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MINI-REVIEW

Current progress on the biodegradation of synthetic plastics: from fundamentals to biotechnological applications

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Abstract Plastic pollution is a global concern due to the long half-life and high resistance of many synthetic plastics to natural biodegradation. Therefore, great effort is required to avoid littering. However, the challenge of managing the ever-increasing quantities of plastic waste is daunting. The biodegradation of synthetic plastics, such as polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), and polyurethane (PUR) by microorganisms is either slow or under investigation as to whether it occurs at all in different environmental niches (e.g., soil, aquatic systems). There is an urgent need to complement the existing knowledge on the biodegradation and biotransformation of synthetic plastics to enable effective bioremediation strategies to mitigate the effects of environmental plastic contamination. Therefore, the aim of this review is to highlight current fundamental and applied research regarding the most promising biodegradation processes for synthetic plastics, the synthesis and applications of the most effective plastic-degrading enzymes, successful biotechnological strategies to improve degradation, such as enzyme engineering and novel reactor designs, and plastic waste bioconversion into value-added products. In addition, this review is intended to depict indications for techno-economic analyses toward the valorization of plastic biodegradation processes and the environmental impacts of synthetic plastic biodegradation. Combining strategies, such as enzymatic plastic degradation followed by microbial biotransformation with the broad array of available pretreatment methods and abiotic factors, can contribute, under confined conditions, to the end-of-life utilization of plastics, consequently leading to more efficient biorecycling processes, and hence, to a circular plastic economy.

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Abbreviations

BHET	Bis(2-hydroxyethyl) terephthalate
CALB	Candida antarctica lipase B
Cu	Cupper
EG	Ethylene glycol
H_2O_2	Hydrogen peroxide
LCA	Life-cycle analysis
LCB	Lignocellulosic biomass
LCC	Leaf-branch compost cutinase
LiPs	Lignin peroxidases
MHET	Mono(2-hydroxyethyl) terephtalate
MnPs	Manganese peroxidases
MSP	Minimum selling price
PCA	Protocatechuate
PEF	Polyethylene furanoate
PLA	Polylactic acid
PE	Polyethylene
PET	Polyethylene terephthalate
PP	Polypropylene
PS	Polystyrene
PU	Polyurethane
PTT	Polytrimethylene terephthalate
PVC	Polyvinyl chloride
SS	Sodium sulfate
TEA	Techno-economic analysis
TPA	Terephthalic acid
TPPB	Two-phase partitioning bioreactor

1 Introduction

Petrochemical plastics have reached an annual estimated production of 359 million tons, and that production over the last 70 years has reached approximately 8.3 billion tons (Kaushal et al. 2021). Upon analyzing these numbers, the management of plastic waste easily becomes unsustainable. Furthermore, it is well known that most petroleum-based plastics persist in the environment for long periods due to their intrinsic properties, including high resistance to microbial degradation (Hopewell et al. 2009; Tokiwa et al. 2009; Amobonye et al. 2021; Zhu et al. 2022).

Saturated polyolefins have a broad range of applications since the versatility of these polymers arises from their cheap petrochemical feedstock origin and efficient catalytic polymerization process, with polyethylene (PE) and polypropylene (PP) being two of the most widely used linear hydrocarbon polymers (Yeung et al. 2021). The recalcitrance of C–C backbone plastics to biodegradation is due to their extremely stable covalent C–C and C–H bonds as well as the absence of reactive functional groups (Fig. 1). In addition, the high molecular weight and hydrophobic nature of C–C polymers hinder biological degradation since extracellular enzymes capable of oxidizing and depolymerizing long carbon chains are required to break down the polymer (Yang et al. 2014). Multiple microorganisms have been found to degrade PE, especially when the plastic polymer is pretreated before being exposed to biological degradation (Restrepo-Flórez et al. 2014; Cowan et al. 2022). The microbial degradation of PP has not been well investigated, and only a few reports describe the degradation of pretreated PP films by soil consortia, bacterial communities, and fungal species (Alariqi et al. 2006; Arkatkar et al. 2009; Auta et al. 2018). Polystyrene (PS) and polyvinyl chloride (PVC) plastics also have C–C bonds in their structure, with PVC being considered one of the most durable synthetic polymers together with PP (Chen et al. 2020). Despite the widespread use of these polymers, there are only a few reports on their effective biodegradability (Wei et al. 2020).

The other group of synthetic polymers, which are categorized as heteroatomic backbone plastics (Wei and Zimmermann 2017), has been observed to be more susceptible to biodegradation processes. This group includes polyethylene terephthalate (PET) and polyurethane (PUR) polymers, which contain hydrolyzable ester and urethane bonds, respectively (Mohanan et al. 2020). PET is the most common type of aromatic polyester; it is widely used as a packaging material and in bottles and fibers. As a sustainable recycling alternative for waste PET materials, microbial polyester hydrolases from fungi and bacteria have already been evaluated for their potential to help solve the challenge of PET waste management. In nature, cutin is an abundant polyester found in plant cuticles. Interestingly, many polyester hydrolases with activity against PET are related to cutin-hydrolyzing esterases, the so-called cutinases (Wei et al. 2014; Zhu et al. 2022). The biodegradation of polyester PUR has been demonstrated primarily by soil fungi, but unlike

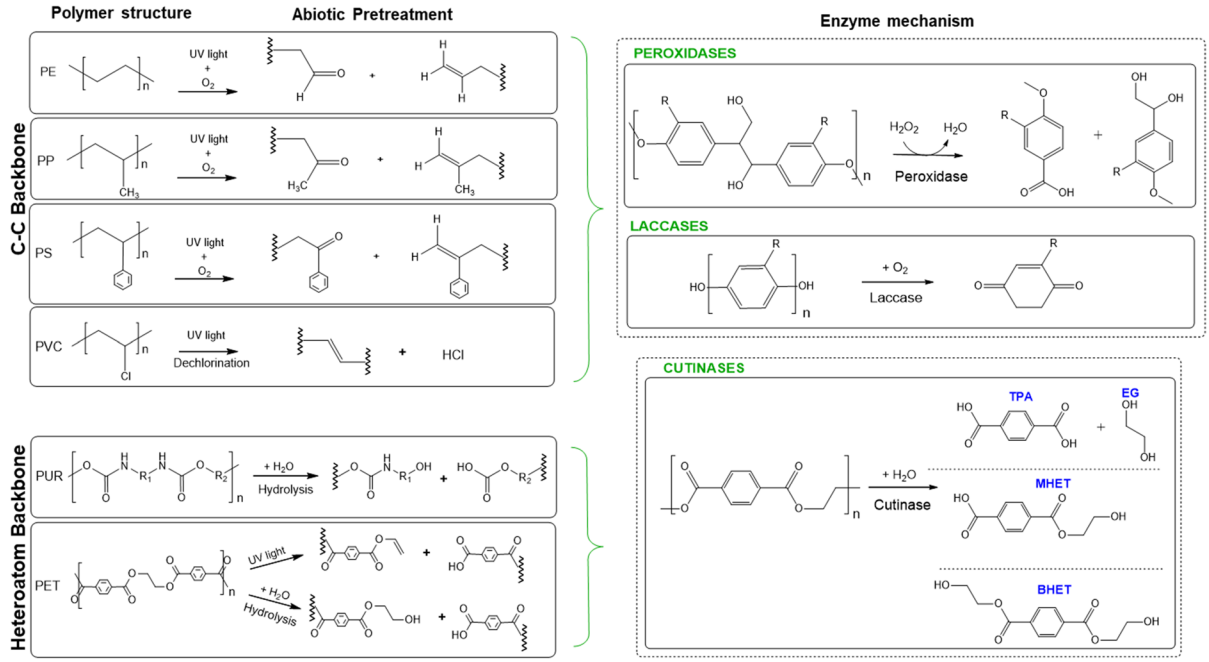

Fig. 1 **A** Chemical structure of synthetic plastics and proposed polymer chain cleavage due to abiotic factors. **B** Catalytic reaction of the most common extracellular enzymes capable of altering the chemical and physical properties of polymers (bio-deterioration) or polymer breakdown (bio-fragmentation)

in PET, the responsible enzymes that contribute to PUR decomposition remain elusive and under investigation (Liu et al. 2021).

The literature is extensive regarding the degradation of plastics, primarily because of the environmental impact they generate and their projected future lacking feasible and sustainable solutions. A comprehensive overview of the bacterial degradation of synthetic polymers was recently published, indicating that important research must include (i) Further screening for microorganisms and biodegradation pathways as well as (ii) Standardizing the corresponding studies and methodologies (Matjašič et al. 2021). Kaushal et al. (2021) summarized recent advances in the enzymatic degradation of the most frequent plastic materials to be attacked by hydrolases and suggested focusing on approaches that enhance these activities. The biodegradation of microplastics by different microorganisms and their respective enzymes has been extensively described (Arpia et al. 2021; Othman et al. 2021). Detailed compilations of studies on the biodegradation of conventional plastics and/or bioplastics by bacteria, fungi, and larvae are also available (Mohanan et al. 2020; Maity et al. 2021). Several studies have focused on integrative degradation processes, proposing the use of synthetic biology (Jaiswal et al. 2020) and the microbial valorization of waste plastics for the biosynthesis of high-value chemicals (Ru et al. 2020). Lastly, a very recent review of biotechnological and molecular advancements in plastic biodegradation provides a comprehensive assessment and future perspectives, including synthetic biology and computational approaches (Priya et al. 2021).

However, for most petroleum-based plastics, little is known about the metabolic pathways, or the mechanisms and enzymes involved. In addition, there are contradictory views on the biodegradation of C–C bonds since it is claimed that the energy required to break C–C bonds is too high for enzymes to overcome. Recently, by using protein engineering, it was possible to obtain a PET hydrolase with significant improvements in the PET degradation rate (Tournier et al. 2020), which would make it possible to develop an industrial biodegradation process for PET. In this way, it has been shown that optimization tools, both molecular and process-related, are of great importance for the biodegradation of polymeric materials.

This review emphasizes the most promising enzymes, microorganisms, and host systems, providing auspicious results with regard to the degradation of synthetic plastics and the main strategies that enable effective biodegradation processes.

The first part of the review presents relevant studies that are organized according to the chemical structure of the polymers and the potential enzymes capable of attacking these structures. Biotechnological advances have led to the continuous improvement of plastic biodegradation processes. Thus, the second part of this review focuses on the most promising strategies with high application potential in the fields of enzyme engineering, process optimization, and reactor design as discussed in the context of subsequent upcycling routes (Fig. 2). The last part of the review focuses on techno-economic aspects of the valorization of plastic biodegradation processes and the environmental implications for the enzymatic degradation of synthetic plastics. All these considerations provide the current framework for selecting suitable microorganisms and enzymes for the efficient biodegradation of the different petroleum-based plastic polymers and provide an overview of up-to-date approaches to tackling the plastic problem with cost-effective solutions.

2 Enzymatic degradation of synthetic plastics

2.1 Insights into the enzymatic cleavage of polymers

The use of living organisms in catalyzing solid substrates is usually a major challenge, resulting in low degradation yields (Andler et al. 2018; Andler 2020). Currently, both bacteria and fungi are host systems for producing enzymes such as laccases, peroxidases, cutinases, and esterases. A major limitation in using enzymes for plastic degradation on an industrial scale is the stability of the enzymes under various conditions, such as high temperatures and extreme pH conditions (Gomes et al. 2013; Al-Tammar et al. 2016). For this reason, many investigators have searched different microorganisms for efficient enzymes to demonstrate their use in industrial applications (Chen et al. 2013; Tournier et al. 2020; Saravanan et al. 2021).

Here, we present the enzymes with the most promising results in the field of plastic degradation. For a

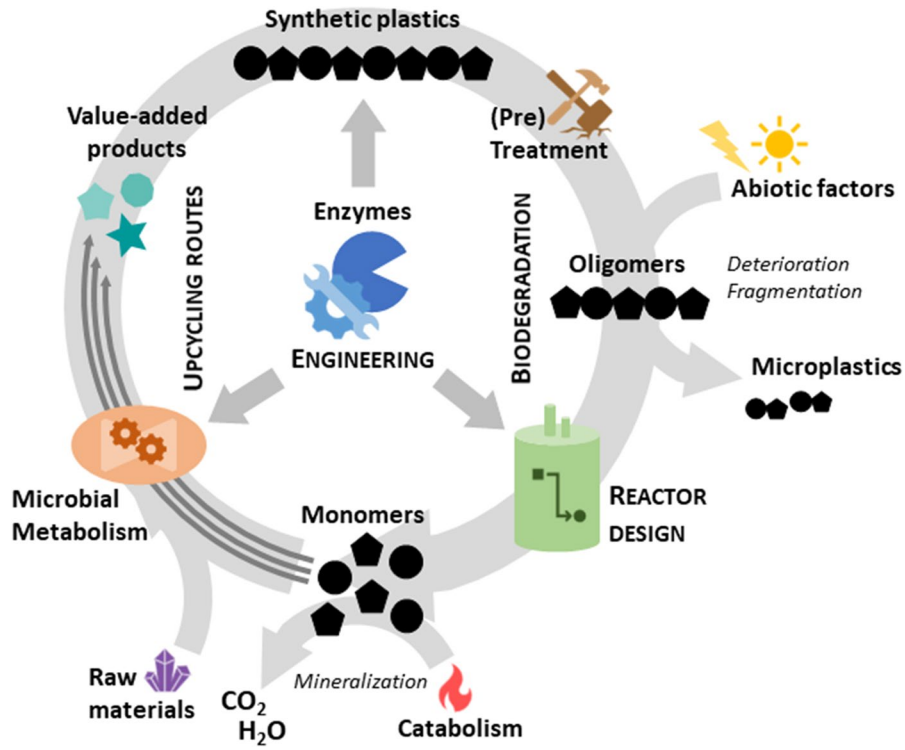

Fig. 2 Schematic overview of the microbial degradation of synthetic plastics and upcycling towards value-added products. Light grey arrows indicate the main routes of synthetic plastics; thin dark grey arrows represent the multiple upcycling routes towards value-added products

better understanding, the studies are organized into two groups according to the nature of the bonds that link the monomers together. The first group includes plastics with a C–C backbone, such as PE, PP, PS, and PVC, while the second group corresponds to plastics with a heteroatomic backbone, such as PUR and PET (Fig. 1). In Table 1, different studies showing enzymes that effectively degrade synthetic plastics, including hydrolases, laccases, and peroxidases, are summarized.

2.1.1 Enzymatic degradation of plastics with a C–C backbone

The biodegradation of plastics with C–C bonds in their structure is poor, primarily due to the lack of hydrolyzable functional groups. This issue represents one of the biggest challenges in the absence of physicochemical pretreatment processes (Restrepo-Flórez et al. 2014). Since enzymes that degrade natural polymers with C–C bonds exist in nature, it has been proposed that these enzymes are prime candidates for the biodegradation of polyolefins (Chen et al. 2020). This is the case for lignin-degrading enzymes, the second most abundant natural polymer (after cellulose) in nature. The main enzymes reported to have the ability to break down this group of polymers are laccases and peroxidases.

Laccases (benzenediol:oxygen oxidoreductase; *p*-diphenol oxidase EC 1.10.3.2) are multicopper oxidase enzymes that were described for the first time in Japanese or Chinese lacquers (*Rhus* sp.) by Yoshida in 1883 (Madzak et al. 2005; Sumathi et al. 2016). These enzymes are widely found in nature and can catalyze the oxidation of various substrates, including phenolic compounds, non-phenolic substrates, and environmental pollutants, by transferring electrons from organic substrates to molecular oxygen (Fig. 1). In nature, a wide variety of microorganisms produce laccases, such as filamentous fungi, some plants, bacteria, and a few insects (Janusz et al. 2020). The functions described for laccases depend on the organism. In plants, laccases act in the degradation of lignin (Alessandra et al. 2010). Fungal laccases play a role in fungal plant pathogen/host interactions, morphogenesis, and stress defense (Moreno et al. 2020; Janusz et al. 2020). Bacterial laccases can confer resistance to UV radiation and oxidation, in addition to participating in sporulation and pigmentation processes (Alessandra et al. 2010; Janusz et al. 2020). The great interest in studying laccases is due to their widespread use in many biotechnological processes, from textile bleaching to pharmaceuticals and the bioremediation of industrial waste (Chandra and Chowdhary 2015; Munk et al. 2015; Roth and Spiess 2015; Ece et al. 2017; Singh and Gupta 2020; Lecourt et al. 2021). According to Chen et al. (Chen et al. 2020), the site with the highest redox potential activity in laccases corresponds to the T1 site, one of the four Cu centers described from the X-ray structure of a laccase from *Trametes trogii*, which should be responsible for the oxidation of the substrate. However, this mechanism is still hypothetical and would work primarily for phenolic lignin substrates. Few studies have been able to associate microbial or fungal laccase with the ability to degrade polyethylene; however, some efforts have been made, especially toward their potential to reduce polymer molecular weights (Cowan et al. 2022).

Peroxidases (EC number 1.11.1.x) are a set of oxidoreductases responsible for promoting the oxidation of organic and inorganic compounds by oxidation–reduction reactions using H_2O_2 as an electron-accepting co-substrate (Fig. 1) (Pandey et al. 2017; Twala et al. 2020). This protein family is very important for industrial and biotechnology processes. Generally, its applicability is linked to the process of dye discoloration, bioremediation, bioenergy, and textile industry activities. Many organisms can produce these sets of enzymes, such as animals, plants, and microorganisms, including *Bacillus subtilis*, *Trametes villosa*, *Phanerochaete chrysosporium*, and *P. tremellosa* (Pandey et al. 2017; Zahmatkesh et al. 2017; Twala et al. 2020; Amobonye et al. 2021). Within this large group, manganese peroxidases (MnPs EC 1.11.1.13) and lignin peroxidases (LiPs EC 1.11.1.14) are the most commonly used peroxidases in C–C backbone plastic degradation processes. These enzymes contain Fe^{III} in their active site, which forms a reactive complex upon reaction with H_2O_2. An electron donor, which could be a C–C polymer, reduces the complex to form a new compound, which is again reduced to regenerate the initial enzyme structure (Chen et al. 2020).

Ligninolytic enzymes have the ability to cleave the C–C bonds of lignin; however, it is difficult to compare these bonds with those present in synthetic polymers. The complex structure of lignin

Table 1 Overview of the most promising plastic-degrading enzymes

Enzyme	Donor microorganism	Host microorganism	Plastic material	Culture medium	Production yield / activity	Purification process	Evidence of biodegradation	Reference
Cutinase (AnCUT2)	*Aspergillus niger* ATCC 10,574	*Pichia pastoris* strain X 33	PCL and PET pellets	Yeast extract peptone dextrose (YPD) agar supplemented with Zeocin (from 100 µg/mL to 2.0 µg/mL)	42 U/mL	NA	SEM analysis shows evidence of corrosion and pitting of the material	Al-Tammar et al. (2016)
Cutinase (CUT-N1)	*Fusarium solani* + *Cellulomonas fimi*	Genetically modified *Eschericha coli*	PET bottles	LB and 2% agar, supplemented with 100 µg/ml ampicillin	1.4 U/mL	NA	PET weight loss of 0.90%	Gomes et al. (2013)
Cutinase (LC-cutinase)	*Thermobifida fusca*	*E. coli* BL21	PCL and PET films	LB medium supplemented with 50 mg of ampicillin L^{-1}	6–8 mg/L	Ammonium sulphate, 10 mM Tris–HCl (pH 7.0); dialysis process from extracellular medium	1.45 mg PET mass loss after 24 h; 9.5 mg PCL mass loss after 6 h	Sulaiman et al. (2012)
Cutinase (Thc_Cut1)	*Thermobifida cellulosilytica*	*P. pastoris*	PBS and PHBV	Buffered glycerol complex	400 ± 20 mg/L	Affinity chromatography	PHBV films presented 3.0% mass change and PBS showed 93.2% mass decrease; PBS film resulted in large weight losses and surface changes	Gamerith et al. (2017)
PETase	*Streptomyces SM 14*	*E. coli* BL21(DE3)	PCL	LB agar medium	NA	NA	Clearing zone in presence of PCL	Almeida et al. (2019)

Table 1 (continued)

Enzyme	Donor microorganism	Host microorganism	Plastic material	Culture medium	Production yield / activity	Purification process	Evidence of biodegradation	Reference
Wild PETase; double mutant PETase (S238F/W159H)	*Ideonella sakaiensis* 201F6	*E. coli* C41(DE3)	PET	2 × TY	10 mg/mL	Ni-affinity chromatography and gel filtration	Pitting and erosion on PET surface; changes in PET relative crystallinity	Austin et al. (2018)
MHETase	*Ideonella sakaiensis* 201F6	*E. coli*	PET	NA	2.5 mg/L	NA	Degradation of around 40% of BHET in presence of 2 µM MHETase	Sagong et al. (2020)
Laccase	*Cochliobolus sp.*	NA	PVC	Czapek Dox	Laccase production: 1.966 nkat/mL; protein activity (2720 mg/mL)	NA	Structural and morphological changes were observed in PVC BTS through the SEM technique	Sumathi et al. (2016)
Laccase	*Bjerkandera adusta* TBB-03	NA	HDPE	Potato dextrose agar containing 2.2-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS); malt extract medium (ME; malt extract 20 g, peptone 1 g L^{-1}, pH 4.5); carbon-liquid medium (LM) and SSF	86.3–211.4 U/L	Filtration of supernatant using 0.2 µm PES syringe filters	Changes in crystallinity were detected by using Raman microspectroscopy. Appearance of pits and cracks in the HDPE surface by SEM	Kang et al. (2019)

Table 1 (continued)

Enzyme	Donor microorganism	Host microorganism	Plastic material	Culture medium	Production yield / activity	Purification process	Evidence of biodegradation	Reference
Laccase	*Trametes versicolor* IFO 6482	NA	PE and nylon-66 membrane	Potato dextrose agar	100-fold (500 nkat)	Ammonium sulphate (AS)–30 to 90% of saturation; dialysis. Elution using 50 mM Tris–HCl buffer containing 100 mM NaCl (pH 7.0)	Decrease in molecular weight from 242,000 to 28,300 (PE) and from 79,300 to 14,700 (nylon-66 membrane). Reduction of the elongation and tensile strength	Fujisawa et al. (2001)
Laccase	*Rhodococcus ruber* C208	NA	LDPE	Synthetic medium (SM) with 0.2 mm LDPE films (3×3 cm)	350 mAu/min	NA	Reduction of average molecular weight by 15–20%. Weight loss of 2.5%	Santo et al. (2013)
Peroxidase	White rot fungus strain IZU-154	NA	Nylon-66 membrane	Potato dextrose agar plates; in CSL-glc medium; nitrogen-limited medium	NA	Ion-exchange chromatography, gel filtration chromatography, and hydrophobic chromatography	Changes in the nylon surface were observed as the presence of deep horizontal grooves	Deguchi et al. (1998)
Peroxidase	*Phanerochaete chrysosporium* NK-1	NA	PVC film	Seaboard dextrose liquid and agar medium; minimum salt medium	67 U/mL	Ammonium sulphate saturation	Polymer weight loss of 31%; intermediates compounds formed after the degradation assay Corrosion and holes on the PVC surface	Khatoon et al. (2018)

Table 1 (continued)

Enzyme	Donor microorganism	Host microorganism	Plastic material	Culture medium	Production yield / activity	Purification process	Evidence of biodegradation	Reference
Peroxidase	*Azotobacter beijerinckii* HM121	NA	PE	NA	2.4 U/mg	NA	Degradation seen in water phase: Rf 0.6 (Mr 1,0) after 5 min and Rf 0 (Mr 350) after 10 min	Nakamiya et al. (1997)

provides a wide variety of C–C bonds, with bond energies in the range of 205–308 kJ mol^{-1} (Guadix-Montero and Sankar 2018). The energy required for the dissociation of the C–C bond of PE is approximately 350 kJ mol^{-1} (Popov and Knyazev 2014). It is therefore unlikely that this enzyme will substantially degrade synthetic polymers with C–C bonds without physicochemical pretreatments. A recent study performed using quantum mechanism calculations analyzed the cleavage of C–C bonds of polymers such as PE and PS. The results suggest that under certain operating conditions, laccase and peroxidase enzymes could abstract a hydrogen anion, which would cause the absence of a hydride anion at the C_β position. This change would result in a significant reduction of the C2–C3 bond, causing bond cleavage (Xu et al. 2019).

The analyzed studies (Table 1) reveal that most enzymatic degradation processes with polymers containing a C–C skeleton do not achieve robust degradation, especially in the absence of physicochemical pretreatments as the first degradation step. Laccase and peroxidase enzymes play a secondary role in attacking the oligomers or degradation products resulting from polymer cleavage. The effectiveness of enzymatic mechanisms for these types of polymers depends largely on whether there is a prior step of incorporating double bonds or oxygen, for which abiotic factors are often necessary (Fig. 1) (Wei et al. 2020). Photoinitiated oxidative degradation is postulated to be the abiotic factor with the greatest effect on plastic waste found in the environment. It causes the appearance of free radicals, which is more difficult to induce for polymers such as PE and PP since they lack double bonds. If radicals are formed, they react with the oxygen in the environment to form radical peroxides (Singh and Sharma 2008). This propagation step leads to chain scission or cross-linking. As a result, carbonyl functional groups such as aldehydes and ketones are obtained, the molecular weight decreases, hydrophilicity increases, and the polymer becomes susceptible to fragmentation, which makes the enzymatic attack possible (Gewert et al. 2015).

Further evidence is needed to show that the biodegradation processes of polyolefins are indeed caused by microorganisms and their enzymes and not by external sources.

2.1.2 *Enzymatic degradation of plastics with heteroatoms in the main chain*

The group of plastics with a heteroatomic backbone, such as PET and PUR, have ester or amide bonds that can be hydrolyzed more easily than C–C bonds (Wei and Zimmermann 2017). As described by Tang et al. (2021), these polymers are susceptible to hydrolytic attack and the mechanisms include photooxidation, hydrolysis, and biodegradation. The main enzymes described for the cleavage of this group of polymers are hydrolases, lipases, esterases, proteases, and ureases (Chen et al. 2020).

Cutin hydrolases or cutinases (EC 3.1.1.74) are inducible extracellular enzymes found in fungi and bacteria (Al-Tammar et al. 2016) that are capable of cleaving the ester bonds of cutin. Their hydrolytic activity can act on several water-soluble esters, plastics, triglycerides, and synthetic fibers (Al-Tammar et al. 2016). Cutinases represent the most common PET hydrolytic enzymes, which systematically belong to the serine hydrolase family next to lipases and carboxylesterases. Microorganisms capable of degrading plant biomass secrete cutinases, which then hydrolyze cutin, thereby releasing cutin monomers. Cutinases are present in both fungi and bacteria and have similar properties and mechanisms. Bacterial enzymes should be placed into a different cutinase subfamily due to differences in sequence and structure, most likely leading to their superior thermostability (Chen et al. 2018).

A recent study of the taxonomic distribution of PET-degrading enzymes showed that bacterial PET hydrolases in marine ecosystems occur predominantly within the phylum *Bacteroidetes*, whereas in terrestrial environments, the phylum *Actinobacteria* dominates (Danso et al. 2018). As an obvious explanation for this narrow distribution of PET hydrolases, the authors indicated that the ability to degrade PET most likely evolved rather recently and is therefore not yet a widespread metabolic tool. The highest number of characterized PET-degrading enzymes thus far are derived from *Thermobifida fusca, Thermomonospora curvata, Fusarium solani,* and *Ideonella sakaiensis* (Wei et al. 2014; Tournier et al. 2020).

Among *Actinobacteria*, PET-degrading enzymes from *Thermobifida* species (*T. cellulosilytica*, *T. alba*, and *T. halotolerans*) have been identified as well as one from the phylum *Thermomonospora* (*T. curvata*) and one from *Saccharomonospora* (*S. viridis*). The closely related cutinases Thc_CutI and Thc_Cut2 from *T. cellulosilytica* have been shown to exhibit distinct hydrolytic efficiencies on PET, which is explained by the differences in their electrostatic and hydrophobic surface properties (Herrero Acero et al. 2011, 2013). The extracellular hydrolases Tcur1278 and Tcur0390 from *T. curvata* show similar catalytic and structural properties to cutinases from *T. fusca* and *T. cellulosilytica* and are able to degrade poly(ε-caprolactone) and PET (Wei et al. 2014). The cutinase-like enzyme Cut190 from *S. viridis*, which was isolated from compost in Okayama (Japan), has been shown to catalyze surface hydrolysis efficiently and degrade the inner block of PET (Kawai et al. 2014; Kawabata et al. 2017).

The cutinase-like PET hydrolase, designated PETase (EC 3.1.1.101.), catalyzes the degradation of PET to bis(2-hydroxyethyl) terephthalate (BHET), mono(2-hydroxyethyl) terephthalate (MHET), and terephthalic acid (TPA) (Fig. 1). MHET is then metabolized by a unique hydrolase named MHETase (EC 3.1.1.102) to yield TPA, which can be used by the central metabolism via the TPA degradation pathway. Although PETase is most similar to the PET hydrolase from *T. fusca*, it shows superior hydrolytic activity and substrate specificity toward PET compared to previously described cutinases. The crystal structure of PETase reveals significant differences, such as an additional disulfide bond (Chen et al. 2018). MHETase does not exhibit activity toward PET and is not homologous to any of the known MHET-degrading enzymes, which usually also degrade PET. Next to the MHETase-encoding gene in the genome of *I. sakaiensis*, there is a whole gene cluster that is almost identical to the TPA degradation gene clusters tph_{I} and tph_{II} of *Comamonas* sp. strain E6. The corresponding enzymes TPA 1,2-dioxygenase and protocatechuate (PCA) dehydrogenase are assumed to catalyze the downstream metabolism of the TPA monomer (Yoshida et al. 2016). Liu and colleagues (Liu et al. 2018) isolated the PETase protein from *I. sakaiensis* and expressed it in an *E. coli* system. They described the conservation of the catalytic machinery of α/β hydrolase and its specific substrate interaction. In this study, to improve the degradation of PET through PETase activity, several mutations were generated at specific sites in the PETase structure: substrate binding pockets (W130, M132, W156,

I180, Q90, S185, and S209), triad center residues (S131, D177, H208), and residues involved in the correct folding of the active site (W68, Q153, R94, the N212). As a result, the authors found that the mutations W68, Q153, R94, and N212 may contribute to a decrease in the hydrolytic activity of PETase. In addition, mutations Q90, M132, and W156 in the PETase protein could hinder PET recognition and therefore lead to a decrease in its hydrolytic activity. Lastly, mutations Y58A, W130A, W130H, and A180I increased PETase activity and were able to generate different changes on the PET material surface (Liu et al. 2018).

Lipases (EC 3.1.13) have been described as catalysts for the hydrolysis of both PET and PUR (Wilkes and Aristilde 2017). The effect of exploiting different *Pseudomonas* strains for the degradation of a PUR of commercial interest was studied. After biochemical and mutational analyses, two extracellular lipases (PueA and PueB) were identified as being involved in the degradation process (Hung et al. 2016). A lipase from *Thermomyces lanuginosus* was studied in detail regarding the surface modification of PET. This enzyme efficiently hydrolyzed PET, leading to the formation of superficial polar groups and, consequently, enhanced the hydrophilicity of the material (Brueckner et al. 2008; Gricajeva et al. 2022). In addition, lipase B from *Candida antarctica* (CALB), which is one of the most studied and versatile lipases, was highly efficient in catalyzing the depolymerization of PET (Carniel et al. 2017).

Apart from lipases and cutinases, esterases have also been shown to hydrolyze PET and PUR. True esterases (EC 3.1.1.3 carboxyl ester hydrolases) comprise a diverse group of enzymes, which typically hydrolyze the ester bonds of shorter chain fatty acids than lipases. They are known to show a wide substrate range and facilitate the utilization of carbon sources or other catabolic pathways (Gricajeva et al. 2022). PET degradation has been achieved using the serine esterase PmC from *P. mendocina* (Ronkvist et al. 2009) and the *p*-nitrobenzyl esterase BsEstB from *B. subtilis* (Ribitsch et al. 2011) as well as esterases from *T. alba* and *T. halotolerans*. The thermoactive Est119 from *T. alba* was classified as an esterase (Hu et al. 2010), as was Thh_Est from *T. halotolerans* (Ribitsch et al. 2012). Esterases were previously believed to be less efficient in degrading polyesters than cutinases or lipases, especially in hydrolyzing the polymer surface (Oeser et al. 2010; Ribitsch et al. 2012). PUR is postulated to be cleaved by esterase activity. The bacterial enzyme urethanase exhibited esterase and protease activity and was able to hydrolyze urethane compounds (Akutsu-Shigeno et al. 2006; Liu et al. 2021).

Similar to polymers with a C–C backbone, photoinitiation reactions are key to the biodegradation of PUR in the environment. This oxidation occurs in the α-methylene position and leads to the formation of hydroperoxides (Gewert et al. 2015). Subsequent enzymatic reactions can then hydrolyze the ester or urethane bonds, with the latter being catalyzed at lower degradation rates. The enzymatic activity of urethanases is known to require the presence of aryl esters or carbamates, but the substrate recognition pattern of these enzymes remains unknown (Chen et al. 2020).

Due to the hydrolyzable ester or amide bonds that allow PET and some PUR polymers to be effectively biodegraded into defined oligomers and monomers (Wei et al. 2020), abiotic factors are not strictly needed for proper biodegradation.

3 Strategies for efficient polymer biodegradation

Enzymatic plastic degradation is a field that is being investigated intensively. Two main aspects are being investigated: the enhancement of already existing enzymes and the identification of novel enzymes useful for the degradation of polymers that are not yet useable for enzymatic cleavage. Here, we present selected biotechnological approaches with high potential to improve the enzyme degradation of synthetic plastics and the valorization of plastic degradation products.

3.1 Protein engineering and enzymatic degradation strategies

Knowledge of the three-dimensional structure of an enzyme is a prerequisite to designing improved biocatalysts rationally. Ideally, crystal structures should be obtained, but the rapid development of three-dimensional model building algorithms has allowed for a prompt advance. Most contributions address substrate affinity, either with the abovementioned binding domains or by modifying surface

hydrophobicity and charge, according to the structure of the catalytic site (Herrero Acero et al. 2013; Gricajeva et al. 2022). PET-degrading enzymes must cleave the ester bond. Since biological polymers such as cutin naturally contain ester bonds, cutinases have been applied to the degradation of PET. One example is a cutinase from *Thermobifida*, which belongs to the most studied models (Roth et al. 2014). However, over the last four years, studies on the two-enzyme system PETase and MHETase from *I. sakaiensis* (Yoshida et al. 2016) have emerged and have allowed for a clearer understanding of the hydrolytic mechanism (Han et al. 2017; Joo et al. 2018). PETase breaks down PET into MHET and BHET. MHETase cleaves MHET and releases the original monomers TPA and EG.

In a subsequent study, the X-ray crystal structure of the *I. sakaiensis* PETase revealed features common to both cutinases and lipases while exhibiting a more open active-site cleft than homologous cutinases. The authors exchanged two active-site residues to conserved amino acids in cutinases and were able to thus narrow the binding cleft. This change led to improved PET degradation, which suggested that the *I. sakaiensis* PETase is not fully optimized for crystalline PET degradation, despite presumably evolving in a PET-rich environment (Austin et al. 2018).

One of the most recent achievements is the construction of chimeric proteins that include regions of both PETase and MHETase, the performance of which is improved compared to the individual enzymes (Knott et al. 2020). The idea of building chimeric enzymes arose from the fact that the two enzymes act synergistically when placed in the same reaction system. This example is an interesting prospect for the development of more efficient enzymes for plastic degradation in the future.

The use of enzyme mixtures is also an interesting approach to improving results. Carniel et al. (2017) achieved an eight-fold increase in TPA yield when they used both CALB lipase and HiC. Bermúdez-García et al. (2019) described the role of the different cutinases produced by *Aspergillus nidulans* and the differences in the products obtained after cutin hydrolysis. They observed that when a mixture of two was used, ANCUT1 and ANCUT3, in a specific order, the TPA yields from this cutinase-treated PET increased by 40 times.

To date, the most active wild-type thermophilic PET hydrolase is leaf-branch compost cutinase (LCC) (Wei et al. 2019), a polyester hydrolase that originates from a plant compost metagenome (Sulaiman et al. 2012). More recently, a novel metagenomic hydrolase (PHL7) was isolated from plant compost that showed the ability to hydrolyze completely amorphous post-consumer PET packaging films with high efficiency (Sonnendecker et al. 2022). In 2020, a depolymerization degree of > 50% was reported after 24 h at 70–72 °C, with amorphous PET films in reaction tubes (Falkenstein et al. 2020) by applying an enzyme concentration of the wild-type LCC in the range of 1–2 mg_{enzyme}/g_{PET}. Tournier et al. used an improved LCC and were able to achieve 90% PET depolymerization into monomers over 10 h at 65 °C with a productivity of 16.7 g of terephthalate per liter per hour with an enzyme concentration of 3 mg_{enzyme}/g_{PET} in a bioreactor. The amorphized post-consumer PET facilitated easier access for the enzyme (Tournier et al. 2020). Using amorphous PET films for LCC-catalyzed hydrolysis in a stirred tank reactor, Tiso et al. obtained over 47% depolymerization within the first 24 h at 70 °C (Tiso et al. 2021a). While all these studies focused on PET hydrolysis at elevated temperatures, there have also been efforts to engineer PET hydrolases to function at ambient temperatures. Cui et al. generated a PETase called DuraPETase, which exhibits a melting temperature that is elevated by 31 °C and features enhanced degradation toward semicrystalline PET films at mild temperatures (over 300-fold) (Cui et al. 2021). Based on machine learning-guided engineering, Lu et al. (2022) succeeded in generating a PET hydrolase variant (FAST-PETase) robust to changes in pH and temperature, which was shown to degrade untreated post-consumer PET almost entirely within one week (Lu et al. 2022).

Further developments have been made in terms of plastic degradation monitoring. Frank et al. established a real-time noninvasive analytical method to monitor PET degradation by measuring the changes in the dielectric properties of PET films. Compared to optical methods, this technique is also insensitive to changes in the solution composition, thus enabling both high temporal resolution and parallel processing (Frank et al. 2022).

Enzymatic degradation of PET appears to be closest to industrial application. It is interesting to note that the thermochemical recycling of this polymer is

a reality worldwide, especially in the case of beverage bottles. However, this recycling process results in the deterioration of its mechanical properties (Ragaert et al. 2017). Other promising approaches to enzymatic plastic degradation include the use of polyurethanases and polyamidases to degrade nylon as well as laccases and the multiple copper-binding enzymes that degrade PVC, PE, and PS. PET, nylon, PVC, PE, and PS together represent approximately half of the synthetic plastics market (Grand View Research 2021, Plastic Market Size, Growth & Trends Report, 2021–2028).

Several studies have shown the growth of different microorganisms on these polymers using them as carbon sources. However, there are very few reports that explore the use of enzyme extracts or supernatants. More detailed information has recently become available on the production of laccases by several microorganisms, particularly by basidiomycetes, and the application of these preparations in polymer degradation. Santo et al. (2013) reported obtaining laccase from *R. ruber* and achieving the degradation of PE films, as assayed by weight loss. The discovery of numerous sources of laccases and the cloning of several genes in widely accepted models, such as *Pichia pastoris*, leads to the belief that economic sources of these enzymes will be available in a not distant future and that enzymatic degradation processes may be developed. Moreover, a recent high-throughput RNA-seq study reconstructed the whole metabolic pathway behind PE degradation in *Rhodococcus* bacteria. In addition to the identification of different multicopper oxidase laccase-like enzymes involved in the first step of oxidation, other oxidative systems were also detected (Zampolli et al. 2021). The fact that these enzymes are used in the bioremediation of several toxic products further widens the market. In addition, laccases are even able to degrade PVC (Sumathi et al. 2016).

Knowledge about polyurethanes has also advanced in several respects. In addition to the growing number of studies showing new species that can degrade different forms of this polymer, the role of enzymes in its degradation is more deeply understood. Enzyme structure studies have yielded new models, and the results pave the way for the design of more efficient catalysts (do Canto et al. 2019). Lastly, an increasing number of studies are investigating the sources, genetic regulation, and just recently, the structure of amidases; the mechanisms that lead to nylon degradation are well understood and more efficient, and thermostable mutants have been designed (Negoro et al. 2018).

3.2 Reactor design for polymer degradation

Studies on bioreactor design in plastic biodegradation processes are scarce. This subject must be addressed at the laboratory scale and will allow for the scale-up of the biodegradation processes of persistent polymers. Optimizing the reactor design helps to adapt to the necessary conditions, such as the mixing efficiency as well as mass and heat transfer, which are key processes for effective enzymatic hydrolysis. The optimized bioreactor must ensure the efficient interaction between the substrate and the catalyst, which is reflected in the degree of bioconversion of the initial substrate to the degradation products. Furthermore, a balance between transfer conditions and biological sensitivity to shear stress is essential to avoid losses in enzyme activity (García-Aguirre et al. 2009).

For the enzymatic hydrolysis of lignocellulosic biomass (LCB), the use and optimization of the reactor design have been widely studied, with stirred tank bioreactors and membrane bioreactors being the most commonly used designs (Pino et al. 2018). The outcome of these studies can serve as a reference to apply similar strategies for plastic degradation processes since the challenges involved in the use of solid substrates and the difficulties of the enzymatic degradation process are comparable for LCB and synthetic plastic materials. One of the determining factors is the solid loading in the system because it is reported that up to 12–15% (w/w) solids appear to be the loading limit that still allows for adequate mixing in a stirred tank reactor. Higher solid loading, however, leads to problems in transfer phenomena, resulting in a non-Newtonian fluid and a decrease in enzyme efficiency (Hodge et al. 2009; Du et al. 2014). For these cases, alternative bioreactor configurations have been proposed, such as the use of horizontal rotating tubular bioreactors or the exchange of the impellers of stirred tank reactors with a peg mixer, an anchor impeller, or a double helical impeller (Pino et al. 2018).

Of the few examples found in the literature regarding reactor design in synthetic plastic degradation processes, an interesting description was given by Barth et al. (2015) showing the advantages

of performing PET degradation in an ultrafiltration membrane reactor to avoid product inhibition of the enzyme. In addition, two key factors were crucial: buffer and pH control as well as agitation within the reactor. Enzymatic reactors do not require high temperatures or pressures, but certainly, the reactor must withstand the pretreatment conditions and temperatures over a range of 60–80 °C and thus must have a temperature control system. According to Andrić et al. (2010), product inhibition has been identified as one of the main obstacles to enzyme-based reactions, directly affecting biocatalytic conversion. Under this scenario, membrane reactors provide several advantages, such as product removal, reuse of enzymes, and fed-batch feeding of enzymes. However, some issues, such as membrane fouling and issues with scale-up, still make it challenging to set up successful processes.

The use of two-phase partitioning bioreactors (TPPB) has proven to be efficient for the degradation of water-insoluble recalcitrant compounds. The proper functioning of TPPB depends primarily on the immiscible solvent to be incorporated, for which the partition coefficient must be appropriate and specific for the degradation system. In addition, it is important that the solvent of choice does not significantly affect the activity of the enzyme. There are two operation possibilities when using TPPB, depending on whether the substrate is (i) Dissolved in the organic solvent or (ii) In solid form in the aqueous phase. In the first case, the appropriate diffusion of the substrate from the solvent to the aqueous phase is required considering that the enzymatic reaction occurs in the aqueous phase. The rate of substrate transfer is essential in this case, in which mass transfer is strongly interface-dependent and directly affects the rate of biodegradation (Eibes et al. 2007). In the second case, the aim is to keep the solid substrate in the aqueous phase without contact with the solvent, thus preventing its deterioration or dissolution. This second model aims for the degradation products of the substrate to migrate into the solvent and thus prevent product inhibition (Andrić et al. 2010).

A recent study showed the design of a multiphase enzymatic reactor for the biotransformation of poly(*cis*-1,4-isoprene) rubber (Andler et al. 2020). The tested setups allowed for the isolation of the rubber particles immersed in the aqueous phase from the organic phase to prevent deterioration of the rubber particles due to the solvent in use. During the assay, an oxygenase, the latex clearing protein from *G. polyisoprenivorans* strain VH2 ($Lcp1_{VH2}$), was added to the aqueous phase containing rubber particles. After five days of incubation, 42–52% of the initial polymer mass was transformed into oligoisoprenoids as degradation products.

3.3 Microbial conversion of plastic monomers to value-added products

In a fully circular plastic bioeconomy, the products of plastic biodegradation must be valorized. For conventional repolymerization, the monomers must be purified to exclude contaminants and, in many cases, to obtain pure single monomer-containing fractions. In contrast to the recycling of plastic waste material, microbes can be used for a process called upcycling. Here, hydrolysates are used for the de novo synthesis of valuable compounds that do not retain the molecular structure of the monomers in use. In nature, biological polymer degradation usually does not yield high-value products for subsequent processing since microbes metabolize monomers directly and generate biomass and CO_2. Efficient plastic upcycling thus involves metabolic engineering. In theory, the complete arsenal of biosynthetic pathways is available for the conversion of degraded polymers into value-added products. This concept of a metabolic funnel, called bow-tie metabolism, was presented in the context of plastic degradation by Tiso et al. (2021b), who evaluated the potential use of plastic monomers as microbial substrates (Fig. 2) (Sudarsan et al. 2014; Tiso et al. 2021b).

Whole-cell plastic degradation usually comprises two steps: depolymerization and subsequent metabolization of mono- and oligomers, but conventional synthetic plastics are highly calcitrant to microbial depolymerization (Tiso et al. 2021b). Sugar polymers such as cellulose and aromatic polymers such as lignin are employed as carbon sources by many microbes, whereas the commercial degradation of lignocellulose and subsequent monomer use have not yet been reached. Since the challenges are similar, some of the already established solutions for lignocellulosic biotechnology might also be beneficial for the microbial or whole-cell depolymerization of plastics (Ellis et al. 2021). For biopolymer degradation, microbes dispose of intrinsic enzymes for

depolymerization, but this is usually not the case for conventional recalcitrant plastics. In many cases, conventional (or synthetic) plastics have high glass transition temperatures, which entails the need to perform enzymatic degradation separately from the microbial metabolization of the monomers.

The subsequent metabolization of the resulting monomers is not readily available in nature; however, a few metabolic pathways are present in specialized microorganisms. For ethylene glycol (EG) derived from PET, various organisms have been described that use EG as the sole source of carbon and energy under both aerobic and anaerobic conditions (Fincher and Payne 1962; Gaston and Stadtman 1963). Several research groups are working on establishing anabolic routes for molecules that are not metabolized thus far, such as TPA and EG from PET (Kenny et al. 2008; Narancic et al. 2021) or monomers from polyurethanes, adipic acid (Ackermann et al. 2021) and 1,4-butanediol (Li et al. 2020). Recently, Tamoor and co-workers (2021) discussed the involvement of different enzymes in the recycling and bioconversion of commercial polymers composed of a mixture of polylactic acid and polyethylene terephthalate (PLA-PET). These enzymes include PETase and MHETase from *I. sakaiensis*; esterases produced by *Bacillus* and *Nocardia*; and lipases from *T. lanuginosus*, *C. antarctica*, *Triticum aestivum*, and *Burkholderia* spp. LCCs generate monomers that can be upcycled into small molecules with added value, such as cyclic acetals, 1,3-propanediol, and vanillin.

The valorization of plastic biodegradation products via cost-effective technologies is urgently needed to achieve a circular economy system in which not only plastic monomers are useful substrates but also intermediates derived from subsequent mineralization processes can be used as new raw materials in further upcycling routes. Unfortunately, the global economy is not yet ready to embrace the overall process fully because of (i) The lack of cost-effective and adequate technologies to manage the different plastic polymers, (ii) The need for well-characterized and widely available monomer feedstocks for standardized and reproducible upcycling systems, and (iii) The kinetic and thermodynamic limitations of plastic deconstruction and biodegradation. Another misleading aspect is that upcycling concepts often overlap with recycling, i.e., obtaining monomers to make additional plastic products (Hou et al. 2021). Thus, further plastic wastes are generated and circularly reproduce the plastic waste issue to be addressed.

4 Techno-economic valorization of plastic biodegradation

Techno-economic analysis (TEA) allows for a prediction of the necessary capital and operating costs associated with the process to project a minimum selling price (MSP). TEA is widely used in the analysis of new products; however, its application in biological or enzymatic recycling processes has only been employed to a limited extent. To incorporate TEA into biodegradation processes, it is necessary to apply the concept of upcycling and identify value-added products based on the products of enzymatic degradation.

One of the important economic factors revealed by TEA of enzymatic recycling processes are the enzyme production costs. These costs depend on factors/parameters such as the enzyme type, expression strategy, production scale, and purification process (Ferreira et al. 2018; Tournier et al. 2020). It is estimated that the production value of enzymes can be in the range of $25–$110/kg, although enzymes such as fungal cellulases can have lower prices of approximately $5/kg (Klein-Marcuschamer et al. 2012). Another important aspect to consider when working with waste, such as plastic waste, are the costs associated with the pretreatment, which produces a clean substrate with physicochemical characteristics that favor the enzymatic process.

Recently, a TEA, life-cycle analysis (LCA), and socioeconomic impact study were performed for a PET recycling process based on enzymatic depolymerization (Singh et al. 2021). In this study, the PET recycling process was divided into three sections: (i) Feedstock pretreatment, (ii) Enzymatic PET depolymerization, and (iii) Product and co-product recovery. Within the general characteristics for modeling, a processing capacity of 150 Mt of PET flakes per day was considered, with a recyclable PET fraction of 0.95 after discarding contaminants such as labels, caps, and adhesives. The pretreatment included an extrusion process followed by a size reduction process with a microgranulator. The enzymatic depolymerization process was performed using a PET hydrolase in a series of 950 m^3 stirred tank reactors

with a solid loading of 15% as a base case. For product recovery, a series of unit operations, including crystallization, salt recovery, and distillation were considered to achieve the recovery of the main product, TPA, and two byproducts, EG and sodium sulfate. The modeling assumed a recovery of 90% of the TPA and 50% of the EG with a selling price of 0.66 USD/kg for TPA, 0.96 USD/kg for EG, and 0.15 USD/kg for sodium sulfate, considering the market price of the last five years. The analysis showed that the total capital investment for the plant design amounts to 67 M USD. The most influential costs on the final TPA price were the downstream processing steps for product recovery with 29% of the total costs, while the pretreatment and depolymerization processes reached a similar share with 20% of the total costs each. The operating costs were estimated at 44 M USD, with feedstock, electricity, chemicals, filter maintenance, activated carbon bed, and membrane replacement costs predominating. The TEA results indicated a TPA selling price of 1.93 USD/kg, which is competitive with the manufacturing price of virgin TPA. In addition, the socioeconomic benefits were highlighted, in that the total supply of energy was reduced by 69–83% and greenhouse gas emissions were reduced by 17–43%.

Another study reported TEA for upcycling PET into two bio-based polymers: polyethylene furanoate (PEF) and polytrimethylene terephthalate (PTT) (Roux and Varrone 2021). The depolymerization products EG and PTA were used as precursors of the production of PEF and PTT, respectively. In addition, cellulose extracted from LCB was used for PEF production, while crude glycerol was used for PTT production. Considering waste streams of 68,000 tpa of PET, 132,000 tpa of cellulose, and 65,000 tpa of glycerol, the results of the designed process reached a production of 59,000 tpa of PEF and 53,000 tpa of PTT. The analysis established that the MSP estimated for these second generation-derived polymers was 3.13 USD/kg. Although the calculated price was three times higher than the current selling price of PET, the physicochemical and recyclability properties of PEF and PTT are similar or even superior to those of PET (Kurian 2005; Fei et al. 2020).

The presented cases demonstrate that through the valorization of existing plastic waste streams, it is possible to transition toward a more sustainable plastic industry, with PET being the model polymer. However, industrial validation is still lacking, and there are still important limitations due to the difficulty of generating defined degradation products of polymers with greater resistance to the depolymerization process.

5 Environmental implications of enzymatic degradation of synthetic plastics

Plastics can be found ubiquitously in different environments due to the multiplicity of their sources and transport routes within and across freshwater and terrestrial ecosystems. The final fate of plastic waste is a consequence of different processes: (i) The accumulation of plastic materials in environmental compartments poses a risk not only to specific ecosystems but also to human health. This is especially the case for the most common polymers that often contain additional solubilizers, additives, and other chemical agents to improve their mechanical and physical characteristics (Danso et al. 2019). (ii) Abiotic oxidation occurs through different pathways, including UV radiation, temperatures, and oxygen levels (Mohanan et al. 2020). This result implies not only the partial degradation or activation of plastic polymers but also the consequent release of harmful compounds, including volatile organic compounds (VOCs), that can interact with the surrounding ecosystem (La Nasa et al. 2021). (iii) When plastic is properly collected and transported to waste treatment plants, chemical or mechanical recycling and incineration are the conventional treatment methods for plastic waste, although the majority of plastic waste has always been disposed of in landfills (Zhang et al. 2021). Although the waste-to-energy process has also been adopted to recover energy from waste treatment, it only covers a small fraction of polymer waste and yields a multiplicity of environmental consequences, such as toxic gas production (furans and dioxins) and heavy metal-contaminated ash. (iv) Recycling and/or biodegradation processes involving microorganisms, or their enzymes are the most eco-friendly methods that have not yet been established (Lee and Liew 2021). In fact, in plastic-contaminated environments, microbial communities can adapt and break down polymers into simpler compounds by biochemical transformations. Several processes are involved in the microbial attack: Biodeterioration affects the superficial part

of the polymer and is also enhanced by abiotic and environmental factors. Biofragmentation of the biodeteriorated plastics involves a depolymerization process, generating plastic fragments with lower molecular weights or oxidized molecules. The assimilation routes are activated by microorganisms that form biofilms on the plastic surface and/or produce active catalytic enzymes able to degrade or biotransform the synthetic polymers. Lastly, during the mineralization process the oxidized plastic derivatives are transported into the cells and diverse enzymatic reactions lead to complete degradation into oxidized metabolites, which include CO_2 and H_2O (Amobonye et al. 2021). Therefore, plastic polymer biodegradation would be the preferred strategy under specific environmental conditions and in the presence of microbial communities able to cope with their enzymatic arsenals.

6 Conclusion

The biodegradation of synthetic plastics has been studied extensively, and the examples illustrated in this review show that the basic tools for developing enzymatic degradation processes at both the molecular and process strategy levels are already available. However, to achieve feasible biotechnological processes, biodegradation rates must be improved. Screening for enzymes to identify novel activities and establish higher degradation activities on heteroatoms as well as C–C backbone plastics will be fundamental. In addition, it will be crucial to improve the efficiency of plastic biodegradation processes: (i) Engineering existing enzymes and microorganisms will help to establish higher degradation rates. (ii) Applying degradation strategies with multiple enzymes will take advantage of synergistic effects that have still scarcely been studied. (iii) Focusing more in-depth studies on the optimization of the reactor design will improve mass transfer conditions and avoid potential product inhibition. (iv) Lastly, constructing metabolic pathways to upcycle the obtained plastic monomers to high-value products efficiently closes the loop and primarily contributes to the economic feasibility of the overall process. Assessing these strategies combined with the broad array of available pretreatment methods and abiotic factors will additionally lead to higher biodegradation rates and consequently more efficient biorecycling processes. Eventually, the biological recycling of plastic materials has the potential to close the plastic cycle from monomers to new products and lead to a sustainable, zero-pollution system.

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Declarations

Conflict of interest The authors declare that they have no competing interests.

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