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Research review paper

Biodegradation and up-cycling of polyurethanes: Progress, challenges, and prospects

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ABSTRACT

Polyurethanes (PUR) are ranked globally as the 6th most abundant synthetic polymer material. Most PUR materials are specifically designed to ensure long-term durability and high resistance to environmental factors. As the demand for diverse PUR materials is increasing annually in many industrial sectors, a large amount of PUR waste is also being generated, which requires proper disposal. In contrast to other mass-produced plastics such as PE, PP, and PET, PUR is a family of synthetic polymers, which differ considerably in their physical properties due to different building blocks (for example, polyester- or polyether-polyol) used in the synthesis. Despite its xenobiotic properties, PUR has been found to be susceptible to biodegradation by different microorganisms, albeit at very low rate under environmental and laboratory conditions. Discovery and characterization of highly efficient PUR-degrading microbes and enzymes capable of disassembling PUR polymer chains into oligo- and monomeric compounds is of fundamental importance for a circular plastic economy. In this review, the main methods used for screening PUR-degrading microbes and enzymes are summarized and compared in terms of their catalytic mechanisms. Furthermore, recycling and upcycling strategies of waste PUR polymers, including microbial conversion of PUR monomers into value added products, are presented.

1. Introduction

Polyurethane (PUR) is a versatile class of synthetic polymeric materials, ranked as the 6th most common type of plastic used worldwide. In 2018, PUR accounted for 7.9% of the total plastic end-user market (359 million tons) (Plastics Europe, 2019). PUR can be catalytically synthesized by reacting different isocyanates and polyols. The variability in monomers used allows the synthesis of PUR with tailored physical properties and subsequently a huge range of applications. The majority of PUR is flexible or rigid foamed polymers with applications in many sectors, such as building and construction, automotive industry, and medical devices (Furtwengler et al., 2018).

The tremendous demand for PUR will result in the equivalent amount of solid waste, out of which a large fraction is currently not recycled and ends up in landfills and incineration (Mahajan and Gupta, 2015). As most of PUR is a thermosetting polymer, which can be considered as a giant molecule internally cross-linked, a decomposition under natural conditions is very unlikely causing its preservation presumably for more than hundreds of years in dumping sites. As a result of slow decay, PUR wastes may continuously release environmental pollutants, such as 4,4′-methylenedianiline (MDA) and 2,4′-toluene diamine (TDA). Notably, these diamines were classified by the European Chemicals Agency as "substances of very high concern", specifically in the category of "carcinogenic, mutagenic or toxic to reproduction" (European Chemicals Agency, 2019). Besides, the additivities used in the PUR production for improved application properties and resistance to environmental factors like oxidation may also be released to and have a negative impact on the natural environment. For example, some PUR-based liquid formulations contain additives like secondary alcohols and glycol ethers that function as solvents or coalescent agents. Glycol ethers present in a high quantity are toxic for many microbial species, and also considered potentially hazardous for human health (Gaytán et al.,

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2019). Furthermore, due to the small pile-up density of PUR, landfill use causes a waste of land resources (Cregut et al., 2013). Zero plastics to landfill by 2025 has been proposed in the Plastics Europe's position paper, and ten European countries have banned communal waste in landfills already (Plastics Europe, 2019). Currently, incineration is another commonly used method to dispose waste plastics. The technical solutions exist and are implemented in modern combustion plants to avoid release of dioxins and carbon monoxide originating from incomplete plastic combustion (Cregut et al., 2013).

Compared to these traditional waste disposal methods, recycling is a much more desirable approach for PUR end-of-life processing. Mechanical recycling is applied currently as a dominant approach, but it has a significant disadvantage in generating "down-cycled" less-valuable products. Prominent examples are carpet backings. Alternatively, chemical recycling can be used, obtaining basic hydrocarbon units known as monomers to be used as synthesis feedstocks in the chemical industry. As a result, it is thinkable to synthesize high value products, hence upcycle PUR (Hicks et al., 1994). Chemical decomposition of polymers obtained by polycondensation involves disassembling reactions such as hydrolysis, glycolysis or aminolysis. Hydrolysis was the first process developed to recycle PUR waste, in particular for flexible PUR foams. The main disadvantage of hydrolysis is the required energy for high pressure and temperature, while the products are of low value (Yang et al., 2012). Glycolysis is the most widely used chemical recycling method for PUR, mainly for rigid and flexible PUR foam. The aim is to recover polyols for the production of new PUR material and have been applied at a pilot-scale or in large industrial plants. Due to a lack of phase separation, polyols yielded in this way can only replace virgin polyols used in producing rigid and semi-rigid PUR foams but not the flexible ones (Simon et al., 2018). Aminolysis of PUR waste is carried out at an elevated temperature in the presence of ammonia or ammonium hydroxide. Ammonia exhibits higher nucleophilicity than water (applied in hydro-lysis) or glycol (applied in glycolysis). As a result of aminolysis, polyols, amines, and unsubstituted urea are obtained. Polyols produced by this process can be reused to synthesize, for example, rigid PUR foams (Datta and Włoch, 2017).

In recent years, biodegradation using microorganisms or enzymes has become a promising alternative for plastic recycling due to the mild and environmentally friendly reaction conditions required (Wierckx et al., 2015; Wei and Zimmermann, 2017). Moreover, this approach can provide new knowledge on the fate of the landfilled or littered PUR waste undergoing microbial degradation (Wei et al., 2020). In the last two decades, many microbial enzymes with the ability to degrade polyethylene terephthalate (PET) have been reported (Rolf-Joachim et al., 2005; Wei and Zimmermann, 2017; Kawai et al., 2020). A recent breakthrough in this active research area has been published in *Nature* by a French team, who successfully depolymerized >90% of pre-treated PET bottles into monomers within 10 h using an engineered thermophilic cutinase, corresponding to a productivity of about 17 g of terephthalate per liter per hour (Tournier et al., 2020). The selection of a thermophilic enzyme was a prerequisite for achieving this excellent degradation performance (Wei et al., 2019), rather than using its mesophilic counterpart *Is*PETase from *Ideonella sakaiensis* (Yoshida et al., 2016), which attracted increasing interest from public and scientific communities in the last few years. Recently, monomeric products of enzymatic PET degradation were successfully used as substrates for engineered bacteria to produce value-added chemicals (Kenny et al., 2008; Kim et al., 2019; Tiso et al., preprint), thereby providing a sustainable biotechnological up-cycling strategy of plastic waste (Wierckx et al., 2015; Wei et al., 2020). As PUR is the second abundant plastic type with hydrolyzable backbone, it is also envisioned to up-cycle PUR in a similar manner by viable biotechnological approaches. However, due to the high complexity in the polymer structures of PUR, an efficient biodegradation at a promising rate has not yet been reported with many scientific and technical challenges still not fully addressed.

This review systematically describes the recent advances in the development of screening methods for PUR-degrading microorganisms and enzymes, from the selection of suited model substrate to evaluation of the degradation efficacy. Furthermore, microorganisms and enzymes that have been reported to be involved in the PUR biodegradation process are also summarized. Finally, a utilization approach of PUR degradation products aiming at upcycling towards value-added chemicals is proposed.

2. Substrates for screening PUR polymer degraders

2.1. Polyester-PUR particle dispersion

In the literature, three common model substrates were mainly used to explore PUR degrading microbial strains or enzymes (Fig. 1). The advantages and disadvantages of using these three PUR model compounds as substrates are summarized in Table 1. Polyester-polyurethane particle dispersions were most widely used in the screening of PUR-degrading microbes and enzymes. Impranil DLN® is a colloidal polyester-PUR dispersion, a white, milky suspension containing 40% of polymer particles with estimated sizes in the sub-micrometer range between 0.1 and 0.2 μm. Although the proposed structure of Impranil DLN® has been reported, the exact structure is still unknown (Biffinger et al., 2014). When Impranil DLN® is used as the substrate, the PUR degrading ability of a microbial colony can be easily determined through the formation of clear zones on agar plates (Crabbe et al., 1994; Howard et al., 2010; Russell et al., 2011; Ivano et al., 2018; Molitor et al., 2019). Also, other polyester-polyurethane particle dispersions such as Bayhydrol 110 and Bayhydrol 121 were used as substrates. However, since they are transparent, dye indicators are needed for screening strains based on the formation of clear halos. (Howard and Hilliard, 1999; Howard et al., 2001).

Most PUR-degrading microorganisms were isolated and identified using polyester-PUR particle dispersions as substrates, although this approach has some disadvantages. Firstly, the degradation activity of isolated microbes and enzymes on PUR bulk polymers were poor. The number of ester bonds were much more than urethane bonds in polyester-PUR particle dispersions, and the biodegradability of ester bonds is much higher. As a result, a lot of 'false positive' candidates isolated only have polyester hydrolase activities while have no degradation activity of urethane bond. Secondly, the composition and structure of commercial polyester-polyurethane particle dispersions are unclear, making them unsuitable for subsequent studies of the degradation mechanism (Álvarezbarragán et al., 2016).

2.2. PUR in bulk form

PUR in bulk form, such as elastomers, films, and foams (Fig. 1), have also been used as substrates for microbial growth/screening. However, significant microbial degradation of PUR polymers was reported rarely. The degradation performance was mainly characterized by measuring the weight loss of polymers, changes of surface topography, functional groups on the surface, hydrophobicity, crystallinity, and molecular weight distribution (Khan et al., 2017; Magnin et al., 2019a, b). The growth and screening of microbes on bulk PUR polymers require extremely long incubation periods of several weeks or months (Nakajima-kambe et al., 1995; Mathur and Prasad, 2012; Khan et al., 2017). Only a few effective PU-degrading microbial strains, including bacteria and fungi, have been isolated and identified to date. *Comamonas acidovorans* TB-35 was isolated using PUR synthesized by reacting poly (diethylene glycol adipate) with 2,4-tolylene diisocyanate as the sole carbon source. The incubation was conducted for more than 14 days, while the degradation performance was evidenced by a substrate mass loss of 50 mg after seven days (Nakajima-kambe et al., 1995). *Aspergillus tubingensis* was isolated using PUR film as a substrate by incubation for about 27 days on Sabouraud dextrose agar (SDA) plates. Its growth resulted in surface changes of the PUR film, such as cracking, erosion,

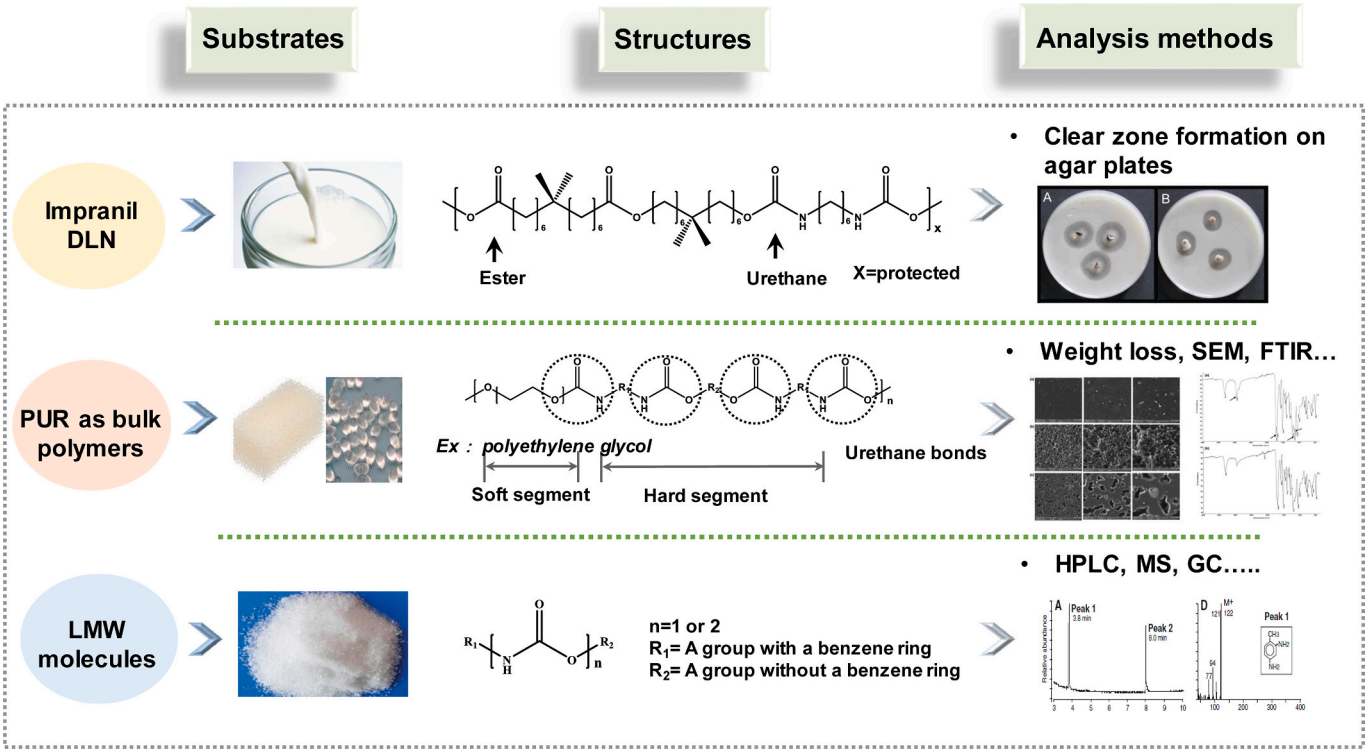

Fig. 1. Selected widely used substrates for the screening, isolation and characterization of PUR-degrading microorganisms and enzymes are shown along with their chemical structures and corresponding analysis methods.

Table 1
Summary of substrates used for the screening of PUR-degrading microorganisms.

PUR types	Substrates	Advantages	Disadvantages
Polyester-PUR particle dispersion	Impranil-DLN®; Bayhydrol 110; Bayhydrol 121	◆ Readily available; ◆ Simple visualization; ◆ Faster	◆ Complex composition; ◆ Poor or no ability to degrade real PUR
LMW urethane-based model molecules	Toluene-2,4- and − 2,6-dicarbamic acid diethyl ester; 1-methoxypropan-2-yl (4-nitrophenyl) carbamate; *p*-toluenesulfonyl isocyanate model substrate	◆ Clear composition; ◆ Simple quantitative analysis; ◆ Faster	◆ Design and synthesis required; ◆ Poor or no ability to degrade real PUR
PUR in bulk form	elastomer; film; foam	◆ Readily available; ◆ Efficient ability to degrade real PUR	◆ The slowest screening process; ◆ Various evaluation methods used together to determine the degradation effect

and pore formation (Khan et al., 2017). The formation or breakage of chemical bonds during the PUR biodegradation process was confirmed using attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy (Khan et al., 2017).

2.3. Low-molecular-weight urethane-based model molecules

Low-molecular-weight (LMW) urethane-based model molecules have urethane bonds and thus partly mimic a segment of the PUR polymer chain. Compared with PUR, the LMW urethane-based molecules are considered more susceptible to biodegradation, and can thus facilitate the screening of degradative microbes and the understanding of the degradation mechanisms (Fig. 2). By screening soil samples for microorganisms that can utilize toluene-2,4-carbamic acid, diethyl ester (a LMW *N*-toluylcarbamate model compound resembling the urethane linkages found in PUR) as the sole carbon source, a fungal strain *Exophiala jeanselmei* REN-11A was found to act most effectively. It completely consumed 300 μM toluene-2,4-carbamic acid diethyl ester within six days of incubation (Owen et al., 1996, Fig. 2a). Similarly, a bacterium that degrades urethane-bond-based compounds was isolated and identified as *Rhodococcus equi* strain TB-60. It degraded 1.5 mM toluene-2,4-carbamic acid dibutyl ester (TDCB) in seven days and released toluene diamine as the degradation product (Fig. 2b; Akutsu-Shigeno et al., 2006). Another model molecule, 1-methoxypropan-2-yl (4-nitrophenyl) carbamate, was used to quickly determine the hydrolytic activity of different amidases on PUR polymers. The hydrolysis product is 4-nitroaniline, a compound that can be easily quantified at 405 nm using a spectrophotometer (Gamerith et al., 2016, Fig. 2c). Recently, an amidase (E4143) and an esterase (E3576) were identified able to hydrolyze the urethane bond in a low-molecular-weight molecule based on *p*-toluenesulfonyl isocyanate (Magnin et al., 2019a, Fig. 2d). The simple synthesis procedure of this model compound will enable its application in the screening of various microorganisms and enzymes. Nonetheless, due to high biodegradability of urethane bond in the LMW model substrates, the strains or enzymes identified in this manner may not necessarily be able to cleave the same bond in PUR polymers.

Therefore, a two-step screening strategy is advised. Preliminary high-throughput screening should be carried out with both LMW urethane-based model molecules and polyester-PUR particle dispersion

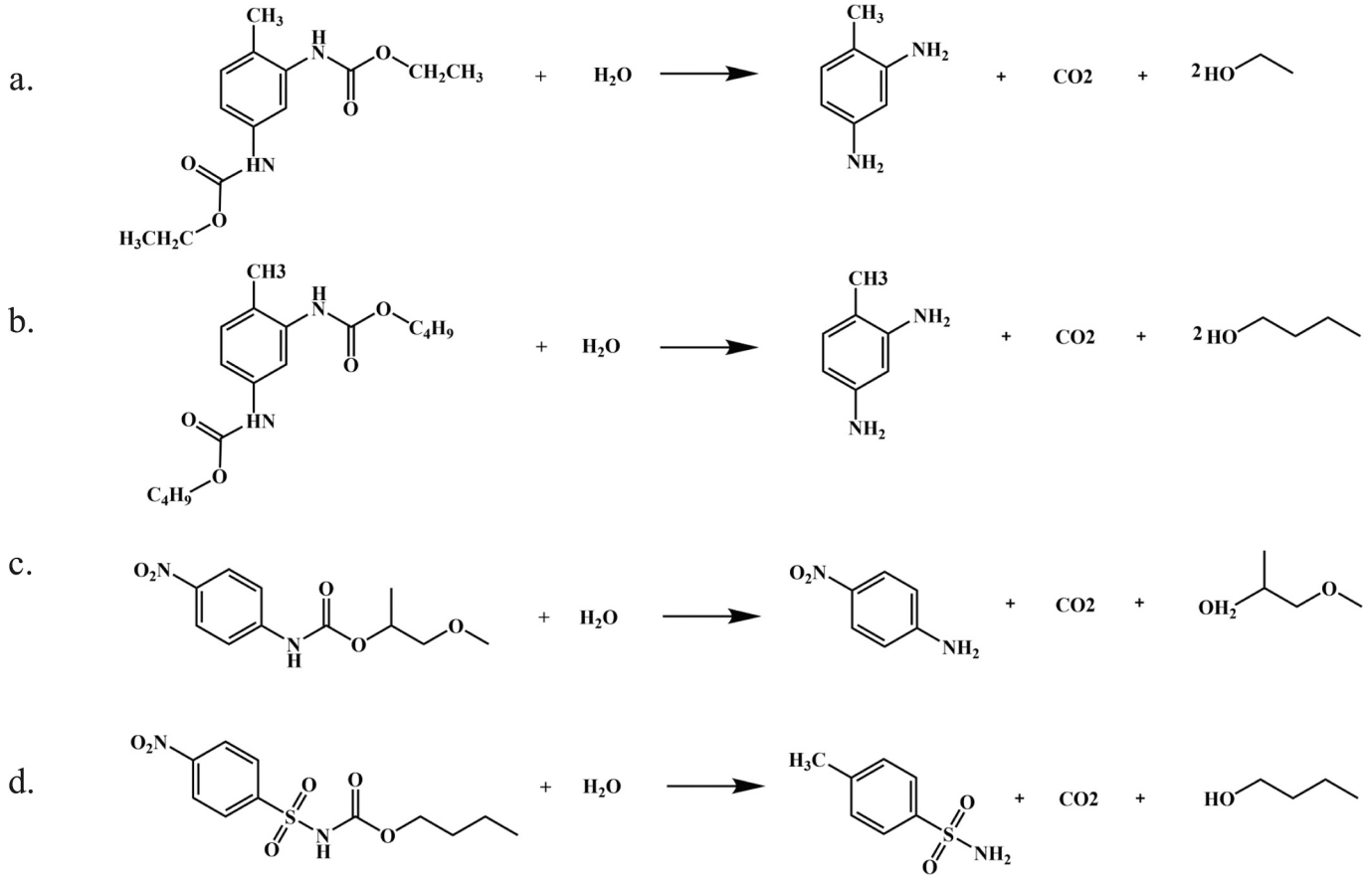

Fig. 2. Hydrolysis of LMW urethane-based model molecules used for the screening and isolation of PUR-degrading microorganisms: (a) toluene-2, 4-carbamic acid diethyl ester; (b) toluene-2,4-carbamic acid dibutyl ester; (c) 1-methoxypropan-2-yl(4-nitrophenyl) carbamate; (d) urethane compound based on *p*-toluene-sulfonyl isocyanate.

as substrates. The microbes and enzymes active on both substrate types will be selected as candidates for further characterizations with bulk PUR polymers in the second step. This approach will help to exclude the 'false positive' candidates which have only polyester hydrolase activities, like the cases of many so far identified 'polyurethanases'. This two-step screening strategy may offer great promise for the isolation and identification of more realistic PUR-degrading microbes and enzymes.

3. Microorganisms involved in the biodegradation of PUR

3.1. Microorganisms that can degrade polyester-based or polyether-based PUR

The reported bacteria capable of degrading polyester-based PUR polymers were mainly identified as members of the genera *Comamonas*, *Pseudomonas*, *Bacillus*, *Acinetobacter*, and *Corynebacterium* (Table 2). *Pseudomonas putida* A12 can utilize Impranil DLN as the sole carbon source and was reported to degrade 92% of the substrate within four days at 30 °C. FTIR analysis provided further evidence of degradation, such as the decreased abundance of ester functional groups and the emergence of amide groups (Peng et al., 2014). *Comamonas* sp. strain TB-35 completely degraded 50 mg of polyester-based PUR into diethylene glycol and adipic acid after seven days of incubation at 30 °C when the polymer was supplied as the sole carbon source. However, the degradation performance was reduced to 48% when no other nitrogen source was added (Nakajima-kambe et al., 1995). Both *Bacillus subtilis* MZA-75 and *Pseudomonas aeruginosa* MZA-85 could not only utilize polyester PUR film as the sole carbon source for growth but also completely mineralize the intermediates 1,4-butanediol (BDO) and adipic acid (AA) into CO_2 and H_2O (Shah et al., 2013a, b). Also, by simultaneous cultivation of the two strains in a mixed culture, 40% weight loss of the polyester PUR film within 30 days has been determined (Shah et al., 2016).

PUR biodegradation capabilities were also found in a wide range of fungal genera, such as *Aspergillus*, *Pestalotiopsis*, *Cladosporium*, *Fusarium*, *Penicillium* (Magnin et al., 2019a, b). Eight fungal strains, which could degrade 74–87% of Impranil DLN in 2 weeks, were able to grow in a mineral medium with Impranil DLN as the sole carbon source. The six best degraders were found to belong to the *Cladosporium cladosporioides* complex, and two others were identified as *Aspergillus fumigatus* and *Penicillium chrysogenum* (Álvarezbarragán et al., 2016). It should be emphasized that strains of *Aspergillus* spp. were reported to have the highest degradation ability on polyester-based PUR in bulk form. *A. tubingensis* isolated from a landfill could degrade the polyester PUR film on a Sabouraud dextrose agar culture plate with high efficiency, resulting in a macroscopic hole on the surface of the film after 21 days of incubation at 37 °C. Furthermore, the polyester PUR film incubated with this fungus broke into small fragments within two months in a mineral salt medium with 2% glucose at 37 °C with an agitation speed of 150 rpm (Khan et al., 2017). A strain of *A. flavus* isolated from landfill soil showed excellent biodegradation ability and could use polyester PUR film as the sole carbon source, which resulted in 60% weight loss by shaking at 120 rpm for 30 days at 28 ± 2 °C (Mathur and Prasad, 2012). Similarly, *Aspergillus* sp. S45 isolated from a landfill could also utilize polyester PUR film as the sole carbon source, reducing the initial weight by 20% after 28 days at 30 °C and 100 rpm (Osman et al., 2018).

However, few microorganisms were reported to degrade polyether PUR, and the biodegradation efficiency was also considerably lower

Table 2
PUR and LMW urethane compounds degrading microorganisms.

Strain	Substrate	Degradation condition	Degradation ability	References
Bacillus spp.; *Pseudomonas* spp.; *Acinetobacter gerneri* P7	DLN	30 °C, without shaking	Transparent hydrolysis circles on DLN agar plates	Ii et al., 1998; Howard et al., 1999; Howard et al., 2012
Pseudomonas putida A12	DLN	30 °C, 100 rpm	Degrade 92% of DLN within 4 days	Peng et al., 2014
Fusarium solani, *Curvularia senegalensis*, *Aureobasidiumpullulans*, *Cladosporium* sp.; *Nectria gliocladioides*, *Penicillium ochrochloron*, *Geomyces pannorum*; *Geomyces pannorum*, *Phoma* sp., *Penicillium inflatum*, *Neonectria ramulariae*, *Penicillium viridicatum*	DLN	30 °C, without shaking	Transparent hydrolysis circles on DLN agar plates	Crabbe et al., 1994; Cosgrove et al., 2007; Barratt et al., 2010
Pestalotiopsis microspora E2712A	DLN	25 °C, with shaking	Degrade nearly 99% of DLN in 2 weeks	Russell et al., 2011
Cladosporium pseudocladospo-rioides, *Cladosporium tenuissimum*, *Cladosporium asperulatum*, *Cladosporium montecillanum*, *Aspergillus fumigatus and Penicillium chrysogenum*	DLN	25 to 30 °C, without shaking	Degrade 74%–87% of DLN in 2 weeks	Álvarezbarragán et al., 2016
Comamonas acidovorans TB-35	Polyester PUR	30 °C, 120 rpm	Degrade 50 mg PUR within 7 days	Nakajima-kambe et al., 1995
Corynebacterium sp. B12	Polyester PUR	Ambient temperature, 150 rpm	Tensile strength and percentage elongation at break of the test material within 3 days	Kay et al., 1993
Bacillus subtilis MZA-75, *Pseudomonas aeruginosa* MZA-85	Polyester PUR film	37 °C, 150 rpm	Weight loss of 40% within 30 days in mixed cultured	Shah et al., 2013a, b, 2016
Aspergillus flavus (ITCC 6051)	Polyester PUR film	28 ± 2 °C,120 rpm	Weight loss of 60.6% within 30 days	Mathur and Prasad, 2012
Aspergillus tubingensis	Polyester PUR film	37 °C, 150 rpm	Degrade the film into pieces within 2 months	Khan et al., 2017
Aspergillus sp. strain S45	Polyester PUR film	37 °C, 100 rpm	Weight loss of 20% in 28 days	Osman et al., 2018
Staphylococcus epidermidis KH11	Polyether PUR elastomer	Not reported	A decrease in elementary nitrogen detected in the polyurethane surfaces.	Jansen et al., 1991
Aspergillus niger, *Cladosporium herbarum*	Polyether PUR foam	25 °C, 100 rpm	A small number of strains growing on the foam	Filip, 1979
Cladosporium pseudocladospo-rioides, *Cladosporium tenuissimum*, *Cladosporium asperulatum*, *Cladosporium montecillanum*, *Aspergillus fumigatus*, *Penicillium chrysogenum*	Polyether PUR foam	25 to 30 °C, without shaking	Weight loss of 10%–65% within 21 days	Álvarezbarragán et al., 2016
Alternaria sp. PURDK2	Polyether PUR foam	30 °C, without shaking	Weight loss of 27.5% in 70 days	Matsumiya et al., 2010
Exophiala jeanselmei REN-11A	LMW urethane compounds	25 °C, with shaking	Degrade 300 μM urethane compounds after 5 days	Owen et al., 1996
Rhodococcus equi strain TB-60	LMW urethane compounds	37 °C, 120 rpm	Degrade 70% of 3 mM urethane compounds over 10 days	Akutsu-Shigeno et al., 2006

(Table 2). Most reported fungi capable of degrading polyether-based PUR are members of the genera *Cladosporium*, *Aspergillus*, and *Alternaria* (Filip, 1979; Matsumiya et al., 2010; Álvarezbarragán et al., 2016).

As early as 1991, Jansen et al. isolated a *Staphylococcus epidermidis* strain that could modify surface properties of a polyether PUR polymer. Furthermore, urease activity was detected in the culture supernatant and suspected to be involved in the polyether PUR degradation (Jansen et al., 1991). *C. tenuissimum* strains A2.PP.5 and A3.I.1, and *C. pseudocladosporioides* strain T1.PL.1 are the three *Cladosporium* strains identified so far with the best PUR degradation activities, resulting in 65, 49, and 45% weight loss of the polyether-PUR foam, respectively (Álvarezbarragán et al., 2016).

3.2. Microorganisms capable of degrading LMW urethane-based model molecules

Table 2 lists the previous studies using urethane-based PUR model molecules to study its biodegradation. Soil samples were screened for microorganisms that can utilize toluene-2,4-carbamic acid, diethyl ester as the sole carbon source, and the soil fungus *Exophiala jeanselmei* strain REN-11A was selected as the most effective one. As shown in Fig. 2a, this strain was first reported to degrade toluene-2,4-carbamic acid diethyl ester based on 2,4-toluene diisocyanate (2,4-TDI) which is one of the most commercially important isomers of TDI. Following 7 days of incubation a total of 0.3 mM of this model substrate was completely degraded, yielding tolulene-2,4-diamine (TDA) as the hydrolysis product (Owen et al., 1996). Further experiments in the same study revealed that the 2,6-TDI based diethyl ester can also be degraded by *Exophiala jeanselmei* strain REN-11A at a similar efficacy. *Rhodococcus equi* strain TB-60 was isolated and found to degrade 1.5 mM TDCB (toluene-2,4-carbamic acid dibutyl ester) (Fig. 2 b) in 7 days by hydrolyzing the urethane bonds and thereby releasing TDA as the degradation product (Akutsu-Shigeno et al., 2006), and in the later incubation period the growth of TB-60 was inhibited by TDA when its concentrations was higher than 1.0 mM. Compared with *E. jeanselmei* REN-11A, which degraded 0.3 mM toluene-2, 4-carbamic acid diethyl ester (Fig. 2a) in 7 days (Owen et al., 1996), the degradation efficiency of *Rhodococcus equi* strain TB-60 was superior.

Besides, the biodegradation of LMW PUR analogs with a different number of benzene rings was also investigated with *R. equi* TB-60, which showed hydrolytic activities on the urethane bonds in MDCB (methylene bisphenyl carbamic acid dibutyl ester) and HDCB (hexamethylene carbamic acid dibutyl ester), releasing MDA and hexamethylene diamine (HDA) as degradation products, respectively. Although the hydrolysis of the urethane bond was independent of the number of benzene rings in the LMW PUR analogues, the biodegradation of real-world PUR polymers was not reported with these strains.

3.3. PUR-degrading enzymes

Microbial attack to PUR plastics is mainly mediated by the enzymatic action of hydrolases, such as esterases, ureases, proteases, and amidases (Magnin et al., 2019b). The properties of the so far identified and characterized enzymes involved in PUR biodegradation are summarized

in Table 3, and the corresponding polymer disassembling reactions are illustrated in Fig. 3.

Esterases are the main enzyme class (EC 3.1) involved in the degradation of polyester-based PUR plastics, in which they hydrolyze the ester bonds in the soft segments, leading to the release of carboxylic acid and alcohol end-groups (Nakajima-kambe et al., 1995; Yang et al., 2013; Schmidt et al., 2017). A membrane-bound PUase enzyme (PudA) from *C. acidovorans* TB-35 was found to possess a hydrophobic PUR-surface-binding domain (SBD) and a catalytic domain (Nakajima-kambe et al., 1995; Akutsu et al., 1998). It was hypothesized that this enzyme degraded PUR in a two-step reaction, with initial hydrophobic adsorption onto the PUR surface *via* its SBD followed by the hydrolysis of PUR ester bonds. Other esterases encoded by the *pulA*, *pueA* and *pueB* genes of *Pseudomonas* sp. were also characterized and found to possess excellent hydrolytic activity on Impranil DLN (Howard et al., 2001; Stern and Howard, 2000; Vega et al., 1999). These ester hydrolases contain the consensus motif of classic serine hydrolases (G-H-S-L-G). Nevertheless, the degradation efficiency of these esterases against bulk PUR polymers was very low or even undetectable (Akutsu et al., 1998; Howard et al., 2001; Stern and Howard, 2000; Vega et al., 1999). The polyester hydrolases TfCut2, Tcur0390 and Tcur1278 isolated from *Thermobifida fusca* KW3 (Wei et al., 2012) and *Thermomonospora curvata* DSM43183 (Wei et al., 2014) as well as LCC identified using a metagenomic library derived from plant compost (Sulaiman et al., 2012), were found to hydrolyze Impranil DLN and thermoplastic polyester PUR (TPU) cubes. The highest DLN hydrolysis rates were obtained with TfCut2 and Tcur0390, while LCC and TfCut2 also showed higher hydrolytic activity on the TPU cubes. At 70 °C, up to 3.2% and 1.9% weight loss of Elastollan B85A-10 (initial weight 80 mg) was obtained with LCC and TfCut2 following incubation for 100 h, respectively (Schmidt et al., 2017).

Proteases and amidases are two additional enzyme classes involved in PUR degradation. They can intrinsically hydrolyze peptide or amide bonds and have been shown to hydrolyze urethane bonds in PUR (Phua et al., 1987; Magnin et al., 2019a). When the polyether PUR elastomer film (Biomer®, Ethicon), which is used in some blood-contacting devices, was treated with the plant protease papain (EC 3.4.22.2) for 1–6 months at 37 °C, a certain degree of degradation occurred at the urethane bonds has been shown by mechanical tests, GPC and FTIR analyses. However, the extremely long degradation time suggested a low PUR-degradation efficiency of papain (Phua et al., 1987). By contrast, α-chymotrypsin showed high degradation activity on a new biodegradable PUR (TEG-HMDI) synthesized from triethylene glycol (TEG) and 1,6-hexamethylene diisocyanate (HMDI). The average molecular weight of this TEG-HMDI PUR decreased by more than 30% after ten days of α-chymotrypsin digestion at 25 °C (Campinez et al., 2013). The proteases bromelain (EC 3.4.4.24) and ficin (EC 3.4.22.3) were found to be more effective than other proteases in the cleavage of urethane bonds in PUR, and segmented polyurethane urea plastics (SPUUs) derived from lysine diisocyanate (LD) (Yamamoto et al., 2007). A few amidases capable of hydrolyzing PUR have also been reported. The combination of two commercial enzymes (esterase E3576 and amidase E4143) improved polyester-PUR degradation compared to using them individually (Magnin et al., 2019a). During this process, the esterase E3576 (EC 3.1) first hydrolyzes the ester bonds to break down the macromolecules into LMW intermediates, which are more accessible for the amidase E4143 (EC 3.5.1.4) to hydrolyze the urethane bonds. Furthermore, an amidase from *Nocardia farcinica* which hydrolyze polyamides (PA) (Guo et al., 2014) and PA-related oligomeric model substrates (Heumann et al., 2009) showed also hydrolytic activity on polyester-based PUR (Gamerith et al., 2016).

Urease hydrolyzes the urea bonds in selected poly(urea-urethane) polymers, releasing two amines and carbon dioxide. However, there are few reports on PUR degradation by ureases, as the urea bonds are hard to be degraded compared to ester bonds. Ureases (EC 3.5.1.5) showed activity on poly(ether urea) PUR, and the degradation was found to be mainly due to the hydrolysis of urea bonds (Phua et al., 1987).

Two bottlenecks hampering the enzymatic degradation of PUR have been recognized in recent years. Firstly, the PUR hydrolases identified to date are mostly polyester hydrolases that can only hydrolyze ester bonds in soft segments of polyester-based PUR. By contrast, a true urethanase that can directly degrade the urethane bonds in PUR polymers has not been reported yet (Wei et al., 2020). In the future, more studies should thus focus on the screening of enzymes with 'polyurethanase' activity, which will greatly reduce the hurdles for biocatalytic degradation of PUR in synergy with the known polyester hydrolases. Secondly, the hydrolysable chemical bonds in PUR polymers are not highly accessible to enzymes due to the insoluble hydrophobic nature. This can potentially be facilitated by introducing specific polymer-binding domains (Van et al., 1986; Fukui et al., 1988; Hansen, 1992). Functional polymer-binding peptides (anchor peptides) can enable the specific binding of whole cells to polymer surfaces to improve the accessibility of insoluble polymers (Dedisch et al., 2019). An *E. coli*-based esterase cell surface display screening system has been developed to enable the directed evolution of polypropylene (PP)-binding peptide LCI, which resulted in a mutant with 12-fold improved PP-binding ability compared to the wild-type LCI (Apitius et al., 2019). Also, ultra-high throughput screening approaches (Apitius et al., 2019) and rational engineering for anchor peptide developments have been reported (Kristin et al., 2018). Tcur1278, a polyester hydrolase derived from *Thermomonospora curvata* DSM 43183 with hydrolytic activity on PET (Wei et al., 2014), has been

Table 3
Enzymes involved in PUR biodegradation.

Microorganism (source)	Enzyme types	Proteins	Optimum temperature (°C)	Optimum pH	Molecular mass (kDa)	Cleavage sites	References
Comamonas acidovorans TB-35	Esterase	PudA	45	6.5	62	Ester bonds	Nakajima-kambe et al., 1995
Pseudomonas fluorescens	Esterase	PulA	Not reported	Not reported	48	Ester bonds	Vega et al., 1999
Pseudomonas chlororaphis	Lipase	PueA	Not reported	Not reported	65	Ester bonds	Stern and Howard, 2000
		PueB	Not reported	Not reported	60	Ester bonds	Howard et al., 2001
Plant compost	Cutinase	LCC	70	8.0	27	Ester bonds	Schmidt et al., 2017
Thermobifida fusca KW3	Cutinase	TfCut2	70	8.0	28	Ester bonds	Schmidt et al., 2017
Thermomonospora curvata DSM43183	Cutinase	Tcur1278	60	8.5	35	Ester bonds	Wei et al., 2014
Thermomonospora curvata DSM43183	Cutinase	Tcur0390	55	8.5	35	Ester bonds	Wei et al., 2014
Rhodococcus equi TB-60	Urethane hydrolase	–	45	5.5	55	Urethane bonds	Akutsu-Shigeno et al., 2006

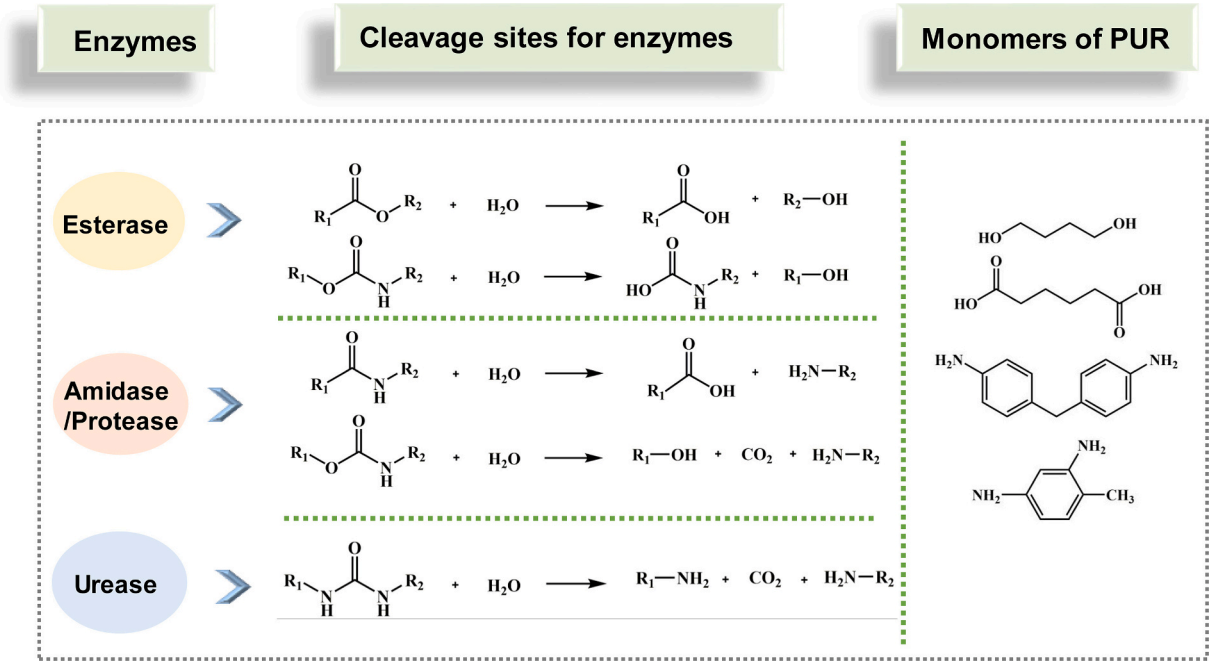

Fig. 3. Mechanisms of the enzymatic hydrolysis of chemical bonds available in PUR. Specific monomers released from PUR are also illustrated.

fused with the anchor peptide tachystatin A2, which led to markedly increased hydrolytic activity on polyester PUR nanoparticles (Impranil DLN SD) compared to the wild-type enzyme, presumably as a result of enhanced substrate adsorption (Islam et al., 2019). Nevertheless, the mechanism through which the binding domains specifically assist the enzyme in recognizing the substrate (urethane/ester-bonds) in the polymer needs to be studied further.

4. Evaluation methods for assessing the PUR degradation efficiency

4.1. Measuring the changes of physical properties

PUR polymers will have altered physical properties as a result of biodegradation such as weight loss, changes of surface topography and crystallinity, hydrophobicity/hydrophilicity, molecular weight distribution, and mechanical properties. Loss of the initial weight can provide the most direct evidence for PUR polymer degradation by microorganisms. However, due to the low biodegradability of most PUR bulk polymers, the extent of weight loss was presumably too low to be demonstrated in many previous degradation experiments (Crabbe et al., 1994; Nakajima-kambe et al., 1995; Matsumiya et al., 2010; Mathur and Prasad, 2012; Álvarezbarragán et al., 2016; Shah et al., 2016; Schmidt et al., 2017; Magnin et al., 2019a). The weight-averaged molecular weight (M_w) and number-averaged molecular weight (M_n) measured by gel permeation chromatography (GPC) are also two important parameters for the evaluation of polymer degradation (Phua et al., 1987; Ziaullah et al., 2013; Schmidt et al., 2017; Magnin et al., 2019a). The changes in tensile strength and elongation at break suggested that PUR degradation led to the deterioration of mechanical properties (Oprea, 2010; Aranguren et al., 2012; Spontón et al., 2013; Zafar et al., 2014; Uscátegui et al., 2016). In addition, the quantification of CO_2 release can be used to determine the rate of mineralization of the degradation products by microbes (Aamerali et al., 2008; Shah et al., 2008, 2016; Osman et al., 2018). Besides, the cleavage of the urethane bond also releases CO_2, which interfere with the accuracy of the mineralization rate.

PUR polymers are semi-crystalline polymers consisting of polyisocyanates (crystalline regions) and polyester/polyether polyols (low-crystalline regions) that can be differentiated by X-ray diffraction (Loredo-Trevino et al., 2012). Many studies found that the crystallinity of PUR polymers was enhanced when the degradation of PUR polymer took place in soft segments due to microbial treatment (Zafar et al., 2014; Osman et al., 2018). The surface hydrophilicity of PUR polymers can be assessed by measuring the water contact angle, which is an important factor for bacterial adhesion on the surface of polymer. Generally, the contact angle values will decrease after biodegradation, indicating an increase of hydrophilicity at the polymer surface (Spontón et al., 2013; Álvarezbarragán et al., 2016; Uscátegui et al., 2016). Scanning electron microscopy (SEM) analysis can directly illustrate the changes of surface morphology, such as the formation of pits, holes, and erosion on the polymer surface (Oprea, 2010; Matsumiya et al., 2010; Howard et al., 2012; Ziaullah et al., 2013; Zafar et al., 2014; Álvarezbarragán et al., 2016; Schmidt et al., 2017).

4.2. Changes of chemical properties

Changes of functional groups on the polymer surface can clearly show which part of the polymer molecule was degraded. Many previous studies reported a decrease in the abundance of carbonyl groups by FTIR, indicating that the degradation mainly takes place in the soft segments (Mathur and Prasad, 2012; Spontón et al., 2013; Biffinger et al., 2014; Khan et al., 2017; Schmidt et al., 2017). The decrease of carbonyl and C-N-H signals at their respective wavenumbers of 1729 cm^{-1}, 1540 cm^{-1} and 1261 cm^{-1} was attributed to fungal enzymatic hydrolysis of the urethane groups (Alvarezbarragán et al., 2016; Magnin et al., 2019b). The disappearance of the isocyanate group signal at 2268 cm^{-1} in PUR incubated with *Aspergillus niger* and *Cladosporium herbarum* also indicated the hydrolysis of urethane groups (Filip, 1979).

In addition, PUR degradation by microorganisms can be verified by the release of low-molecular-weight degradation products into the culture supernatant (Magnin et al., 2019a). When polyester-based PUR synthesized from poly(butylene adipate) and 4,4′-methylene diphenyl diisocyanate (4,4′MDI) was used as the substrate for *P. aeruginosa* strain MZA-85, BDO, and AA monomers were detected as degradation products by gas chromatography–mass spectrometry (GC–MS) (Shah et al., 2013a, b). When thermoplastic polyurethane synthesized from polycaprolactone (PCL) and 4,4'-MDI was used as the substrate, 6-hydroxy

caproic acid and MDA were detected by liquid chromatography coupled with mass spectrometry (LC/ESI/qTOF-MS) (Magnin et al., 2019b). The identified PUR degradation products were mostly reported to be alcohols, carboxylic acids, and amines (Matsumiya et al., 2010; Shah et al., 2013b; Ziaullah et al., 2013; Álvarezbarragán et al., 2016; Shah et al., 2016; Magnin et al., 2019a) (Table 4).

Thus, microorganisms are able to colonize on the surfaces of PUR polymers and initiate their degradation, which will cause changes of polymer characteristics, including both physical and chemical properties. The main changes of PUR polymers as a result of microbial degradation are summarized in Table 4 along with the key techniques used to monitor them. Different researchers have applied various methods for evaluating PUR polymer degradation performance, thereby complicating a comprehensive comparison of the degradation efficacy by different strains (Magnin et al., 2019b). Characterization methods such as SEM, FTIR, and WCA can only provide qualitative evidence. In contrast, the measurement of degradation products or weight loss *versus* time is (semi-)quantitative and can be used to compare the degradation performance. Besides, the distinct types and sources of PUR used as substrates can further complicate the direct comparison of degradation performance. Therefore, standardized evaluation methods towards the degradation of well-defined PUR polymers with uniform properties are urgently needed to promote further research activities focusing on the PUR biodegradation.

5. Valorization of PUR degradation products

5.1. PUR monomer metabolic pathways

The complex structure of PUR leads to a variety of PUR degradation products, including organic acids, organic alcohols, and diamines. The metabolic pathways for some of these PUR degradation products have been reported.

1, 4-butanediol (BDO) is one of the representative organic alcohols as PUR degradation products. *Pseudomonas putida* KT2440 can grow with 1, 4-butanediol as the sole carbon source, albeit very slow. The utilization efficiency of KT2440 for 1BDO can be improved through adaptive laboratory evolution. Li et al. analyzed the biodegradation pathway of BDO through genome sequencing and proteomics analysis of the resulting mutant strain. Initially, 1,4-butanediol is oxidized to 4-hydroxybutyrate, in which the highly expressed dehydrogenase enzymes encoded within the PP_2674-2680 *ped* gene cluster play an essential role. Then, 4-hydroxybutyrate can be metabolized through three possible pathways: i) oxidation to succinate, ii) CoA activation and subsequent oxidation to succinyl-CoA, and iii) beta-oxidation to glycolyl-CoA and acetyl-CoA (Li, 2020).

Adipic acid (AA) is one of the organic acids as PUR degradation products. Its metabolic pathway has been elucidated in *Acinetobacter* (Parke et al., 2001). Firstly, AA is catalyzed by succinyl-CoA transferase (DcaIJ) to form adipyl-CoA. Secondly, 2,3-dihydroadipyl-CoA is generated under the action of enoyl-CoA dehydratase (DcaE), which is then catalyzed by 3-hydroxyacyl-CoA dehydrogenase (DCAA) to form 3-hydroxyadipate-CoA. Finally, succinyl-CoA and acetyl-CoA are generated under the acyl-CoA thiolase catalysis (DcaF), and then enter the TCA cycle to maintain cell growth and metabolism.

2.4′-TDA is one of the degradation products of diamines. Cardenas et al. isolated a strain of *Pseudomonas* TDA1 from the soil of a plastic waste dump, which can grow with PUR oligomer and TDA as carbon and nitrogen sources. Through genomic analysis, the degradation pathway of TDA was preliminary proposed: the methyl group of TDA is oxidized, decarboxylated, and deaminated to form 4-amino-catechol, which may be converted into 5-amino-2-hydroxyl muconic acid in the form of diol, and further degraded and transformed through a metabolic pathway similar to catechuic acid. In the future, a comprehensive proteomic and transcriptome analysis of related genes in the predicted metabolic pathway is needed to accurately determine the degradation pathway of TDA (Cardenas et al., 2020). However, MDA, another important degradation product from the isocyanate chain in PUR, is degraded difficultly more than TDA due to its diphenyl structure. At the same time, the degradation pathway of MDA has not been proposed.

5.2. High-value utilization of PUR monomer

Biotechnological plastic recycling aims to recover raw materials that

Table 4
Evaluation methods of PUR biodegradation.

Characteristics		Techniques used	Property measured	References
Physical properties	Polymer consumption	Gravimetric	Weight loss	Matsumiya et al., 2010; Mathur and Prasad, 2012; Álvarezbarragán et al., 2016; Shah et al., 2016; Schmidt et al., 2017; Magnin et al., 2019a
		CO_2 evolution	Weight loss	Aamerali et al., 2008; Shah et al., 2008, 2016; Osman et al., 2018
	Surface topography	SEM	Topography	Oprea, 2010; Matsumiya et al., 2010; Howard et al., 2012; Ziaullah et al., 2013; Zafar et al., 2014; Álvarezbarragán et al., 2016
	Crystallinity	DSC	Glass transition and melting temperatures	Osman et al., 2018; Zafar et al., 2014
	Hydrophobicity/ Hydrophilicity	Drop shape analysis system	Contact angle values	Spontón et al., 2013; Álvarezbarragán et al., 2016; Uscátegui et al., 2016
	Molecular weight distribution	HT-SEC GPC	Number-averaged molecular weight (M_n) and weight-averaged molecular weights (M_w)	Ziaullah et al., 2013; Schmidt et al., 2017; Magnin et al., 2019a
	Mechanical properties	ASTM D638-10 Instron	Tensile strength and % elongation	Oprea, 2010; Aranguren et al., 2012; Spontón et al., 2013; Zafar et al., 2014; Uscátegui et al., 2016
Chemical properties	Functional groups on the surface	FTIR	Ester-carbonyl index (1740 cm^{-1}) N—H bond index (1540 and 1261 cm^{-1})	Mathur and Prasad, 2012;
			N—H hydrogen bond and OH stretching vibration (str., vib.) band (3400 cm^{-1}) Urea bond index(1613 cm^{-1}) Vinyl-bound incdex (1640 cm^{-1}) C—O stretching (1735 cm^{-1}) NCO group (2268 cm^{-1})	Spontón et al., 2013; Biffinger et al., 2014; Khan et al., 2017; Schmidt et al., 2017
	Metabolites identification	LC–MS GC–MS NMR	Ethylene glycol, diethylene glycol, 1,4-butanediol, adipic acid, polymer, 6-hydroxycaproic acid, 4,4′-diaminodiphenylmethane, 2.4′-toluene diamine (TDA)	Matsumiya et al., 2010; Shah et al., 2013a, 2013b; Ziaullah et al., 2013; Álvarezbarragán et al., 2016; Shah et al., 2016; Magnin et al., 2019a

can be used to synthesize virgin polymers to close the recycling loop (Wei et al., 2020). Compared with mechanical and selected chemical approaches (*e.g.*, dissolution/precipitation) focusing on the reuse of polymers with minimal chain scissions (Vollmer et al., 2020), a high yield of small-molecule products from polymer disassembly is envisaged by biotechnological recycling. Therefore, as an alternative to the closed-loop strategy, an open-loop 'upcycling' strategy aiming to produce value-added chemicals from these degradation products of plastic waste has also been proposed (Blank et al., 2019, Utomo et al., 2020). Moreover, converting plastic waste into value-added and sustainable products is the ultimate goal for a low-carbon circular bioeconomy.

For instance, PET degradation products such as terephthalic acid (TA) and ethylene glycol (EG) can be converted into polyhydroxyalkanoate (PHA) by genetically modified *Pseudomonas putida* (Kenny et al., 2008; Kenny et al., 2012; Tiso et al., 2020). In addition, TA and EG were also converted by a modified *Pseudomonas* sp. GO16 into the engineered extracellular building block hydroxyalkanoyloxyalkanoate (HAA), which can be copolymerized with diisocyanate and butanediol to yield a novel bio-based poly(amide urethane) (bio-PUR) (Tiso et al., 2020). Among them, TA has recently been reported to be biologically converted to various higher-value products than the value of PET, such as gallic acid, pyrogallol, catechol, muconic acid, and vanillic acid *via* protocatechuic acid, using engineered *E. coli*. The other monomer from PET, EG, can be converted to glycolic acid by EG-fermenting *Gluconobacter oxydans* (Kim et al., 2019) or rapidly converted by *P. putida* (Li et al., 2019; Ann et al., 2018).

Similarly, valorization of PUR waste *via* the biotechnological production of value-added products was envisioned. Unlike PET, which contains only TA and EG in its main chain, PUR polymers often have a more complex backbone. Hence, PUR yields a broader spectrum of degradation products, leading to challenges in downstream processing. Degradation products derived from PUR can include amines, alcohols, acids, aromatics, and other residues, such as EG, BDO, AA, MDA, or TDA (Magnin et al., 2019a; Shah et al., 2013a, b) (Fig. 3). EG can be used as a substrate for the production of PHA and glyoxylic acid, which have a wide range of applications in the chemical industry (Mückschel et al., 2012). Carboxylic acids and alcohols can be used for the synthesis of virgin PUR and other polyesters, such as poly(butylene succinate) (PBS), poly(1,3-propylene succinate-*ran*-1,4-butylene succinate) (PPBS) and poly(1,3-propylene adipate-*ran*-1,4-butylene adipate) (PPBA) (Tiso et al., 2020; Debuissy et al., 2017). Two series of biobased high-molecular-weight aliphatic *co*-polyesters were synthesized by trans-esterification with BDO and AA (Debuissy et al., 2017). Amines can be used to synthesize polyamides and virgin PUR (Li et al., 2002; Hablot et al., 2010). Recently, a biotechnological route to utilize PUR monomers as a carbon source and convert to rhamnolipid (RHL) production with a defined microbial mixed culture was proposed (Utomo et al., 2020). The mixed culture contained three *P. putida* KT2440 derivatives, which were engineered to utilize AA, BDO, and EG, respectively. In addition, the *Pseudomonas* sp. TDA1 was used to remove TDA. TDA inhibited the growth of mixed cultures and the utilization of mixed substrate. Reactive extraction of TDA was implemented before the full utilization of remaining PUR monomers as carbon sources. Furthermore, the extracted and recycled TDA could be used for TDI resynthesis and subsequently for virgin PUR synthesis (Cregut et al., 2013). By integrating biodegradation and biotransformation, a green route for future upcycling of PUR waste could be established, enabling the sustainable use of petrochemical resources compared with current PUR recycling (Fig. 4).

6. Challenges and prospects

Microbial and enzymatic degradation of PUR waste is considered a highly attractive and eco-friendly alternative approach for solid waste treatment. However, the microbes and enzymes discovered to date still show very low degradation activity. A number of challenges must be addressed to develop an effective biodegradation and recycling process for PUR waste. Firstly, novel high-throughput and standardized screening methods should be developed to identify microbes with polyether-PUR degrading activity. Secondly, the biocatalytic degradation mechanism of PUR needs to be further elucidated, especially for polyether-based PUR plastics. This knowledge will facilitate protein and strain engineering for enhanced PUR degradation performance, meeting the requirements for industrial applications. The synergistic use of polyesterases and urethane-degrading enzymes in an optimal enzyme cocktail can greatly improve the degradation of mixed PUR waste in a bioreactor. In this context, various protein engineering approaches, such as the recently developed machine-learning-based methods (Cui et al., 2021), should be adopted. Moreover, engineering PUR-specific binding domains that can be introduced to the microbial degradation of solid PUR to promote its accessibility to biocatalysts can also be a useful strategy. Thirdly, it is urgent to establish a highly efficient and cost-effective method for the separation of degradation products from PUR waste, especially for small molecules, including certain alcohols and acids. To this end, toxic substances such as diamines should be removed in real-time during the enzymatic degradation to maximize the biocatalytic capability. Lastly, microbial metabolic routes used to transform the monomers or oligomers into value-added products should be systematically introduced and engineered. The recently identified *Pseudomonas* sp. strain that can grow on PUR oligomers and monomers can serve as a chassis cell with great potential for upcycling (Tiso et al., 2020; Cardenas et al., 2020). Although technical challenges in downstream processing of the PUR degradation products need still to be addressed, the broad spectrum of small molecules yielded will provide the opportunities to be transformed into a variety of high value-added chemicals. The synergistic combination of metabolic pathways for degradation products and synthesis modules in genetically engineered microbes should be optimized to achieve high transformation efficiency in producing value-added chemicals.

7. Conclusion remarks

In conclusion, further studies on the biological degradation of PUR will contribute to mitigating the global plastic crisis. While a biotechnological route for the recycling of PET plastic waste has been recently reported (Tournier et al., 2020), an analogous method for PUR waste is still missing and will require further efforts from the scientific community. An ideal solution, especially for the PUR waste, will certainly benefit from the combination of advanced physicochemical treatment processes under mild reaction conditions that do not generate secondary pollution, highly effective biocatalytic degradation modules, and synthetic-biology-based valorization approaches geared towards the synthesis of value-added products, finally achieving the sustainable use of PUR plastic waste.

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Declaration of Competing Interest

No conflict of interest exits in the submission of this manuscript, and manuscript is approved by all authors for publication. All the authors listed have approved the manuscript that is enclosed. We declare that:

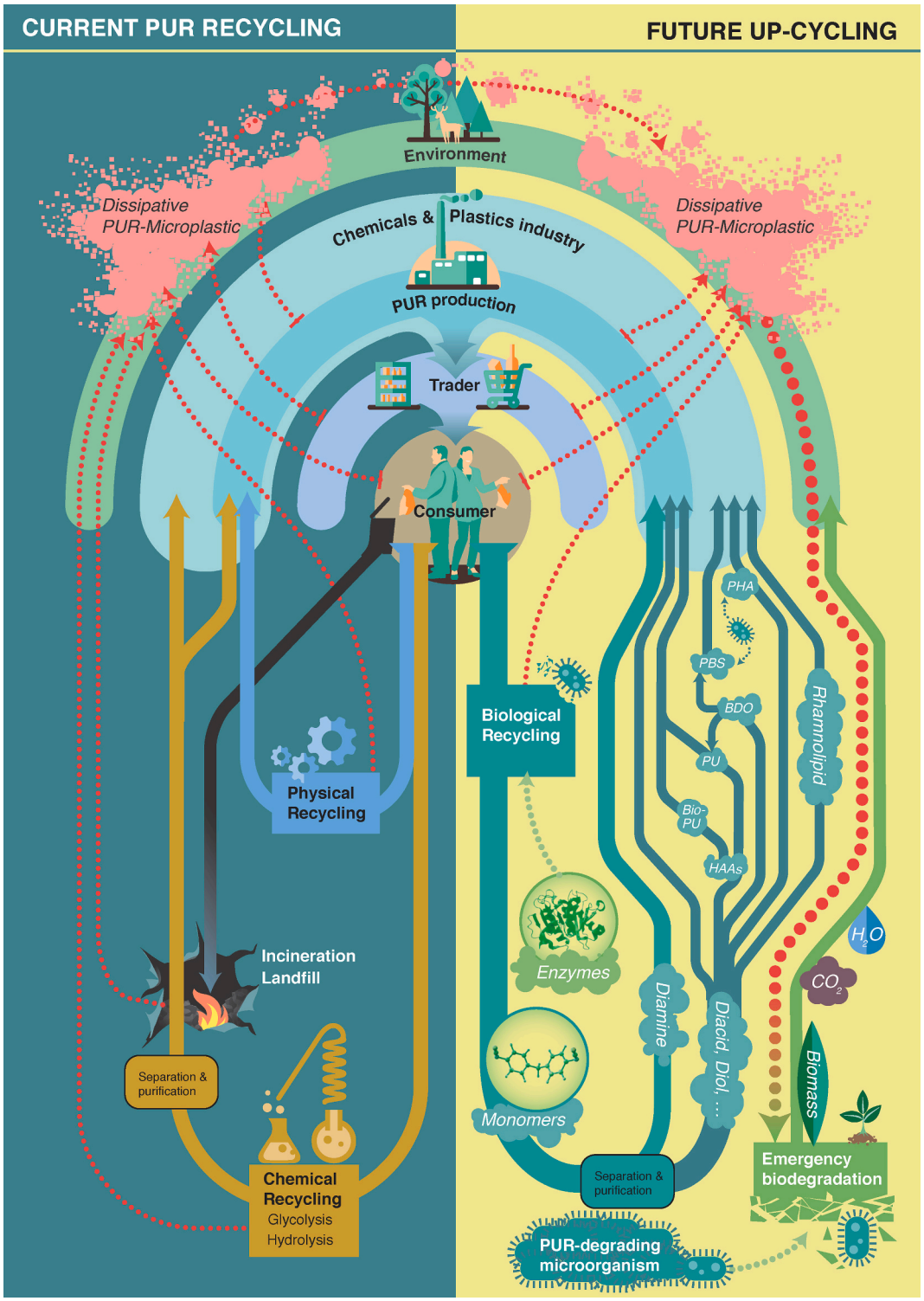

Fig. 4. The current and future scenarios of PUR recycling. The amount of PUR waste sent to recycling is currently low partly as a result of the lack of efficient recycling approaches. Traditional physical and chemical recycling methods lead to downcycled products and considerable environmental pollution. With advances in biotechnology, an upcycling strategy of PUR waste including biological degradation, separation and maximized re-utilization of the small-molecule degradation products is envisioned for the future. A variety of value-added chemicals will be produced including biopolymers such as polybutylene succinate (PBS) and polyhydroxyalkanoate (PHA) using the (derivatized) PUR monomers like 1,4-butanediol (BDO) and hydroxyalkanoyloxy-alkanoate (HAA). In this way, the dependency on fossil fuels for virgin plastic production as well as the rate of landfilling of post-consumer PUR waste will be drastically reduced. As the release of PUR microplastics to environments is still inevitable, the possibility to emergency biodegradation should be taken into account already at the stage of product design and developement.

all of the authors mutually agree for submitting this manuscript to *BIOTECHNOLOGY ADVANCES*; the manuscript is original work of authors.

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