Evaluation of biological degradation of polyurethanes

Audrey Magnin, Eric Pollet, Vincent Phalip, Luc Avérous

Evaluation of biological degradation of polyurethanes

Audrey Magnin[1], Eric Pollet[1], Vincent Phalip[2], Luc Avérous*[,1]

(1) BioTeam/ICPEES-ECPM, UMR CNRS 7515, Université de Strasbourg, 25 rue Becquerel, 67087 Strasbourg Cedex 2, France

(2) Université Lille, INRA, ISA, Université Artois, Université Littoral Côte d'Opale, EA 7394 - ICV - Institut Charles Viollette, 59000 Lille, France

(*) Corresponding author: luc.averous@unistra.fr

1. Abstract

Polyurethanes (PU) are a family of versatile synthetic polymers intended for diverse applications. Biological degradation of PU is a blooming research domain as it contributes to the design of eco-friendly materials sensitive to biodegradation phenomena and the development of green recycling processes. In this field, an increasing number of studies deal with the discovery and characterization of enzymes and microorganisms able to degrade PU chains. The synthesis of short lifespan PU material sensitive to biological degradation is also of growing interest. Measurement of PU degradation can be performed by a wide range of analytical tools depending on the architecture of the materials and the biological entities. Recent developments of these analytical techniques allowed for a better understanding of the mechanisms involved in PU biodegradation. Here, we reviewed the evaluation of biological PU degradation, including the required analytics. Advantages, drawbacks, specific uses, and results of these analytics are largely discussed to provide a critical overview and support future studies.

Keywords: Microbial degradation, enzymatic degradation, polyurethanes, technical review

2. Introduction

In 2019, the International Union of Pure and Applied Chemistry (IUPAC) published a list of ten emerging technologies in Chemistry with the potential to make our planet more sustainable. Among them, technologies permitting the transformation of plastic material into monomers are highlighted. These recycling technologies will help reduce plastic waste and save fossil resources. Despite comfort and incomparable uses to our everyday life, plastic materials are a cause of global and increasing pollution resulting from inadequate behaviors of both producers and users. The massive production involves a polluting exploitation of fossil resources and their poor waste management induces uncontrolled dissemination in the environment. In 2010, more than 275 million metric tons of plastic waste were generated in almost 200 coastal countries, out of which an estimated 5 to 13 million metric tons reached the oceans where plastic waste accumulate (Jambeck et al., 2015). With the problematic of the nano- or microplastic debris, ocean garbage patches are one of the major environmental concerns of this century (Cozar et al., 2014; Eriksen et al., 2013; Law et al., 2010). Even if some very minor studies still question the actual impact of plastic waste (Duis and Coors, 2016), most are warnings of irrevocable environmental damages (Clukey et al., 2018; Darmon et al., 2017; Galloway and Lewis, 2016). Furthermore, by entering

the food chain, plastic materials finally attain human beings, thereby causing health concerns (Barboza et al., 2018; Bouwmeester et al., 2015; Chae and An, 2017).

Among the vast families of resistant plastic materials, we can find the polyurethanes (PUs). Low-density and easily dispersible foams (soft to rigid) represent around 70% of the PU production. The presence of PUs as pollutants in marine ecosystems has been largely attested (Frère et al., 2016; Reddy et al., 2006). In 2016, Turner et al. revealed that over the 70 foamed plastics fragments collected on a Britain beach, 39 were identified as PU (Figure 1), thus pointing out the significant role of PU in plastic pollution (Turner and Lau, 2016).

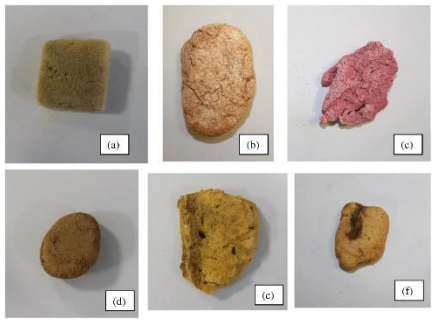


Figure 1 –Foamed plastic debris collected on a Britain beach, pieces a, b d, e and f are PU (Turner and Lau, 2016)

First synthesized in the 1930s by the German chemist Otto Bayer, PU products were commercialized about 10 years later (Bayer, 1948). The use of PU spread during World War II, where it replaced natural rubber for elastomer production. Rapidly, other applications emerged in aviation and textile, which were flourishing markets at the time. Diversification of PU properties allowed to reach other numerous markets. In 2016, 18 million tons of PU were produced worldwide, representing 5.3% of global plastic production (Furtwengler et al., 2018a; PlasticsEurope, 2017). PU rank at the 6th most produced synthetic polymers. About 22 million tons are expected to be produced in 2020 (Akindoyo et al., 2016).

In 2014, the PU foam market was valued at $46.8 billion and is expected to reach $72.2 billion by 2020 (Pillai et al., 2016). Flexible and rigid foams represent respectively 32% and 36% of the global PU production. Flexible foams, renowned for the comfort they provide, are used for the cushioning of furniture, bedding or automotive seats. In the construction area, rigid foams are preferred for thermal insulation and their use increases in agreement with a growing demand for energetically efficient buildings. PU are also widely used as coatings, adhesives, sealants and elastomers (CASE). PU coatings provide a protection layer against weather, abrasion and corrosion. Elastomers are both elastic and flexible and can adopt any desired shape, such as wheels for rollerblades. Biocompatibility of certain types of polyurethanes make them polymers of choice for medical application, for instance, cardiovascular devices or orthopedic prosthesis (Gunatillake et al., 2011; Zhou et al., 2012). The common thread between most of these PU materials is that they are mostly intended for long-term applications. They are mainly designed to resist environmental factors such as microbial degradation, abrasion, hydrolytic (moisture) or UV degradation.

Biodegradation is generally defined as the decomposition/degradation of materials by the means of biological entities such as microorganisms or enzymes. This process is used for numerous industrial applications such as waste water treatment (Watanabe, 2001) or depollution of contaminated site by, for instance, polycyclic aromatic hydrocarbons (Shuttleworth and Cerniglia, 1995). Polymer degradation by microorganisms is performed through several steps (Figure 2). First, materials are fragmented into pieces thanks to abiotic and biotic factors such as UV, hydrolysis, abrasion or pressure exerted by filamentous microorganisms. Growth of filaments into polymer pores provokes cracks. Then, macromolecules are cleaved by enzymatic hydrolysis and/or oxidation, leading to the release of low molar mass molecules such as oligomers and monomers. These molecules are finally assimilated and mineralized by microorganisms to promote microbial growth (Lucas et al., 2008; Shah et al., 2008b). A countless number of mineralization paths exists in nature. The step of enzymatic depolymerization or enzymatic degradation can be reproduced or mimicked *in vitro,* independently of the microbial degradation. Interestingly, the released molecules resulting from enzymatic depolymerization of polymers could be turned into building blocks and high value products for the chemistry market (Wierckx et al., 2015).

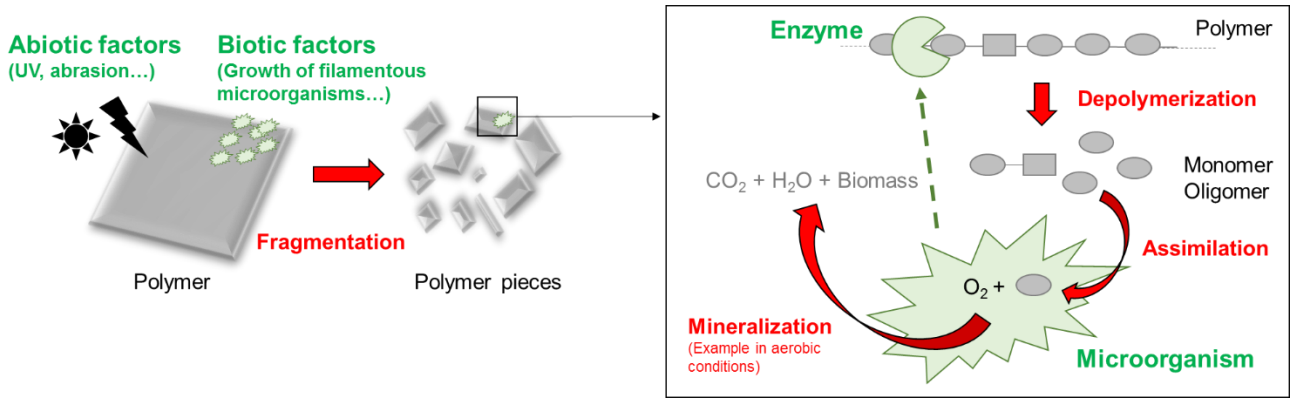


Figure 2 – Polymer biodegradation process

PU are not biodegradable polymers (Wierckx et al., 2018). Even if some PU are partly sensitive to biological degradation, they do not answer, for instance, the requirements of the European norm EN 13432 defining biodegradable and compostable materials (Avérous and Pollet, 2012; Bastioli, 2005). This norm considers a material as biodegradable if the degradation reaches 90% after 6 months, under composting conditions. The non-toxicity of the degradation products is also a requirement of this norm to declare a material as biodegradable or compostable. Biodegradation of PU has been studied since the 1960s. The first scientific publications on this topic aimed to evaluate the microbial degradation susceptibility of PU formulations to promote the development of highly resistant materials (Cooney, 1969; Darby and Kaplan, 1968; Edmonds and Cooney, 1968; Kanavel et al., 1966; Kaplan et al., 1968). Today, this approach is reversed to address the PU materials end-of-life issues. Due to increased environmental concerns, sensitivity to microbial degradation has become a desired feature to reduce the environmental footprint of PU materials, mainly at their ends of life (Prieto, 2016). Meanwhile, the development of bioresorbable PU materials for the biomedical industry raised interest (Pavlova and Draganova, 1993; Špírková et

al., 2017). Currently, PU biodegradation assessments are focused on two main purposes: (i) biodegradation susceptibility of new eco-materials or materials intended for biomedical purposes, thus focusing on the polymer synthesis and (ii) bioremediation or biological recycling of PU, thus focusing on the biological entities capable of degradation.

Techniques used to evaluate the biodegradation of PU are diverse, depending on the type of PU and the degrading entity. Furthermore, conflicting results and conclusions are found in the scientific literature, often due to the difficulty in interpreting the analytical results. Nevertheless, significant advances have recently been made on the evaluation of PU biodegradation and consequently on the understanding of degradation mechanisms.

Review articles recently published on PU biodegradation have mainly focused on the degradation by microorganisms (Mahajan and Gupta, 2015), enzymatic degradation (Loredo-Treviño et al., 2011) or PU biodegradation for recycling (Cregut et al., 2013). Here, we reviewed comprehensively PU biodegradation including used analytics. For a full understanding of the different approaches, a first part is dedicated to the diversity of PU in term of compositions, architectures and corresponding waste management. Secondly, biological entities (microorganisms, enzymes) able to degrade PU and their degradation mechanisms, if known, are reviewed. Finally, analytical techniques used to assess PU biodegradation are gathered. Their applications, advantages and drawbacks are fully discussed.

3. Polyurethane structure and biological degradation susceptibility relationships

3.1. Diversity of the compositions and architectures of PU

Chemical composition and macromolecular architectures are of prime importance for the biodegradation of polymers (Kim and Kim, 1998). The nature of chemical bonds, crystallinity and molar mass are key parameters influencing the polymer susceptibility to biological attacks (Zeng et al., 2016). PUs are characterized by the urethane or carbamate linkage, generally obtained by addition of an isocyanate to a hydroxyl group (Figure 3). For instance, in thermoplastic PU (TPU) synthesis, an excess of polyisocyanate reacts with a polyol, principally long polyester- or polyether-based polyols, with a controlled functionality close to 2. A linear prepolymer with isocyanate end groups is formed, followed by addition of a chain extender, usually a short diol, obtain high molar mass polymers. Molar mass is a parameter influencing the biological degradation susceptibility of polymers. It has been shown that for polymers with the same chemical structures and different molar mass, the higher the molar mass, the lower the biological degradation susceptibility (Philip et al., 2007; Zheng et al., 2005).

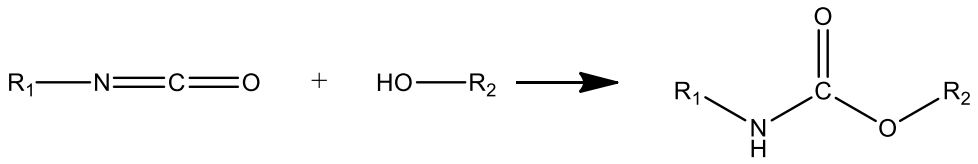
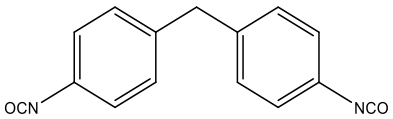
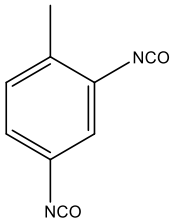
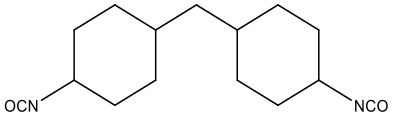
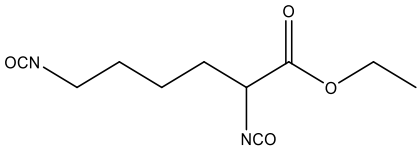
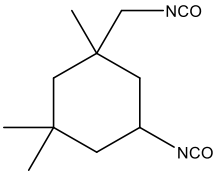
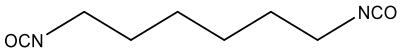
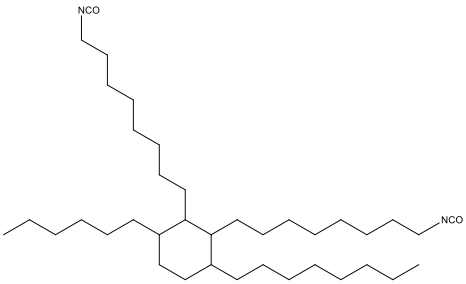


Figure 3 - Polyaddition of an isocyanate and a hydroxyl group to form a urethane bond

The most frequently used isocyanates are bifunctional aromatic molecules such as 4,4'-methylene diphenyl isocyanate (4,4'-MDI) or toluene diisocyanate (2,4-TDI) that give, respectively, a rigid and a more flexible polymer backbone (Table 1) (Delebecq et al., 2013). Due to its chemical structure presenting two aromatic rings, MDI is the most used isocyanate for rigid foams, one of the most prevalent PU-based product (Sabbioni et al., 2012). Aliphatic isocyanates are also of interest such as isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI), lysine diisocyanate (LDI) or 4,4'-methylene dicyclohexyl diisocyanate (H_{12}MDI) (Table 1). They are preferred for medical devices because of the mutagenicity of diamines derived from aromatic diisocyanate hydrolysis (Darby et al., 1978). For the preparation of waterborne polyurethane dispersion, aliphatic isocyanates are chosen due to the high reactivity of aromatic isocyanates with water, making aromatic isocyanates hard to handle in these particular formulations (Noble, 1997). Finally, in the frame of sustainable PUs development, non-isocyanate polyurethane (NIPU) is of growing interest. Indeed, isocyanates derived from phosgene are extremely toxic. NIPU can be obtained by reaction between amines and cyclic carbonates to form polyhydroxy-urethanes, rendering the process of PU synthesis more environment-friendly (Carré et al., 2014; Carré et al., 2015).The high reactivity of isocyanates makes them unstable in water. Consequently, even if free isocyanates remain entrapped in the polymer after its synthesis, they will immediately react with water molecules from the aqueous media. Therefore, no isocyanates can be found either before or after degradation.

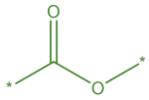
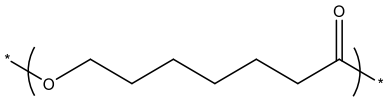
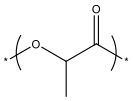
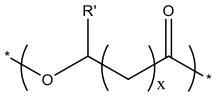
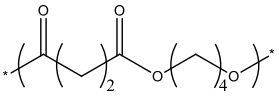
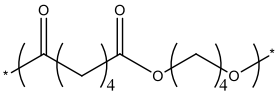
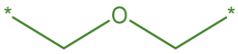
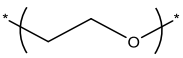
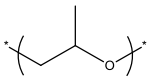
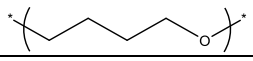
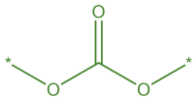
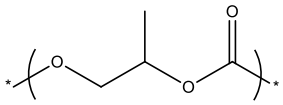
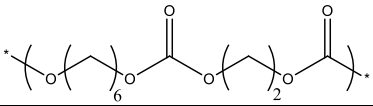
Table 1 – Structure of the some common biobased and fossil-based isocyanates

IUPAC name	Abbrev.	Type	Structure	Potentially biobased	Reference
1-isocyanato-4-[(4-isocyanatophenyl)methyl] benzene	4, 4'-MDI	Aromatic		No	(Shah et al., 2016)
2,4-diisocyanato-1-methyl-benzene	2, 4-TDI	Aromatic		No	(Spontón et al., 2013)
1-Isocyanato-4-[(4-isocyanatocyclohexyl) methyl]cyclohexan	H_{12}MDI	Aliphatic cyclic		No	(Brzeska et al., 2015)
Ethyl Ester L-Lysine Diisocyanate	LDI	Aliphatic linear		Yes	(Zhou et al., 2012)
5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethyl-cyclohexane	IPDI	Aliphatic cyclic		No	(Pereira et al., 2012)
1,6-diisocyanatohexane	HDI	Aliphatic linear		No	(Tang et al., 2001a)
Dimer fatty acid-based diisocyanate	DDI	Aliphatic cyclic		Yes	(Charlon et al., 2014)

Common polyols are polyether, polyester or, more rarely, polycarbonates. Higher flexibility of polyether polyols makes them more convenient for polyurethane production (Krasowska et al., 2012). A non-exhaustive list of polyols with their structures is available in

Table 2. Polyols ordinarily used are fossil-based molecules, but an increasing number of studies deal with bio-based polyols, on agreement with green chemistry principles. Polyols from vegetal sources such as castor oil (Hablot et al., 2008; Trovati et al., 2010), starch (Duarah et al., 2016) or aromatic biopolymers such as tannins or lignin (Ignat et al., 2011; Laurichesse et al., 2014) are increasingly incorporated in PU formulations. Based on short diols such as 1,4-butanediol, ethylene glycol or 1,6-hexanediol, (Akindoyo et al., 2016) chain extenders are used to obtain high-molar mass polymers. Low molar mass diamines can also be used, such as ethylene diamine (Tang et al., 1997), thus generating urea instead of urethane bonds.

177 *Table 2 – Some biobased and fossil-based polyols used for PU synthesis*

Polymer name	Abbrev.	Structure	Potentially biobased	Reference
Polyester				
Poly(caprolactone)	PCL		No	(Yeganeh and Hojati-Talemi, 2007)
Poly(lactic acid)	PLA		Yes	(Izadi-Vasafi et al., 2017)
Poly(hydroxyalkanoates)	PHA		Yes	(Debuissy et al., 2017)
Poly(butylene succinate)	PBS		Yes	(Li et al., 2015)
Poly(butylene adipate)	PBA		Yes	(Shah et al., 2013b)
Polyether				
Poly(ethylene glycol)	PEG		No	(Zhang et al., 2013)
Poly(propylene glycol)	PPG		No	(Chattopadhyay et al., 2008)
Poly(tetramethylene glycol)	PTMEG		No	(Wiggins et al., 2003)
Polycarbonate				
Poly(propylene carbonate)	PPC		No	(Chen et al., 2016)
Poly(1,6-hexyl 1,2-ethyl carbonate)	PHEC		No	(Christenson et al., 2004)

178

PUs can be thermoplastics or thermosets. Thermoplastics are linear or slightly cross-linked/branched structures. Isocyanates, polyols and chain extenders used for TPU synthesis have only two functional groups (diols or diisocyanates). Thermoplastics can be soluble in organic solvent and can be melted, or present a liquid-like behavior with increased temperature. TPUs are commonly described by two types of segments, hard and soft segments. The segments are generally organized with a specific micro-segregation which can lead to micro-crystalline phases. The hard segment (HS) is a block segment with low mobility mainly formed by the isocyanate and the short-chain extender. By contrast, the soft segment (SS) is mainly based on the long polyol part (Figure 4a). TPUs are often semi-crystalline structures (Figure 4b). HS content and chemistry influenced the biodegradation susceptibility of a polycarbonate PU (Tang et al., 2001a, b). Interactions between enzymes and mobile SS are higher than with the HS. Consequently, the higher the HS content, the lower the biological degradation susceptibility.

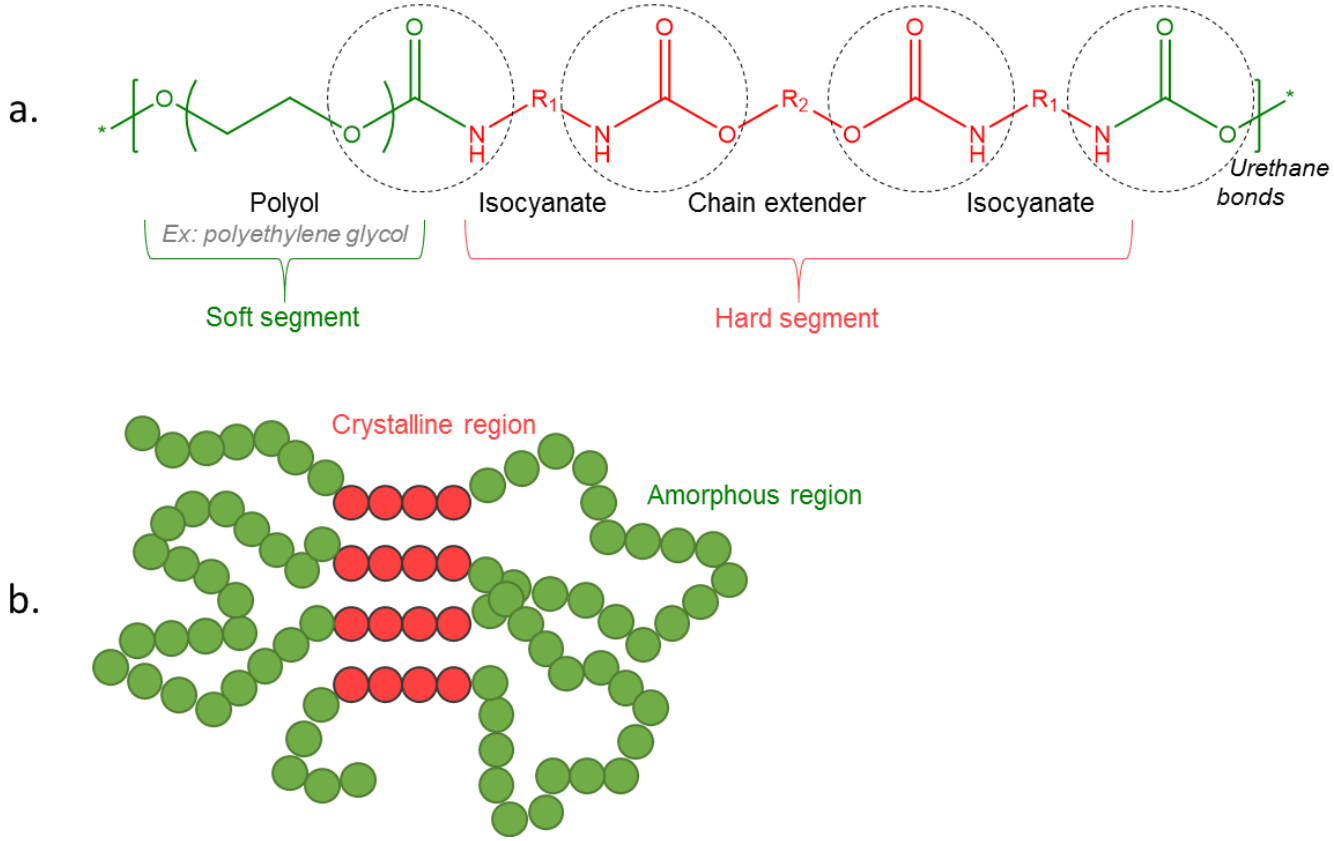


Figure 4 – (a) Schematic representation of a semi-crystalline polymer and (b) linear polyurethane structure

Thermosets are highly cross-linked polymers with 3D structures brought by molecules with a functionality higher than 2. Due to their architecture, thermosets are not soluble, do not melt and are denatured at high temperature, and thus cannot be reshaped by heating, unlike thermoplastics. PU foams are thermoset materials. The alveolar structures of these complex and multicomponent systems are obtained thanks to physical or chemical blowing with air, carbon dioxide, hydrocarbons such as isopentane or other gaseous substances. Foams are structured by

struts and walls defining cell cavities. Cells can be closed (closed-cell foams, mainly rigid e.g. thermal insulation) or open (open-cell foams, mainly soft e.g. damping) (Gautam et al., 2007a). Side reactions during foaming induce the formation of various reversible and irreversible bonds such as urea or isocyanurate moieties (Furtwengler and Avérous, 2018). Isocyanurate linkage is obtained by isocyanate trimerization. Polyisocyanurate foams are increasingly produced because of their better properties such as fire resistance and thermal stability (Arbenz et al., 2016; Furtwengler et al., 2018b). It is then important to consider the bond nature when dealing with foam degradation. Because of the variety of bonds, it is difficult to anticipate and know if the urethane bond was degraded. Also, commercial foams are supplemented with several additives such as fire retardants, antioxidant, processing aids, and anti-microbial compounds (mainly fungicides) that can prevent biodegradation.

Due to the nanometric size of the particles and their hydrophilicity, waterborne PU dispersions (WPUDs) are particularly suitable for biological assays (Figure 5a). To provide hydrophilicity, WPUDs are synthesized using an emulsifier, often the 2,2-dimethylol propionic acid. This molecule contains two hydroxyl groups which react with the isocyanates to form urethane linkage (Figure 5b). The hydroxyl group of the carboxylic acid does not react with isocyanate because of steric hindrance and the lower reactivity (Coutinho et al., 2001). Hydrophilic carboxylic acid then forms a stabilizing top-layer around the hydrophobic polymer (Zhang et al., 2011). Systems containing acrylic polyols are readily dispersed in water (Ionescu, 2005). Acrylic polyols are thus widely used in WPUD formulations. These polyols provide strength and resistance to coatings (Akindoyo et al., 2016). Acrylic polyols are generally based on hydroxyethyl methacrylate or hydroxyethyl acrylate (Figure 5c). The hydroxyl groups of the lateral chains then react with isocyanate for urethane formation.

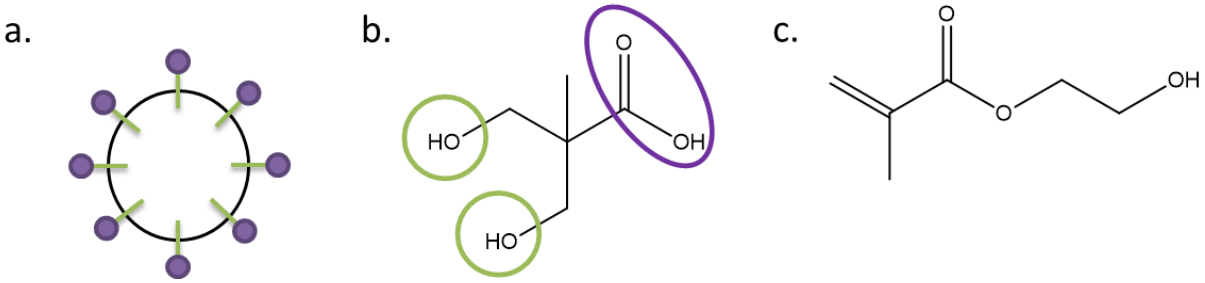


Figure 5 – (a) Schematic structure of a polymer particle, (b) structure of the 2,2-dimethylol propionic acid and (c) structure of the hydroxyethyl methacrylate

3.2. PU waste disposal

The diversity of PUs macromolecular structures and chemistry is a clear obstacle for efficient waste management. To appreciate the importance of PU biodegradation, it is necessary to analyze the current PU waste disposal. PU waste is made of post-consumer products as well as PU production waste, mostly from foam. Indeed, scrap from slabstock foam can reach up to 10% of the production (Simon et al., 2018). In France, scrap PUs were estimated at 13 kTons in 2011 while end-of-life PU volume is about 198 kTons (Boujard et al., 2014). This source of PU waste

mainly arises from construction, furniture, bedding, automotive, shoes and home appliances. Efficient collection and product dismantling are required to recycle these materials, thus limiting their valorization.

PU wastes are mainly treated by three different methods: landfilling, incineration (which can also be considered as quaternary recycling (Ignatyev et al., 2014)) and conventional recycling. Landfill discharge is often the main option but is gradually decreasing, especially in Europe, since it requires large land areas and no value is brought from the waste. European Union aims at reducing municipal waste landfilling to a maximum of 10% by 2030 (Castillo-Gimenez et al., 2019; Makarichi et al., 2018). Landfilling and the absence of waste management lead generally to pollution (Jambeck et al., 2015).

Incineration presents the advantage of being a mature technique, practiced for several decades. Energy is recovered by burning waste and can totally or partly offset the energy spent in the heating process. Even if some CO2 emission exists and may cause greenhouse effect and contribute to global warming, new generations of plants are equipped with dry and wet air pollution control system to make this process as clean as possible (Brunner and Rechberger, 2015; Makarichi et al., 2018). Because of the low value recovered it is hardly considered as recycling. It is a proper solution to reduce landfill volumes, yet incineration is not a satisfying strategy since the richness from the chemical architecture is fully lost.

Depending on the nature (thermoplastics vs. thermosets), recycling processes differ. TPUs can be heated and remolded therefore making the physical recycling process easier. However, it is estimated that only 1% of PU are recycled thanks to physical methods (Behrendt and Naber, 2009). The recycling of PU foams is more challenging since foams cannot be remolded. The main path for foam recycling is regrinding. In 2002, more than 380 kTons were used for carpet underlay (Zia et al., 2007).

Chemical recycling can address both thermoplastic and thermoset architectures (Simón et al., 2016; Wang et al., 2011). Glycolysis appears as the most promising technique (Simon et al., 2018). Glycolysis is a transesterification reaction. The ester group of the urethane bond is interchanged by the hydroxyl group of a diol (glycol) added in large excess (Simón et al., 2013). Simón et al., developed a glycolysis process allowing polyether polyol recovery from high resilience PU foams (Simón et al., 2016). These polyols can then serve as building blocks for the synthesis of second-generation polymers. The major limits of chemical recycling are the processing temperature that leads to high energy consumption (in the example mentioned above, the glycolysis temperature is 190°C) and the side chemical reactions occurring on the urethane bond during the chemical reactions (Gadhave et al., 2019).

Biological recycling is a growing route with high potential that might answer the need for PU recycling in the coming years. This is a soft process that can be implemented at low temperatures (less than 70°C) (Mueller, 2006; Valerio, 2010). This process is catalyzed by biological entities, namely enzymes. The resulting degradation products may then be valorized. Efficient enzymatic depolymerization of poly(ethylene terephthalate) (PET) has been demonstrated at 60°C leading to the release of valuable building blocks such as terephthalic acid and mono(2-hydroxyethyl)-terephthalate (Gamerith et al., 2017). This result, based on PET, can be considered as the first

benchmark for PU. For instance, the company Carbios (France) is starting the biological recycling of PET for the synthesis of second-generation polymers.

4. Actors of the PU biodegradation: Biological entities and associated mechanisms

4.1. Microorganisms

Biodegradation involving microorganisms can be performed by a microbial community or a single strain (Figure 6). Microorganisms can form biofilms on the polymer surface by adhesion (Sivan, 2011). Once colonized, the material constitutes a source of carbon and nitrogen thus promoting microbial growth.

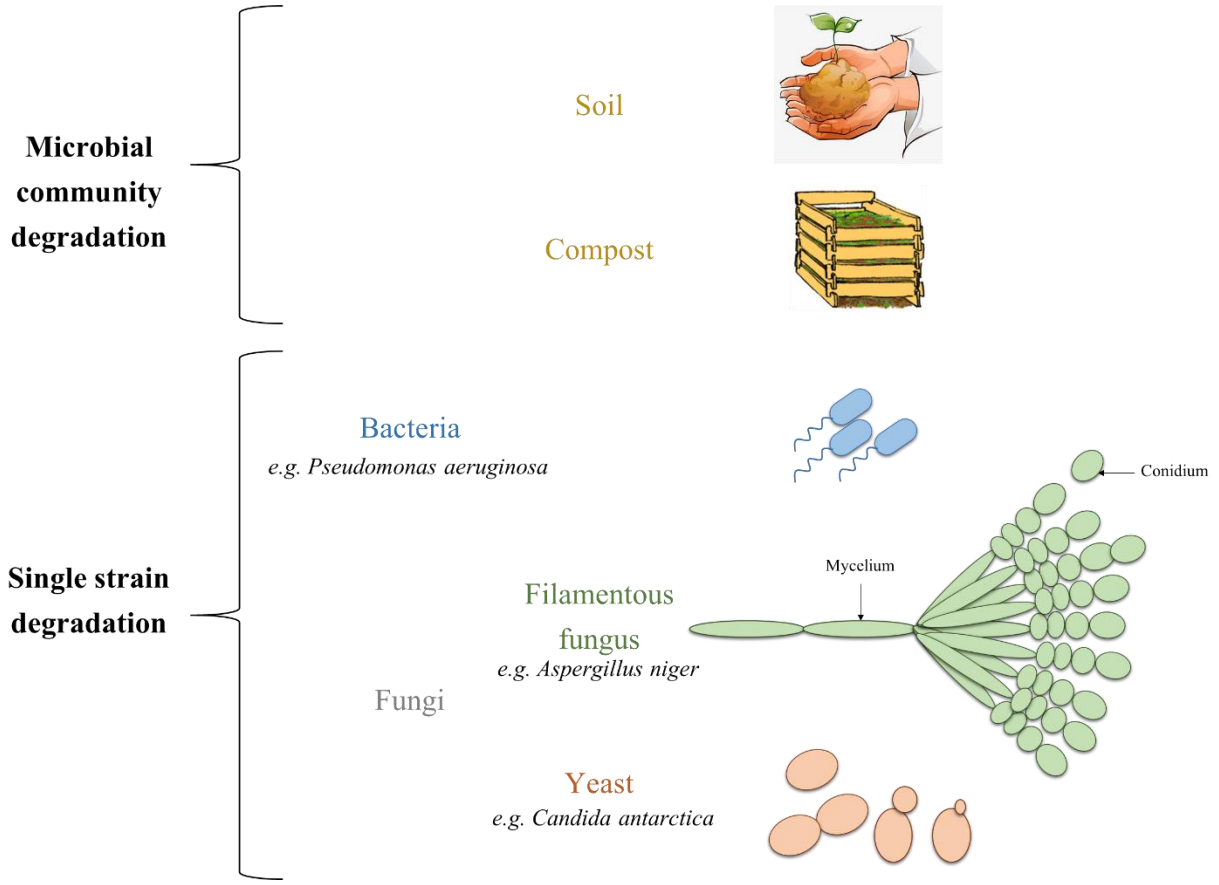


Figure 6 – Different paths for microbial PU degradation

4.1.1. PU degradation by microbial communities

A microbial community is a group of microorganisms sharing a common living place. These microorganisms interact in different ways such as mutualism, predation or competition (Faust and Raes, 2012). Mutualism, also called symbiosis, may occur during the microbial degradation of

xenobiotic, such as synthetic polymers, leading to an improved degradation (Tsoi et al., 2019; Vaclavkova et al., 2007). Comparison of degradation skills of a strain of fungi (*Aspergillus niger*) and a strain of bacteria (*Pseudomonas aeruginosa*) revealed a slightly higher TPU degradation with the bacteria but, above all, an impressive synergistic effect was observed when the polymer was incubated with both strains (Fernandes et al., 2016). Weight losses were approximately doubled for polyester TPU incubated with both microorganisms compared to single strain incubation. PU substrates degraded by communities range from simple structures such as thermoplastic polyester PU (Genovese et al., 2016) to recalcitrant material such as polyether PU foam (Ge et al., 2000). As PU are recalcitrant material, degradation experiments by microbial communities are often performed on a long time scale going from 28 days (Bentham et al., 1987) to two years of incubation (Seal and Pantke, 1988). The predominant systems for studying PU degradation have been composting and soil burial (Table 3 – PU degradation by microbial communities and associated PU substrates. These ecosystems are rich in degrading microorganisms. Other strategies to obtain communities that are more acclimated to PU are also developed. For instance, Cregut et al., selected microbial communities from the soil of a PU foam industrial plant (Cregut et al., 2014).

Table 3 – PU degradation by microbial communities and associated PU substrates

Microbial communities	PU substrates	Time of incubation	Reference
Composting	Polyester PU foam	50 days	(Gómez et al., 2014)
	Thermoplastic polyester PU	90 days	(Genovese et al., 2016; Kucharczyk et al., 2016)
		12 weeks	(Zafar et al., 2013)
		24 months	(Krasowska et al., 2012)
	Thermoset polyester PU	90 days	(Das et al., 2017)
Microbial communities from Garbage Landfill Leakage Water	Polyester PU foam	3 months	(Filip, 1978)
	Polyether PU foam	3 months	(Filip, 1978)
Microbial communities from sewage water of a latex rubber factory	Polyester PU foam	60 days	(Rattanapan et al., 2016)
Microbial communities from soil of a PU foam industrial plant	Polyether PU foam	28 days	(Cregut et al., 2014)
Mixed culture of *Aspergillus niger* and *Pseudomonas aeruginosa*	Thermoplastic polyester PU	30 days	(Fernandes et al., 2016)
Soil burial	Polyester PU	383 days	(Aranguren et al., 2012)
		24 months	(Seal and Pantke, 1988)
	Polyester PU foam	28 days	(Bentham et al., 1987)
		320 days	(Gómez et al., 2014)
	Polyether PU foam	6 months	(Ge et al., 2000)

	Polyether PU foam	12 months	(Zhang et al., 2013)
	PU coating	12 months	(Lu et al., 2016)
	Thermoplastic polyester PU	44 days	(Barratt et al., 2003)
		12 weeks	(Zafar et al., 2013)
		16 weeks	(Huang et al., 2016)
		140 days	(Umare and Chandure, 2008)
		5 months	(Cosgrove et al., 2007)
		6 months	(Fernandes et al., 2016)
	Thermoplastic polyester PU	12 months	(Oprea et al., 2016; Tajau et al., 2016)
	Thermoplastic polyether PU	12 months	(Oprea et al., 2016)
Soil microbial communities, bioaugmentation with PU-degrading fungi	Thermoplastic polyester PU	4 weeks	(Cosgrove et al., 2010)
Vermiculite inoculated with degrading microorganisms, notably *Pseudomonas aeruginosa* and *Achromobacter marplatensis*	Polyester PU	383 days	(Aranguren et al., 2012)

4.1.2. Single-strain degradation

Single species of bacteria and fungi can be isolated and identified using molecular tools. These isolated strains are then used alone for PU degradation assays (Khan et al., 2017; Nair and Kumar, 2007). Another approach is to establish a collection of microorganisms and to screen it for the identification of PU-degrading strain. For instance, Russell *et al*. collected endophytic fungi from wood of the Ecuadorian Amazonian rainforest (Russell et al., 2011). Equatorial are hot and humid environments, and above-all, well-known for the tremendous richness of their biodiversity. PU debris were sampled in e.g., dump-site for isolation of already adapted microorganisms (Álvarez-Barragán et al., 2016; Oceguera-Cervantes et al., 2007).

Bacteria

Bacteria are mainly studied for the degradation of TPU and coatings (Table 4). Only a few publications described the bacterial degradation of polyester-based PU foams, notably by *Pseudomonas aeruginosa* (Cooney, 1969; Gautam et al., 2007c; Hedrick and Crum, 1968; Kay et al., 1991) or by a strain of Corynebacterium (Kay et al., 1991). *Pseudomonas* is the most studied genus. The strain of *P. aeruginosa* ATCC 13388 is the only recommended strain by the ASTM for testing material resistance to bacterial degradation (ASTM code G22-76: Standard Practice for Determining Resistance of Plastics to Bacteria) (Gu and Gu, 2005; Kay et al., 1991). Other *Pseudomonas* species such as *P. chlorographis* or *P. putida* were described as PU-degrading entities (Gautam et al., 2007c; Peng et al., 2014). Furthermore, *Pseudomonas* strains are known to be of high interest in white biotechnology (Wierckx et al., 2015).

Table 4 – PU-degrading bacteria and associated PU substrates

Species and/or strains	PU substrates	References
Acinetobacter gerneri P7	Polyester PU coating (Impranil)	(Howard et al., 2012)

Alicycliphilus sp. BQ1	Polyester PU coating	(Oceguera-Cervantes et al., 2007)
Alicycliphilus sp. BQ8	Polyester PU coating	(Oceguera-Cervantes et al., 2007)
	Polyester PU foam	(Pérez-Lara et al., 2016)
Arthrobacter sp.	Thermoplastic polyester PU	(Shah et al., 2008a)
Arthrobacter calcoaceticus ATCC 31012	Polyester PU coating	(El-Sayed et al., 1996)
Arthrobacter calcoaceticus NAV-2	Polyester PU coating	(El-Sayed et al., 1996)
Arthrobacter globiformis	Polyester PU coating	(El-Sayed et al., 1996)
Bacillus sp.	Polyester PU coating (Impranil)	(Ii et al., 1998)
	Thermoplastic polyester PU	(Shah et al., 2008a)
Bacillus amyloliquefaciens	Thermoplastic poly(ether urea) PU	(Rafiemanzelat et al., 2015)
Bacillus pumilus NMSN-1d	Polyester PU coating (Impranil)	(Nair and Kumar, 2007)
Bacillus subtilis MZA-75	Thermoplastic polyester PU	(Shah et al., 2016)
		(Shah et al., 2013b)
Chryseobacterium meningosepticum	Polyester PU foam	(Cangemi et al., 2008)
Comamonas acidovorans TB-35	Thermoplastic polyester PU	(Akutsu et al., 1998; Nakajima-Kambe et al., 1997; Nakajima-Kambe et al., 1995)
	Thermoplastic polyether PU	(Nakajima-Kambe et al., 1995)
Corynebacterium sp.	Thermoplastic polyester PU	(Kay et al., 1993)
		(Shah et al., 2008a)
	Polyester PU foam	(Kay et al., 1991)
Escherichia coli	Thermoplastic poly(ether urea) PU	(Rafiemanzelat et al., 2013)
Micrococcus sp.	Thermoplastic polyester PU	(Shah et al., 2008a)
	Thermoplastic poly(ether urea) PU	(Rafiemanzelat et al., 2013)
Pseudomonas sp.	Polyester PU foam	(Spontón et al., 2013)
	Thermoplastic polyester PU	(Shah et al., 2008a)
Pseudomonas aeruginosa	Thermoset poly(amido amine) PU	(Gogoi and Karak, 2015)
	Thermoset polyester PU	(Duarah et al., 2016)
	Polyester PU coating (Impranil)	(Mukherjee et al., 2011)
	Thermoset poly(ester amide) PU	(Gogoi and Karak, 2017)
	Polyester PU foam	(Cooney, 1969; Edmonds and Cooney, 1968)
Pseudomonas aeruginosa ATCC 13388	Polyester PU foam	(Kay et al., 1991)
Pseudomonas aeruginosa ATCC 9027	Thermoplastic polyester PU	(Fernandes et al., 2016)
Pseudomonas aeruginosa MTCC 7814	Thermoset polyester PU	(Bayan and Karak, 2017; Gogoi and Karak, 2014)
Pseudomonas aeruginosa MZA-85	Thermoplastic polyester PU	(Shah et al., 2016; Shah et al., 2013a)
Pseudomonas aeruginosa NAV-6	Polyester PU coating	(El-Sayed et al., 1996)
Pseudomonas cepacia	Polyester PU coating	(El-Sayed et al., 1996)
Pseudomonas chlororaphis ATCC 55729	Polyester PU foam	(Gautam et al., 2007c)
Pseudomonas fluorescens	Polyether PU coating	(Crookes-Goodson et al., 2013)
	Polyester PU coating (Impranil)	(Howard and Blake, 1998; Vega et al., 1999)
Pseudomonas protegens Pf-5	Polyester PU coating (Impranil)	(Biffinger et al., 2014)
	Thermoplastic polyether PU	(Barlow et al., 2016)
Pseudomonas putida	Polyester PU coating (Impranil)	(Peng et al., 2014)
Pseudomonas putida ATCC 17484	Polyester PU coating	(El-Sayed et al., 1996)

Rhodococcus equi strain TB-60	Model urethane molecule (toluene-2,4-dicarbamic acid dibutyl ester)	(Akutsu-Shigeno et al., 2006)
Staphylococcus aureus	Poly(ether urea) PU	(Rafiemanzelat et al., 2013)
	Undefined PU	(Curia et al., 2014)
Staphylococcus epidermidis strain KH 11	Thermoplastic polyether PU	(Jansen et al., 1991)

Fungi

It is possible to appraise only the fungal activity of a consortium or isolate only fungal strain by adding antibacterial molecules which prevent bacterial growth. For instance, 50 µg/mL of chloramphenicol can be added to the medium to prevent bacterial growth and therefore perform analysis only on fungal strains (Zafar et al., 2013). Microorganisms from the fungi kingdom described as PU degrading entities are almost only filamentous fungi. Strains belonging to the genus of *Alternaria* (Magnin et al., 2018; Matsumiya et al., 2010; Oprea et al., 2018), *Aspergillus* (Khan et al., 2017; Magnin et al., 2018; Mathur and Prasad, 2012; Osman et al., 2018) and *Cladosporium* (Álvarez-Barragán et al., 2016) are frequently isolated for PU degradation (Table 5). Only one study on yeast was found, describing the growth of *Cryptococcus sp.* MTCC 5455 on fish waste to produce a lipase with activity on PU (Thirunavukarasu et al., 2015). Five strains are recommended by the American Society for Testing and Materials (ASTM) to evaluate the fungal resistance of a material: *Aspergillus niger* ATCC 9642, *Aureobasidium pullulans* ATCC15233, *Chaetomium globosum* ATCC6205, *Gliocladium virens* ATCC9645, *Penicillum pinophilum* ATCC11797 (ASTM code: G21 - 90 Standard Practice for Determining Resistance of Synthetic Polymetric Materials to Fungi) (Gu and Gu, 2005). Oprea et al. who developed new bio-based materials and tested their fungal degradation susceptibility with the strain of *Chaetomium globosum* (Oprea, 2010; Oprea and Doroftei, 2011; Oprea et al., 2016). Only a few studies are based on this norm and mentioned these strains. However, using such reference fungal strains would allow better reproducibility and comparison of results in-between studies.

A review on the biodegradation of fossil-based polymers interestingly shows the significant importance of the abiotic effect of fungal biodegradation (Lucas et al., 2008). The formation of filaments exerts physical pressure leading to polymer breaking. Filament apices penetrate in the material increasing the size of pores and provoking cracks. For instance, rifts under the form of a fungal filament network were observed by microscopy on the surface of a TPU incubated two months with a strain of *Penicillium brasilianum* (Magnin et al., 2018). Fungal degradation has been demonstrated on both polyester- and polyether-based PU, on TPU, foams and coatings. However, mechanisms of degradation have not been fully elucidated. The importance of each biotic and abiotic steps in fungal degradation still needs to be clarified.

363 *Table 5 – PU-degrading fungi and associated PU substrates*

Species and/or strain	PU substrates	Reference
Alternaria sp.	Thermoplastic polyester PU	(Magnin et al., 2018)
Alternaria Solani Number Ss.1-3	Thermoplastic polyester PU	(Ibrahim N. Ibrahim, 2009)
Alternaria sp. strain PURDK2	Polyether PU foam	(Matsumiya et al., 2010)
Alternaria tenuissima	Thermoplastic polyether PU	(Oprea et al., 2018)
Aspergillus sp.	Polyester PU foam	(Cangemi et al., 2006; Cangemi et al., 2008)
Aspergillus flavus	Thermoplastic polyester PU	(Mathur and Prasad, 2012)
Aspergillus fumigatus	Polyester PU coating (Impranil)	(Álvarez-Barragán et al., 2016)
	Polyether PU foam	(Álvarez-Barragán et al., 2016)
	Thermoplastic polyester PU	(Osman et al., 2018)
Aspergillus niger	Polyether PU foam	(Filip, 1979)
Aspergillus niger ATCC 9642	Thermoplastic polyester PU	(Kanavel et al., 1966)
Aspergillus section flavi	Thermoplastic polyester PU	(Magnin et al., 2018)
Aspergillus tubingensis	Thermoplastic polyester PU	(Khan et al., 2017)
Aureobasidium pullulans	Polyester PU coating (Impranil)	(Crabbe et al., 1994)
Chaetomium globosum	Thermoset polyester PU	(Oprea and Doroftei, 2011)
	Thermoplastic polyester PU	(Oprea et al., 2016)
Cladosporium sp.	Polyester PU coating (Impranil)	(Crabbe et al., 1994)
	Polyether PU foam	(Cooney, 1969; Edmonds and Cooney, 1968)
Cladosporium tenuissimum	Polyester PU coating (Impranil)	(Álvarez-Barragán et al., 2016)
	Polyether PU foam	(Álvarez-Barragán et al., 2016)
Cladosporium asperulatum	Polyester PU coating (Impranil)	(Álvarez-Barragán et al., 2016)
	Polyether PU foam	(Álvarez-Barragán et al., 2016)
Cladosporium herbarum	Polyether PU foam	(Filip, 1979)
Cladosporium montecillanum	Polyester PU coating (Impranil)	(Álvarez-Barragán et al., 2016)
	Polyether PU foam	(Álvarez-Barragán et al., 2016)
Cladosporium pseudocladosporioides	Polyester PU coating (Impranil)	(Álvarez-Barragán et al., 2016)
	Polyether PU foam	(Álvarez-Barragán et al., 2016)
Cryptococcus laurentii	Polyester PU coating (Impranil)	(Zicht, 2017)
Curvularia senegalensis	Polyester PU coating (Impranil)	(Crabbe et al., 1994)
Exophiala jeanselmei	Model urethane molecule (N-tolylcarbamate)	(Owen et al., 1996)
Fusarium solani	Polyester PU coating (Impranil)	(Crabbe et al., 1994)
Gliocladium roseum	Thermoplastic polyester PU	(Shuttleworth and Seal, 1986)
Penicillium chrysogenum	Polyester PU coating (Impranil)	(Álvarez-Barragán et al., 2016)
	Polyether PU foam	(Álvarez-Barragán et al., 2016)
Penicillium section lanata-divaricata	Thermoplastic polyester PU	(Magnin et al., 2018)
Pestalotiopsis microspora	Polyester PU coating (Impranil)	(Russell et al., 2011)

364

4.2. Enzymes

Enzymes are biological catalysts (biocatalysts). Enzymes identified as PU degrading entities originate from microorganisms but also mammalian cells such as lipase porcine pancreas (Ng et al., 2017) or from plants such as papain from *Carica papaya* (Ferris et al., 2010). Enzymes used for PU degradation assays are either commercial enzymes or enzymes over-expressed in heterologous microorganisms. In this latter case, they correspond to enzymes identified in PU-degrading microorganisms for which the encoding genes were cloned into model organism. Enzymes are then over-expressed and even purified in some cases. Enzymes are mainly described for the depolymerization of TPU or coatings (Table 6 – PU-degrading enzymes and associated PU substrates). As far as we know, only one publication has addressed the enzymatic degradation of foams (Ng et al., 2017) all other studies involved degradation by microorganisms. A set of different poly(ester ether) PU foam containing PCL, PEG and polyester from palm oil was studied by enzymatic degradation. A maximal weight loss of 70% was measured after 28 days of incubation with lipase from porcine pancreas for a polymer with 7.7% of PCL, 34.8% of PEG and 7.5% of polyester from palm oil.

Table 6 – PU-degrading enzymes and associated PU substrates

EC number	Enzyme name in the publication	Type of PU	Reference
EC 1.10.3.2	Laccase	Thermoplastic polyester PU	(Ignat et al., 2011)
EC 1.11.1.7	Fungal peroxidase	Thermoplastic polyester PU	(Ignat et al., 2011)
EC 3	Tcur0390 (*Thermomonospora curvata* DSM43183 hydrolase)	Thermoplastic polyester PU	(Schmidt, J. et al., 2017)
	Tcur1278 (*Thermomonospora curvata* DSM43183 hydrolase)	Thermoplastic polyester PU	(Schmidt, J. et al., 2017)
EC 3.1	*Bacillus subtilis* esterase	Polyester PU (Impranil)	(Rowe and Howard, 2002)
	Comamonas acidovorans TB-35 esterase	Polyester PU (Impranil)	(Allen et al., 1999)
	Curvularia senegalensis esterase	Polyester PU (Impranil)	(Crabbe et al., 1994)
	E3576 (esterase)	Polyester PU Impranil	(Magnin et al., 2019)
		Thermoplastic polyester PU	(Magnin et al., 2019)
	Pseudomonas fluorescens esterase	Polyester PU (Impranil)	(Biffinger et al., 2015)
	PudA (*Comamonas acidovorans* TB-35 esterase)	Thermoplastic polyester PU	(Akutsu et al., 1998; Nomura et al., 1998)
	PulA (*Pseudomonas fluorescens* esterase)	Polyester PU (Impranil)	(Ruiz and Howard, 1999)
EC 3.1.1	*Cryptococcus sp.* MTCC 5455 lipase	Thermoplastic polyester PU	(Thirunavukarasu et al., 2015)
	Lipase	Thermoplastic poly(ester ether) PU	(Feng et al., 2017)
	Lipase AK	Thermoplastic polyester PU	(Zhou et al., 2012)
		Thermoset poly(ester ether) PU	(Jiang et al., 2007)
	Lipase PS	Thermoplastic polycarbonate PU	(Chen et al., 2016)
		Thermoplastic polyester PU	(Xu et al., 2014)
	Lipolase 100L	Polyester PU coating	(Pilch-Pitera, 2012)
	Novozym 51,032	Polyester PU coating	(Pilch-Pitera, 2012)

	Novozym 735	Polyester PU coating	(Pilch-Pitera, 2012)
	Palatase 20,000	Polyester PU coating	(Pilch-Pitera, 2012)
	Pseudomonas cepacia lipase	Thermoplastic poly(ester ether) PU	(Zhou and Xie, 2017)
		Thermoset polyester PU	(Schöne et al., 2016)
	Pseudomonas sp. lipase	Polyester PU (Impranil)	(Biffinger et al., 2015)
		Thermoplastic polyester PU	(Daemi et al., 2016)
	PueA (*Ps chlororaphis* lipase)	Polyester PU (Impranil)	(Howard et al., 2007; Hung et al., 2016; Langlois and Howard, 2002; Ruiz et al., 1999; Stern and Howard, 2000)
	PueB (*Pseudomonas chlororaphis* lipase)	Polyester PU (Impranil)	(Howard et al., 2007; Howard et al., 2001; Hung et al., 2016; Ruiz et al., 1999)
	Rhizopus arrhizus lipase	Thermoplastic polyester PU	Tokiwa (Tokiwa et al., 1988)
	Rhizopus delemar lipase	Thermoplastic polyester PU	Tokiwa (Tokiwa et al., 1988)
	Thermomyces lanuginosus lipase	Thermoplastic poly(ester urea) PU	(Fang et al., 2014)
		Thermoset polyester PU	(Wu et al., 2016)
EC 3.1.1.1	Esterase	Thermoplastic polyether PU	(Smith et al., 1987)
	Porcine liver esterase	Thermoplastic polyester PU	(Li and Yang, 2006)
EC 3.1.1.3	*Candida antarctica* lipase	Thermoplastic polyester PU	(Takamoto et al., 2001)
		Polyester PU coating	(Liu et al., 2016)
	Candida cylindracea lipase	Thermoplastic polyester PU	(Kim and Kim, 1998)
	Candida rugosa lipase	Thermoplastic polyester PU	(Li et al., 2015)
		Polyester PU (Impranil)	(Gautam et al., 2007b)
	Porcine pancreas lipase	Polyester PU foam	(Ng et al., 2017)
		Thermoplastic poly(ester ether) PU	(Brzeska et al., 2015)
		Thermoplastic polyester PU	(Brzeska et al., 2015)
		Thermoplastic polyether PU	(Ferris et al., 2010)
EC 3.1.1.13	Cholesterol esterase	Thermoplastic poly(ester urea) PU	(Santerre et al., 1993; Santerre et al., 1994; Wang et al., 1997a)
		Thermoplastic poly(ether urea) PU	(Santerre et al., 1994)
		Thermoplastic polycarbonate PU	(Christenson et al., 2006; Tang et al., 2001a, b; Tang et al., 2003)
		Thermoplastic polyester PU	(Woo et al., 2000)
		Thermoplastic polyether PU	(Christenson et al., 2006)
EC 3.1.1.74	LC cutinase (LCC)	Thermoplastic polyester PU	(Schmidt, J. et al., 2017)
	TfCut 2 (*Thermobifida fusca* KW3 cutinase)	Thermoplastic polyester PU	(Schmidt, J. et al., 2017)
		Thermoset polyester PU	(Wu et al., 2016)
EC 3.4	*Bacillus sp.* Protease	Polyester PU (Impranil)	(Biffinger et al., 2015)
EC 3.4.11.1	Leucine aminopeptidase	Thermoplastic polyester PU	(Ratner et al., 1988)
		Thermoplastic polyether PU	(Ratner et al., 1988)
EC 3.4.14.1	Cathepsin C	Thermoplastic polyether PU	(Smith et al., 1987)
EC 3.4.21.1	Chymotrypsin	Thermoplastic poly(ester ether) PU	(Ciardelli et al., 2004)
		Thermoplastic poly(ester urea) PU	(Elliott et al., 2002)

		Thermoplastic polyester PU	(Ratner et al., 1988; Yamamoto et al., 2007)
		Thermoplastic polyether PU	(Campinez et al., 2013; Ferris et al., 2010; Ratner et al., 1988; Smith et al., 1987)
EC 3.4.21.36	Porcine pancreatic elastase	Thermoplastic poly(ester urea) PU	(Guan et al., 2008; Labow et al., 1996)
		Thermoplastic poly(ether urea) PU	(Labow et al., 1996)
EC 3.4.21.62	Subtilisin	Thermoplastic polyamide PU	(Huang et al., 2016)
EC 3.4.21.64	Protease K	Thermoplastic polyester PU	(Dogan et al., 2017; Yamamoto et al., 2007)
EC 3.4.22.2	Papain	Thermoplastic poly(ether urea) PU	(Zhao et al., 1987)
		Thermoplastic polyester PU	(Ratner et al., 1988; Yamamoto et al., 2007)
		Thermoplastic polyether PU	(Campinez et al., 2013; Ferris et al., 2010; Phua et al., 1987; Ratner et al., 1988; Smith et al., 1987)
		poly(ether urethane urea) elastomer	(Marchant et al., 1987)
EC 3.4.22.3	Ficin	Thermoplastic polyester PU	(Yamamoto et al., 2007)
		Thermoplastic polyether PU	(Smith et al., 1987)
EC 3.4.4.24	Bromelain	Thermoplastic polyester PU	(Smith et al., 1987; Yamamoto et al., 2007)
EC 3.4.21.37	Human neutrophil elastase	Thermoplastic poly(ester urea) PU	(Labow et al., 1996)
		Thermoplastic poly(ether urea) PU	(Labow et al., 1996)
EC 3.4.24	Collagenase	Thermoplastic polyester PU	(Zhang et al., 1994)
		Thermoplastic polyether PU	(Mendoza-Novelo et al., 2013)
EC 3.5.1.4	E4143 (amidase)	Thermoplastic polyester PU	(Magnin et al., 2019)
	Nocardia farcinica polyamidase	Thermoplastic polyester PU	(Gamerith et al., 2016)
EC 3.5.1.5	Urease	Thermoplastic polyether PU	(Phua et al., 1987)
No EC number	Pancreatine (enzyme mixture)	Thermoplastic polyester PU	(Zhang et al., 1994)

Enzymatic degradation assays on PU using oxidase enzymes (Enzyme Classification 1, EC 1) e.g., fungal peroxidase (EC 1.11.1.7) and laccase (E.C. 1.10.3.2) have been performed with success on a polyester PU (Ignat et al., 2011). All the other assays dealing with enzymatic degradation of PU relies on hydrolytic enzymes (EC 3). Several hydrolytic mechanisms have indeed been highlighted for PU degradation. The most common is the hydrolysis of the polyester moieties of polyester-based PU by esterases (EC 3.1). Ester hydrolysis leads to the release of a carboxylic acid and an alcohol (Figure 7a). Other esterases such as lipases (EC 3.1.1) (Fang et al., 2014; Schöne et al., 2016), cutinases (EC 3.1.1.74) (Schmidt, J. et al., 2017; Yang et al., 2013) or unspecific esterases (EC 3.1) (Kang et al., 2011) have been described as polyester PU degrading enzymes. Esterase has also been described as hydrolyzing the urethane linkage. Some of these studies refer to a mechanism resulting in carbamic acid and alcohol chain-ends after hydrolysis (Mahajan and Gupta, 2015; Wei and Zimmermann, 2017). However, this mechanism does not seem conceivable because of the instability of the carbamic acid which immediately breaks down into an amine with the release of a molecule of carbon dioxide (Ionescu, 2005; Ozaki, 1972) (Figure 7b). Moreover, most of the assays involving esterases concern polyester-based PU and do not allow

differentiation between ester and urethane bond hydrolysis. To evaluate the urethane bond hydrolysis by an esterase, assays must be performed on substrates that do not contain ester bonds. Publications describing slight esterase activity on polyether PU and showing the potential ability of esterase to hydrolyze the urethane bond are scarce (Santerre et al., 1994; Smith et al., 1987). A cholesterol lipase was reported to display activity on a PU based on triethylene glycol and 1,4-di-S-benzyl-D,L-dithiothreitol (Ferris et al., 2010). Urease (EC 3.5.1.5) also showed activity on poly(ether urea) PU (Phua et al., 1987) but the degradation is mainly attributed to the urea bond hydrolysis (Figure 7c). Amidases (EC 3.5.1.4) and proteases hydrolyze amide or peptidic bonds leading to the release of a carboxylic acid and an amine (Figure 7d). These enzymes appeared to be also efficient for the hydrolysis of the urethane bond leading to the release of an amine, an alcohol and a carbon dioxide molecule (Figure 7e). Proteases such as papain (EC 3.4.22.2) (Campinez et al., 2013; Ferris et al., 2010; Marchant et al., 1987; Yamamoto et al., 2007), bromelain (EC 3.4.22.32/33) (Yamamoto et al., 2007), ficain (EC 3.4.22.3) (Yamamoto et al., 2007) and chymotrypsin EC 3.4.21.1 (Ciardelli et al., 2004; Elliott et al., 2002; Ferris et al., 2010) are also described for the degradation of PU. Recently, an amidase drew attention. This enzyme was isolated from *Nocardia farcinica* with the specificity of being able to hydrolyze polyamides (Guo et al., 2014) but also both the ester and amide bonds of non-water soluble model substrates (Heumann et al., 2009) and polyester-based PUs (Gamerith et al., 2016). Even if esterase is the main class of enzyme describes for PU degradation, others such as amidase or oxidase are rising interest for the full degradation of PU material.

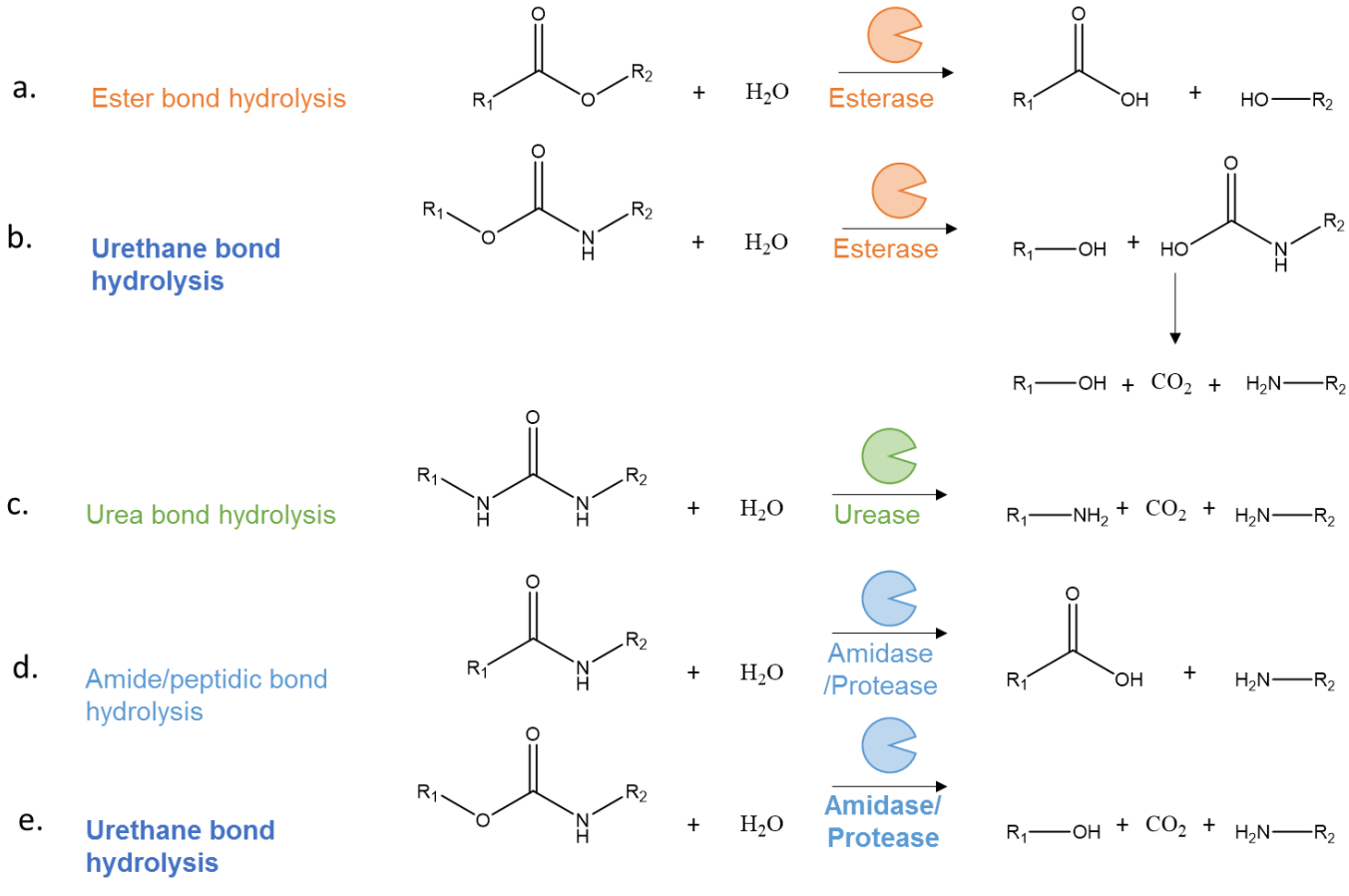


Figure 7 – Main mechanisms of enzymatic degradation of PU

An alternative strategy aiming at discovering efficient PU-degrading enzymes was recently published. Metagenomics tools allowing to screen bovine rumen microbiota were developed to select enzymes with activity towards carbamate insecticides and PUs (Ufarte et al., 2017). The main advantage of this strategy is the possibility of studying enzymes from uncultivable microorganisms that are predominant in microbial communities, and thus having potential access to new degrading enzymes.

To date, PU depolymerization using enzymes is not efficient enough for the development of recycling processes. Recent publications on this topic aimed to improve the efficiency of the depolymerization reactions. Complementary activities of enzymes presented above justify testing cocktail of enzymes with different activities. A mixture of an esterase and an amidase revealed a synergistic effect between these two enzymes for the degradation of a polyester PU. Corresponding product analysis showed that hydrolysis of ester moieties from the SS by the esterase released low molar mass molecules containing urethane bonds that are then hydrolyzed by the amidase (Magnin et al., 2019). Another strategy for enzymatic depolymerization improvement is to use protein engineering. This approach already proved itself on PET-degrading enzymes. As an example, decreased inhibitor sensitivity of a PET-degrading cutinase has been successfully achieved by amino-acid modification into the catalytic site (Wei et al., 2016). Thermostability is also a key parameter for polymer degradation (Kawai et al., 2014). Ribitsch et al., fused a PET-degrading enzyme (a cutinase from *Thermomyces cellullosylitica*) with a binding module of a PHA depolymerase from *Alcaligenes faecalis* (Ribitsch et al., 2013) to improve enzyme/polymer interactions. This binding domain was recently added to the amidase from *Nocardia farcinica* to improve the degradation of polyester PU pellets (Gamerith et al., 2016). These improvements will help reaching efficient depolymerization processes for PU biorecycling.

5. Analytical solutions for the measurement of polyurethane biodegradation

The great diversity of PU structures and biological entities gives rise to numerous analytical approaches to evaluate PU biological degradation. The methods have evolved lately with powerful tools for a better understanding of the mechanisms of PU biodegradation. This chapter offers an overview of the different techniques. The implementation of tools using urethane-based model molecules is first addressed. Then, the degradation of more complex substrates, such as TPU and PU foams, is presented.

5.1. Biological degradation of urethane-based model molecules

For the development of bioremediation or biological recycling processes, degradation of model molecules is generally the first step as it allows easy identification of efficient degrading entities. Urethane-based model molecules are readily hydrolysable and generally propose a simplified hydrolysis detection. These model molecules can be either low molar mass molecules or hydrophilic PU dispersion.

5.1.1. Analysis of low molar mass molecules

To cover the degradation of different PU structures, tracking the urethane bond hydrolysis appears as a relevant solution. Low molar mass molecules containing a single urethane linkage can be designed for this purpose. Urethane-based molecules are not soluble in water. Pre-dilution in organic solvents such as ethanol (Akutsu-Shigeno et al., 2006) or DMSO (Gamerith et al., 2016) is thus required.

Low molar mass N-tolylcarbamate molecules correspond to toluene with urethane linkage on one or two carbons of the aromatic ring bound to ethanol moieties (Owen et al., 1996). In Owen et al., aromatic amines resulting from the N-tolylcarbamate hydrolysis were extracted in chloroform and quantified by Gas Chromatography coupled with Mass Spectrometry (GC/MS). This assay revealed that the degrading activity of the *Exophiala jeanselmei* strain REN-11A depends on the position of the urethane(s) around the aromatic ring. Toluene-2,4- and -2,6-dicarbamic acid diethyl ester were the most readily biodegradable molecules (Figure 8).

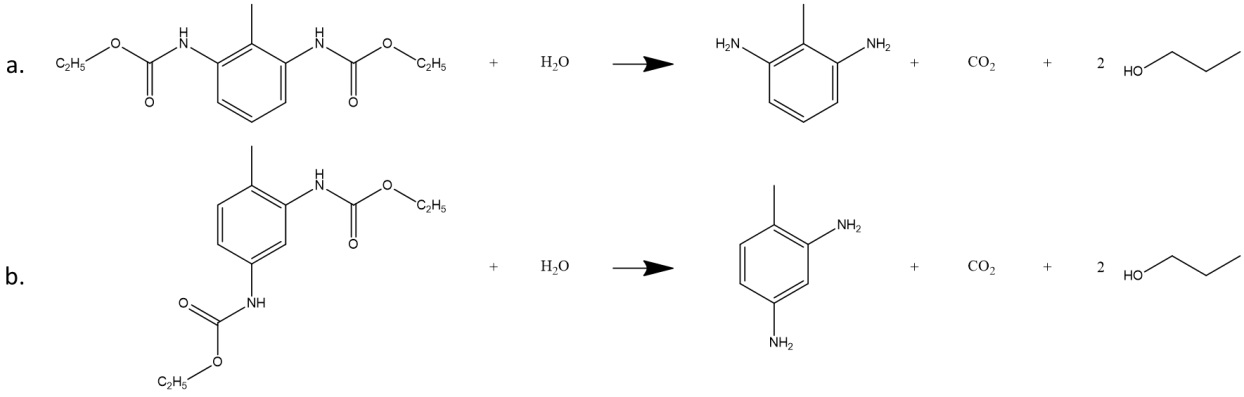


Figure 8 – Hydrolysis of (a) the toluene-2,6-dicarbamic acid diethyl ester into 2,6-toluene diamine and propanol and (b) the toluene-2,4-dicarbamic acid diethyl ester into 2,4-toluene diamine and propanol

Akutsu-Shigeno et al., also described a set of molecules bearing a single urethane bond formed by reacting a di-isocyanate (2,4-TDI, 4,4'-MDI and HDI) with butanol (Akutsu-Shigeno et al., 2006). These compounds were degraded by both *Rhodococcus equi* strain TB-60 and a purified urethane-degrading enzyme secreted by this bacterium. Degradation products were extracted with ethyl acetate and analyzed by GC/MS except for the HDI-based model molecules which degradation products were extracted with toluene under alkaline conditions. Because of the difficulties to detect aliphatic amines in GC/MS, amines coming from HDI-based molecules hydrolysis were derivatized using heptafluorobutyric acid anhydride following the method of Skarping et al. (Skarping et al., 1988).

Coupling a 96-wells microplate assay with HPLC analysis was proposed for the development of a medium-throughput screening (Magnin et al., 2019). A model molecule based on p-Toluenesulfonyl isocyanate was synthesized for this microplate assay (Figure 9). Both the substrate and the degradation products were analyzed by HPLC. Finally, 55 enzymes were screened resulting in the identification of two amidases able to hydrolyze the urethane bond.

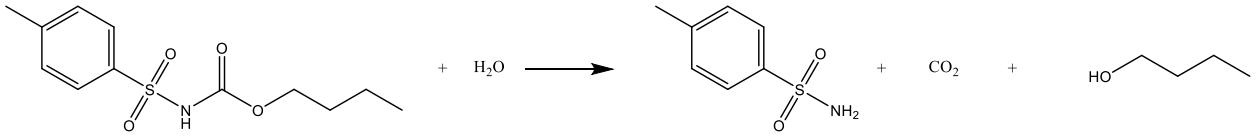


Figure 9 – Hydrolysis of p-Toluenesulfonyl isocyanate model substrate (Magnin et al., 2019)

To avoid the setup of complex analytical procedures such as GC/MS, Gamerith et al., proposed the synthesis of a model molecule based on 4-nitrophenol (Gamerith et al., 2016). Molecules based on this aromatic compound are well known as model substrates for enzymes such as esterase (4-nitrophenyl acetate) or amidase (4-nitroacetanilide). 1-methoxypropan-2-yl (4-nitrophenyl) carbamate was synthesized (Figure 10) and the subsequent hydrolysis leads to the release of 4-nitroaniline that can be tracked and quantified by UV-vis absorbance measurements at 405 nm.

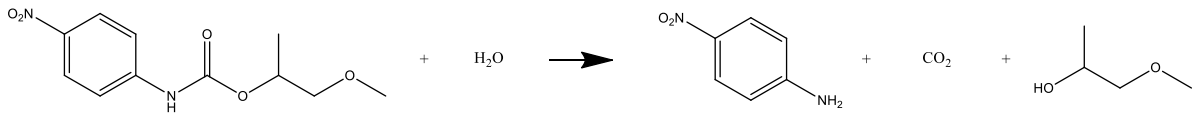


Figure 10 - Hydrolysis of the 1-methoxypropan-2-yl (4-nitrophenyl) carbamate leading to 4-nitroaniline and 1-methoxy-2-propanol (Gamerith et al., 2016)

The use of low molar mass urethane substrates is a good way to identify efficient degrading entities. However, the low steric hindrance of these molecules makes them far from being representative of actual PU materials which often present organized and crystalline structures and are much more hydrophobic. Activity assays on real and complex polymers must then be performed with the identified degrading entities.

5.1.2. Waterborne polyurethane dispersions as a PU-based model

WPUD are particularly suitable to assess the degradation ability of enzymes and microorganisms thanks to the polymer particles nanometric size and homogeneity in water. Indeed, their specific surface is higher than for previously described polymers, thus maximizing interactions between the degrading entity and the polymer. Moreover, all biodegradation reactions occur in aqueous media. The most famous WPUD is the Impranil-DLN®, commercialized by Covestro (Germany) for textile coating applications. Particle size is estimated to range between 0.1 to 0.2 µm (Biffinger et al., 2015). This dispersion appears as a white, milky suspension containing 40% of polymer. The exact composition and structure of Impranil-DLN® are not precisely known. A tentative structure has been proposed by Biffinger et al. based on polyhexane/neopentyl adipate polyester and HDI (Figure 11). Diethylene glycol is also a component of Impranil-DLN® (Gautam et al., 2007b).

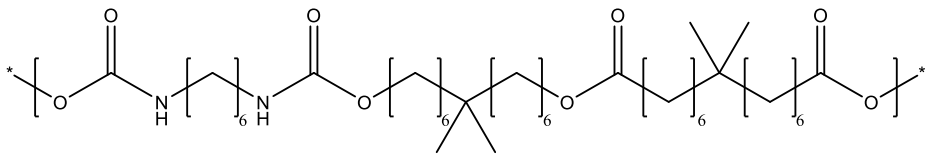


Figure 11 – Impranil-DLN® tentative structure adapted from Biffinger et al., 2015 (Biffinger et al., 2015)

Impranil-DLN® has been widely studied as a PU-based model since it presents the particularity to become translucent when hydrolyzed as a result of water-soluble molecules being released in the medium. Impranil-DLN® was used as "polyurethane biodegradation benchmark" for the first time in 1994 (Crabbe et al., 1994). Screening of soil fungi was performed on a plate where Impranil-DLN® was mixed with an agar medium. Fungi were allowed to grow on it and a transparent halo appeared after a few days when the microorganism was producing degrading enzymes. This agar plate technique has subsequently been used intensively (Howard et al., 2001; Peng et al., 2014; Rowe and Howard, 2002; Vega et al., 1999) (Figure 12a & b). Impranil-DLN® is also suitable for assays in liquid media for both microorganisms (Álvarez-Barragán et al., 2016; Russell et al., 2011) (Figure 12c) and enzymes (Gautam et al., 2007b; Schmidt, J. et al., 2017).

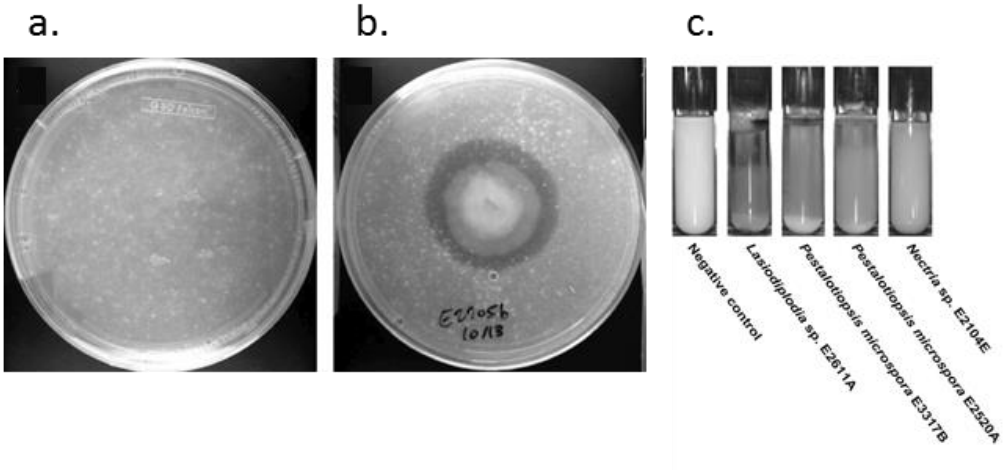


Figure 12 – Hydrolysis of Impranil-DLN®. Degradation assay in agar plate (a) negative control and (b) Pleosporales sp. strain E2705B after two weeks of incubation. (c) Assay in liquid media. Adapted from Russel et al. (Russell et al., 2011)

As the exact polymer structure is unknown, it is difficult to appraise the mechanism of degradation. Biffinger et al., used NMR and FT-IR to offer quantitative analysis of alcohol and carboxylic acid release after the ester bond cleavage (Biffinger et al., 2015). They also highlighted that polymer aggregation can occur when incubated with enzymes without any measurable degradation. Observation of the polymer is thus not sufficient to conclude on enzymatic degradation activity. Ufarté et al., proposed to use Matrix Assisted Laser Desorption Ionisation - Time of Flight/Mass Spectrometry (MALDI-TOF/MS) to identify degradation by-products. Three peaks at m/z 682, 683 and 782 were specific of the bacterial degradation of Impranil-DLN®. All

seemed to correspond to the formula $C_{36}H_{68}O_8N_2$, ionized with either Na^+ or I^-. The peak at m/z 683 could correspond to the isotope form of the molecule at m/z 682. However, no specific chemical structure has been suggested. Alvarez-Barragan et al., presented the analysis of degradation by-products by GC/MS (Álvarez-Barragán et al., 2016). Almost none of the products identified correspond to the Impranil putative structure shown above (Figure 11) suggesting that the structure is much more complex than expected. The only corresponding molecule is HDI. However, HDI cannot be a degradation product as isocyanates are not stable in water. A possible explanation would be the detection of either hexane diamine (HDA) or HDI-derivatives.

Despite some important limitations, Impranil-DLN® is thus a good model substrate to identify degrading entities that have a great chance to be efficient afterwards on polyester PUs. It provides a first approach that must then be confirmed. Hung et al. (2016) did not only present Impranil-DLN® as a model but also as a common coating which integrity can be affected by microbial degradation (Hung et al., 2016). Esterase and lipase are mainly involved in the enzymatic degradation of Impranil-DLN®. However, up to now, there is no clear evidence that these enzymes, improperly called "Polyurethanase" (Ruiz et al., 1999; Stern and Howard, 2000), effectively hydrolyze the urethane bond.

Few other WPUDs have been tested for degradation activities. Bayhydrol 110 (Covestro, Germany) is a polyester PU dispersion presenting the same clarification properties as Impranil-DLN®: translucent halo appeared when incubated with a strain of *Pseudomonas chlorographis* on an agar plate containing this WPUD (Howard et al., 2001). Poly Lack (Sayer Lack Mexicana, Mexico), a polyether PU, was also tested on agar plate containing the polymer and minimal media (Álvarez-Barragán et al., 2016). Strains able to grow on Poly Lack as sole carbon source were isolated, yet, no clarification zone could have been observed on this polymer.

5.2. Biological degradation of TPU and PU foams

The most mainstream PU systems, i.e. TPU and PU foams, have been tested in biodegradation assays. These products present a wide and varied range of chemical structures and groups. When the purpose is to evaluate the susceptibility to biological degradation of a material, the structure and formulation are precisely described in the study. In contrast, bioremediation and biological recycling studies on PU mainly involve commercial products of complex and often unknown chemical structure, additives and composition. The biological degradation experiments described in the literature are mainly partial, leading to the recovery of the degraded polymer and, possibly, soluble degradation products released in the aqueous media (Figure 13). Techniques developed to evaluate the biological degradation of polymers can thus be oriented towards the efficiency of the entire degradation system with the analysis of the degraded polymer products (soluble and insoluble).

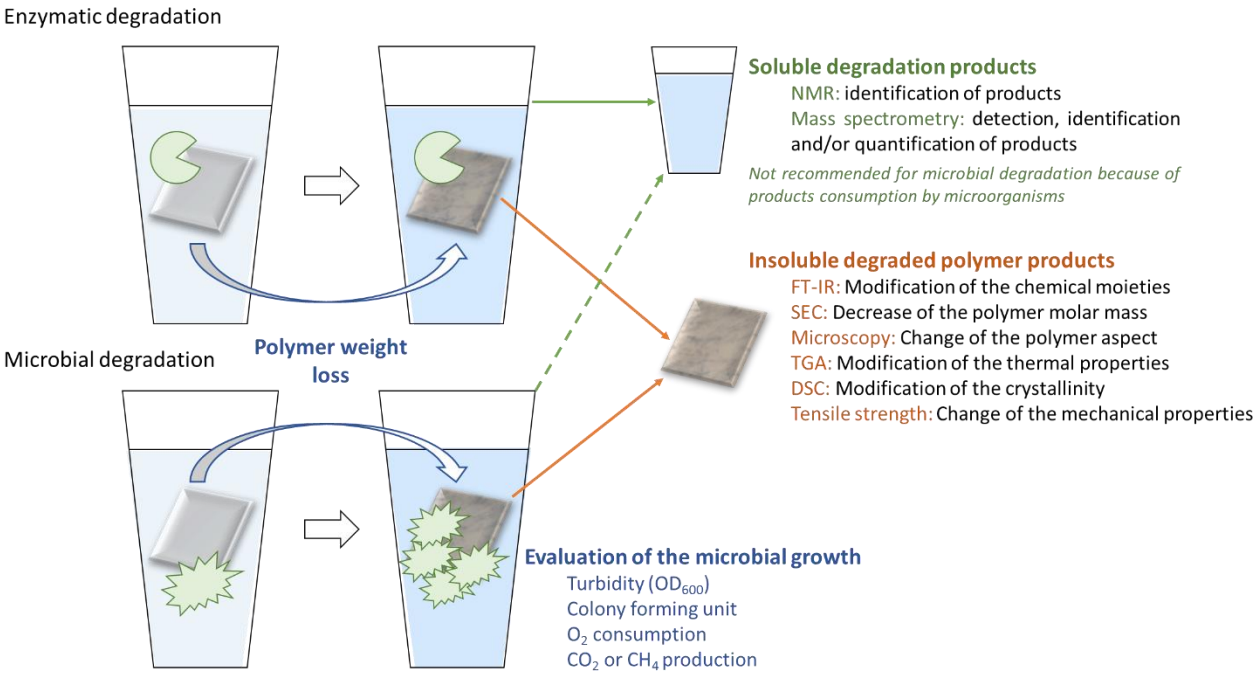


Figure 13 – Strategies and diversity of the analytical methods for TPU and PU foam biodegradation monitoring

Samples structures and preparation

Evaluation of PU foam degradation is more challenging than that of TPU, since foams are highly complex systems based on crosslinked architectures with different components and additives. Side reactions during synthesis and foaming steps can also lead to the formation of isocyanurate and other bonds. Foam analysis is limited by their insolubility in solvent.

PUs shape drives the specific surface and thus the bioavailability which is of importance for the biological degradation. Thanks to their alveolar structure, bioavailability is greater for foams, especially for open-cell foams, as microorganisms can easily circulate inside the material. Foams can also be ground to increase bioavailability (Cregut et al., 2014). TPUs for degradation assays can be used as thin films obtained by coating after solubilizing in an appropriate solvent, pouring on glassware and solvent evaporation (Chen et al., 2016; Woo et al., 2000). Thin films obtained can reach a few dozen micrometers (Phua et al., 1987). TPU films can also be obtained by thermoforming (Zhou and Xie, 2017). TPU cubes (Nakajima-Kambe et al., 1995), pellets (Cosgrove et al., 2007) or sheets (Ibrahim N. Ibrahim, 2009) are also used for PU degradation assays.

Preparation of samples

It is not recommended to sterilize TPUs by autoclaving for microbial experiments as most of the TPU becomes liquid-like or very soft at autoclaving temperatures (121°C). Degradation can occur e.g., a study comparing autoclaved and non-autoclaved poly(ether urea) PU material revealed that no weight loss was observed after autoclaving but a surface alteration appeared, leading to bias in degradation measurement (Rafiemanzelat et al., 2015). Alternatives such as rinsing with ethanol (Cosgrove et al., 2010; Mathur and Prasad, 2012), UV exposure (Gogoi and Karak, 2014)

or both (Osman et al., 2018) are thus frequently employed to sterilize the samples. Because of better thermal resistance of thermosetting materials, foams can be tested after autoclaving (Álvarez-Barragán et al., 2016).

5.2.1. Evaluation of the global biodegradation efficiency

The most widespread method to evaluate global biodegradation is the weight loss of the PU. Samples are weighted before and after degradation assay to evaluate the weight of degradation products released in the liquid media. It is a straightforward and easy method to implement, although some bias can be noticed. For instance, if the degradation is too superficial and too low to lead to detectable product release, the test will be considered as inefficient as no weight loss will be measured. Therefore, weight loss measurement must be associated with a surface analysis of the sample (Rafiemanzelat et al., 2015) in case of a low degradation extent, or to analyze the early steps of the degradation. It is necessary to remove all the biological materials that can remain on the polymer surface. Hard washing with ethanol is generally performed (Mathur and Prasad, 2012; Urgun-Demirtas et al., 2007). Non-ionic surfactants such as TritonX-100 (Polyethylene glycol tert-octylphenyl ether) (1% v/v) have also been suggested to remove reversibly bounded enzymes and cells (Ciardelli et al., 2004). This cleaning step is particularly challenging for the fungal degradation of foams as filaments could be deeply trapped into the bulk structure of the samples. It was recently suggested to use 0.88% (wt/vol) sodium hypochlorite for 18 h to destroy and remove the remaining mycelium (Álvarez-Barragán et al., 2016). When enzymatic degradations are performed, kinetic weight loss is generally set up (Dogan et al., 2017; Zhou and Xie, 2017). In such experiments, a loss of enzymatic activity is often observed with time. This loss of activity may be due to the thermal denaturation of enzymes (Pastorino et al., 2004) or to the release of inhibiting compounds (Barth et al., 2015). To cope with this phenomenon, enzymatic solutions are frequently renewed at regular time intervals (Phua et al., 1987). Between the removal step and the renewal step, polymer pieces are usually washed, dried and weighed.

As a parameter of global assay efficiency, the evaluation of the ability of a microorganism to grow on PUs when the polymer is used as the sole source of carbon (or carbon and nitrogen) is common practice (Cooney, 1969). Indeed, microbial development means that microorganisms can depolymerize PUs and metabolize degradation products for growth. It is possible to quantitatively follow the bacterial growth through the McFarland method which estimates the number of bacteria thanks to turbidity measurement using UV-vis at 600 nm (Bayan and Karak, 2017; Fernandes et al., 2016; Gogoi and Karak, 2014). Colony forming unit (CFU) is another method to count bacteria: after being incubated with polymers, bacteria are sampled, diluted and poured on an agar plate containing a rich medium (Crookes-Goodson et al., 2013; Urgun-Demirtas et al., 2007). Colonies are counted after overnight incubation. The dry or wet weight of the biomass corresponding to microorganisms growth can be measured (Oceguera-Cervantes et al., 2007). This technique could be particularly suitable for bacteria that form aggregates or for filamentous fungi.

Mineralization of polymers by microorganisms in aerobic conditions leads to the production of CO_2 with O_2 consumption. Online sensors are used to measure both evolutions. These variations must be compared to a negative control made without polymers (Cregut et al., 2014) or with an

inert polymer such as low-density polyethylene (Rattanapan et al., 2016), and to a conventional biodegradable positive control such as cellulose (Gómez et al., 2014) or sodium benzoate (Rattanapan et al., 2016) incubated with the same inoculum. For instance, low O_2 consumption and CO_2 release were measured during the 28 days of degradation of a ground polyether PU foam revealing low degradation by an acclimated microbial consortium (Cregut et al., 2014). CO_2 release during PU mineralization is associated with pressure increase. The pressure can be measured by a Sturm test (Standard OECD 301 B) (Shah et al., 2016). This test is used for readily biodegradable materials and usually lasts 28 days. Rattanapan et al., used this assay to measure the biodegradation of a biobased polyester PU foam with long incubation time (60 days) (Rattanapan et al., 2016). In fact, after 30 days, 7 to 11% of degradation was measured while a higher degradation rate occurred during the last 30 days leading to a maximal degradation yield of 46 wt%. Under anaerobic digestion, CH_4 is produced proportionally to polymer consumption. Gomez et al., proposed to compare the biological degradation susceptibility of polyether PU foams under composting, soil burial and anaerobic digestion according to three ASTM standard methods based on CO_2 or CH_4 measurement (Gómez et al., 2014). These methods are ASTM D5988-03 (Standard Test Method for Determining Aerobic Biodegradation in Soil of Plastic Materials or Residual Plastic Materials After Composting) (International, 2003b), the ASTM D5338-98 (Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions) (International, 2003a) and the ASTM D5511-02 (Standard test method for determining anaerobic biodegradation of plastic materials under high-solid anaerobic-digestion conditions) (International, 2002). The most pronounced degradation was observed for a bio-based PU foam after 320 days of soil burial. Methods involving CO_2, O_2 or CH_4 measurement present a low throughput. Incubation time is superior to 28 days. Moreover, a pressure or gas monitor is required for each reaction which is generally performed in flasks from 2 to 5 liters (recommendation for OECD 301 series). These methods are mainly oriented towards the evaluation of the biological sensitivity or resistance of newly synthesized or commercial PUs, especially foams. These techniques are not suitable for screening of PU degrading entities.

5.2.2. Study of the degraded polymers samples and insoluble products

The first assessment of polymer degradation is a naked eye observation, sometimes sufficient to evaluate the degradation onset. Change in color, roughness or shape can be noticed (Pilch-Pitera, 2012). These observations can be completed by surface analysis such as spectroscopy and/or microscopy, polymer molar mass evolution by SEC or modifications of physical properties.

Spectroscopy techniques

FT-IR (Fourier-transform infrared spectroscopy) analysis relies on the fact that most molecules absorb in the infrared region. This absorption corresponds specifically to the vibration modes of the different bonds present in the analytes. Absorption spectra thus provide information on the chemical structure of the polymer as a fingerprint. FT-IR is particularly popular for PU degradation analysis because of its accuracy and rapidity and because FT-IR is a non-destructive method: the sample is recovered without damage after the analysis. Surface analysis can be easily performed to measure superficial biological degradation. Different issues can be encountered in the analysis and interpretation of a spectrum. For instance, partial similarities between bonds e.g., urethane and ester groups complicate the spectra interpretation for polyester PUs. Moreover, both

hydroxyl (OH) moieties, resulting from ester and urethane degradation, and amine (NH) moieties, resulting from urethane degradation, absorb around 3400 cm^{-1}. For polyester PUs, the increase of this large band is generally attributed to ester- or both ester and urethane hydrolysis (Oprea, 2010; Spontón et al., 2013), but it has also already been interpreted exclusively as the cleavage of the urethane bond (Umare and Chandure, 2008).

Similarly, it is difficult to interpret changes in spectra presenting carbonyl bonds (C=O) that appear in ester (1750-1725 cm^{-1}), urethane (1700 cm^{-1}) and urea bonds (1630 cm^{-1}). In polyester PUs, there is often a unique broad signal representing both urethane and ester carbonyl bonds. Its decrease is generally attributed to ester bond hydrolysis (Schmidt, J. et al., 2017; Shah et al., 2016) but sometimes has been attributed only to urethane bond hydrolysis in polyester PUs (Gómez et al., 2014; Ozsagiroglu et al., 2012). The signal at 1530 cm^{-1} is generally attributed to the nitrogen of the urethane moieties. A comparison of the polyester PU based on PCL and the constitutive PCL polyester showed that the signal at 1530 cm^{-1} only appeared on the PU spectrum thus confirming that this signal is attributed to the urethane (Magnin et al., 2019). Oprea *et al.* suggested that an increase of this signal is related to urethane bond hydrolysis (Oprea, 2010) while others suggested that a decrease of this signal attests to urethane bond degradation (Oceguera-Cervantes et al., 2007; Sarkar and Lopina, 2007). It is also conceivable that an increase of this signal is correlated to the increase of the urethane proportion in the polymer after the biological hydrolysis of the soft segment. Concluding on the variation of this signal upon degradation appeared therefore complicated. Other peaks are sometimes considered as proof of PU degradation. For instance, the emergence of a peak at 2250 cm^{-1} after degradation has been attributed to isocyanate (NCO) release (Shah et al., 2016) (Figure 14b). However, isocyanates are unstable in water and cannot be released through biological degradation in aqueous media. This signal could correspond to atmospheric CO_2 resulting from improperly done FT-IR background spectra (Gerakines et al., 1994). Since high variation on FT-IR spectra interpretations are observed through the literature, especially concerning polyester PUs, additional methods must be used to confirm urethane bond cleavage for PU degradation.

Kay *et al.*, suggested to consider the decrease of the ratio ester (C=O) /ether (1720 cm^{-1}/1125 cm^{-1}), the ratio urethane (NH)/ether (1630 cm^{-1}/1125cm^{-1}) and the ratio aryl (C=C)/ether in order to provide a semi-quantitative analysis of the degradation of a polyether PU (Kay et al., 1993). The ratio ester/ether decreases after degradation with a strain of *Corynebacterium* while the ratio urethane/ether and aryl/ether remain stable meaning that the ester bonds are affected by the bacterial degradation. Zhang et al., have used the band at 1463 cm^{-1} corresponding to CH_2 moieties to normalize their results (Zhang et al., 1994). The decrease of the normalized signals of 1239 cm^{-1}/1463 cm^{-1} revealed an alteration of the polyester part of an arterial prosthesis made in polyester PU after 100 days of incubation with pancreatin and collagenase. However, no change of the normalized signal of 1695cm^{-1}/1463cm^{-1} showed the stability of the urethane moieties.

Recently, a Raman spectroscopy has been applied to monitor the biodegradation of a polyether polyurethane foam which is among the most recalcitrant PU (Cregut et al., 2013). This technique allowed conclusions to be drawn on the amorphous region degradation of the foam by a microbial consortium while the crystalline region remained unaffected.

Microscopy

For the assessment of morphological surface modification of PUs, microscopy, particularly scanning electron microscopy (SEM) is employed. SEM allows for a qualitative evaluation of the degradation on the surface after biological treatment by observation of cracks or holes on the degraded polymers. Enzymatic degradation generally leads to cracks (Figure 14a) or holes (Figure 14b) homogeneously spread at the TPU surface (Ozsagiroglu et al., 2012; Schmidt, J. et al., 2017) while degradation with a microbial consortium leads to irregularities (Figure 14c) (Das et al., 2017; Thirunavukarasu et al., 2015; Zafar et al., 2013). For instance, Das et al., showed the appearance of cracks at the surface of a polyester TPU degraded under composting conditions. Depth of the cracks, corresponding to fungal mycelium development, increased until the formation of holes (Das et al., 2017).

SEM observations of the fungal mycelium propagation inside a PU foam highlights the higher biodegradability of open-cell foams compared to closed-cell foams. The strut of cells appeared distended, leading to the collapse of the alveolar structure (Figure 14d) (Álvarez-Barragán et al., 2016). Degradation is efficient in a PDB medium (Potatoes Dextrose Broth, rich medium) but it is specified that no degradation was observed by either weight loss or microscopy in minimal media. Small holes appeared when foams were incubated with one of the three tested strains, confirming enzymatic action. Holes in the walls and struts of the foam structure were already described previously (Figure 14e) (Gautam et al., 2007c).

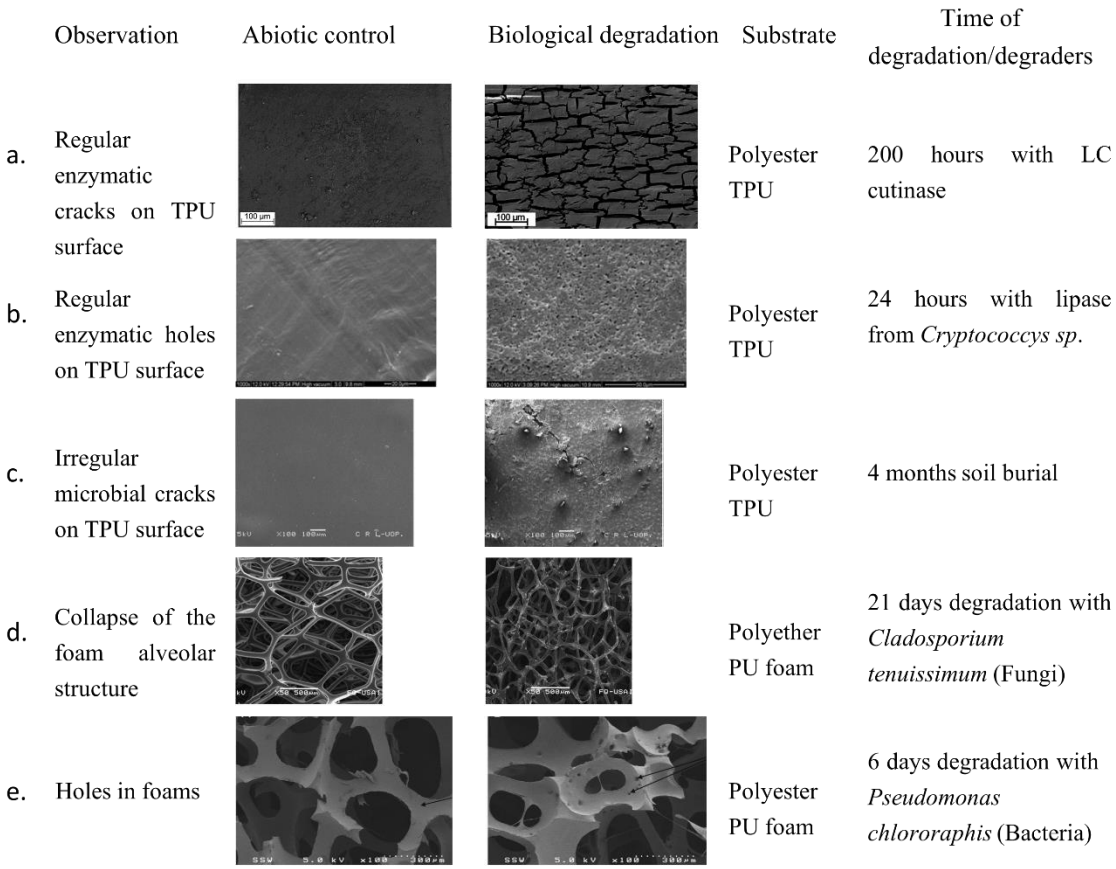


Figure 14 – SEM images showing the morphological modifications of (a, b and c) thermoplastics PU and (d and e) PU foams degraded by (a and b) enzymes, (c) microbial communities or (d and e) single strains. Photographs are adapted from (a) Schmidt et al., 2017, (b) Thirunavukarasu et al., 2015, (c) Khan et al., 2017, (d) Alvarez-Barragan et al., 2016 and (e) Gautam et al., 2007

SEM is also used to evaluate microbial growth. For instance, *Micrococcus* biofilm formation on the surface of a poly(ether urea) PU was shown by microscopy (Rafiemanzelat et al., 2013). SEM can cope with the limitation of available assays to evaluate fungal growth on carbon depleted media containing polymers. Huang et al. indeed highlighted a higher fungal growth on the surface of an adhesive containing 70% of a polyester PU than the one containing 40% (Huang et al., 2016).

Size Exclusion Chromatography (SEC)

SEC analysis allows the determination of the molar mass distribution of polymers. This quantitative analysis is more powerful than weight loss because it can appraise the change of polymer mass distribution from the beginning of chains cut off even if soluble products are not released. This measurement relies on the separation of the polymer chains in a column according to their length. The polymer is solubilized in an organic solvent such as THF, chloroform, dimethylformamide (DMF), then the solution runs through a fixed column packed with porous beads (gel) with different sizes pores. Short chains pass through the pores while longer chains cannot enter and are eluted more rapidly, then the higher the retention time, the lower the molar mass is. Detection can be performed with a UV diode array detector and/or refractive index (RI) detector. UV-vis analysis is efficient for PU containing aromatic rings such as 4,4'-MDI- or TDI-

based PUs (generally at 254 nm). Since the sample must be soluble in an organic solvent, this method is not suitable for PU foams. Analysis and comparison of chromatograms can be performed to evaluate PU degradation (Christenson et al., 2006; Rafiemanzelat et al., 2013). Molar masses are usually determined with polystyrene standards. Because of its aromatic rings, this standard is adapted to both UV and RI detection. Three main parameters are usually considered with the number average molar mass (M_n), the weight average molar mass (M_w) and the dispersity (Đ) (ratio of M_w over M_n).

Polymer degradation leads to changes in the molar mass distribution. The most common observed variation on PU biodegradation studies is a decrease of the M_w whereas M_n remains unchanged, leading to a decreasing Đ value (Schmidt, J. et al., 2017). M_w being more sensitive to long polymer chains contribution, this is consistent with the cleavage of the long chains into lower molar mass molecules. In Ferris et al., only the M_w was found to decrease (Ferris et al., 2010). Changes in molar mass distribution reveal global degradation in the bulk material and not only what is occurring at the surface of the polymer (Shah et al., 2013a; Shah et al., 2013b). Rafiemanzelat et al. described a bi-modal SEC profile with a high and a low molar mass distribution after 4 months soil burial degradation of a poly(ether urea) PU (Rafiemanzelat et al., 2013) resulting from the cleavage of the long polymer chains into shorter ones (Figure 15). The decrease of the peak area corresponding to the main polymer chain in favor of lower molar mass chains, after fungal degradation of two polyester PUs, has also been reported (Magnin et al., 2019).

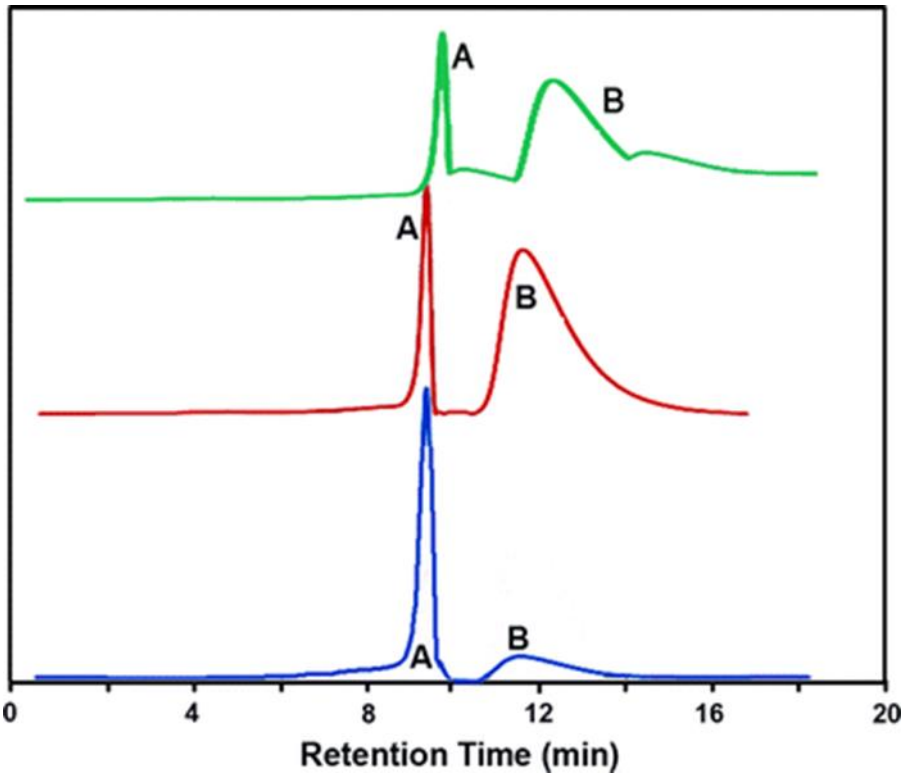


Figure 15 – SEC chromatograms of a poly(ether urea) PU before (bottom), after 4 months (middle) and after 6 months (top) of soil burial (Rafiemanzelat et al., 2013). A et B correspond respectively to the long and the short polymers chains.

Throughput of SEC analysis is rather low since a run generally lasts around one hour. Only a few publications on PU biodegradation offered robust SEC data with several repetitions of the analysis (Kuang and Mather, 2018; Magnin et al., 2019; Schmidt, J. et al., 2017).

Modifications of the physical and physico-chemical properties of PU degraded materials

Observation of modifications in the physical and physicochemical properties of a sample can be an indirect method of assessing biodegradation since the polymer chain cleavage often affects some of these properties. These assays are thus used as complementary methods. Loss of mechanical properties such as uniaxial tensile strength is generally observed after significant biological degradation of a material. Tensile test measurement allows, for example, to evaluate material elasticity and the behavior at break (Phua et al., 1987). For instance, after 24 months of composting, a decrease of the tensile strength from 20 to 10 MPa was measured for a poly(ether urea) TPU. In similar degradation conditions, samples of polyester PU were already broken down into pieces and cannot be evaluated by uniaxial tensile tests (Krasowska et al., 2012). This technique was also adapted for flexible PU foams. The tensile strength increased and the elongation at break decreased after 60 days of incubation with a strain of *Pseudomonas* for polyester PU foams (Spontón et al., 2013) (Figure 17, PU-1 and PU-2). In contrast, no change in static mechanical properties was observed for the polyether PU foam before and after degradation (Figure 17, PU-3). The polyether PU is thus more stable than the polyester PU.

PUs thermal stability may also be affected by biological degradation. This property can be measured by thermogravimetric analysis (TGA) where the weight evolution of a sample is recorded while the temperature is increased in a furnace, under air (oxidative) or N_2 (non-oxidative) environments. For most polymers, the analysis temperatures range from 0 to 600-800°C. Weight loss variations correspond to specific structure degradation and/or distinct mechanisms. The first derivative of the TGA curve (DTG) gives curve with different peaks, to determine different specific temperatures for each maximum in the case of a multistep degradation, for instance. The maximum thermal degradation temperature can be used to compare thermal stability between samples. For polyester TPUs, the first window from 100 to 300°C corresponds to the release of volatile compounds such as additives. Although urethane bonds present a reversibility at around 200°C (Delebecq et al., 2013), urethane bonds degradation induces a weight loss between 300 and 400°C while ester bond cleavage results in a weight loss between 400 and 500°C (Cangemi et al., 2006; Mathur and Prasad, 2012). A decrease in weight loss occurring between 400 and 500°C was observed after biological degradation (Mathur and Prasad, 2012). This revealed a decrease in the ester bond content per polymer and thus evidenced the biological hydrolysis of these linkages. Beyond the type of linkage affected, TGA may, therefore, provide information on the material part affected. For instance, a poly(ether urea) PU was incubated for one month with a strain of *Bacillus.* The observed changes in the material thermal stability attested for a higher proportion of hard segments and consequently a degradation occurring preferentially at the SS domains containing ether bonds (Rafiemanzelat et al., 2015).TGA is perfectly appropriate to analyze cross-linked foams. In their study, Gomez et al., compared the composting of a fossil-based and a biobased PU foam (Gómez et al., 2014). TGA

was combined with MS analysis to identify the gaseous products of thermal degradation. They found that a bio-based, aliphatic polyester PU is more sensitive to biodegradation than the fossil-based, polyester ether PU with aromatic rings.

Differential scanning calorimetry (DSC) is a thermal analysis which appraises the phase transitions of material. Glass transition temperature (T_g) is the temperature over which the amorphous region of a polymer transitions from a hard to a more mobile/viscous state. Working above the glass transition temperature (T_g) is an advantage for polymer degradation as it promotes chain mobility of the amorphous zone of semi-crystalline material. Temperature changes depending on the biological degrading-entities. Temperature of composting process can reach up to 58°C (Genovese et al., 2016) while degradation with single strain of bacteria or fungi are generally performed between 25 and 37°C. Enzymatic reaction can be performed at 60 or 70°C (Schmidt, J. et al., 2017). The melting temperature (T_m) is defined as the temperature of transition from a solid to a liquid state, which corresponds to the fusion of the crystalline regions. In practice, the area of this fusion peak allows determining the crystallinity of the material. The crystallinity of a poly(ether-urea) PU was found to increase after 4 months of soil incubation because of the decrease in the amorphous region preferentially degraded (Rafiemanzelat et al., 2013). This modification was accompanied by an increase in the T_m (Figure 19). Similarly, Osman et al., observed a shift of T_m from 191 to 196°C after the fungal degradation of a polyester PU (Osman et al., 2018). In addition to this change, a decrease of T_g was measured. Pilch-Pitera et al., also measured a lower T_g after PU degradation with an enzyme, associated with lower rigidity of the material (Pilch-Pitera, 2012).

Biological degradation can alter the hydrophobicity of a PU material. Degradation induces exposure of hydrophilic moieties on the polymer surface such as alcohol and carboxylic acid. Moreover, disruption (cracks, holes) observed on the material surface offers a higher surface area of access for water and thus higher hydrophilicity. To evaluate the hydrophobic/hydrophilic balance, a drop of known liquid, generally water, is deposited on the polymer surface and the contact angle is measured. With a hydrophilic material, the drop of water will collapse and the contact angle will be low. A shift from 90° to 63° has been measured after 320 days of soil burial of a polyester PU (Aranguren et al., 2012). Therefore, this polyester PU is more hydrophilic after biological degradation.

5.2.3. Analysis of the soluble degradation products

The identification of soluble degradation products found in the liquid phase is the best route to understand PU degradation mechanisms. Enzymatic degradation is more relevant than microbial degradation in this case. Indeed, with microbial degradation, the quantifications are biased by the possible assimilation of some degradation products by the microorganisms. Consequently, the recovered products are those that cannot be metabolized by the microorganisms.

Quantification of these products is possible with the measurement of the Total Organic Carbon (TOC) of the soluble fraction (Yamamoto et al., 2007). This measurement can be performed only for enzymatic reactions as the amount of carbon brought by the enzyme remains stable in time contrary to microbial cultures which involve growth and thus an increase of the carbon content. Yamamoto et al., used this method to evaluate the degradation of several PUs based on LDI with

various proteases. For instance, 518 ppm of carbon from degradation products were released after the degradation of a PU based on LDI and ethylene glycol, representing 44% of the theoretical carbon of the polymer. Another way to measure the release of soluble degradation products is the use of radiolabeled polymers. They were synthesized with ^{14}C molecules such as ^{14}C-TDI, ^{14}C ethylene diamine, ^{14}C 1,4-butanediol or ^{14}C 1,6-HDI (Santerre et al., 1994; Woo et al., 2000). The increase of radiolabeled-based molecules in the supernatant is quantified in counts per minute (CPM). This is a very sensitive method, but the cost and the hazardous exposure to radioactivity for the experimenter limit its usage. Both TOC and radioactivity measurements allow precise quantification of the degradation products release, but these techniques do not give information about the chemical structure of the corresponding degradation products.

Another indirect way to assess PU biodegradation is to monitor the toxicity of the soluble fraction resulting from the release of toxic degradation by-products. This is the case of 4,4'-methylene dianiline (MDA), coming from the hydrolysis of MDI-based PU, which is known to be carcinogenic (McQueen and Williams, 1990). The toxicity of the soluble fraction containing degradation products can be evaluated using Microtox® bio-assay. This assay relies on a naturally luminescent bacterium, *Photobacterium phosphoreum*. The parameter consider is the IC_{50} which is, in this case, the volume of the soluble fraction that induces a decrease of the luminescence of 50% (Spontón et al., 2013). A liquid medium of a polyester PU foam incubated for 60 days with *Pseudomonas sp,* presented an IC_{50} of 13.29% (V/V) thus attesting the release of toxic products during the degradation, probably MDA or MDA-based molecules.

The efficient recovery of the degradation products for their analysis is an important issue. Indeed, the liquid fraction of a degradation assay is a mixture containing salts, enzymes, and eventually microbial cellular debris and degradation products which are molecules released from the polymer. Several strategies were suggested to recover only the degradation products from PU degradation assays. This recovery can be performed by solvent extraction using, for example, ethyl acetate (Shah et al., 2016), acetonitrile (Tang et al., 2003) or ethyl ether (Spontón et al., 2013). Instead of solvent extraction, selective recovery of degradation products can also be achieved by removing enzymes using filtration (Wang et al., 1997a). Gamerith et al., added one volume of methanol and acidified the supernatant to pH 3.5 so that proteins precipitated and could be removed by centrifugation (Gamerith et al., 2016).

High Performance Liquid Chromatography (HPLC) with UV detection (Thirunavukarasu et al., 2015) and mass spectrometry analyses associated with liquid chromatography (LC-MS) (Elliott et al., 2002; Wang et al., 1997b) or with gas chromatography (GC-MS) (Pérez-Lara et al., 2016) are methods of choice to identify the degradation products. These methods coupled a chromatographic, for the separation of the mix of degradation products and an analytical method such as the mass spectrometry. Detected degradation products highly depend on the initial structure of polymers. Some chemical structures of identified degradation products are shown in Figure 16. Thirunavukarasu et al., monitored the degradation of 50 mg of a poly(diethylene glycol adipate)-based PU by quantifying diethylene glycol and adipic acid with HPLC analysis. After 4 days of PU incubation with a *Cryptococcus sp.* lipase, about 25 mg of adipic acid and about 8 mg of diethylene glycol were released (Thirunavukarasu et al., 2015). The detection of specific amines appears as the best way to confirm the cleavage of urethane bonds. It is interesting to notice that

the degradation of a PCL-based TPU (based on TDI as isocyanate starting material) with cholesterol esterase leads to the release of low molar mass urethane molecules containing TDI-based moieties but no TDA was detected (Wang et al., 1997a) (Figure 16). Then, the urethane bond has not been cleaved. MDA was the unique aromatic amine released from polycarbonate-based PUs synthesized with diverse diisocyanates (HDI, HMDI and MDI) after hydrolysis with cholesterol esterase (Tang et al., 2003). This enzyme is thus able to cleave urethane linkages of MDA based PU but not HDI- and HMDI-based PU. Gamerith et al., used liquid chromatography/electrospray/time-of-flight mass spectrometry (LC/ESI/TOF-MS) and also detected MDA as well as MDA derivatives after the hydrolysis of a polyester PU incubated with a *Nocardia farcinica* polyamidase enzyme. Using the same procedure, Magnin et al., quantified MDA at 0.3 mg/L after incubation of a PCL-based TPU for 50 days with an amidase (Magnin et al., 2019).

NMR analysis was used for the identification of degradation products from the enzymatic hydrolysis of a polyester PU based on PCL. 6-hydroxycaproic acid was predominantly identified showing the efficient depolymerization of the ester linkage of the SS into the constitutive building block by the esterase E3576 (Magnin et al., 2019).

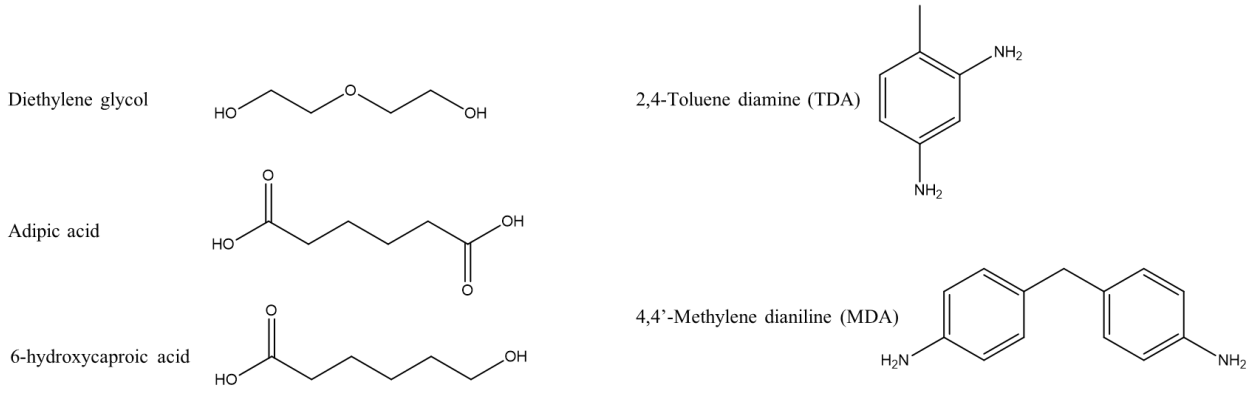


Figure 16 – Degradation products identified after PU biological degradation

6. Conclusion: The challenge of PU biological degradation: the urethane bond hydrolysis

PU are versatile polymers with high variability of structures, chemical compositions, formulations, morphologies, shapes, with a direct impact on the biodegradation mechanisms and kinetics. From the published literature, a large variety of potential or efficient biological degrading entities can be identified among fungi, bacteria or enzymes. Because of the diversity of substrates and analytical tools, a direct comparison of these degrading entities does not appear as an easy task. Microbial degradation of PUs remains a complex and rather obscure process. For instance, analysis of the set of enzymes produced by microorganisms during degradation often fails to understand the mechanisms involved in PU degradation.

To tackle the degradation of the widest range of PU, the urethane bond cleavage appears as the key parameter. However, only a few techniques provide undeniable proof of urethane bond

cleavage. Detection of amines derived from isocyanates as degradation products seems to be the main direct way to prove urethane bond hydrolysis. For that purpose, the recent development of new techniques such as LC/ESI/TOF-MS helps going forward in the resolution of this issue. Once mastered, the efficient enzymatic hydrolysis of the urethane bond will undoubtedly pave the way for a biological recycling of PU. Indeed, besides giving information on the degradation mechanism, released molecules resulting from PU biological depolymerization can also be considered as valuable products and used as building blocks for second-generation polymer synthesis. In the review of Cregut *et al.*, the economic value of major building blocks was evaluated, showing the interest of recovering molecules such as diethylene glycol, adipic acid or trimethylol propane, which are products often identified after PU biological degradation (Figure 16) (Cregut et al., 2013).

Applicability of the biological recycling on mainstream PU waste still needs to be attested. As far as we know, only one study deals with the biodegradation of a real PU waste. Gautam *et al.,* described the successful degradation of a waste polyester PU foam with a strain of *Pseudomonas chlororaphis* (Gautam et al., 2007c). Attempts to work with "real" PU waste (and no PU-based models) have recently been performed by Alvarez-Barragan *et al.* by studying the degradation of polyether-PU foam synthesized with and without the addition of a fire retardant tris(1,3-dichloro-2-propyl)phosphate (TDCPP) (Álvarez-Barragán et al., 2016). The TDCPP-containing foam was found to be less sensitive to biodegradation thus highlighting the need for considering thoroughly the presence of additives in real PU biological degradation assessment.

Polluting waste management such as landfilling will no longer be suitable solution. Limitation of the pollution linked to PU waste is an outcome deeply needed and expected from recycling. An efficient biological recycling path for PUs will support the economic value of PU waste towards the development of a circular economy for plastic material.

Funding:

The work for this review was fully supported by the Fondation pour la Recherche en Chimie (the Frontier Research in Chemistry Foundation) with the project "Biocycling" (2019-2020), in the continuation of a previous H2020 project (P4SB).

7. References

Akindoyo, J.O., Beg, M.D.H., Ghazali, S., Islam, M.R., Jeyaratnam, N., Yuvaraj, A.R., 2016. Polyurethane types, synthesis and applications – a review. RSC Advances 6(115), 114453-114482.

Akutsu-Shigeno, Y., Adachi, Y., Yamada, C., Toyoshima, K., Nomura, N., Uchiyama, H., Nakajima-Kambe, T., 2006. Isolation of a bacterium that degrades urethane compounds and characterization of its urethane hydrolase. Applied Microbiology and Biotechnology 70(4), 422-429.

Akutsu, Y., Nakajima-Kambe, T., Nomura, N., Nakahara, T., 1998. Purification and properties of a polyester polyurethane-degrading enzyme from *Comamonas acidovorans* TB-35. Applied and Environmental Microbiology 64(1), 62-67.

Allen, A.B., Hilliard, N.P., Howard, G.T., 1999. Purification and characterization of a soluble polyurethane degrading enzyme from *Comamonas acidovorans*. International Biodeterioration & Biodegradation 43(1-2), 37-41.

Álvarez-Barragán, J., Dominguez-Malfavon, L., Vargas-Suarez, M., Gonzalez-Hernandez, R., Aguilar-Osorio, G., Loza-Tavera, H., 2016. Biodegradative Activities of Selected Environmental Fungi on a Polyester Polyurethane Varnish and Polyether Polyurethane Foams. Applied and Environmental Microbiology 82(17), 5225-5235.

Aranguren, M.I., González, J.F., Mosiewicki, M.A., 2012. Biodegradation of a vegetable oil based polyurethane and wood flour composites. Polymer Testing 31(1), 7-15.

Arbenz, A., Frache, A., Cuttica, F., Avérous, L., 2016. Advanced biobased and rigid foams, based on urethane-modified isocyanurate from oxypropylated gambier tannin polyol. Polymer Degradation and Stability 132, 62-68.

Avérous, L., Pollet, E., 2012. Biodegradable polymers, Environmental silicate nano-biocomposites. Springer, pp. 13-39.

Barboza, L.G.A., Dick Vethaak, A., Lavorante, B.R.B.O., Lundebye, A.-K., Guilhermino, L., 2018. Marine microplastic debris: An emerging issue for food security, food safety and human health. Marine Pollution Bulletin 133, 336-348.

Barlow, D.E., Biffinger, J.C., Cockrell-Zugell, A.L., Lo, M., Kjoller, K., Cook, D., Lee, W.K., Pehrsson, P.E., Crookes-Goodson, W.J., Hung, C.S., Nadeau, L.J., Russell, J.N., 2016. The importance of correcting for variable probe-sample interactions in AFM-IR spectroscopy: AFM-IR of dried bacteria on a polyurethane film. Analyst 141(16), 4848-4854.

Barratt, S., Ennos, A., Greenhalgh, M., Robson, G., Handley, P., 2003. Fungi are the predominant micro-organisms responsible for degradation of soil-buried polyester polyurethane over a range of soil water holding capacities. Journal of Applied Microbiology 95(1), 78-85.

Barth, M., Oeser, T., Wei, R., Then, J., Schmidt, J., Zimmermann, W., 2015. Effect of hydrolysis products on the enzymatic degradation of polyethylene terephthalate nanoparticles by a polyester hydrolase from *Thermobifida fusca*. Biochemical Engineering Journal 93, 222-228.

1018 Bastioli, C., 2005. Handbook of biodegradable polymers. iSmithers Rapra Publishing.

1019 Bayan, R., Karak, N., 2017. Renewable resource modified polyol derived aliphatic hyperbranched
1020 polyurethane as a biodegradable and UV-resistant smart material. Polymer International 66(6),
1021 839-850.

1022 Bayer, O., 1948. Annalen549, 286 (1941). Angewandte Chemie A 59, 257.

1023 Behrendt, G., Naber, B.W., 2009. The chemical recycling of polyurethanes. Journal of the
1024 University of Chemical Technology and Metallurgy 44(1), 3-23.

1025 Bentham, R., Morton, L., Allen, N., 1987. Rapid assessment of the microbial deterioration of
1026 polyurethanes. International Biodeterioration 23(6), 377-386.

1027 Biffinger, J.C., Barlow, D.E., Cockrell, A.L., Cusick, K.D., Hervey, W.J., Fitzgerald, L.A., Nadeau, L.J.,
1028 Hung, C.S., Crookes-Goodson, W.J., Russell, J.N., 2015. The applicability of Impranil®DLN for
1029 gauging the biodegradation of polyurethanes. Polymer Degradation and Stability 120, 178-185.

1030 Biffinger, J.C., Barlow, D.E., Pirlo, R.K., Babson, D.M., Fitzgerald, L.A., Zingarelli, S., Nadeau, L.J.,
1031 Crookes-Goodson, W.J., Russell, J.N., 2014. A direct quantitative agar-plate based assay for
1032 analysis of *Pseudomonas protegens* Pf-5 degradation of polyurethane films. International
1033 Biodeterioration & Biodegradation 95, 311-319.

1034 Boujard, C., Foray, N., Caudron, J., 2014. Panorama du marché du polyuréthane et état de l'art de
1035 ses techniques de recyclages. Report 1202C0079, ADEME.

1036 Bouwmeester, H., Hollman, P.C., Peters, R.J., 2015. Potential health impact of environmentally
1037 released micro-and nanoplastics in the human food production chain: experiences from
1038 nanotoxicology. Environmental Science & Technology 49(15), 8932-8947.

1039 Brunner, P.H., Rechberger, H., 2015. Waste to energy--key element for sustainable waste
1040 management. Waste Management 37, 3-12.

1041 Brzeska, J., Heimowska, A., Sikorska, W., Jasińska-Walc, L., Kowalczuk, M., Rutkowska, M., 2015.
1042 Chemical and Enzymatic Hydrolysis of Polyurethane/Polylactide Blends. International Journal of
1043 Polymer Science 2015, 1-8.

1044 Campinez, M.D., Aguilar-de-Leyva, A., Ferris, C., de Paz, M.V., Galbis, J.A., Caraballo, I., 2013. Study
1045 of the properties of the new biodegradable polyurethane PU (TEG-HMDI) as matrix forming
1046 excipient for controlled drug delivery. Drug Development and Industrial Pharmacy 39(11), 1758-
1047 1764.

1048 Cangemi, J.M., Claro Neto, S., Chierice, G.O., Santos, A.M.d., 2006. Study of the biodegradation of
1049 a polymer derived from castor oil by scanning electron microscopy, thermogravimetry and
1050 infrared spectroscopy. Polímeros 16(2), 129-135.

1051 Cangemi, J.M., Santos, A.M.d., C Neto, S., Chierice, G.O., 2008. Biodegradation of polyurethane
1052 derived from castor oil. Polímeros 18(3), 201-206.

Carré, C., Bonnet, L., Avérous, L., 2014. Original biobased nonisocyanate polyurethanes: solvent- and catalyst-free synthesis, thermal properties and rheological behaviour. RSC Advances 4(96), 54018-54025.

Carré, C., Bonnet, L., Avérous, L., 2015. Solvent- and catalyst-free synthesis of fully biobased nonisocyanate polyurethanes with different macromolecular architectures. RSC Advances 5(121), 100390-100400.

Castillo-Gimenez, J., Montanes, A., Picazo-Tadeo, A.J., 2019. Performance and convergence in municipal waste treatment in the European Union. Waste Management 85, 222-231.

Chae, Y., An, Y.J., 2017. Effects of micro- and nanoplastics on aquatic ecosystems: Current research trends and perspectives. Marine Pollution Bulletin 124(2), 624-632.

Charlon, M., Heinrich, B., Matter, Y., Couzigné, E., Donnio, B., Avérous, L., 2014. Synthesis, structure and properties of fully biobased thermoplastic polyurethanes, obtained from a diisocyanate based on modified dimer fatty acids, and different renewable diols. European Polymer Journal 61, 197-205.

Chattopadhyay, D.K., Raju, N.P., Vairamani, M., Raju, K.V.S.N., 2008. Structural investigations of polypropylene glycol (PPG) and isophorone diisocyanate (IPDI) based polyurethane prepolymer by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF)-mass spectrometry. Progress in Organic Coatings 62(2), 117-122.

Chen, Y., Liu, Z., Han, S., Han, J., Jiang, D., 2016. Poly(propylene carbonate) polyurethane self-polishing coating for marine antifouling application. Journal of Applied Polymer Science 133(28).

Christenson, E.M., Anderson, J.M., Hiltner, A., 2004. Oxidative mechanisms of poly(carbonate urethane) and poly(ether urethane) biodegradation: in vivo and in vitro correlations. Journal of Biomedical Materials Research Part A 70(2), 245-255.

Christenson, E.M., Patel, S., Anderson, J.M., Hiltner, A., 2006. Enzymatic degradation of poly(ether urethane) and poly(carbonate urethane) by cholesterol esterase. Biomaterials 27(21), 3920-3926.

Ciardelli, G., Rechichi, A., Cerrai, P., Tricoli, M., Barbani, N., Giusti, P., 2004. Segmented polyurethanes for medical applications: synthesis, characterization and in vitro enzymatic degradation studies, Macromolecular Symposia. Wiley Online Library, pp. 261-272.

Clukey, K.E., Lepczyk, C.A., Balazs, G.H., Work, T.M., Li, Q.X., Bachman, M.J., Lynch, J.M., 2018. Persistent organic pollutants in fat of three species of Pacific pelagic longline caught sea turtles: Accumulation in relation to ingested plastic marine debris. Science of the Total Environment 610-611, 402-411.

Cooney, J., 1969. Effects of polyurethane foams on microbial growth in fuel-water systems. Applied Microbiology 17(2), 227-231.

Cosgrove, L., McGeechan, P.L., Handley, P.S., Robson, G.D., 2010. Effect of biostimulation and bioaugmentation on degradation of polyurethane buried in soil. Applied of Environemental Microbiology 76(3), 810-819.

1090 Cosgrove, L., McGeechan, P.L., Robson, G.D., Handley, P.S., 2007. Fungal communities associated
1091 with degradation of polyester polyurethane in soil. Applied of Environemental Microbiology
1092 73(18), 5817-5824.
1093 Coutinho, F., Delpech, M.C., Alves, L.S., 2001. Anionic waterborne polyurethane dispersions based
1094 on hydroxyl-terminated polybutadiene and poly (propylene glycol): Synthesis and
1095 characterization. Journal of Applied Polymer Science 80(4), 566-572.
1096 Cozar, A., Echevarria, F., Gonzalez-Gordillo, J.I., Irigoien, X., Ubeda, B., Hernandez-Leon, S., Palma,
1097 A.T., Navarro, S., Garcia-de-Lomas, J., Ruiz, A., Fernandez-de-Puelles, M.L., Duarte, C.M., 2014.
1098 Plastic debris in the open ocean. Proceedings of the National Academy of Sciences 111(28),
1099 10239-10244.
1100 Crabbe, J.R., Campbell, J.R., Thompson, L., Walz, S.L., Schultz, W.W., 1994. Biodegradation of a
1101 colloidal ester-based polyurethane by soil fungi. International Biodeterioration & Biodegradation
1102 33(2), 103-113.
1103 Cregut, M., Bedas, M., Assaf, A., Durand-Thouand, M.J., Thouand, G., 2014. Applying Raman
1104 spectroscopy to the assessment of the biodegradation of industrial polyurethanes wastes.
1105 Environmental Science and Pollution Research 21(16), 9538-9544.
1106 Cregut, M., Bedas, M., Durand, M.J., Thouand, G., 2013. New insights into polyurethane
1107 biodegradation and realistic prospects for the development of a sustainable waste recycling
1108 process. Biotechnol Adv 31(8), 1634-1647.
1109 Crookes-Goodson, W.J., Bojanowski, C.L., Kay, M.L., Lloyd, P.F., Blankemeier, A., Hurtubise, J.M.,
1110 Singh, K.M., Barlow, D.E., Ladouceur, H.D., Matt Eby, D., Johnson, G.R., Mirau, P.A., Pehrsson, P.E.,
1111 Fraser, H.L., Russell, J.N., Jr., 2013. The impact of culture medium on the development and
1112 physiology of biofilms of *Pseudomonas fluorescens* formed on polyurethane paint. Biofouling
1113 29(6), 601-615.
1114 Curia, R., Milani, M., Didenko, L., Avtandilov, G., Shevlyagina, N., Smirnova, T., 2014. Beyond the
1115 biodestruction of polyurethane: *S. aureus* uptake of nanoparticles is a challenge for toxicology.
1116 Microscopy: Advances in Scientific Research and Education 1, 16-23.
1117 Daemi, H., Rajabi-Zeleti, S., Sardon, H., Barikani, M., Khademhosseini, A., Baharvand, H., 2016. A
1118 robust super-tough biodegradable elastomer engineered by supramolecular ionic interactions.
1119 Biomaterials 84, 54-63.
1120 Darby, R.T., Kaplan, A.M., 1968. Fungal susceptibility of polyurethanes. Applied Microbiology
1121 16(6), 900-905.
1122 Darby, T., Johnson, H., Northup, S., 1978. An evaluation of a polyurethane for use as a medical
1123 grade plastic. Toxicology and Applied Pharmacology 46(2), 449-453.
1124 Darmon, G., Miaud, C., Claro, F., Doremus, G., Galgani, F., 2017. Risk assessment reveals high
1125 exposure of sea turtles to marine debris in French Mediterranean and metropolitan Atlantic
1126 waters. Deep Sea Research Part II: Topical Studies in Oceanography 141, 319-328.

Das, S., Pandey, P., Mohanty, S., Nayak, S.K., 2017. Evaluation of biodegradability of green polyurethane/nanosilica composite synthesized from transesterified castor oil and palm oil based isocyanate. International Biodeterioration & Biodegradation 117, 278-288.

Debuissy, T., Pollet, E., Avérous, L., 2017. Synthesis and characterization of block poly(ester-ether-urethane)s from bacterial poly(3-hydroxybutyrate) oligomers. Journal of Polymer Science Part A: Polymer Chemistry 55(11), 1949-1961.

Delebecq, E., Pascault, J.P., Boutevin, B., Ganachaud, F., 2013. On the versatility of urethane/urea bonds: reversibility, blocked isocyanate, and non-isocyanate polyurethane. Chemical Reviews 113(1), 80-118.

Dogan, S.K., Boyacioglu, S., Kodal, M., Gokce, O., Ozkoc, G., 2017. Thermally induced shape memory behavior, enzymatic degradation and biocompatibility of PLA/TPU blends: "Effects of compatibilization". Journal of the Mechanical Behavior of Biomedical Materials 71, 349-361.

Duarah, R., Singh, Y.P., Mandal, B.B., Karak, N., 2016. Sustainable starch modified polyol based tough, biocompatible, hyperbranched polyurethane with a shape memory attribute. New Journal of Chemistry 40(6), 5152-5163.

Duis, K., Coors, A., 2016. Microplastics in the aquatic and terrestrial environment: sources (with a specific focus on personal care products), fate and effects. Environmental Sciences Europe 28(1), 2.

Edmonds, P., Cooney, J., 1968. Microbial growth in a fuel-water system containing polyesterurethane foam. Applied Microbiology 16(2), 426.

El-Sayed, A.H.M., Mahmoud, W.M., Davis, E.M., Coughlin, R.W., 1996. Biodegradation of polyurethane coatings by hydrocarbon-degrading bacteria. International Biodeterioration & Biodegradation 37(1-2), 69-79.

Elliott, S., Fromstein, J., P. Santerre, J., Woodhouse, K., 2002. Identification of biodegradation products formed by L-phenylalanine based segmented polyurethaneureas. Journal of Biomaterials Science, Polymer Edition 13(6), 691-711.

Eriksen, M., Maximenko, N., Thiel, M., Cummins, A., Lattin, G., Wilson, S., Hafner, J., Zellers, A., Rifman, S., 2013. Plastic pollution in the South Pacific subtropical gyre. Marine Pollution Bulletin 68(1-2), 71-76.

Fang, J., Ye, S.H., Shankarraman, V., Huang, Y., Mo, X., Wagner, W.R., 2014. Biodegradable poly(ester urethane)urea elastomers with variable amino content for subsequent functionalization with phosphorylcholine. Acta Biomaterialia 10(11), 4639-4649.

Faust, K., Raes, J., 2012. Microbial interactions: from networks to models. Nature Reviews Microbiology 10(8), 538-550.

Feng, X., Wang, G., Neumann, K., Yao, W., Ding, L., Li, S., Sheng, Y., Jiang, Y., Bradley, M., Zhang, R., 2017. Synthesis and characterization of biodegradable poly (ether-ester) urethane acrylates for controlled drug release. Materials Science and Engineering: C 74, 270-278.

1164 Fernandes, I.P., Barbosa, M., Amaral, J.S., Pinto, V., Rodrigues, J.L., Ferreira, M.J., Barreiro, M.F.,
1165 2016. Biobased Additives as Biodegradability Enhancers with Application in TPU-Based Footwear
1166 Components. Journal of Renewable Materials 4(1), 47-56.

1167 Ferris, C., Violante de Paz, M., Zamora, F., Galbis, J.A., 2010. Dithiothreitol-based polyurethanes.
1168 Synthesis and degradation studies. Polymer Degradation and Stability 95(9), 1480-1487.

1169 Filip, Z., 1978. Decomposition of polyurethane in a garbage landfill leakage water and by soil
1170 microorganisms. European Journal of Applied Microbiology and Biotechnology 5(3), 225-231.

1171 Filip, Z., 1979. Polyurethane as the sole nutrient source for *Aspergillus niger* and *Cladosporium*
1172 *herbarum*. European Journal of Applied Microbiology and Biotechnology 7(3), 277-280.

1173 Frère, L., Paul-Pont, I., Moreau, J., Soudant, P., Lambert, C., Huvet, A., Rinnert, E., 2016. A semi-
1174 automated Raman micro-spectroscopy method for morphological and chemical characterizations
1175 of microplastic litter. Marine Pollution Bulletin 113(1-2), 461-468.

1176 Furtwengler, P., Avérous, L., 2018. Renewable polyols for advanced polyurethane foams from
1177 diverse biomass resources. Polymer Chemistry 9(32), 4258-4287.

1178 Furtwengler, P., Boumbimba, R.M., Avérous, L., 2018a. Elaboration and Characterization of
1179 Advanced Biobased Polyurethane Foams Presenting Anisotropic Behavior. Macromolecular
1180 Materials and Engineering.

1181 Furtwengler, P., Matadi Boumbimba, R., Sarbu, A., Avérous, L., 2018b. Novel Rigid
1182 Polyisocyanurate Foams from Synthesized Biobased Polyester Polyol with Enhanced Properties.
1183 ACS Sustainable Chemistry & Engineering 6(5), 6577-6589.

1184 Gadhave, R.V., Srivastava, S., Mahanwar, P.A., Gadekar, P.T., 2019. Recycling and Disposal
1185 Methods for Polyurethane Wastes: A Review. Open Journal of Polymer Chemistry.

1186 Galloway, T.S., Lewis, C.N., 2016. Marine microplastics spell big problems for future generations.
1187 Proceedings of the National Academy of Sciences 113(9), 2331-2333.

1188 Gamerith, C., Herrero Acero, E., Pellis, A., Ortner, A., Vielnascher, R., Luschnig, D., Zartl, B.,
1189 Haernvall, K., Zitzenbacher, S., Strohmeier, G., Hoff, O., Steinkellner, G., Gruber, K., Ribitsch, D.,
1190 Guebitz, G.M., 2016. Improving enzymatic polyurethane hydrolysis by tuning enzyme sorption.
1191 Polymer Degradation and Stability 132, 69-77.

1192 Gamerith, C., Zartl, B., Pellis, A., Guillamot, F., Marty, A., Acero, E.H., Guebitz, G.M., 2017.
1193 Enzymatic recovery of polyester building blocks from polymer blends. Process Biochemistry 59,
1194 58-64.

1195 Gautam, Bassi, A., Yanful, E., 2007a. A review of biodegradation of synthetic plastic and foams.
1196 Applied Biochemistry and Biotechnology 141(1), 85-108.

1197 Gautam, Bassi, A.S., Yanful, E.K., 2007b. Candida rugosa lipase-catalyzed polyurethane
1198 degradation in aqueous medium. Biotechnology Letters 29(7), 1081-1086.

1199 Gautam, Bassi, A.S., Yanful, E.K., Cullen, E., 2007c. Biodegradation of automotive waste polyester
1200 polyurethane foam using *Pseudomonas chlororaphis* ATCC55729. International Biodeterioration
1201 & Biodegradation 60(4), 245-249.

1202 Ge, J., Zhong, W., Guo, Z., Li, W., Sakai, K., 2000. Biodegradable polyurethane materials from bark
1203 and starch. I. Highly resilient foams. Journal of Applied Polymer Science 77(12), 2575-2580.

1204 Genovese, L., Soccio, M., Gigli, M., Lotti, N., Gazzano, M., Siracusa, V., Munari, A., 2016. Gas
1205 permeability, mechanical behaviour and compostability of fully-aliphatic bio-based multiblock
1206 poly(ester urethane)s. RSC Advances 6(60), 55331-55342.

1207 Gerakines, P.A., Schutte, W., Greenberg, J., van Dishoeck, E.F., 1994. The infrared band strengths
1208 of H2O, CO and CO2 in laboratory simulations of astrophysical ice mixtures. Astronomy &
1209 Astrophysics.

1210 Gogoi, G., Karak, N., 2017. Waterborne hyperbranched poly(ester amide urethane) thermoset:
1211 Mechanical, thermal and biodegradation behaviors. Polymer Degradation and Stability 143, 155-
1212 163.

1213 Gogoi, S., Karak, N., 2014. Biobased Biodegradable Waterborne Hyperbranched Polyurethane as
1214 an Ecofriendly Sustainable Material. ACS Sustainable Chemistry & Engineering 2(12), 2730-2738.

1215 Gogoi, S., Karak, N., 2015. Bio-based high-performance waterborne hyperbranched polyurethane
1216 thermoset. Polymers for Advanced Technologies 26(6), 589-596.

1217 Gómez, E.F., Luo, X., Li, C., Michel, F.C., Li, Y., 2014. Biodegradability of crude glycerol-based
1218 polyurethane foams during composting, anaerobic digestion and soil incubation. Polymer
1219 Degradation and Stability 102, 195-203.

1220 Gu, J.-G., Gu, J.-D., 2005. Methods Currently Used in Testing Microbiological Degradation and
1221 Deterioration of a Wide Range of Polymeric Materials with Various Degree of Degradability: A
1222 Review. Journal of Polymers and the Environment 13(1), 65-74.

1223 Guan, J., Fujimoto, K.L., Wagner, W.R., 2008. Elastase-sensitive elastomeric scaffolds with variable
1224 anisotropy for soft tissue engineering. Pharmaceutical Research 25(10), 2400-2412.

1225 Gunatillake, P.A., Adhikari, R., Felton, G., 2011. Biodegradable polyurethanes: design, synthesis,
1226 properties and potential applications. Biodegradable Polymers: Processing, Degradation and
1227 Applications, 431-470.

1228 Guo, Y., Chen, S., Su, L., Wu, J., Chen, J., 2014. Cloning, expression, and characterization of
1229 polyamidase from *Nocardia farcinica* and its application to polyamide modification.
1230 Biotechnology and Bioprocess Engineering 18(6), 1067-1075.

1231 Hablot, E., Zheng, D., Bouquey, M., Avérous, L., 2008. Polyurethanes based on castor oil: kinetics,
1232 chemical, mechanical and thermal properties. Macromolecular Materials and Engineering
1233 293(11), 922-929.

1234 Hedrick, H., Crum, M., 1968. Effects of jet-fuel microbial isolates on a polyurethane foam. Applied
1235 and Environmental Microbiology 16(12), 1826-1830.

Heumann, S., Eberl, A., Fischer-Colbrie, G., Pobeheim, H., Kaufmann, F., Ribitsch, D., Cavaco-Paulo, A., Guebitz, G.M., 2009. A novel aryl acylamidase from *Nocardia farcinica* hydrolyses polyamide. Biotechnology Bioengineering 102(4), 1003-1011.

Howard, G., Mackie, R., Cann, I., Ohene-Adjei, S., Aboudehen, K., Duos, B., Childers, G., 2007. Effect of insertional mutations in the pueA and pueB genes encoding two polyurethanases in *Pseudomonas chlororaphis* contained within a gene cluster. Journal of Applied Microbiology 103(6), 2074-2083.

Howard, G.T., Blake, R.C., 1998. Growth of *Pseudomonas fluorescens* on a polyester–polyurethane and the purification and characterization of a polyurethanase–protease enzyme. International Biodeterioration & Biodegradation 42(4), 213-220.

Howard, G.T., Crother, B., Vicknair, J., 2001. Cloning, nucleotide sequencing and characterization of a polyurethanase gene (pueB) from *Pseudomonas chlororaphis*. International Biodeterioration & Biodegradation 47(3), 141-149.

Howard, G.T., Norton, W.N., Burks, T., 2012. Growth of *Acinetobacter gerneri* P7 on polyurethane and the purification and characterization of a polyurethanase enzyme. Biodegradation 23(4), 561-573.

Huang, J., Sun, J., Zhang, R., Zou, R., Liu, X., Yang, Z., Yuan, T., 2016. Improvement of biodegradability of UV-curable adhesives modified by a novel polyurethane acrylate. Progress in Organic Coatings 95, 20-25.

Hung, C.S., Zingarelli, S., Nadeau, L.J., Biffinger, J.C., Drake, C.A., Crouch, A.L., Barlow, D.E., Russell, J.N., Jr., Crookes-Goodson, W.J., 2016. Carbon Catabolite Repression and Impranil Polyurethane Degradation in *Pseudomonas protegens* Strain Pf-5. Applied and Environmental Microbiology 82(20), 6080-6090.

Ibrahim N. Ibrahim, A.M., Khalid M. Hameed, Ismail M. Saadoun, Hamzah M Maswadeh and Toshiaki Nakajima-Kambe 2 3, 2009. Polyester-polyurethane Biodegradation by Alternaria Solani, Isolated from Northern Jordan Advances in Environmental Biology 3(2), 162-170.

Ignat, L., Ignat, M., Ciobanu, C., Doroftei, F., Popa, V.I., 2011. Effects of flax lignin addition on enzymatic oxidation of poly(ethylene adipate) urethanes. Industrial Crops and Products 34(1), 1017-1028.

Ignatyev, I.A., Thielemans, W., Vander Beke, B., 2014. Recycling of polymers: a review. ChemSusChem 7(6), 1579-1593.

Ii, R.C.B., Norton, W.N., Howard, G.T., 1998. Adherence and growth of a *Bacillus* species on an insoluble polyester polyurethane. International Biodeterioration & Biodegradation 42(1), 63-73.

International, A., 2002. ASTM D5511-02, Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials Under High-Solids Anaerobic-Digestion Conditions. West Conshohocken.

International, A., 2003a. ASTM D5338-98(2003), Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions. West Conshohocken.

International, A., 2003b. ASTM D5988-03, Standard Test Method for Determining Aerobic Biodegradation in Soil of Plastic Materials or Residual Plastic Materials After Composting. West Conshohocken.

Ionescu, M., 2005. Chemistry and technology of polyols for polyurethanes. iSmithers Rapra Publishing.

Izadi-Vasafi, H., Sadeghi, G.M.M., Babaei, A., Ghayoumi, F., 2017. A novel biodegradable polyurethane based on hydroxylated polylactic acid and tung oil mixtures. I. Synthesis, physicochemical and biodegradability characterization. Fibers and Polymers 17(3), 311-323.

Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., Law, K.L., 2015. Plastic waste inputs from land into the ocean. Science 347(6223), 768-771.

Jansen, B., Schumacher-Perdreau, F., Peters, G., Pulverer, G., 1991. Evidence for degradation of synthetic polyurethanes by *Staphylococcus* epidermidis. Zentralblatt für Bakteriologie 276(1), 36-45.

Jiang, X., Li, J., Ding, M., Tan, H., Ling, Q., Zhong, Y., Fu, Q., 2007. Synthesis and degradation of nontoxic biodegradable waterborne polyurethanes elastomer with poly (ε-caprolactone) and poly (ethylene glycol) as soft segment. European Polymer Journal 43(5), 1838-1846.

Kanavel, G., Koons, P., Lauer, R., 1966. Fungus Resistance of Millable Urethans. Rubber Chemistry and Technology 39(4), 1338-1346.

Kang, C.H., Oh, K.H., Lee, M.H., Oh, T.K., Kim, B.H., Yoon, J., 2011. A novel family VII esterase with industrial potential from compost metagenomic library. Microbial Cell Factories 10, 41.

Kaplan, A.M., Darby, R.T., Greenberger, M., Rodgers, M., 1968. Microbial deterioration of polyurethane systems. Developments in Industrial Microbiology 82, 362-371.

Kawai, F., Oda, M., Tamashiro, T., Waku, T., Tanaka, N., Yamamoto, M., Mizushima, H., Miyakawa, T., Tanokura, M., 2014. A novel Ca 2+-activated, thermostabilized polyesterase capable of hydrolyzing polyethylene terephthalate from *Saccharomonospora viridis* AHK190. Applied Microbiology and Biotechnology 98(24), 10053-10064.

Kay, M., McCabe, R., Morton, L., 1993. Chemical and physical changes occurring in polyester polyurethane during biodegradation. International Biodeterioration & Biodegradation 31(3), 209-225.

Kay, M., Morton, L., Prince, E., 1991. Bacterial degradation of polyester polyurethane. International Biodeterioration 27(2), 205-222.

Khan, S., Nadir, S., Shah, Z.U., Shah, A.A., Karunarathna, S.C., Xu, J., Khan, A., Munir, S., Hasan, F., 2017. Biodegradation of polyester polyurethane by *Aspergillus tubingensis*. Environmental Pollution 225, 469-480.

Kim, Y.D., Kim, S.C., 1998. Effect of chemical structure on the biodegradation of polyurethanes under composting conditions. Polymer Degradation and Stability 62(2), 343-352.

Krasowska, K., Janik, H., Gradys, A., Rutkowska, M., 2012. Degradation of polyurethanes in compost under natural conditions. Journal of Applied Polymer Science 125(6), 4252-4260.

Kuang, W., Mather, P.T., 2018. A latent crosslinkable PCL-based polyurethane: Synthesis, shape memory, and enzymatic degradation. Journal of Materials Research, 1-14.

Kucharczyk, P., Pavelková, A., Stloukal, P., Sedlarík, V., 2016. Degradation behaviour of PLA-based polyesterurethanes under abiotic and biotic environments. Polymer Degradation and Stability 129, 222-230.

Labow, R.S., Erfle, D.J., Santerre, J.P., 1996. Elastase-induced hydrolysis of synthetic solid substrates: poly (ester-urea-urethane) and poly (ether-urea-urethane). Biomaterials 17(24), 2381-2388.

Langlois, P., Howard, G.T., 2002. A single glycine-rich repeat of *Pseudomonas chlororaphis* Polyurethanase A mediates secretion of a GST fusion protein in *Escherichia coli*. International Biodeterioration & Biodegradation 50(2), 121-126.

Laurichesse, S., Huillet, C., Avérous, L., 2014. Original polyols based on organosolv lignin and fatty acids: new bio-based building blocks for segmented polyurethane synthesis. Green Chemistry 16(8), 3958-3970.

Law, K.L., Morét-Ferguson, S., Maximenko, N.A., Proskurowski, G., Peacock, E.E., Hafner, J., Reddy, C.M., 2010. Plastic accumulation in the North Atlantic subtropical gyre. Science 329(5996), 1185-1188.

Li, B.H., Yang, M.C., 2006. Improvement of thermal and mechanical properties of poly (L-lactic acid) with 4, 4-methylene diphenyl diisocyanate. Polymers for Advanced Technologies 17(6), 439-443.

Li, S.-L., Wu, F., Wang, Y.-Z., Zeng, J.-B., 2015. Biobased Thermoplastic Poly(ester urethane) Elastomers Consisting of Poly(butylene succinate) and Poly(propylene succinate). Industrial & Engineering Chemistry Research 54(24), 6258-6268.

Liu, K., Su, Z., Miao, S., Ma, G., Zhang, S., 2016. Enzymatic waterborne polyurethane towards a robust and environmentally friendly anti-biofouling coating. RSC Advances 6(38), 31698-31704.

Loredo-Treviño, A., Gutiérrez-Sánchez, G., Rodríguez-Herrera, R., Aguilar, C.N., 2011. Microbial Enzymes Involved in Polyurethane Biodegradation: A Review. Journal of Polymers and the Environment 20(1), 258-265.

Lu, P., Zhang, Y., Jia, C., Li, Y., Zhang, M., Mao, Z., 2016. Degradation of polyurethane coating materials from liquefied wheat straw for controlled release fertilizers. Journal of Applied Polymer Science 133(41).

Lucas, N., Bienaime, C., Belloy, C., Queneudec, M., Silvestre, F., Nava-Saucedo, J.E., 2008. Polymer biodegradation: mechanisms and estimation techniques. Chemosphere 73(4), 429-442.

Magnin, A., Hoornaert, L., Pollet, E., Laurichesse, S., Phalip, V., Avérous, L., 2018. Isolation and characterization of different promising fungi for biological waste management of polyurethanes. Microbial Biotechnology.

Magnin, A., Pollet, E., Perrin, R., Ullmann, C., Persillon, C., Phalip, V., Avérous, L., 2019. Enzymatic recycling of thermoplastic polyurethanes: Synergistic effect of an esterase and an amidase and recovery of building blocks. Waste Management 85, 141-150.

Mahajan, N., Gupta, P., 2015. New insights into the microbial degradation of polyurethanes. RSC Advances 5(52), 41839-41854.

Makarichi, L., Jutidamrongphan, W., Techato, K.-a., 2018. The evolution of waste-to-energy incineration: A review. Renewable and Sustainable Energy Reviews 91, 812-821.

Marchant, R., Zhao, Q., Anderson, J., Hiltner, A., 1987. Degradation of a poly (ether urethane urea) elastomer: infra-red and XPS studies. Polymer 28(12), 2032-2039.

Mathur, G., Prasad, R., 2012. Degradation of polyurethane by *Aspergillus flavus* (ITCC 6051) isolated from soil. Appl Biochem Biotechnol 167(6), 1595-1602.

Matsumiya, Y., Murata, N., Tanabe, E., Kubota, K., Kubo, M., 2010. Isolation and characterization of an ether-type polyurethane-degrading micro-organism and analysis of degradation mechanism by *Alternaria sp*. Journal of Applied Microbiology 108(6), 1946-1953.

McQueen, C.A., Williams, G.M., 1990. Review of the genotoxicity and carcinogenicity of 4, 4'-methylene-dianiline and 4, 4'-methylene-bis-2-chloroaniline. Mutation Research/Reviews in Genetic Toxicology 239(2), 133-142.

Mendoza-Novelo, B., González-García, G., Mata-Mata, J.L., Castellano, L.E., Cuéllar-Mata, P., Ávila, E.E., 2013. A biological scaffold filled with silica and simultaneously crosslinked with polyurethane. Materials Letters 106, 369-372.

Mueller, R.-J., 2006. Biological degradation of synthetic polyesters—Enzymes as potential catalysts for polyester recycling. Process Biochemistry 41(10), 2124-2128.

Mukherjee, K., Tribedi, P., Chowdhury, A., Ray, T., Joardar, A., Giri, S., Sil, A.K., 2011. Isolation of a *Pseudomonas aeruginosa* strain from soil that can degrade polyurethane diol. Biodegradation 22(2), 377-388.

Nair, S., Kumar, P., 2007. Molecular characterization of a lipase-producing *Bacillus pumilus* strain (NMSN-1d) utilizing colloidal water-dispersible polyurethane. World Journal of Microbiology and Biotechnology 23(10), 1441-1449.

Nakajima-Kambe, T., Onuma, F., Akutsu, Y., Nakahara, T., 1997. Determination of the polyester polyurethane breakdown products and distribution of the polyurethane degrading enzyme of *Comamonas acidovorans* strain TB-35. Journal of Fermentation and Bioengineering 83(5), 456-460.

1381 Nakajima-Kambe, T., Onuma, F., Kimpara, N., Nakahara, T., 1995. Isolation and characterization
1382 of a bacterium which utilizes polyester polyurethane as a sole carbon and nitrogen source. FEMS
1383 Microbiology Letters 129(1), 39-42.

1384 Ng, W.S., Lee, C.S., Chuah, C.H., Cheng, S.-F., 2017. Preparation and modification of water-blown
1385 porous biodegradable polyurethane foams with palm oil-based polyester polyol. Industrial Crops
1386 and Products 97, 65-78.

1387 Noble, K.-L., 1997. Waterborne polyurethanes. Progress in organic coatings 32(1-4), 131-136.

1388 Nomura, N., Shigeno-Akutsu, Y., Nakajima-Kambe, T., Nakahara, T., 1998. Cloning and sequence
1389 analysis of a polyurethane esterase of *Comamonas acidovorans* TB-35. Journal of Fermentation
1390 and Bioengineering 86(4), 339-345.

1391 Oceguera-Cervantes, A., Carrillo-Garcia, A., Lopez, N., Bolanos-Nunez, S., Cruz-Gomez, M.J.,
1392 Wacher, C., Loza-Tavera, H., 2007. Characterization of the polyurethanolytic activity of two
1393 *Alicycliphilus sp.* strains able to degrade polyurethane and N-methylpyrrolidone. Applied and
1394 Environmental Microbiology 73(19), 6214-6223.

1395 Oprea, S., 2010. Dependence of fungal biodegradation of PEG/castor oil-based polyurethane
1396 elastomers on the hard-segment structure. Polymer Degradation and Stability 95(12), 2396-2404.

1397 Oprea, S., Doroftei, F., 2011. Biodegradation of polyurethane acrylate with acrylated epoxidized
1398 soybean oil blend elastomers by *Chaetomium globosum*. International Biodeterioration &
1399 Biodegradation 65(3), 533-538.

1400 Oprea, S., Potolinca, V.O., Gradinariu, P., Joga, A., Oprea, V., 2016. Synthesis, properties, and
1401 fungal degradation of castor-oil-based polyurethane composites with different cellulose
1402 contents. Cellulose 23(4), 2515-2526.

1403 Oprea, S., Potolinca, V.O., Gradinariu, P., Oprea, V., 2018. Biodegradation of pyridine-based
1404 polyether polyurethanes by the *Alternaria tenuissima* fungus. Journal of Applied Polymer Science
1405 135(14), 46096.

1406 Osman, M., Satti, S.M., Luqman, A., Hasan, F., Shah, Z., Shah, A.A., 2018. Degradation of Polyester
1407 Polyurethane by *Aspergillus sp.* Strain S45 Isolated from Soil. Journal of Polymers and the
1408 Environment 26(1), 301-310.

1409 Owen, S., Otani, T., Masaoka, S., Ohe, T., 1996. The Biodegradation of Low-molecular-weight
1410 Urethane Compounds by a Strain of *Exophiala jeanselmei*. Biosci Biotechnol Biochem 60(2), 244-
1411 248.

1412 Ozaki, S., 1972. Recent advances in isocyanate chemistry. Chemical Reviews 72(5), 457-496.

1413 Ozsagiroglu, E., Iyisan, B., Guvenilir, Y.A., 2012. Biodegradation and characterization studies of
1414 different kinds of polyurethanes with several enzyme solutions. Polish Journal of Environmental
1415 Studies 21(6), 1777-1782.

Paabo, M., Levin, B.C., 1987. A review of the literature on the gaseous products and toxicity generated from the pyrolysis and combustion of rigid polyurethane foams. Fire and Materials 11(1), 1-29.

Pastorino, L., Pioli, F., Zilli, M., Converti, A., Nicolini, C., 2004. Lipase-catalyzed degradation of poly(ε-caprolactone). Enzyme and Microbial Technology 35(4), 321-326.

Pavlova, M., Draganova, M., 1993. Biocompatible and biodegradable polyurethane polymers. Biomaterials 14(13), 1024-1029.

Peng, Y.-H., Shih, Y.-h., Lai, Y.-C., Liu, Y.-Z., Liu, Y.-T., Lin, N.-C., 2014. Degradation of polyurethane by bacterium isolated from soil and assessment of polyurethanolytic activity of a *Pseudomonas putida* strain. Environmental Science and Pollution Research 21(16), 9529-9537.

Pereira, A., Santos, M.C.M., Costa, V., Pianetti, G.A., Da Silva, G., 2012. Development and validation of a high performance liquid chromatographic method for determination of triamcinolone acetonide from polyurethane intraocular implants. Int J Pharm Pharm Sci 4(4), 132-136.

Pérez-Lara, L.F., Vargas-Suárez, M., López-Castillo, N.N., Cruz-Gómez, M.J., Loza-Tavera, H., 2016. Preliminary study on the biodegradation of adipate/phthalate polyester polyurethanes of commercial-type by *Alicycliphilus sp.* BQ8. Journal of Applied Polymer Science 133(6), n/a-n/a.

Philip, S., Keshavarz, T., Roy, I., 2007. Polyhydroxyalkanoates: biodegradable polymers with a range of applications. Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology 82(3), 233-247.

Phua, S., Castillo, E., Anderson, J., Hiltner, A., 1987. Biodegradation of a polyurethane in vitro. Journal of Biomedical Materials Research Part A 21(2), 231-246.

Pilch-Pitera, B., 2012. Examination of the Enzyme Resistance of Polyurethane Powder Coatings. Journal of Polymers and the Environment 21(1), 215-223.

Pillai, P.K.S., Li, S., Bouzidi, L., Narine, S.S., 2016. Metathesized palm oil polyol for the preparation of improved bio-based rigid and flexible polyurethane foams. Industrial Crops and Products 83, 568-576.

PlasticsEurope, 2017. Plastics – the Facts 2017: An analysis of European plastics production, demand and waste data.

Prieto, A., 2016. To be, or not to be biodegradable... that is the question for the bio-based plastics. Microbial Biotechnology 9(5), 652-657.

Rafiemanzelat, F., Fathollahi Zonouz, A., Emtiazi, G., 2013. Synthesis of new poly(ether-urethane-urea)s based on amino acid cyclopeptide and PEG: study of their environmental degradation. Amino Acids 44(2), 449-459.

Rafiemanzelat, F., Jafari, M., Emtiazi, G., 2015. Study of Biological Degradation of New Poly(Ether-Urethane-Urea)s Containing Cyclopeptide Moiety and PEG by *Bacillus amyloliquefaciens* Isolated from Soil. Appl Biochem Biotechnol 177(4), 842-860.

Ratner, B., Gladhill, K., Horbett, T., 1988. Analysis of in vitro enzymatic and oxidative degradation of polyurethanes. Journal of Biomedical Materials Research 22(6), 509-527.

Rattanapan, S., Pasetto, P., Pilard, J.-F., Tanrattanakul, V., 2016. Preparation and properties of bio-based polyurethane foams from natural rubber and polycaprolactone diol. Journal of Polymer Research 23(9).

Reddy, M.S., Shaik, B., Adimurthy, S., Ramachandraiah, G., 2006. Description of the small plastics fragments in marine sediments along the Alang-Sosiya ship-breaking yard, India. Estuarine, Coastal and Shelf Science 68(3-4), 656-660.

Ribitsch, D., Yebra, A.O., Zitzenbacher, S., Wu, J., Nowitsch, S., Steinkellner, G., Greimel, K., Doliska, A., Oberdorfer, G., Gruber, C.C., Gruber, K., Schwab, H., Stana-Kleinschek, K., Acero, E.H., Guebitz, G.M., 2013. Fusion of binding domains to Thermobifida cellulosilytica cutinase to tune sorption characteristics and enhancing PET hydrolysis. Biomacromolecules 14(6), 1769-1776.

Rowe, L., Howard, G.T., 2002. Growth of *Bacillus subtilis* on polyurethane and the purification and characterization of a polyurethanase-lipase enzyme. International Biodeterioration & Biodegradation 50(1), 33-40.

Ruiz, C., Howard, G.T., 1999. Nucleotide sequencing of a polyurethanase gene (pulA) from *Pseudomonas fluorescens*. International Biodeterioration & Biodegradation 44(2-3), 127-131.

Ruiz, C., Main, T., Hilliard, N.P., Howard, G.T., 1999. Purification and characterization of two polyurethanase enzymes from *Pseudomonas chlororaphis*. International Biodeterioration & Biodegradation 43(1-2), 43-47.

Russell, J.R., Huang, J., Anand, P., Kucera, K., Sandoval, A.G., Dantzler, K.W., Hickman, D., Jee, J., Kimovec, F.M., Koppstein, D., Marks, D.H., Mittermiller, P.A., Nunez, S.J., Santiago, M., Townes, M.A., Vishnevetsky, M., Williams, N.E., Vargas, M.P., Boulanger, L.A., Bascom-Slack, C., Strobel, S.A., 2011. Biodegradation of polyester polyurethane by endophytic fungi. Applied and Environmental Microbiology 77(17), 6076-6084.

Sabbioni, G., Dongari, N., Schneider, S., Kumar, A., 2012. Synthetic approaches to obtain amino acid adducts of 4,4'-methylenediphenyl diisocyanate. Chemical Research in Toxicology 25(12), 2704-2714.

Santerre, J., Labow, R., Adams, G., 1993. Enzyme–biomaterial interactions: effect of biosystems on degradation of polyurethanes. Journal of Biomedical Materials Research Part A 27(1), 97-109.

Santerre, J., Labow, R., Duguay, D., Erfle, D., Adams, G., 1994. Biodegradation evaluation of polyether and polyester-urethanes with oxidative and hydrolytic enzymes. Journal of Biomedical Materials Research Part A 28(10), 1187-1199.

Sarkar, D., Lopina, S.T., 2007. Oxidative and enzymatic degradations of l-tyrosine based polyurethanes. Polymer Degradation and Stability 92(11), 1994-2004.

Schmidt, C., Krauth, T., Wagner, S., 2017. Export of plastic debris by rivers into the sea. Environmental Science & Technology 51(21), 12246-12253.

Schmidt, J., Wei, R., Oeser, T., Dedavid e Silva, L., Breite, D., Schulze, A., Zimmermann, W., 2017. Degradation of Polyester Polyurethane by Bacterial Polyester Hydrolases. Polymers 9(12), 65.

Schöne, A.-C., Kratz, K., Schulz, B., Lendlein, A., 2016. Polymer architecture versus chemical structure as adjusting tools for the enzymatic degradation of oligo(ε-caprolactone) based films at the air-water interface. Polymer Degradation and Stability 131, 114-121.

Seal, K.J., Pantke, M., 1988. Microbiological testing of plastics: ongoing activities of IBRG plastics project group to improve standard test procedures. International Biodeterioration 24(4-5), 313-320.

Shah, A.A., Hasan, F., Akhter, J.I., Hameed, A., Ahmed, S., 2008a. Degradation of polyurethane by novel bacterial consortium isolated from soil. Annals of Microbiology 58(3), 381.

Shah, A.A., Hasan, F., Hameed, A., Ahmed, S., 2008b. Biological degradation of plastics: a comprehensive review. Biotechnology Advances 26(3), 246-265.

Shah, Z., Gulzar, M., Hasan, F., Shah, A.A., 2016. Degradation of polyester polyurethane by an indigenously developed consortium of *Pseudomonas* and *Bacillus* species isolated from soil. Polymer Degradation and Stability 134, 349-356.

Shah, Z., Hasan, F., Krumholz, L., Aktas, D.F., Shah, A.A., 2013a. Degradation of polyester polyurethane by newly isolated *Pseudomonas aeruginosa* strain MZA-85 and analysis of degradation products by GC–MS. International Biodeterioration & Biodegradation 77, 114-122.

Shah, Z., Krumholz, L., Aktas, D.F., Hasan, F., Khattak, M., Shah, A.A., 2013b. Degradation of polyester polyurethane by a newly isolated soil bacterium, *Bacillus subtilis* strain MZA-75. Biodegradation 24(6), 865-877.

Shuttleworth, K.L., Cerniglia, E., 1995. Environmental aspects of PAH biodegradation. Applied Biochemistry and Biotechnology 54(1-3), 291-302.

Shuttleworth, W.A., Seal, K.J., 1986. A rapid technique for evaluating the biodeterioration potential of polyurethane elastomers. Applied Microbiology and Biotechnology 23(5), 407-409.

Simon, D., Borreguero, A.M., de Lucas, A., Rodriguez, J.F., 2018. Recycling of polyurethanes from laboratory to industry, a journey towards the sustainability. Waste Management 76, 147-171.

Simón, D., de Lucas, A., Rodríguez, J.F., Borreguero, A.M., 2016. Glycolysis of high resilience flexible polyurethane foams containing polyurethane dispersion polyol. Polymer Degradation and Stability 133, 119-130.

Simón, D., García, M.T., de Lucas, A., Borreguero, A.M., Rodríguez, J.F., 2013. Glycolysis of flexible polyurethane wastes using stannous octoate as the catalyst: Study on the influence of reaction parameters. Polymer Degradation and Stability 98(1), 144-149.

Sivan, A., 2011. New perspectives in plastic biodegradation. Curr Opin Biotechnol 22(3), 422-426.

Skarping, G., Dalene, M., Mathiasson, L., 1988. Trace analysis of airborne 1, 6-hexamethylenediisocyanate and the related aminoisocyanate and diamine by glass capillary gas chromatography. Journal of Chromatography A 435, 453-468.

Smith, R., Williams, D., Oliver, C., 1987. The biodegradation of poly (ether urethanes). Journal of Biomedical Materials Research Part A 21(9), 1149-1165.

Špírková, M., Hodan, J., Kobera, L., Kredatusová, J., Kubies, D., Machová, L., Poręba, R., Serkis, M., Zhigunov, A., Kotek, J., 2017. The influence of the length of the degradable segment on the functional properties and hydrolytic stability of multi-component polyurethane elastomeric films. Polymer Degradation and Stability 137, 216-228.

Spontón, M., Casis, N., Mazo, P., Raud, B., Simonetta, A., Ríos, L., Estenoz, D., 2013. Biodegradation study by *Pseudomonas sp.* of flexible polyurethane foams derived from castor oil. International Biodeterioration & Biodegradation 85, 85-94.

Stern, R.V., Howard, G.T., 2000. The polyester polyurethanase gene (pueA) from *Pseudomonas chlororaphis* encodes a lipase. FEMS Microbiology Letters 185(2), 163-168.

Tajau, R., Salleh, M.Z., Salleh, N.G.N., Abdurahman, M.N., Salih, A.M., Fathy, S.F., Azman, A.A., Hamidi, N.A., 2016. Soil burial biodegradation studies of palm oil-based UV-curable films, AIP Conference Proceedings. AIP Publishing, p. 040008.

Takamoto, T., Shirasaka, H., Uyama, H., Kobayashi, S., 2001. Lipase-catalyzed hydrolytic degradation of polyurethane in organic solvent. Chemistry Letters 30(6), 492-493.

Tang, Y., Labow, R., Santerre, J., 2001a. Enzyme-induced biodegradation of polycarbonate-polyurethanes: Dependence on hard-segment chemistry. Journal of Biomedical Materials Research Part A 57(4), 597-611.

Tang, Y., Labow, R., Santerre, J., 2001b. Enzyme-induced biodegradation of polycarbonate polyurethanes: Dependence on hard-segment concentration. Journal of Biomedical Materials Research Part A 56(4), 516-528.

Tang, Y., Labow, R.S., Santerre, J.P., 2003. Isolation of methylene dianiline and aqueous-soluble biodegradation products from polycarbonate-polyurethanes. Biomaterials 24(17), 2805-2819.

Tang, Y., Santerre, J., Labow, R., Taylor, D., 1997. Application of macromolecular additives to reduce the hydrolytic degradation of polyurethanes by lysosomal enzymes. Biomaterials 18(1), 37-45.

Thirunavukarasu, K., Purushothaman, S., Gowthaman, M.K., Nakajima-Kambe, T., Rose, C., Kamini, N.R., 2015. Utilization of fish meal and fish oil for production of *Cryptococcus sp.* MTCC 5455 lipase and hydrolysis of polyurethane thereof. Journal of Food Science and Technology 52(9), 5772-5780.

Tokiwa, Y., Suzuki, T., Takeda, K., 1988. Two types of lipases in hydrolysis of polyester. Agricultural and Biological Chemistry 52(8), 1937-1943.

Trovati, G., Sanches, E.A., Neto, S.C., Mascarenhas, Y.P., Chierice, G.O., 2010. Characterization of polyurethane resins by FTIR, TGA, and XRD. Journal of Applied Polymer Science 115(1), 263-268.

Tsoi, R., Dai, Z., You, L., 2019. Emerging strategies for engineering microbial communities. Biotechnology advances.

Turner, A., Lau, K.S., 2016. Elemental concentrations and bioaccessibilities in beached plastic foam litter, with particular reference to lead in polyurethane. Marine Pollution Bulletin 112(1-2), 265-270.

Ufarte, L., Laville, E., Duquesne, S., Morgavi, D., Robe, P., Klopp, C., Rizzo, A., Pizzut-Serin, S., Potocki-Veronese, G., 2017. Discovery of carbamate degrading enzymes by functional metagenomics. PLoS One 12(12), e0189201.

Umare, S.S., Chandure, A.S., 2008. Synthesis, characterization and biodegradation studies of poly(ester urethane)s. Chemical Engineering Journal 142(1), 65-77.

Urgun-Demirtas, M., Singh, D., Pagilla, K., 2007. Laboratory investigation of biodegradability of a polyurethane foam under anaerobic conditions. Polymer Degradation and Stability 92(8), 1599-1610.

Vaclavkova, T., Ruzicka, J., Julinova, M., Vicha, R., Koutny, M., 2007. Novel aspects of symbiotic (polyvinyl alcohol) biodegradation. Applied microbiology and biotechnology 76(4), 911.

Valerio, F., 2010. Environmental impacts of post-consumer material managements: recycling, biological treatments, incineration. Waste Management 30(11), 2354-2361.

Vega, R.E., Main, T., Howard, G.T., 1999. Cloning and expression in Escherichia coli of apolyurethane-degrading enzyme from *Pseudomonas fluorescens*. International Biodeterioration & Biodegradation 43(1-2), 49-55.

Wang, F., Zheng, Z., Wang, W., Gu, Z., Wang, J., Wang, X., 2014. Trypsin-inspired poly (urea-urethane) s containing phenylalanine-lysine ethyl ester-phenylalanine units. Polymer Degradation and Stability 100, 86-92.

Wang, G., Labow, R., Santerre, J., 1997a. Biodegradation of a poly (ester) urea-urethane by cholesterol esterase: Isolation and identification of principal biodegradation products. Journal of Biomedical Materials Research: An Official Journal of The Society for Biomaterials and The Japanese Society for Biomaterials 36(3), 407-417.

Wang, G., Santerre, J., Labow, R., 1997b. High-performance liquid chromatographic separation and tandem mass spectrometric identification of breakdown products associated with the biological hydrolysis of a biomedical polyurethane. Journal of Chromatography B: Biomedical Sciences and Applications 698(1-2), 69-80.

Wang, X., Chen, H., Chen, C., Li, H., 2011. Chemical degradation of thermoplastic polyurethane for recycling polyether polyol. Fibers and Polymers 12(7), 857-863.

Watanabe, K., 2001. Microorganisms relevant to bioremediation. Current Opinion in Biotechnology 12(3), 237-241.

Wei, R., Oeser, T., Schmidt, J., Meier, R., Barth, M., Then, J., Zimmermann, W., 2016. Engineered bacterial polyester hydrolases efficiently degrade polyethylene terephthalate due to relieved product inhibition. Biotechnol Bioeng 113(8), 1658-1665.

Wei, R., Zimmermann, W., 2017. Microbial enzymes for the recycling of recalcitrant petroleum-based plastics: how far are we? Microbial Biotechnology 10(6), 1308-1322.

Wierckx, N., Narancic, T., Eberlein, C., Wei, R., Drzyzga, O., Magnin, A., Ballerstedt, H., Kenny, S.T., Pollet, E., Avérous, L., 2018. Plastic Biodegradation: Challenges and Opportunities, Consequences of Microbial Interactions with Hydrocarbons, Oils, and Lipids: Biodegradation and Bioremediation. Springer, pp. 1-29.

Wierckx, N., Prieto, M.A., Pomposiello, P., de Lorenzo, V., O'Connor, K., Blank, L.M., 2015. Plastic waste as a novel substrate for industrial biotechnology. Microbial Biotechnology 8(6), 900-903.

Wiggins, M.J., Anderson, J.M., Hiltner, A., 2003. Biodegradation of polyurethane under fatigue loading. Journal of Biomedical Materials Research Part A 65(4), 524-535.

Woo, G., Mittelman, M., Santerre, J., 2000. Synthesis and characterization of a novel biodegradable antimicrobial polymer. Biomaterials 21(12), 1235-1246.

Wu, Y., Wang, L., Guo, B., Shao, Y., Ma, P.X., 2016. Electroactive biodegradable polyurethane significantly enhanced Schwann cells myelin gene expression and neurotrophin secretion for peripheral nerve tissue engineering. Biomaterials 87, 18-31.

Xu, W., Ma, C., Ma, J., Gan, T., Zhang, G., 2014. Marine biofouling resistance of polyurethane with biodegradation and hydrolyzation. ACS applied materials & interfaces 6(6), 4017-4024.

Yamamoto, N., Nakayama, A., Oshima, M., Kawasaki, N., Aiba, S.-i., 2007. Enzymatic hydrolysis of lysine diisocyanate based polyurethanes and segmented polyurethane ureas by various proteases. Reactive and Functional Polymers 67(11), 1338-1345.

Yang, S., Xu, H., Yan, Q., Liu, Y., Zhou, P., Jiang, Z., 2013. A low molecular mass cutinase of *Thielavia terrestris* efficiently hydrolyzes poly(esters). Journal of Industrial Microbiology & Biotechnology 40(2), 217-226.

Yeganeh, H., Hojati-Talemi, P., 2007. Preparation and properties of novel biodegradable polyurethane networks based on castor oil and poly(ethylene glycol). Polymer Degradation and Stability 92(3), 480-489.

Zafar, U., Houlden, A., Robson, G.D., 2013. Fungal communities associated with the biodegradation of polyester polyurethane buried under compost at different temperatures. Applied and Environmental Microbiology 79(23), 7313-7324.

Zeng, S.H., Duan, P.P., Shen, M.X., Xue, Y.J., Wang, Z.Y., 2016. Preparation and degradation mechanisms of biodegradable polymer: a review. IOP Conference Series: Materials Science and Engineering 137, 012003.

Zhang, Y., Asif, A., Shi, W., 2011. Highly branched polyurethane acrylates and their waterborne UV curing coating. Progress in Organic Coatings 71(3), 295-301.

Zhang, Y., Fu, Y., Zhou, S., Kang, L., Li, C., 2013. A straightforward ninhydrin-based method for collagenase activity and inhibitor screening of collagenase using spectrophotometry. Analytical Biochemistry 437(1), 46-48.

Zhang, Z., King, M., Guidoin, R., Therrien, M., Doillon, C., Diehl-Jones, W.L., Huebner, E., 1994. In vitro exposure of a novel polyesterurethane graft to enzymes: A study of the biostability of the Vascugraft® arterial prosthesis. Biomaterials 15(14), 1129-1144.

Zhao, Q., Marchant, R., Anderson, J., Hiltner, A., 1987. Long term biodegradation in vitro of poly (ether urethane urea): a mechanical property study. Polymer 28(12), 2040-2046.

Zheng, Y., Yanful, E.K., Bassi, A.S., 2005. A review of plastic waste biodegradation. Critical Reviews in Biotechnology 25(4), 243-250.

Zhou, L., Liang, D., He, X., Li, J., Tan, H., Li, J., Fu, Q., Gu, Q., 2012. The degradation and biocompatibility of pH-sensitive biodegradable polyurethanes for intracellular multifunctional antitumor drug delivery. Biomaterials 33(9), 2734-2745.

Zhou, X.-M., Xie, W.-J., 2017. Synthesis and characterization of poly(ester ether urethane)s block copolymers based on biodegradable poly(butylene succinate) and Poly(ethylene glycol). Polymer Degradation and Stability 140, 147-155.

Zia, K.M., Bhatti, H.N., Ahmad Bhatti, I., 2007. Methods for polyurethane and polyurethane composites, recycling and recovery: A review. Reactive and Functional Polymers 67(8), 675-692.

Zicht, T.J., 2017. Detection and Analysis of Polyurethane Biodegradation due to *Cryptococcus laurentii*. Wright State University.