastics type 7 (“others”) includes the nominally biodegradable plastics PLA, polyhydroxybutyrate (PHB), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), Mater-Bi and polycaprolactone (PCL). The presence of a filler component (e.g., starch, PLA, etc.) or accelerating

conditions (e.g., UV pretreatment, thermal pretreatment, or microbial incubation) in each study is noted. Two of the papers used to construct Figure 8 studied the degradation of blends of polypropylene<sup>132</sup> and polyethylene<sup>149</sup> with a biodegradable filler (5 or 10 wt % starch, respectively). The authors assumed that the filler indirectly increases the degradation rate of the plastic, possibly by causing the surface area of the plastic to increase as the starch component degrades. The problems of inferring plastics degradation rates in this way are discussed further below. Data for PET, PP, and PS degradation are sparse. Finally, only one report for PVC degradation met our criteria, regardless of the environment, and it found no measurable degradation after 32 years.<sup>148</sup>

Considering only the nonzero values, the SSDR values for all plastics types, regardless of environment, vary over several orders of magnitude. Overall, the average reported values for accelerated degradation in each environmental condition are slightly higher than their nonaccelerated counterparts, as expected, although the differences may not be statistically significant. For accelerated degradations (filled circles, Figure 8), involving polymer pretreatment or a filler, the rates still vary by about an order of magnitude in most cases. The variation is especially noticeable for LDPE decomposing on land, where the range is a factor of 50. The highest reported accelerated SSDR for LDPE,  $83 \mu\text{m year}^{-1}$ , is for a blend with 20 wt % PLA decomposing under composting conditions ( $37^\circ\text{C}$ ).<sup>144</sup> The lowest reported accelerated SSDR for LDPE is  $3.7 \mu\text{m year}^{-1}$ , measured after addition of *P. aeruginosa* to the soil. Interestingly, the SSDR for the LDPE/PLA blend ( $83 \mu\text{m year}^{-1}$ ) is higher than the SSDR for pure PLA ( $21 \mu\text{m year}^{-1}$ ),<sup>138</sup> both measured in composting conditions at  $37^\circ\text{C}$ . However, the durations of the two experiments differed (28 days for the LDPE/PLA blend, compared to 365 days for the pure PLA). The discrepancy could also be due to differences in crystallinity, since blending can increase the volume fraction of amorphous regions, which show higher degradation rates.<sup>57</sup>

Extrapolated degradation rates for plastics blended with degradable fillers (e.g., starch) assume constant degradation rates, but this may be highly inaccurate. Such fillers are typically degraded by microorganisms first. Once the readily accessible filler is consumed, the remaining plastics degrades much more slowly through a combination of environmental degradation (e.g., photo-oxidative, hydrolysis, etc.) and microbial action.<sup>150</sup> The degradation should therefore be described as a multiphase kinetic process.<sup>151</sup> The variable durations and rates of these phases depend on the dimensions of the material, type and concentration of the filler, degradation environment and conditions, etc. Abiotic degradation of plastics may be enhanced relative to the unfilled polymer due to greatly increased surface area after removal of the filler.<sup>150</sup> Despite the convenience of shorter time scales, great caution should be used when interpreting degradation kinetics of blended polymers, and they should not be used to infer mechanisms and degradation rates for pure polymers.

Although biodegradable plastics such as PHB and PLA show large average SSDRs in compost and landfill conditions ( $59$  and  $21 \mu\text{m year}^{-1}$ , respectively), their degradation in marine environments is significantly slower and may even be comparable to the degradation rates of their petrochemical counterparts. For example, the average SSDR of PLA in the marine environment,  $7.5 \mu\text{m year}^{-1}$ , is similar to the averages for HDPE ( $4.3 \mu\text{m year}^{-1}$ ) and LDPE ( $15 \mu\text{m year}^{-1}$ ). Although PLA and other “biodegradable” plastics are expected

to fully degrade in industrial composting conditions ( $\geq 60^\circ\text{C}$ , and moist), the temperature in marine environments rarely exceeds  $20^\circ\text{C}$  and therefore lacks the thermal energy for depolymerization. In soil conditions, however, the average SSDR of PLA is notably higher ( $21 \mu\text{m year}^{-1}$ ) than the corresponding values for petrochemical-based plastics (e.g., HDPE,  $1.0 \mu\text{m year}^{-1}$ ). Temperatures in landfills have been reported to reach  $80\text{--}100^\circ\text{C}$ ,<sup>152</sup> which is sufficient to degrade plastics like PLA as long as moisture is present.

**Extrapolated Degradation Times.** Two methods have been widely used to estimate polymer lifetimes, defined here as the time required for complete degradation (>99% loss of the initial polymer mass): (1) Arrhenius extrapolation of accelerated aging result, and (2) extrapolation based on initial rates measured under environmentally relevant conditions. Both make important and often poorly justified assumptions which limit their validity.

The first method assumes that degradation rate constants have Arrhenius-like temperature dependences.<sup>153</sup> A polymer lifetime at ambient temperature is extrapolated from the faster degradation rates that are more readily measured at higher temperatures, ca.  $25\text{--}200^\circ\text{C}$ . For example, the lifetime of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) at  $25^\circ\text{C}$  in distilled water was predicted to be 300 d, based on extrapolation of decreases in tensile strength<sup>154,155</sup> and molecular weight measured at temperatures of  $25\text{--}50^\circ\text{C}$ .<sup>156</sup> However, lifetime estimation by Arrhenius extrapolation assumes that the same degradation mechanism is operative at all relevant temperatures. For PE and PP, the Arrhenius plots are nonlinear,<sup>157–159</sup> suggesting a change in mechanism and/or rate-determining step with temperature.<sup>160</sup>

Arrhenius extrapolation is less useful for estimating biodegradation rates, because enzymatic degradation processes take place only under biologically relevant reaction conditions; they usually do not occur at elevated temperatures. Therefore, biodegradation lifetimes are generally predicted by the second method, using initial degradation rates obtained over prolonged measurement times instead.<sup>148,161</sup> For instance, the degradation rates of LDPE–starch blends were calculated by measuring weight loss as a function of time over a period of 125 days in composting conditions, and this rate was used to predict the complete degradation time using a linear extrapolation.<sup>120</sup> However, since relatively rapid biodegradation of the starch component should be followed by much slower degradation of the remaining LDPE, extrapolation based on initial measurements could be highly misleading. The accuracy of the method is compromised by the occurrence of several phases of degradation, with very different rates.<sup>162</sup> Thus, information on degradation rates for each component in a mixture is necessary to make accurate lifetime estimates.

Although extrapolation from initial rates is inaccurate, it is the simplest method to estimate plastics lifetimes in the environment. The approach requires knowledge of the rate law but does not account for dependence on the shape of the material. The shrinking core model (common in TGA studies of phase transformations) assumes that the volume, and hence the surface area, change as the reaction proceeds.<sup>163</sup> While it may be more realistic, it does not take into account changes in surface roughness, which may be considerable. Applications of the shrinking core model to plastics degradation have so far focused on high temperature catalytic degradation, which is not directly relevant to plastics degradation in the natural environment.<sup>164,165</sup>

Table 1. Estimated Half-Lives of Common Plastic Items<sup>a</sup>

Plastics type	Common applications	Typical thickness ( $\mu\text{m}$ )	Estimated Specific Surface Degradation Rate (min-max; $\mu\text{m year}^{-1}$ ) <sup>b</sup>			Estimated half-lives (min-max; year)			
			Land (buried)	Land (accel. by UV/heat) <sup>c</sup>	Marine (accel. by UV/heat) <sup>c</sup>	Land (buried)	Land (accel. by UV/heat) <sup>c</sup>	Marine (accel. by UV/heat) <sup>c</sup>	
1. PET	Single-use water bottle	500	0	—	—	>2500 <sup>d</sup>	—	—	2.3
2. HDPE	Plastic bottles	500	1.0 (0.91–1.1)	1.3 (0.55–2.6)	4.3 (0–11)	250 (230–280)	190 (95–460)	58 (23 to >2500)	26 (12–55)
2. HDPE	Pipes	10,000	1.0 (0.91–1.1)	1.3 (0.55–2.6)	4.3 (0–11)	5000 (4600–5500)	3900 (1900–9000)	1200 (450 to >2500)	530 (230–1100)
3. PVC	Pipes	10,000	0	—	—	>2500 <sup>d</sup>	—	—	—
4. LDPE	Plastic bags	100	11	22 (1.6–83)	15 (0–37)	4.6	2.3 (0.6–32)	3.4 (1.4 to >2500)	5 (4.2–5.5)
5. PP	Food storage container	800	—	0.51	7.5	—	780	53	87
6. PS	Insulating packaging	20,000	0	—	—	>2500 <sup>d</sup>	—	—	—
7. Others	Biodegradable plastic bag	100	270 (20–1400)	320	16 (7.5–29)	0.19 (0.035–2.5)	0.16	3.1 (1.7–6.7)	0.29

<sup>a</sup>Half-life refers to conversion of the first 50% of the polymer mass, assuming pseudo-zeroth-order kinetics (i.e., invariant SA). According to eq 10, assuming cylindrical geometry and decreasing radius (but not height) over time predicts half-lives that are twice as long. Entries shown as (–) correspond to conditions for which no published data were found. Values in parentheses correspond to the range based on published reports. All values were rounded to two significant figures. <sup>b</sup>Values of  $0 \mu\text{m year}^{-1}$  correspond to reports in which no degradation was observed; however it is likely that the duration of the experiment was too short to measure an appreciable weight loss. These values were included in calculations of average degradation rates and in the corresponding time ranges for complete degradation. <sup>c</sup>C corresponds to data collected in the presence of a degradation accelerant (e.g., UV pretreatment, thermal pretreatment, or microbial incubation) and/or for plastics containing a rapidly degrading filler (e.g., starch, PLA, etc.). <sup>d</sup>>2500 indicates that the relevant studies detected no measurable degradation, possibly due to the duration of the experiment being too short, allowing only an estimated lower limit for the extrapolated degradation time. The value 2500 years was obtained by calculating a SSDR based on the sensitivity of the balance used in the study and extrapolating a half-life for the thinnest material (100  $\mu\text{m}$ , ca. 2500 years).

Since experimental assessment of polymer degradation rate laws would require kinetic studies that last multiple decades or even longer, we assume a simple first-order dependence on SA (eq 3) and further assume that SA is constant over time (i.e., pseudo-zeroth-order behavior). However, we must point out that these assumptions have substantial consequences and can lead to extrapolation errors that represent decades or even centuries of additional lifetime. For example, a 100  $\mu\text{m}$  thick film with a SSDR of 1  $\mu\text{m year}^{-1}$  would require 100 years to degrade completely following a pseudo-zeroth-order rate law (constant surface area), while the same film would be 99% degraded in nearly 500 years if the reaction is first-order degradation. The error is much less important at lower extents of the reaction: using the same SSDR, pseudo-zeroth-order degradation would require 50 years to reach 50% completion, compared to 68 years for first-order degradation.

In addition, we note that the polymer is likely to have undergone extensive chemical and morphological changes as the reaction approaches high conversion. For example, disintegration into smaller pieces (e.g., microplastics) may alter the rate of reaction dramatically. Although little is known about the details of such processes, recent reports suggest that mechanical forces can cause the flaking of weathered, or oxidized, surfaces, leading to ablation, in addition to macro-fragmentation.<sup>166</sup> Studies of several polymer types in a weathering chamber revealed exponential growth in the numbers of nanometer- and micron-sized particles released over several weeks.<sup>125,167</sup> However, since nearly two-thirds of microplastics in the ocean are estimated to originate from the washing of synthetic fabrics and the abrasion of rubber tires,<sup>168</sup> fragmentation of bottles, bags, pipes, and other large rigid pieces may not be major sources of microplastics and nanoplastics.

No extrapolation model is likely to describe the rates of complex phenomena involved in polymer degradation accurately. Consequently, we choose to compare degradation rates by calculating the first half-life, or the time in which the material loses 50% of its original mass. The values are still associated with large uncertainties but are probably much more accurate than attempting to extrapolate the time for “complete” degradation. Subsequent half-lives may be very different from the first half-life, depending on the rate law. In addition, the representativeness of literature values for degradation rates is unknown, and averaging them does not allow us to assess uncertainties in a statistically meaningful way. Nevertheless, in view of the public interest in estimated plastics lifetimes, we averaged the available SSDRs for each plastics type under each type of degradation condition in Figure 8 in order to estimate a first half-life for several common household plastic items, shown in Table 1. Ranges for these half-lives, obtained by multiplying SSDRs based on reported minimum and maximum values for degradation rates by the typical thickness of each plastics type for the specified application, highlight the large uncertainty in the extrapolation. The degradation was assumed to be unidirectional, proceeding from the exterior of the material toward the center. According to Table 1, common single-use plastics items like LDPE plastic bags and HDPE milk bottles and laundry detergent containers have estimated half-lives of 5 and 250 years, respectively, in landfill/compost/soil conditions. In the marine environment, the estimated half-lives are shorter, at 3.4 and 58 years, respectively. All values are subject to additional uncertainty because some data suggest much longer lifetimes, based on

degradation rates that were immeasurably slow in both landfill/compost/soil and marine environments. For heavier industrial items like HDPE pipes, complete degradation may require thousands of years, regardless of the environment (we note that the durability of such items is often desirable for their intended purpose).

In order to obtain estimated times for complete degradation, we can assume a constant rate of degradation, a constant surface area:volume ratio, a constant reaction order, uniform crystallinity, and a mechanism for microplastic degradation identical to that of the parent material. These assumptions make such estimates highly uncertain. Nevertheless, the complete degradation of an HDPE bottle is estimated to require 500 and 116 years in the land and marine environments, respectively.

**Environmental Effects on Degradation Rates.** Prolonged exposure to environmental factors such as moisture, heat, light, or microbial action causes polymers to be abraded into smaller pieces (eventually to microplastics) as well as cleaved into small molecules.<sup>11</sup> The effect of a particular environmental factor on the degradation rate depends strongly on the type of plastic. For example, some studies of petrochemical-based polymers show that degradation rates are lower in the marine environment compared to landfills.<sup>169,170</sup> The differences are typically attributed to lower ambient temperatures and low dissolved oxygen concentrations in the marine environment.<sup>25</sup> However, our literature analysis shows that average degradation rates for HDPE and LDPE are actually slightly higher in marine environments compared to degradation on land (Table 1), although the differences could be statistically insignificant due to the large uncertainties of the averages. The effects of lower temperatures and oxygen concentrations in the ocean may be outweighed by the more intense UV radiation, relative to a landfill.

In other situations, plastics exposed to sunlight on land can experience “heat buildup”, reaching temperatures higher than the surrounding air and experiencing accelerated degradation.<sup>171</sup> Temperatures in some landfills and industrial composters have been reported to reach 80–100 °C,<sup>152</sup> accelerating degradation rates provided sufficient oxygen and/or moisture are present for the thermal-oxidative degradation and hydrolysis pathways, respectively. For example, PLA undergoes ester hydrolysis under industrial composting conditions ( $\geq 60$  °C), although it is very slow to degrade at lower temperatures.<sup>56</sup> Consequently, PLA appears to be just as recalcitrant as its petrochemical counterparts in marine environments, where temperatures are well below 60 °C (Figure 8).

Landfill/soil/compost conditions typically apply to buried materials that experience little solar UV radiation, hindering photodegradation. Biofouling can hinder the rate of photodegradation by decreasing sunlight penetration.<sup>25,139,171</sup> In the ocean, biofouling can also increase the overall density of plastic pieces, causing them to sink<sup>172,173</sup> (although some plastics, including PET, PVC, PLA, do not float anyway).<sup>174–177</sup> The process may be time dependent, as plastic debris has been observed to undergo repeated cycles of sinking and floating. After the fouled plastic debris sinks in the water column, it can undergo defouling due to the absence of sunlight needed to maintain the film, causing the density to decrease and the debris to resurface.<sup>174</sup> Such studies have been largely conducted on petrochemical-based plastics, but similar changes in buoyancy are expected to affect the degradation kinetics of

biodegradable plastics as well. Interestingly, average photo-degradation rates for “biodegradable” plastics do not differ much from those for petrochemical-based plastics.

**Effects of Accelerating Conditions. UV Irradiation.** Solar UV radiation is necessary to initiate photo-oxidation of most polymers,<sup>37</sup> which proceeds via a radical chain mechanism that results in bond cleavage and a decrease in molecular weight (see above). Shorter chains, often with oxygen-containing functional groups at the chain ends, are more prone to attack by microorganisms and mineralization due to their increased hydrophilicity (which enhances microbial adhesion).<sup>178</sup> Several experimental studies reported synergy between photo-oxidation and biodegradation of polyethylene.<sup>179–181</sup> In another study, the abundance of carbonyl groups in polyethylene increased upon exposure to UV radiation for 60 h, then decreased when the photo-oxidized polyethylene was subsequently incubated with microorganisms, suggesting microbial degradation.<sup>182</sup>

**Transient Thermal Treatment.** Moderate heating in air enhances rates of polyolefin oxidative degradation significantly. The increase in polymer hydrophilicity arising from incorporation of oxygen-containing functional groups facilitates surface attachment of microorganisms.<sup>27,178</sup> In a study conducted in a soil culture over 12 months, films of LDPE, HDPE, or PP that were thermally pretreated at 80 °C for 10 days showed enhanced biodegradation rates of 12, 4.5, and 2.7  $\mu\text{m year}^{-1}$ , respectively, compared to 6.3, 1.8, and 0.1  $\mu\text{m year}^{-1}$ , respectively, without thermal pretreatment.<sup>130</sup> In the marine environment, LDPE and HDPE films thermally pretreated at 80 °C in an oven for 10 days showed 4- to 7-fold increases in marine bacterial colonization compared to the untreated materials over six months. Higher mass losses were also observed for thermally pretreated LDPE and HDPE (17% and 5.5%, respectively), compared to the untreated materials (10% and 1%, respectively) over the same time period.<sup>135</sup>

**Humidity.** Elevated humidity levels accelerate polyester degradation by promoting hydrolysis. For example, chain scission of a PET in a plastic bottle was 5 times greater at 60 °C and 100% relative humidity compared to 45% relative humidity. However, at temperatures of 80 °C or higher, there was no significant increase in the rate of hydrolysis with increased humidity, since the rate of thermal-oxidative degradation outpaces that of hydrolysis at these elevated temperatures.<sup>153</sup> Humidity has also been shown to accelerate the photodegradation of PLA,<sup>183</sup> and polyolefins such as PE,<sup>184</sup> PP,<sup>185</sup> and PVC,<sup>186</sup> by promoting an increase in the concentration of hydroxyl radicals.

## CONCLUSIONS

Each year, 400 Mt of plastic waste is generated, of which 175 Mt enters landfills and the natural environment.<sup>1</sup> The amount of plastics that enters landfills and the environment is sufficient for rebuilding the currently standing Great Wall of China with a span of 6000 km<sup>187</sup> every 12 months. Despite this massive scale, the literature on plastics degradation under environmental conditions is disproportionately thin. Relatively little has been reported in the literature regarding the following: How quickly do plastics degrade in the environment? What are the degradation pathways? What are the factors affecting the degradation processes? What are the degradation byproducts? When juxtaposed, existing literature on plastics degradation rates shows a wide range of numbers.

Furthermore, the various degradation byproducts may include larger molecules, as well as microscale and nanoscale plastics with increased bioavailability and associated potential adverse impacts to ecosystems throughout the food web. Additional research is needed to better understand the mechanisms of polymer degradation under various environmental conditions. Given the long life-span of plastics, methods to use short-term experimental results to predict long-term degradation pathways and methods to simulate degradation, for example, using modern computational chemistry techniques, must also be further refined and vetted.

Our review highlights the need to standardize the metrics and the experimental conditions used in plastics degradation research. Studies on plastics degradation often omit key information, such as the temperature, microbial loading, and the size and shape of the sample, which are essential to interpret the results properly. These deficiencies, combined with the sparseness of the literature, limit the ability to conduct meaningful meta-analyses. The SSDR metric proposed here is a step in that direction; however, it only measures how much material, or mass, is lost from the sample. Therefore, neither structural changes nor the extent of mineralization of plastics can be addressed using SSDR alone. Furthermore, extrapolations are fraught with uncertainty. We anticipate the need for development and implementation of multiple well-defined standard metrics to quantify the rates of polymer degradation in the environment.

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### Notes

The authors declare no competing financial interest.

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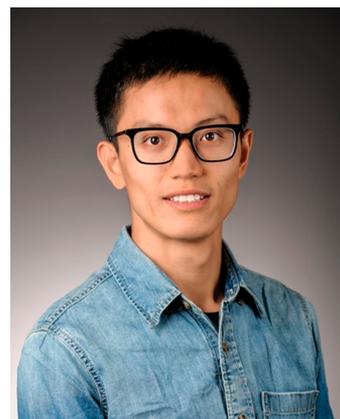
Ali Chamas is completing his Ph.D. in Chemistry at the University of California, Santa Barbara. He received his B.S. in biochemistry also from the University of California, Santa Barbara. His research focuses on kinetic and mechanistic studies of catalytic lignin depolymerization and recently plastic waste upcycling. Ali has been the recipient of several awards and fellowships, including the U.S. Department of Energy, Office of Science Graduate Student Research Program for in-residence research at the Pacific Northwest National Laboratory. The UC Santa Barbara Crossroads Fellowship has allowed him to work in a multidisciplinary team on understanding plastic waste degradation.



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Yang Qiu is a Ph.D. student at the Bren School of Environmental Science and Management at the University of California, Santa Barbara. Yang has been working in the field of industrial ecology for his Ph.D., and his research focuses on understanding the economic and environmental trade-offs of low-carbon transitions in the energy system. Additionally, he is also interested in understanding the implication of technology development on consumption and circularity of critical metals.



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