



Plastic Biodegradation: Challenges and Opportunities

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Abstract

Plastics are extremely useful materials that have transformed our society in a myriad of ways. However, the widespread use of these materials has led to a staggering amount of plastic pollution in man-made and natural environments. The biodegradation of plastics is a key factor to reduce the impact of this plastic pollution. On the one hand, organisms are emerging that can degrade relatively recalcitrant plastics. On the other hand, biodegradable plastics are being developed that are intrinsically more amenable to microbial attack. In this chapter we provide an overview of the natural fates of these two types of plastics, the molecular bonds that occur in them, and the enzymatic activities associated with their degradation. Finally, an outlook is provided for the biotechnological utilization of plastics waste as a substrate, either using these enzymes or through thermochemical pretreatment.

1 Introduction

To date 8.3 billion metric tons (MT) of virgin plastics have been produced (Geyer et al. 2017), of which 6.3 billion MT became waste. Of this waste about 9% has been recycled, while 12% was incinerated. The other 79% of plastic waste is stored in landfills or was directly released into the environment (Geyer et al. 2017).

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Worryingly, according to the report “The New Plastic Economy: Rethinking the future of plastics” by the Ellen MacArthur Foundation, approximately 40% of the remaining plastic waste is landfilled with a potentially staggering 32% directly released to the environment (Ellen MacArthur Foundation et al. 2016). The plastic pollution arising from mismanagement of waste has been a source of concern since the 1970s. Since then, plastic production has greatly increased and so has the pollution of marine environments (Derraik 2002). Plastic polymers are found in all oceanic niches ranging from beaches and the surfaces to shallow seabed and abysses (Barnes et al. 2009; Ryan et al. 2009). Plastic materials are dangerous to marine species due to entanglement and ingestion of litter (Derraik 2002) and also due to toxicological effects of the micro-plastic particles resulting from the degradation of larger polymers. These particles tend to facilitate the aggregation of other organic materials and contaminants changing their bioavailability, which results in the loss of fitness of marine species through decreased feeding, fecundity, and growth (Galloway et al. 2017).

The sources of marine pollution vary, and although initial reports pointed to fishing and merchant fleets (Horsman 1982), recreational boats (UNESCO 1994), and beachgoers (Pruter 1987) as the largest polluters, it is unlikely that the combination of these sources accounts for the amount of plastic disposed of in the ocean. Recent efforts modeling global inputs of plastics into the ocean estimate that the contribution due to mismanagement of waste in coastal countries was 12.7 million MT (Jambeck et al. 2015) in 2010. Fresh waters are also heavily contaminated by plastics (Dris et al. 2015), and rivers contribute an estimated 1.4–2.4 million MT to ocean plastic pollution per annum (Lebreton et al. 2017).

The recycling rates of different kinds of plastics also give an overview of the magnitude of the problem. When considering plastic used for packaging, polyethylene terephthalate (PET) has the highest rate of recovery (70% in Europe), although only 7% of it is recycled bottle to bottle (World Economic Forum et al. 2015). In 2015 the USA only recycled 30% of PET bottles, whereas bottles made of high-density polyethylene (HDPE) had a slightly higher recycling rate of 34.4%. The recycling rates of polypropylene (PP), low-density polyethylene (LDPE), and polyvinyl chloride (PVC) are much lower (18%, 4.1%, and 3.3%, respectively) (ACC and APR 2016). These figures are far from the recycling rates of other materials in the USA such as lead acid batteries (98.9%), steel cans (70.7%), and aluminum cans (55.1%) (US EPA 2016) and well below those of some European countries such as Germany where in 2015 thanks in part to the German “pfandpflichtige PET-Verpackungen” (PET mandatory deposit scheme) over 92% of PET bottles were recycled and 26% of the recycled “R-PET” has been used for new PET bottles (GVM 2016).

Recycling rates vary greatly depending on the country, the management policies, and the nature of the plastic item (Fig. 1). Taking Europe as an example, countries such as Malta, Cyprus, and Greece achieve recycling rates of waste plastic below 20% with no documented incineration, resulting in extremely high rates of plastics ending in landfill or environmental release. In stark contrast, nine countries in Europe have banned landfill of plastic between 1996 and 2006, and by 2014 all of

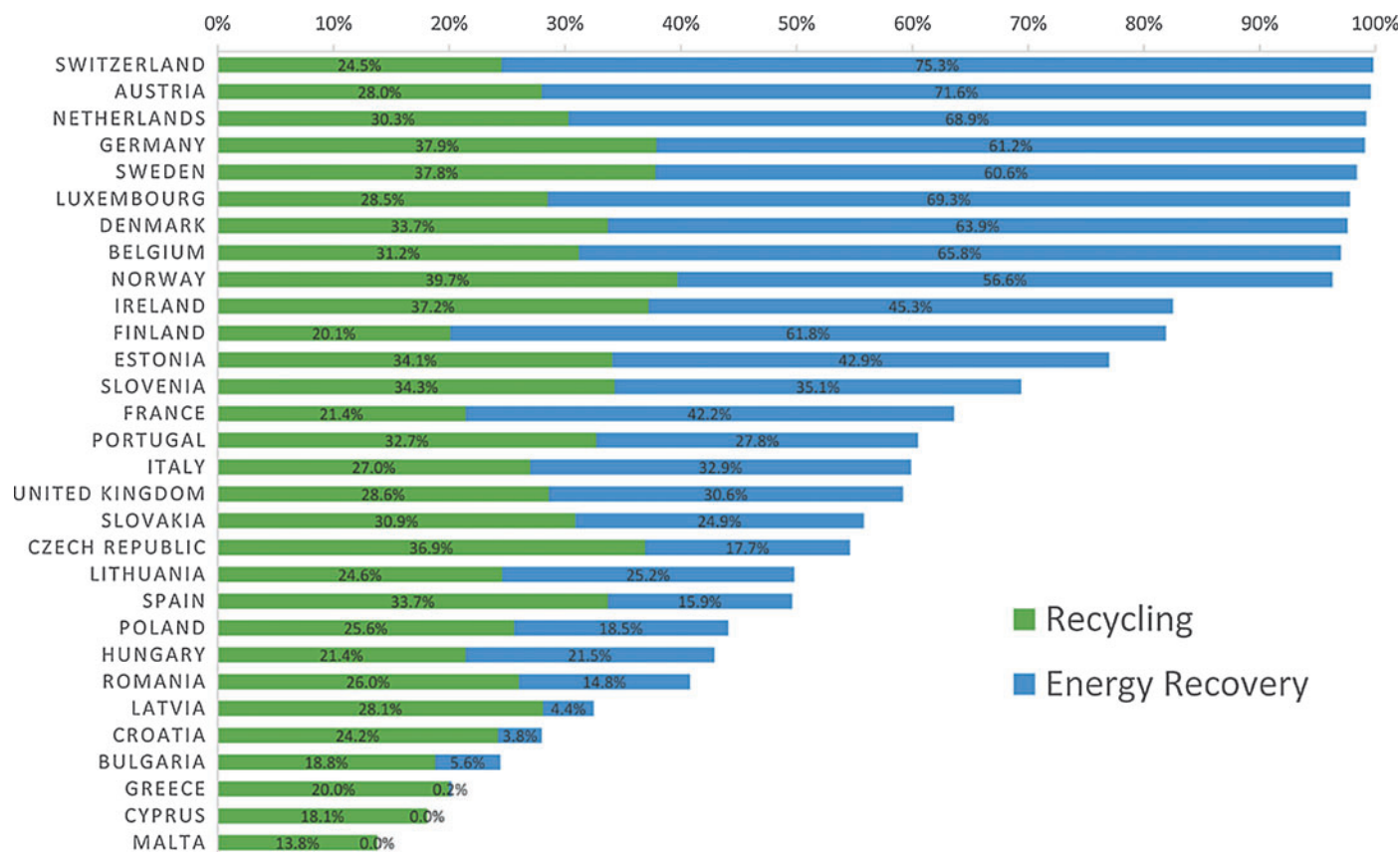


Fig. 1 Recovery of postconsumer plastic waste from the EU28 + 2 countries in 2014. Numbers are based on (PlasticsEurope 2016)

these countries had achieved recycling and incineration rates over 95% (PlasticsEurope 2016). For example, Sweden has a total recycling fraction of about 30% of the postconsumer plastic recovered, while the rest is incinerated (PlasticsEurope 2016). The change in consumer awareness and political agendas in the EU is ongoing, which can be seen in a 64% and 46% increase in recycling and incineration, respectively, alongside a 38% reduction in landfill across the EU between 2006 and 2014 (PlasticsEurope 2016). While these figures show that with proper legislation and regulation significant strides can be made in improving plastic recycling rates, they and the trends they show are highly specific to consumer packaging polymers and overlook many plastics that do not have existing recycling and collection technologies, such as polyurethanes (PU). However, only about 30% of waste plastic is recycled at best according to European figures, with all the major improvements in landfill and environmental release statistics being driven by increased rates of incineration. An obvious but important observation about plastic waste incineration is that these materials are limited in nature and costly to produce and to recover. This means that once they are incinerated, they leave the value chain, for good.

We hence require new ways of lowering the impact of waste plastic on the environment. In this chapter we discuss new value chains for plastic waste use, including ever more advanced chemical and biotechnological recycling or even upcycling routes. An alternative strategy that relies on a different material property is the use of biodegradable plastics. Biodegradable plastics can, similarly to their oil-derived counterparts, be recycled, be incinerated, or, when released to the environment, be rapidly degraded by microbial enzymes.

2 Natural Fates of Plastics

2.1 Biodegradable Plastics

Biodegradable plastics generate a lot of interest due to the ever-increasing levels of plastic waste accumulated in various environments. By definition, biodegradable plastic is decomposed by the action of living organisms. Similar to petrochemical nondegradable counterparts, biodegradable plastic is not a single material, rather a family of different materials with various properties and applications. This diversity is reflected in different biodegradation routes and rates. Polylactic acid (PLA), polyhydroxyalkanoates (PHA), and cellulose are biobased and biodegradable materials perceived as a potential solution to plastic littering. The advantage of these materials, in addition to their environmental degradation, is that they can be produced from renewable and sustainable resources (Cerrone et al. 2015; Walsh et al. 2015; Succinity 2016; Müller et al. 2017) and can also be degraded in the environment. It is worth noting that there are plastic polymers derived from oil such as polycaprolactone (PCL) and poly(butylene adipate-co-terephthalate) (PBAT), which are biodegradable. Others, like polybutylene succinate (PBS), can be both bio- and petroleum based (Succinity 2016), whereas polyethylene (PE) and polyethylene

terephthalate (PET), which represented 47.2% of global bioplastic production in 2014 (European Bioplastics 2016), can be total or partially biobased but are not biodegradable. Therefore, the origin of a polymer does not determine its biodegradability characteristics.

2.1.1 Polylactic Acid

Biodegradable plastics offer new end-of-life management options creating new possibilities for a sustainable society. One of the management options that has been extensively researched is industrial composting (Emadian et al. 2017). While some polymers such as polyhydroxybutyrate (PHB) are home compostable (Greene 2014), polymers such as PLA require higher temperatures used in industrial composting (around 60 °C) to allow complete biodegradation in a reasonable time (Farah et al. 2016). The microorganisms involved in the biodegradation of bioplastics are widely distributed and can be found among aerobic and anaerobic bacteria, archaea, and eukaryotic organisms (Tokiwa and Suzuki 1981; Suyama et al. 1998; Emadian et al. 2017).

Out of the different bioplastics, PLA is a polyester widely used for packaging, and some commercial variants, such as NatureWorks' polymer Ingeo™, are certified for industrial composting (NatureWorks 2017). There are many identified enzymes active toward PLA, i.e., serine proteases from *Amycolatopsis* specific to poly(L-lactic acid) and thermophilic lipases from thermophilic *Bacillus* strains specific for poly(D-lactic acid) (Kawai 2010). However, nonenzymatic hydrolysis is still the main route of PLA degradation (Tsuji 2002), and similar biotic and abiotic PLA degradation rates demonstrated that PLA degradation is not enhanced by the presence of microorganisms (Agarwal et al. 1998). Microbial degradation of PLA is challenging for different reasons. For instance, temperatures above the glass transition temperature of the plastic ($T_g = 55\text{--}62\text{ °C}$) are usually required for the onset of PLA hydrolysis making its degradation difficult at ambient temperatures. Additionally, degradation rates of PLA depend on the molecular weight of the polymer, and, while high-molecular-weight PLA is mechanically stronger, it is also less susceptible to biodegradation (Ho et al. 1999).

2.1.2 Polyhydroxyalkanoates

PHAs are polyesters produced by a range of bacteria. Commercial PHAs represented less than 2% of the global bioplastic market in 2014 (European Bioplastics 2016). With over 150 known PHA monomers, (*R*)-3-hydroxyalkanoic acids, PHAs have highly diverse material properties. Their crystallinity ranges from 30% to 70%, and melting temperature ranges from 50 °C to 180 °C (Madison and Huisman 1999). They are generally divided into short-chain-length (scl) polymers, containing (*R*)-3-hydroxyalkanoic acids with four or five carbon atoms, and medium-chain-length (mcl) polymers of (*R*)-3-hydroxyalkanoic acids containing 6–12 carbon atoms (Sudesh et al. 2000). The key enzymes involved in microbial intracellular and extracellular degradation of PHA are depolymerases (Jendrossek and Handrick 2002), which can also be employed in the in vitro enzymatic degradation of PHAs (Jendrossek and Handrick 2002; Calabia and Tokiwa 2006; Rhee et al. 2006). The

environmental fate of some members of the PHA family, such as PHB, has been studied in detail. For instance, polymers mainly composed of PHB or copolymers of PHB and other compounds (3-hydroxyvalerate, 4-hydroxybutyrate, or 3-hydroxyhexanoate) can be degraded to completion in soil and sludges (Wang et al. 2004; Sridewi et al. 2006; Volova et al. 2017). Other PHA polymers, such as medium-chain-length PHA (mcl-PHA¹) can be degraded as well although at a lower extent (3–17% weight loss) in different soils after 112 days (Lim et al. 2005).

2.1.3 Cellulose

Cellulose-based bioplastics are gaining attention due to their excellent mechanical properties and the sustainability of their life cycle (Wang et al. 2016). Cellulose is the most common biopolymer in nature accounting for 1.5 trillion tons of the annual biomass production (Klemm et al. 2002). Applications of cellulose are limited by its low solubility. However, it is possible to produce cellulose plastics using solvents such as N-methylmorpholine N-oxide or ionic liquids (Lindman et al. 2010), followed by shaping the resulting dissolved cellulose into fibers or films. Even though cellulose is ubiquitously present, it made only 1.6% of the total bioplastic production in 2014 (European Bioplastics 2016). While cellulose forms insoluble crystalline microfibrils, which are quite resistant to enzymatic hydrolysis (Beguin and Aubert 1994), regenerated cellulose was shown to completely degrade in soil in 2 months (Zhang et al. 1996) due to the action of microorganisms producing a battery of enzymes collectively named cellulases with different specificities (Glass et al. 2013).

2.1.4 Polybutylene Succinate

Polybutylene succinate (PBS) used to be produced exclusively from fossil resources. However, it is now possible to obtain a fully biobased PBS polymers by polycondensation reactions of succinic acid and 1,4-butanediol and PBS copolymers, respectively, by adding a third monomer, e.g., sebacic or adipic acid, all produced from renewable feedstocks (Bechthold et al. 2008; Babu et al. 2013). The melting temperature of PBS is similar to PE and PP, and it is less brittle than PLA (Tokiwa and Pranamuda 2002; Succinity 2016). In addition, PBS is certified as compostable under industrial conditions (Succinity 2016), and it is biodegradable by microbial lipases and cutinases mainly produced by *Actinomyces* and fungi (Tokiwa and Pranamuda 2002; Abe et al. 2010).

2.1.5 Polycaprolactone

The petroleum-based PCL is a hydrophobic, semicrystalline polymer of good solubility, low melting temperature (59–64 °C), and good blend compatibility and as such is a very attractive candidate for applications in the biomedical field, particularly tissue engineering (Woodruff and Hutmacher 2010). There is a wide diversity of PCL-degrading microorganisms (Chen et al. 2000), which are

¹mcl-PHA monomer composition: C6:C8:C10:C12:C14:C16 = 6.9:58.4:26.7:6.5:1:0.5.

distributed in various environments (Nishida and Tokiwa 1993; Suyama et al. 1998), and as with PBS, PCL is degraded through the enzymatic activity of lipases and cutinases.

2.1.6 Polybutylene Adipate Terephthalate

Polybutylene adipate terephthalate (PBAT) is a well-known petroleum-based bioplastic. Along with PCL and PBS, it makes up 13% of bioplastics manufactured in 2014 globally (European Bioplastics 2016). This polymer is flexible and hydrophilic and can be processed easily, with typical application in packaging and the biomedical field. PBAT biodegradation was demonstrated by a thermophilic strain, *Thermomonospora fusca* (Witt et al. 2001), and one of the PBAT-containing materials, Ecoflex[®] used for packaging, is certified as compostable (BASF 2017).

2.2 Non-biodegradable Plastics

Many plastics are designed to be durable, i.e., to resist abiotic and microbial degradation. However, once the materials are released into the environment, their longevity turns into a problem. Generally, plastics consisting of C–C chains only or containing ether bonds connecting the building blocks are considered not easily amenable to microbial degradation. Prominent examples of such non-hydrolyzable plastics are polystyrene (PS), PP, PE, PVC, and PU. In addition to those chemical structures resisting enzymatic attacks, the low bioavailability of plastics made of synthetic polymers also hampers the initiation of biodegradation. However, their bioavailability can be increased by the action of abiotic factors like UV light and high temperatures facilitating biodegradation (Gilan et al. 2004; Hakkarainen and Albertsson 2004; Hadad et al. 2005; Krueger et al. 2017). In this sense, it is possible to enhance biodegradation by the use of material blends of combined polymers (e.g., PE and starch) (Cacciari et al. 1993), but here we will focus on the degradation of neat plastic polymers.

2.2.1 Polystyrene

The versatile polymer PS can be degraded to a certain extent. Reports on bacterial (Sielicki et al. 1978; Mor and Sivan 2008) or fungal (Kaplan et al. 1979; Krueger et al. 2017) degradation of PS revealed only minor effects on the building blocks or the polymer, respectively. In contrast to this, it was reported recently that mealworm gut bacteria metabolized almost half of the provided PS to CO₂ within 16 days (Yang et al. 2015a). However, in bacterial pure cultures of *Exiguobacterium* sp. strain YT2 isolated from mealworm gut, the ability to degrade PS pieces within 60 days dropped down to about 7% (Yang et al. 2015b). Recently, oxidative biodegradation of polystyrene sulfonate (PSS) by brown-rot basidiomycetes obtained up to 50% reduction of molecular mass number-average within 20 days. The PSS depolymerization was shown to be carried out by an extracellular hydroquinone-driven Fenton reaction (Krueger et al. 2015b). On the contrary, the very poor bioavailability of

polystyrene and its inert basic structure did not allow significant degradation of PS via biologically driven Fenton chemistry (Krueger et al. 2017).

2.2.2 Polyethylene

The different reports on PE degradation should sometimes be treated with caution because often the material is weathered to facilitate the biotic process of degradation. In addition, in many investigations, LDPE is used that is more branched and of lower crystallinity than the more commonly used HDPE. The higher number of branched molecules of LDPE can improve biodegradation, although this effect is not as important as the aforementioned weathering.

Some studies reported bacterial biodegradation of PE material but treated the polymer with acid (Rajandas et al. 2012) or subjected it to photooxidation or high temperatures beforehand (Albertsson et al. 1995; Koutny et al. 2006; Fontanella et al. 2010). In addition to this, fungal biodegradation of PE films was reported mostly on pretreated material (Pometto et al. 1992; Yamada-Onodera et al. 2001; Volke-Sepulveda et al. 2002). One study on the biodegradation of PE by the thermophilic bacterium *Brevibacillus borstelensis* strain 707 revealed that within 30 days at 50 °C, weight loss of the PE material was about 11% and could almost be increased threefold when the photooxidized polymer was used (Hadad et al. 2005). The following studies all utilized untreated PE and therefore relied only on biotic degradation. For example, the strain *Rhodococcus ruber* C20 caused an 8.8% weight loss on a branched LDPE film (0.2 mm thick) within 30 days of incubation (Gilan et al. 2004; Santo et al. 2013). In the same time range, the assessed weight loss of a HDPE material was nearly 12% for *Arthrobacter* sp. and 15% for *Pseudomonas* sp. (Balasubramanian et al. 2010). Another *Pseudomonas* sp. strain mineralized up to 28.6% of the carbon of a low-molecular-weight PE material within 80 days at 37 °C (Yoon et al. 2012). As shown with PS, a PE-degrading *Bacillus* sp. strain was isolated from waxworm gut. A 60-day incubation of this strain with a PE film resulted in a loss of 10% weight of PE, and soluble putative degradation products were found in the media (Yang et al. 2014). Recently, it was found that larvae of the wax moth can also feed on bags made of PE, but a potential underlying microbial activity was not investigated (Bombelli et al. 2017).

2.2.3 Polypropylene

PP is also difficult to degrade as reflected by the low weight losses of the polymer after treatments reported by most studies. For instance, after 1 year of incubation in soil or seawater, the observed gravimetric loss was below 1% (Artham et al. 2009). Weight loss was increased to approximately 10% when PP was pretreated at high temperatures. A similar pattern was observed by the same research group after incubation of PP with *Bacillus* and *Pseudomonas* strains. After 1 year, the pretreated material lost about 2.5% in weight, whereas there was no notable difference with the untreated one (Arkatkar et al. 2010). Considerably higher degradation of pretreated PP resulting in a 10–19% weight loss after 1 year could be achieved using fungi (Jeyakumar et al. 2013). However, values dropped to 5% when untreated material was supplied.

2.2.4 Polyvinyl Chloride

So far, no successful biodegradation of polyvinyl chloride (PVC) has been reported. An impressive example of this high recalcitrance was observed when a sample of PVC was buried in soil for 32 years and no significant degradation was detected (Otake et al. 1995). Consistent with these negative results is the observation that neither an incubation in soil lasting for months (Santana et al. 2012) nor the addition to liquid fungal cultures caused significant degradation of PVC films (Ali et al. 2014).

2.2.5 Polyurethane








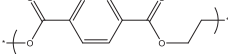
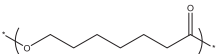

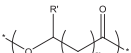
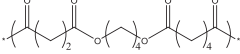
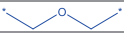
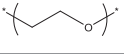


With a market of around 18 million tons a year, PUs are mainly used for long-term applications, including foams for furniture and insulation (soft or rigid foams based on open or closed cells, respectively). Coating, elastomers (TPU), adhesives, and sealants also use PUs. PU is mainly obtained by reactions between polyols (typically polyesters and polyethers) and polyisocyanates (aromatic and aliphatic) and is characterized by the synthesis of urethane or carbamate linkages. By varying these compounds, an infinite variety of PU architectures can be obtained. Most PUs present a complex formulation with several ingredients. PUs contain soft and hard segments, consisting of long polyols and isocyanate, respectively. According to the polyester-polyols structures, some biodegradability properties can be obtained (Krasowska et al. 2012). Numerous studies report the biodegradation of PU based on polyester-polyols by either enzymes, bacteria, or fungi (Wang et al. 1997; Russell et al. 2011; Shah et al. 2013). Polyether-polyols are, on the contrary, more resistant to biodegradation, although recent works describe the biodegradation of polyether-polyol-based PU foams by filamentous fungi from the *Cladosporium* (Álvarez-Barragán et al. 2016) or *Alternaria* genus (Matsumiya et al. 2010) using mechanisms not clearly elucidated.

3 Plastic-Degrading Enzymes

Depending on the type of chemical bonds present in the polymer, plastics such as PET, PU, and PE can be modified or even completely degraded by enzymes (Wei and Zimmermann 2017a). Their enzymatic degradability greatly depends on the type of molecular bonds present in the polymer (Table 1).

Plastics containing hydrolyzable bonds in their backbones, e.g., ester or urethane bonds, are depolymerized by polyester hydrolases, lipases, and proteases. Aromatic moieties in the backbones of, e.g., PET and PU, result in a higher resistance to biodegradation compared to their analogues containing aliphatic building blocks (Marten et al. 2005; Wei and Zimmermann 2017a,b). Synthetic polymers such as PE containing only carbon-carbon bonds in their backbones are recalcitrant to biological attack (Wei and Zimmermann 2017a), and, as explained before, their degradation in the environment has mainly been observed as the result of a combination of abiotic and biotic effects (Lucas et al. 2008). Among the biotic factors, several

Table 1 Chemical structures of typical plastics and putative degrading enzymes

Polymer name (abbreviation)	Structure	Putative enzymes
Vinyl polymers (polyolefins, styrenics, acrylates...)		
Poly(ethylene) (PE)		Laccase (EC 1.10.3.2): Santo et al. (2013); Manganese peroxidase (MnP, EC 1.11.1.13): Iiyoshi et al. (1998);
Poly(propylene) (PP)		Laccase (EC 1.10.3.2): Jeyakumar et al. (2013)
Poly(vinyl chloride) (PVC)		
Poly(styrene) (PS)		Hydroquinone peroxidase (EC 1.11.1.7): Nakamiya et al. (1997)
Poly(methyl methacrylate) (PMMA)		
Polyesters		
Poly(ethylene terephthalate) (PET)		Cutinase (EC 3.1.1.74): Ronkvist et al. (2009); Wei et al. (2014a); Yoshida et al. (2016); Wei et al. (2016) Lipase (EC 3.1.1.3): Eberl et al. (2009); Carboxylesterase (EC 3.1.1.1): Billig et al. (2010)
Poly(caprolactone) (PCL)		Cutinase (EC 3.1.1.74): Murphy et al. (1996); Wei et al. (2014b)
Poly(lactic acid) (PLA)		Lipase, cutinase, carboxylesterase, alkaline protease: Hajighasemi et al. (2016)
Poly(hydroxyalkanoate) (PHA)		PHA depolymerase: Kim et al. (2007)
Poly(butylene succinate co-adipate) (PBSA)		Cutinase (EC 3.1.1.74): Hu et al. (2016); Shinozaki et al. (2013) Lipase (EC 3.1.3): Thirunavukarasu et al. (2016)
Polyethers		
Poly(ethylene glycol) (PEG)		Dehydrogenases: White et al. (1996); Kawai (2002)
Poly(tetramethylene glycol) (PTMEG)		Dehydrogenases: White et al. (1996); Kawai (2002)
Polyamides		

(continued)

Table 1 (continued)

Polymer name (abbreviation)	Structure	Putative enzymes
Polyamide 6.6 (PA6.6)		Manganese peroxidase (EC 1.11.1.13): Deguchi et al. (1998), Friedrich et al. (2007); Laccase (EC 1.10.3.2): Fujisawa et al. (2001) Nylon hydrolase (EC 3.5.1.117): Negoro et al. (2012)
Polyamide 11 (PA11)		
Polyurethanes		
Polyester-polyol polyurethane		Cutinase (EC 3.1.1.74): Schmidt et al. (2017); Esterase (EC 3.1.1.1): Akutsu et al. (1998); Aryl acylamidase (EC 3.5.1.13): Akutsu-Shigeno et al. (2006); Elastase (EC 3.4.21.36): Labow et al. (1996); Urethanase (EC 3.5.1.75): Ruiz et al. (1999), Matsumiya et al. (2010)
Polyether-polyol polyurethane		Aryl acylamidase (EC 3.5.1.13): Akutsu-Shigeno et al. (2006) Elastase (EC3.4.21.36): Labow et al. (1996); Urethanase (EC 3.5.1.75): Ruiz et al. (1999), Matsumiya et al. (2010)
Polycarbonates		
Poly(bisphenol A carbonate) (PBPA)		
Poly(trimethylene carbonate) (PTMC)		Lipase: Matsumura et al. (2001), Suyama and Tokiwa (1997)

oxidoreductases have been shown to be involved in the biodegradation of PE (Sivan 2011; Restrepo-Flórez et al. 2014).

3.1 Cutinases

Cutinases (EC 3.1.1.74) catalyze the hydrolysis of cutin, an aliphatic polyester found in the plant cuticle (Chen et al. 2013). This group of polyester hydrolases are part of the superfamily of α/β hydrolases and show activity against several polyester plastics (Fig. 2) (Wei et al. 2014c; Wei and Zimmermann 2017a,b). Similar to lipases, cutinases display a catalytic triad composed of Ser-His-Asp. Unlike other enzymes of the family, the active site of cutinases is exposed to the solvent because the enzyme lacks the typical lid structure of lipases (Chen et al. 2013; Wei et al. 2014c). Depending on their origin, homology, and structure, plastic-degrading cutinases can

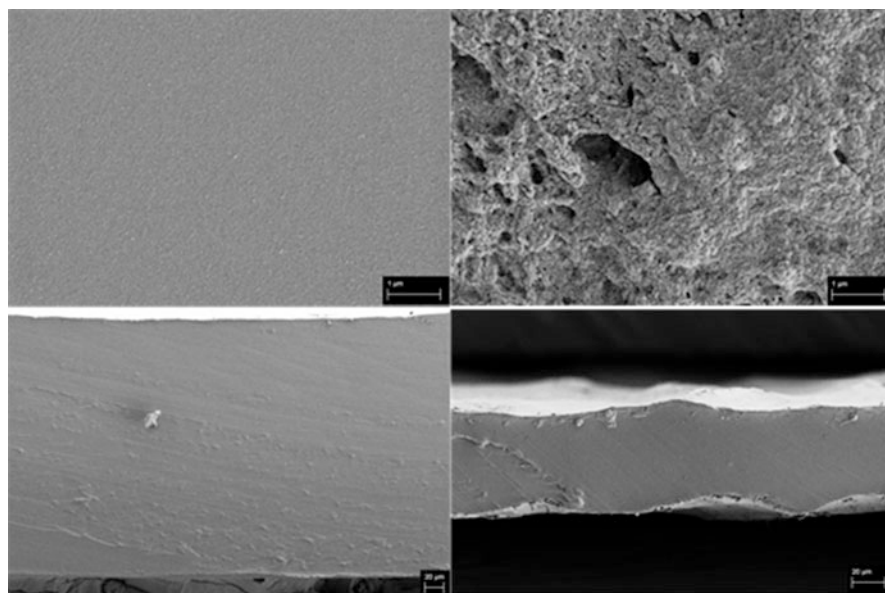


Fig. 2 SEM images of amorphous PET films exposed to the enzymatic hydrolysis catalyzed by TfCut2 from *Thermobifida fusca* KW3 (Wei et al. 2016) resulting a weight loss of 87% (b, d) as well as the negative control sample in the absence of TfCut2 (a, c). The comparison of the upper images indicates the progress of the enzymatic surface erosion. The lower images of cross sections show that the films become significantly thinner as a result of the enzymatic hydrolysis. Image kindly provided by Dr. Daniel Breite and Dr. Agnes Schulze, Leibniz Institute of Surface Modification, Permoserstr. 15, 04318 Leipzig, Germany

be divided into fungal (Ronkvist et al. 2009; Baker et al. 2012) and bacterial (Wei et al. 2014c). Fungal cutinases are mainly used in the hydrolysis and surface modifications of PET films and fibers (Vertommen et al. 2005; Araujo et al. 2007; Nimchua et al. 2007; Ronkvist et al. 2009; Zimmermann and Billig 2011). Among these enzymes, the cutinase from *Thermomyces insolens* showed the highest activity against low crystalline PET films due to its outstanding activity and thermal stability at 70 °C near the glass transition temperature of PET (Ronkvist et al. 2009). Bacterial cutinases and their homologues with PET-hydrolyzing activity have been isolated from various *Thermobifida* species (Zimmermann and Billig 2011; Wei et al. 2014c; Then et al. 2015), *Thermomonospora curvata* (Wei et al. 2014b), *Saccharomonospora viridis* (Kawai et al. 2014), *Ideonella sakaiensis* (Yoshida et al. 2016), as well as the metagenome isolated from plant compost (Sulaiman et al. 2012).

As mentioned above, the efficient hydrolysis of PET and PU by polyester hydrolases requires of high reaction temperatures of up to 70 °C (Then et al. 2016; Schmidt et al. 2017). At this temperature, the chains in the amorphous regions of the polymers become more flexible and prone to be accessed by the enzyme (Wei and Zimmermann 2017b). This process can be facilitated if the thermal stability of the enzymes is increased by adding bivalent metal ions (Then et al. 2015, 2016) and

phosphate anions (Schmidt et al. 2016) to the reaction medium, as well as by genetically engineering the thermolabile amino acid residues of the enzyme (Then et al. 2015, 2016). Moreover, the hydrolysis of PET plastics by polyester hydrolases could be strongly improved by the micronization of the plastic material in a pretreatment step to increase the accessible surface area of the substrate (Wei et al. 2014a; Gamerith et al. 2017). The accumulation of the low-molecular-weight products resulting from the hydrolysis reaction can lead to the inhibition of the enzymes (Barth et al. 2015a,b; Gross et al. 2017). This limitation can be overcome by the addition of a second enzyme hydrolyzing the products of the first reaction (Barth et al. 2016; Carniel et al. 2017) or by their continuous removal in an ultrafiltration membrane reactor (Barth et al. 2015b). It is also possible to obtain genetically modified polyester hydrolases insensitive to product inhibition in order to increase the efficiency of PET hydrolysis (Wei et al. 2016).

3.2 Lipases

Lipases (EC 3.1.1.3) are also part of the superfamily of α/β hydrolases and, like cutinases, display a Ser-His-Asp catalytic triad (Brady et al. 1990). There are multiple examples of microbial lipases capable of hydrolyzing aliphatic polyesters or aliphatic-aromatic co-polyesters (Tokiwa and Suzuki 1981; Marten et al. 2003; Marten et al. 2005; Herzog et al. 2006). For instance, lipases from *Thermomyces lanuginosus* have been shown to degrade PET and poly(trimethylene terephthalate) (Vertommen et al. 2005; Eberl et al. 2009; Ronkvist et al. 2009). Compared to cutinases, lipases exhibit lower hydrolytic activity against PET, possibly due to their lid structure covering the buried hydrophobic catalytic center, which restricts the access of aromatic polymeric substrates to the active site of the enzyme (Guebitz and Cavaco-Paulo 2008; Eberl et al. 2009; Zimmermann and Billig 2011). Lipases from *T. lanuginosus* (Eberl et al. 2009) and *Candida antarctica* (Carniel et al. 2017) also degrade low-molecular-weight degradation products of PET. The latter enzyme has been applied together with the cutinase from *T. insolens* for an improved production of terephthalic acid resulting from the hydrolysis of PET (Carniel et al. 2017).

3.3 Carboxylesterases

Bacterial carboxylesterases (EC 3.1.1.1) from *Bacillus licheniformis*, *Bacillus subtilis*, and *Thermobifida fusca* are known to hydrolyze PET oligomers and their structural analogues (Billig et al. 2010; Oeser et al. 2010; Ribitsch et al. 2011; Llsdorf et al. 2015; Barth et al. 2016). For example, the carboxylesterase TfCa from *T. fusca* is capable of releasing water-soluble products from high-crystalline PET fibers (Billig et al. 2010; Zimmermann and Billig 2011). These serine esterases also belong to the superfamily of α/β hydrolases, and, compared to the polyester hydrolases, they are significantly larger in size and display a much more buried hydrophobic substrate-binding pocket (Billig et al. 2010). Due to their high activity

against PET oligomers, they have been employed for the removal of inhibitory low-molecular-weight degradation products of PET in combination with polyester hydrolases (Billig et al. 2010; Oeser et al. 2010; Ribitsch et al. 2011; LÜlsdorf et al. 2015; Barth et al. 2016).

3.4 Proteases

Several proteases, for example, from *Pseudomonas chlororaphis* and *Pseudomonas fluorescens*, have been reported to degrade polyester PU (Labow et al. 1996; Ruiz et al. 1999; Matsumiya et al. 2010). In addition to the microbial enzymes, other proteases are known to be active against PU such as papain (EC 3.4.22.2), a cysteine protease from papaya, which can hydrolyze amide and urethane bonds (Phua et al. 1987). The porcine pancreatic elastase (EC 3.4.21.36) has been shown to release degradation products from both polyester and polyether PU as a result of the cleavage of hydrolyzable ester, urethane, and urea bonds in the soft segment domains of the polymer (Labow et al. 1996).

3.5 Lignin-Modifying Enzymes

Laccases (EC 1.10.3.2), manganese peroxidases (MnP, EC 1.11.1.13), and lignin peroxidases (LiP, EC 1.11.1.14) are involved in the degradation of lignin, a complex cross-linked aromatic polymer composed of phenylpropanoid units (Ruiz-Dueñas and Martinez 2009). Several of these oxidoreductases are known to be involved in the biodegradation of PE (Restrepo-Flórez et al. 2014; Krueger et al. 2015a). In the presence of copper ions, a thermostable laccase from *Rhodococcus ruber* C208 degraded, both in culture supernatants and in cell-free extracts, UV-irradiated PE films (Santo et al. 2013). This resulted in an increased amount of carbonyl groups and a reduction of the molecular weight within the amorphous part of the PE films. Another laccase isolated from *Trametes versicolor* degraded a high-molecular-weight PE (PE-HMW) membrane in the presence of 1-hydroxybenzotriazole, which mediated the oxidation of non-phenolic substrates by the enzyme (Fujisawa et al. 2001). In other examples, PE-HMW was also degraded by a combination of MnP from the white-rot fungi *Phanerochaete chrysosporium* ME-446 and MnP from isolate IZU-154 (Iiyoshi et al. 1998; Ehara et al. 2000), or cell-free supernatant of a *Phanerochaete chrysosporium* MTCC-787 culture containing both extracellular LiP and MnP, respectively. In this latter case, the combination of enzymes allowed to degrade 70% of a pre-oxidized PE-HMW sample within 15 days of reaction (Mukherjee and Kundu 2014).

4 Thermochemical Plastic Depolymerization

Advances in waste management technologies are promoting the growth of a world-wide industry developing waste-to-bioprocesses. As mentioned before, petroleum-based plastic wastes contain carbon fractions that are very resistant to biodegradation. In this context, thermochemical conversion techniques, other than incineration (combustion), such as gasification and pyrolysis are becoming widely accepted as suitable alternatives (Arena 2012; Messenger 2012; Tanigaki et al. 2013). Pyrolysis and gasification are thermal processes that, similar to incineration, use high temperatures to break down wastes, but consuming less oxygen than traditional mass-burn incineration. Whereas in the conventional pyrolysis process waste is thermally degraded in an almost complete absence of air, gasification is a process in which materials are exposed to some oxygen, but not enough to allow combustion.

4.1 Integrating Thermochemical Degradation of Plastic Waste into Biological Upcycling Processes

Aerobic microbial approaches can be applied to further upgrade the products of thermochemical plastic waste treatment to more value-added chemicals and biopolymers. In particular, bacteria such as the metabolically versatile *Pseudomonas* are able to use the thermochemical by-products as substrates for production of biodegradable polymers such as PHA. In one example, a two-step chemo-biotechnological process was used for converting PS to biodegradable mcl-PHA (Ward et al. 2006). In this approach, pyrolysis of PS was carried out at 520 °C to form styrene oil which was then converted by *Pseudomonas putida* CA-3 to PHA. A yield of 62.5 mg of PHA per gram of styrene oil was obtained. Another study investigated the conversion of the plastic PET using pyrolysis at 450 °C (Table 2) (Kenny et al. 2008). Following this step, the solid fraction containing terephthalic acid (>50%) was supplied as a substrate for the production of PHA using soil bacteria. Similarly, PE can also be used as a substrate for pyrolysis-mediated remediation as recently demonstrated with the conversion of postconsumer PE waste into mcl-PHA (Guzik et al. 2014). In this work, pyrolysis of PE in the absence of air produced a set of low-molecular-weight C8-C32 paraffin compounds. In a following step, the products of pyrolysis were emulsified in the presence of biosurfactants (rhamnolipids) and used as feedstock for *Pseudomonas aeruginosa* PAO-1, which accumulated up to 25% of the dry cell weight in the form of PHA.

4.2 Biological Conversion Processes of Syngas from Pyrolyzed Plastic Waste

An important product of gasification and pyrolysis of plastic waste is syngas (aka synthesis gas). Syngas contains mainly CO, H₂, and to a lesser extent CO₂ and other

Table 2 Fraction yields (wt%) of mixed plastic waste (MPW)^a and PET waste (PETW)^b and composition of the syngas fraction (vol%) with conventional pyrolysis (CP) and microwave-induced pyrolysis (MIP) at different temperatures

Product composition	MPW CP 400 °C	MPW MIP 400 °C	PETW CP 450 °C	MPW CP 800 °C	MPW MIP 800 °C
Solids	79.8	47.9	77	11.2	35.2
Oil	9.2	19.9	6.3	36.8	20.3
Gases	11	32.2	18	53	44.5
Syngas (% of the gas fraction)	35.5	32.7	16.7	30.1	46.2
With H ₂ (%)	0	9.1	0.2	9.2	26.6
With CO (%)	7.3	8.8	3.5	9.6	11.5
With CO ₂ (%)	28.2	14.8	13	11.3	8.1

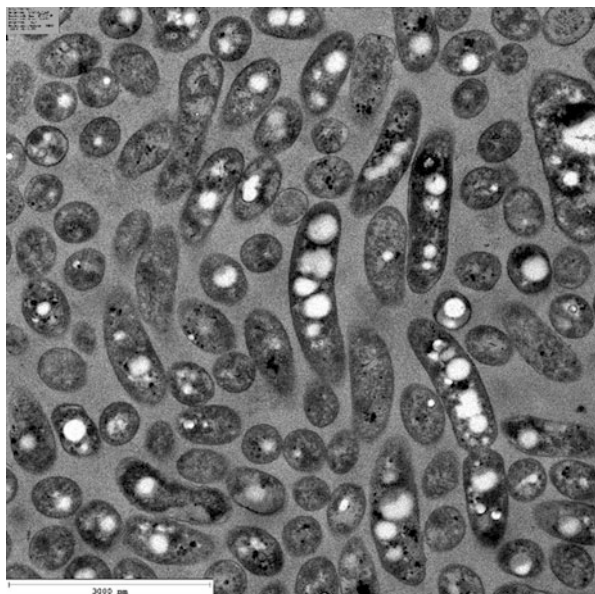
^aData selection taken from (Beneroso et al. 2015)^bData taken from (Kenny et al. 2008)

gases. As recently reviewed by (Drzyzga et al. 2015), syngas has been used as a feedstock for the production of bulk chemicals such as acetic acid, butyric acid, or biofuels (e.g., ethanol and butanol) either by chemical catalytic conversion (e.g., Fischer-Tropsch (FT) synthesis) or biological conversion processes (e.g., syngas fermentation).

There are other emerging thermal waste conversion technologies such as microwave-induced pyrolysis (MIP). MIP is one of the most attractive alternatives due to the higher waste conversion and product yields and, at the same time, much lower energy consumption of the process (Fernandez et al. 2011; Byun et al. 2012; Zhang et al. 2012). MIP not only overcomes the disadvantages of CP, such as slow heating and necessity of feedstock shredding, but also improves the quality of the final pyrolysis products. Table 2 shows a comparison between the syngas produced by MIP or CP of mixed plastic waste and waste PET at different temperatures. The data generally demonstrate that MIP is more efficient than CP in many pyrolytic processes of plastic waste, as shown by the higher total amount of syngas produced, which also contains a higher proportion of CO and H₂. In addition, MIP significantly saves processing time and energy compared with CP and often produces lower amounts of unwanted compounds such as CH₄ or hydrocarbons with two or more C atoms (including aromatics) at the highest temperatures (Beneroso et al. 2015).

Regardless of the method used for the production of syngas, in *syngas fermentation*, microorganisms are responsible for the conversion of syngas (the C1 and H₂ fractions) to a diversity of chemical building block compounds (Munasinghe and Khanal 2010; Bengelsdorf et al. 2013; Latif et al. 2014; Drzyzga et al. 2015). Chemicals produced from syngas fermentation include a wide set of compounds such as H₂, CH₄, carboxylic acids (e.g., acetic acid, butyric acid), as well as alcohols and diols (e.g., ethanol, butanol, butanediol) (Köpke et al. 2011a,b; Dürre 2016). Syngas fermentation can produce monomer compounds useful for biopolymer synthesis, such as C4 compounds (e.g., butanediol, succinate, hydroxybutyrate), or

Fig. 3 PHA-producing strain of *Rhodospirillum rubrum* grown with syngas plus acetate as carbon and energy sources



it can directly produce biopolymers, such as PHAs, polyhydroxybutyrate (PHB), or poly(hydroxybutyrate-*co*-hydroxyvalerate (Do et al. 2007; Choi et al. 2010). Several anaerobic bacteria are able to use C1 gases such as CO and CO₂ by fermentation, converting them to chemicals, usually acetate, through the acetyl-CoA pathway (Müller 2003). These bacteria are named acetogens and include (among others) species such as *Acetobacterium woodii*, *Alkalibaculum bacchi*, *Butyribacterium methylotrophicum*, and many species of the genus *Clostridium* (e.g., *C. ljungdahlii*, *C. aceticum*, *C. thermoaceticum*, *C. autoethanogenum*, *C. ragsdalei*, *C. carboxidivorans*) (Diender et al. 2015; Dürre and Eikmanns 2015).

Besides acetogenic bacteria, *Rhodospirillum rubrum* appears particularly well suited for growth with CO-/CO₂-containing syngas. *R. rubrum*, the type strain of the *Rhodospirillaceae* family, is capable of growth under the broad variety of conditions containing syngas (Do et al. 2007). *R. rubrum* can utilize CO under anaerobic conditions as the sole carbon and energy source. Part of the CO₂ produced is assimilated into cell material (including the stored PHA; Revelles et al. 2016a,b), and the remaining CO₂, along with H₂, is released from the cells. The enrichment of H₂ during syngas fermentation has made *R. rubrum* a particularly attractive organism for the bioconversion of syngas into value-added products, and the feasibility of these processes has been demonstrated with the production of PHA (Fig. 3) in continuous stirred tank reactors fed with syngas (Do et al. 2007; Choi et al. 2010).

5 Research Needs

Recent studies have shown that plastics that are traditionally considered non-biodegradable, such as PET and PE, can be degraded and metabolized by microbes. Several enzymes capable of hydrolyzing the ester-containing PET and other polyester plastics such as PU have been identified (Wei and Zimmermann 2017b), and the monomers resulting from the reaction can be used as a carbon source by different microorganisms. This constitutes a paradigm shift in what can be considered biodegradable plastic. Notwithstanding these developments, it is clear that environmental plastic pollution is a major issue. Even if new plastic-eating organisms are now emerging in this man-made niche through evolution, these plastics remain highly recalcitrant due to their molecular inaccessibility, macroscopic structure, and the low observed rates of degradation. The rate of accumulation thus far greatly exceeds the rate of biodegradation, and we should not assume that nature will take care of the problem for us.

The problem of plastic waste pollution is primarily one of waste management, which currently is of low priority in many countries. This is caused by the low value of plastic waste, which is comparable to the price of virgin plastics. One solution to this problem is to add value to plastic waste, by using it as a carbon source in biotechnological processes. Such upcycling of plastic waste creates an opportunity to improve the efficiency of resource usage and contribute to a circular economy (European Commission 2017), likely resulting in a transformative technology with an outstanding potential to deliver social and economic benefits. The feasibility of this approach has already been demonstrated in lab-scale processes for the chemobiotechnological conversion of PS (Goff et al. 2007), PET (Kenny et al. 2008, 2012), and PE (Guzik et al. 2014). In these two-step technologies, the oil obtained by plastic waste pyrolysis is used as a feedstock for microbial production of PHA. The aforementioned plastic-modifying enzymes are key to achieving a complete biological process for plastic waste upcycling into biodegradable plastic, but, in addition, suitable microorganisms capable of assimilating the hydrolysis products are required. The combination of these two elements would give rise to a customizable microbial platform capable of converting plastic waste. It is worth noting, however, that the metabolism of these monomers is not trivial, since plastics are generally made up of molecules that are not common in nature and thus are not always readily metabolized by microbes.

Alternatively, thermochemical depolymerization methods such as pyrolysis would lead to completely different substrates, with strong focus on syngas. With the recent developments of efficient and inexpensive methods to sequence complete microbial genomes, the genetics of many syngas-fermenting microorganisms is becoming better understood. This knowledge in combination with the newest tools in systems biology can be applied to these microorganisms to enhance the production of chemical compounds from gaseous C1 compounds through metabolic and genetic manipulations (Köpke et al. 2010; Latif et al. 2014). Additionally, methods such as media and reactor design optimization are being pursued to enhance chemical production from existing and newly isolated CO/CO₂-fermenting

microorganisms. The application of all these technologies will contribute to make microbial fermentative production of chemical building block compounds cost-effective when compared with other technologies (Wilkins and Atiyeh 2011). To highlight the potential of syngas fermentation, in the last decade, we have witnessed its application in the production of biofuels (mainly bioethanol) at pilot or industrial scales (e.g., LanzaTech Inc., USA).

The challenge of the bio-utilization of plastic waste is similar to that faced by lignocellulosic biotechnology, which relies mostly on enzymatic hydrolysis and monomer metabolism as key enabling factors. Therefore, much can be learned from developments in this field. We thus expect that major research efforts will be needed to find and engineer efficient plastic-degrading enzymes and associated processes. Also, research is needed toward characterizing the microbial degradation of a wide variety of plastic monomers, varying from long-chain aliphatics derived from PE to α,ω -alcohols and α,ω -acids, as well as complex aromatics derived from PET and PU. In principle, when these two steps, namely, the enzymatic hydrolysis and the subsequent degradation of the monomers, have been taken, the substrate in virtually any current sugar-based biotech process could be replaced with plastic waste. Initially, research will be focused on relatively pure plastics of a single type (i. e., PET), but the real strength of microbial plastic utilization will lie in the ability to utilize mixed waste streams which are inaccessible to traditional recycling techniques.

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