Microbial Degradation of Marine Plastics: Current State and Future Prospects

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Abstract

Millions of tons of plastics entering the sea each year are a substantial environmental problem. It is expected that ocean plastic pollution will increase when considering the rapidly rising rates in global plastic production, in contrast to the relatively slow growth in plastic recycling rates, and future projections of increasing population densities in coastal areas. However, a significant discrepancy exists between the vast quantities of plastic entering the ocean and the orders of magnitude lower amounts afloat at the sea surface, indicating a substantial sink for ocean plastics. Plastics are probably degraded in a multi-step process facilitated by abiotic and biotic factors. Abiotic factors, such as shear stress

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induced by wave action, solar ultraviolet radiation, and heat embrittle and fragment plastics. Fragmentation of macroplastics results in micro and nanoscale particles. Photooxidation causes the release of chain scission products from the polymer matrix, e.g., nanoplastics, low-molecular-weight polymer fragments, and hydrocarbon gases. Biodegradation of plastics is mediated by microbes that have enzymes capable of inducing (1) chain scission and depolymerization, and (2) assimilate and terminally oxidize the intermediate products of initial degradation. Plastic degradation products from UV radiation could be a useful carbon source for microbes, while the role of marine microbes as initial degraders is not well understood. Several terrestrial microorganisms (bacteria, fungi) are known to degrade specific plastic polymers. For example, the bacterium *Ideonella sakaiensis* hydrolyses polyethylene terephthalate (PET) with a novel cutinase (termed PETase) and utilizes the degradation products as energy and carbon source. In the marine environment, complex hydrocarbon-degrading bacteria have repetitively been found in association with plastics. These bacteria have genes encoding for monooxygenases, peroxidases, and dehydrogenases, enzymes which can, in principle, facilitate the initial breakdown of plastics. Most commonly applied methods to investigate plastic biodegradation are based on monitoring weight loss of plastic over time, determining chemical changes of the polymer, investigating colonization of plastics by microbes, and measuring CO_2 production rates. However, these evaluation methods often lack rigor in confirming initial depolymerization, assimilation, and mineralization. This chapter provides an overview of plastic biodegradation in the marine realm. Identified and potential microbial plastic degraders will be covered. Their metabolic and enzymatic capabilities will be highlighted with respect to valorization their potential in the future.

Keywords

Plastic pollution · Plastic polymers · Microbial plastic degradation

5.1 Introduction

5.1.1 Plastics: The Marvel and The Global Problem

The term ‘plastics’ is commonly used to refer to a diverse group of chemically synthesized materials, long chains of repetitive monomers that have a unique chemical structure and specific physicochemical characteristics (Cole et al. 2011; Thompson 2015; PlasticsEurope 2019). Plastics can be subdivided into thermoplastics, thermoset plastics and elastomers. Thermoplastics can be remolded upon heating, in contrast to thermoset plastics and elastomers. Thermoplastics are the most abundant plastic types and are the main subject of this chapter.

The invention of plastics dates back to the late nineteenth century when Alexander Parkes synthesized the first plastic, termed ‘Parkesine’ from cellulose (Parkes

1866). In 1907, Leo Baekeland produced one of the first fully synthetic plastic, became ‘Bakelite’ (Baekeland 1909), but only in the mid-twentieth century, plastics were more widely used in many industrial processes (Ryan 2015). The technological advancements and increasing demand for durable and versatile products that were effortless to manufacture at minimal costs created a niche for plastics to take over a role that was traditionally occupied by natural materials such as wood, leather, stone and glass. Nowadays, plastics are an essential part of human lives and even fulfil the needs of short-lived products that became characteristic of our ‘throw-away’ culture. Countless modifications of the virgin polymer structure, co-polymerizations and mixture of additives such as fillers, plasticizers, colourants, stabilizers, flame retardants and reinforcing fibres (among others) have enabled the development of a vast diversity of plastic formulations. These additives affect the properties of the polymer and serve the purpose to tailor polymer characteristics needed for the intended application (Deanin 1975). Polymers are used for packaging, construction and building, the automotive and electronic industry as well as agriculture and fishing, household, sports, warfare or medical applications, among many others (Fig. 5.1). Production of plastics has thus turned into a global multi-billion € business in less than 100 years. Currently, the most produced plastic types are polyethylene (PE), polypropylene (PP), polyvinylchloride (PVC), polyurethane (PU), polyethylene terephthalate (PET), polystyrene (PS) and polyamides (PA) (Fig. 5.2). In addition to conventional plastics of petrochemical origin, biobased plastics, i.e. plastics made from renewable sources such as cellulose, lactic acid, caprolactone, proteins, food waste and starch offer an alternative to conventional plastics. The market share of biobased plastics is rising but still comparably minor with 2.11 million tonnes produced in 2019 (Bioplastics 2019) accounting for about 1% of the global plastic production.

The invention of plastics created an unprecedented turning point in the evolution of humankind. Plastics, initially considered as the marvel of materials, controversially turned into a colossal and growing environmental hazard of the twenty-first century. Plastic production increased exponentially since mass production began in the 1950s. Solely in 2018, nearly 360 million tons were produced worldwide (PlasticsEurope 2019). Out of the world’s plastics production, around 20% was manufactured in Europe and 50% in Asia, with China alone producing 30% (PlasticsEurope 2019). Unfortunately, the enormous increase in plastic production has not been accompanied by efficient waste management strategies in many countries. Since 2006, plastic waste recycling rates have only doubled, and about 25% of plastic post-consumer waste still ended up in landfills (PlasticsEurope 2019). In many tropical countries, plastic with other waste is either directly discarded to the environment or incinerated albeit in non-adequate infrastructures. While the latter prevents plastic debris from entering the environment, it dramatically contributes to other environmental problems because of the released greenhouse gases and probably more importantly, toxic fumes. These can also pose a direct hazard to human health (Wright and Kelly 2017). The prevalent popularity of plastics, in contrast to the failures of post-consumer waste management, makes plastics an indispensable material with a negative reputation—from an environmental point of view.

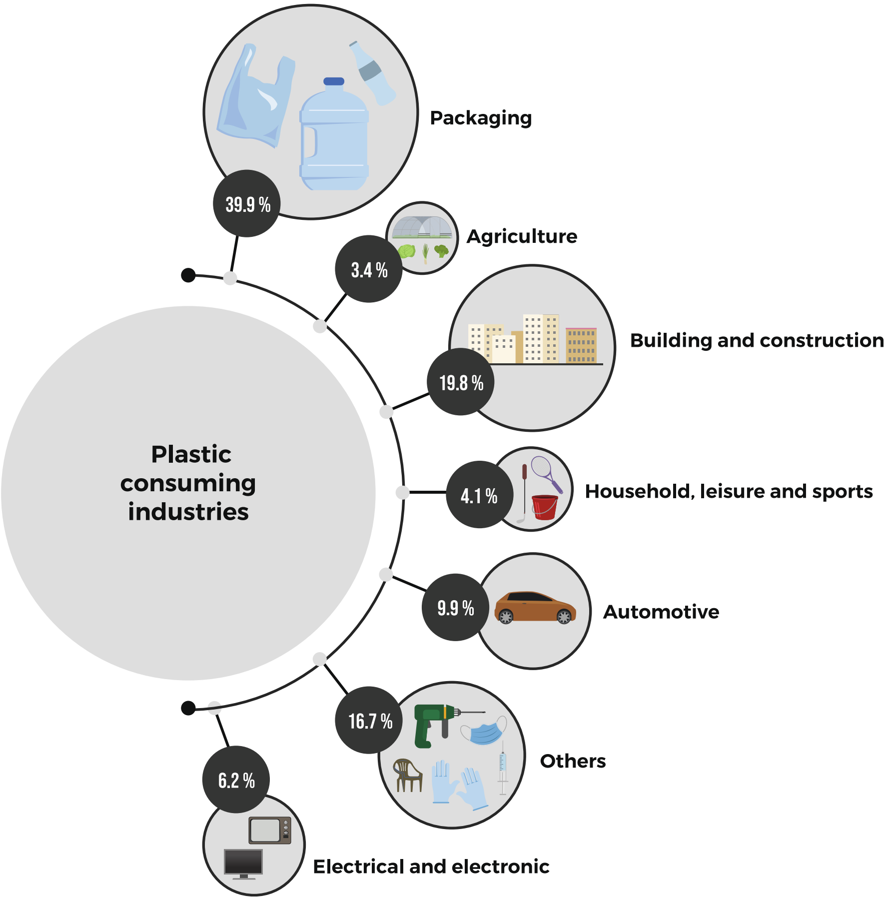
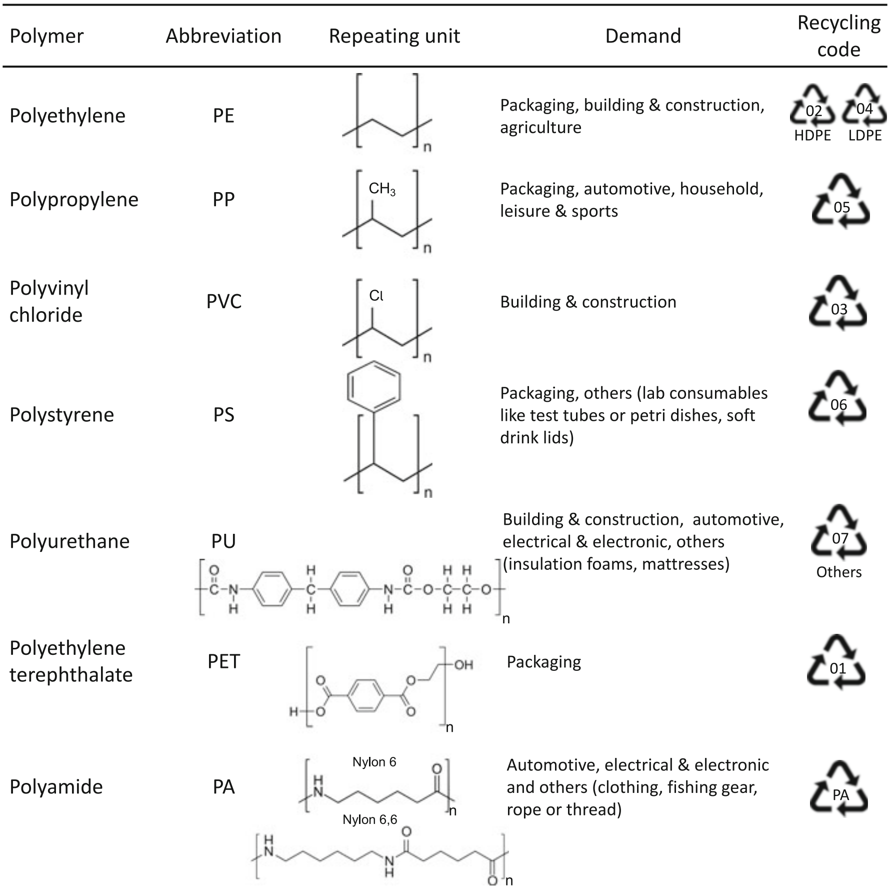


Fig. 5.1 Use of plastics by segments, based on 2018 data of 51.2 millions of tons as input for total European plastics converters demand (PlasticsEurope 2019)

5.2 The Oceans Plastic Problem

Improperly managed plastic waste often gets transported to the ocean (Jambeck et al. 2015; Geyer et al. 2017; Lebreton et al. 2017). First reports of plastic pollution in the marine environment date back to the early 1970s (Heyerdahl 1971; Carpenter et al. 1972; Carpenter and Smith 1972; Cundell 1973), and since about two decades, it has become an even more relevant and intensely investigated research topic. The quantity of plastic released into the marine realm is linked to the quantity of globally produced plastics, but even closer related to the amount of plastic waste generated in coastal areas, and the strategies enforced in those areas to manage plastic waste (Jambeck et al. 2015). For 2010, it has been estimated that the 4.8–12.7 Mt of plastic



Polymer	Abbreviation	Repeating unit	Demand	Recycling code
Polyethylene	PE	n	Packaging, building & construction, agriculture	02 HDPE 04 LDPE
Polypropylene	PP	CH_3 n	Packaging, automotive, household, leisure & sports	05
Polyvinyl chloride	PVC	Cl n	Building & construction	03
Polystyrene	PS	n	Packaging, others (lab consumables like test tubes or petri dishes, soft drink lids)	06
Polyurethane	PU	O C N H H C H N H O C O H C H H C H O n	Building & construction, automotive, electrical & electronic, others (insulation foams, mattresses)	07 Others
Polyethylene terephthalate	PET	OH O O H O O n	Packaging	01
Polyamide	PA	Nylon 6 H N O n Nylon 6,6 H N O N H O n	Automotive, electrical & electronic and others (clothing, fishing gear, rope or thread)	PA

Fig. 5.2 Polymer molecules of plastic reoccurring in marine environments. These can be categorized based on the chemical structure into carbon-carbon backbone based (PE, PP, PS, PVC) or polymers with heteroatoms in the main chain (PET, PC, PA, PUR)

waste generated in that year ended up in the oceans (Jambeck et al. 2015). Partially, plastic waste is transported via rivers, which were found to contribute to 1.15 to 2.41 Mt of plastics to the oceans annually (Lebreton et al. 2017). Catastrophic events, such as hurricanes or floods, can also transport substantial amounts of plastics into the marine environment (Law 2017). Other pathways for plastic entering the oceans include atmospheric transport, beach littering, maritime cargo loss, and loss of commercial fishing gear. By now, no ocean habitat has remained untouched from plastic pollution: plastics were found in as remote areas as Arctic Sea ice (Peeken et al. 2018) and the deep sea (Van Cauwenberghe et al. 2013; Ramirez-Llodra et al. 2014; Peng et al. 2020). Considering the exponentially rising rates of global plastic production in contrast to the relatively slow growth of plastic recycling rates, and considering future projections of increasing population densities in coastal areas, it seems probable that the problem of oceans plastic pollution will increase.

However, in stark contrast to the expected, possibly hundreds of millions of metric tons of plastic debris that should be present in the sea (Jambeck et al. 2015), field measurements and modelling data estimate that 0.09–0.25 Mt (van Sebille et al. 2015) to 0.4–4 Mt (when considering an underestimation of macroplastics in global budgets (Lebreton et al. 2018)) of plastics are afloat in the ocean.

Several theories have been developed to explain the 'missing plastic paradox': (1) polymers, with a higher density than water, are removed by vertical transport to deeper depths/sediments. The overgrowth of floating particles with biofilms (Andrady 2011; Tu et al. 2020; Zhao et al. 2020) as well as the entanglement of plastic particles in marine snow (Porter et al. 2018) increases the density of the initially floating polymer to a point where it sinks. As a result of these biofouling-induced buoyancy changes, the amounts of plastics exported from the surface ocean to deeper water layers or sediment could be substantial. Accumulation of up to 1.9 million (microplastics) particles per m^2 sediment have been measured (Kane et al. 2020). Based on modelling and observations, this removal mechanism could be size-dependent, with smaller particles being less abundant at the surface or removed faster (Cozar et al. 2014; Kooi et al. 2017). However, the number of studies on plastic fallout as well as sedimentation is limited, and abundances of sinking/sedimented plastic detected are variable and in some cases seem even to be insubstantial (Martin et al. 2017; Willis et al. 2017; Barrett et al. 2020; Egger et al. 2020). Besides, vertical transport should not lead to disproportionation of polymer types with PE and PP dominating surface waters and polyesters and PA deeper waters and sediments (Erni-Casola et al. 2019). (2) Estimates of ocean plastic concentrations are often based on observations of floating macroplastics (i.e. plastic pieces >5 mm) or microplastics (i.e. plastic pieces 1μm to 5 mm) typically from surface trawls using nets with a mesh size of typically >300μm. However, a considerable contribution to ocean plastic pollution is attributed to smaller size classes of microplastic and possibly also nano plastics (1–1000 nm). Using nets with a mesh size of 100μm resulted in 2.5-fold and tenfold greater microplastic concentrations than with 333μm and 500μm meshes, respectively (Lindeque et al. 2020). Besides, more plastic is found in samples when improved detection methods and techniques are applied (Anger et al. 2018). (3) Finally, plastics may also be degraded by physicochemical processes, e.g. photooxidation through UV radiation, which leads to the incorporation of oxygen atoms into the polymer as well as chain scission (Gewert et al. 2018). Possibly, microbial degradation of polymers could also constitute a sink for ocean plastic debris as several microbes have been shown to degrade plastics (Yamada-Onodera et al. 2001; Gilan et al. 2004; Sheik et al. 2015; Yoshida et al. 2016; Paço et al. 2017). Nevertheless, ocean plastic degradation and the contribution of the above-mentioned factors to the 'missing plastic paradox' have not been enumerated (Fig. 5.3).

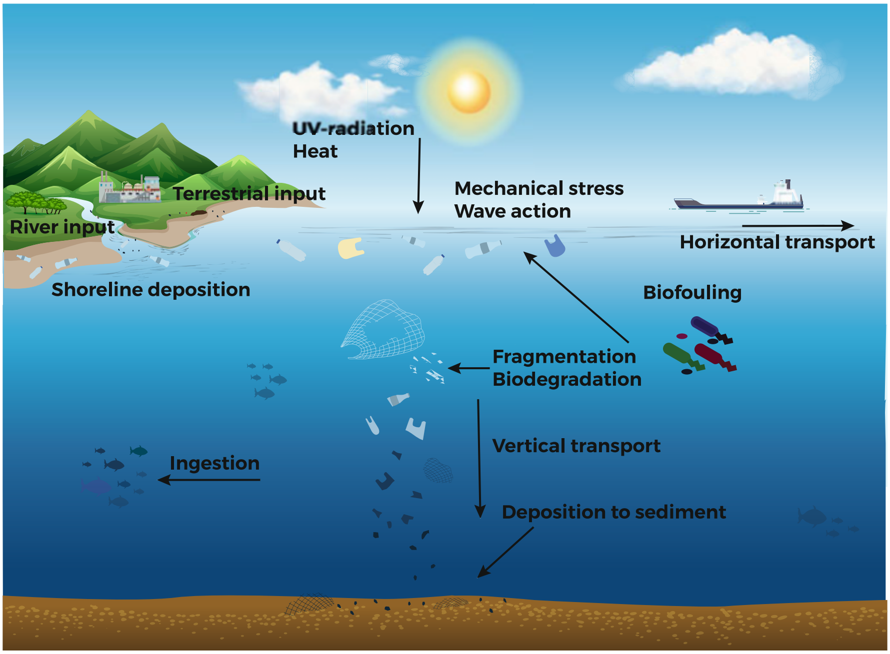


Fig. 5.3 Pathways of plastic input into the ocean and the potential further fate of plastic marine debris

5.2.1 Impacts of Plastic on Marine Life

Plastics in the oceans introduce various problems (Wayman and Niemann 2021). This includes socio-economic losses caused by the visually repulsive littering of shorelines, and physical and biochemical damage inflicted on marine mammals, fish, seabirds and other eukaryotic and possibly prokaryotic life. The effects of plastic interactions with marine life are largely dependent on the characteristics of the debris, for example size, shape, type and concentration of additives added to the basic polymer (Law 2017). First scientific records of plastics being ingested by marine fauna date back to the late 1960s, when gastrointestinal tracts of Laysan albatrosses *Phoebastria immutabilis* were inspected for plastic items in their body cavities (Kenyon and Kridler 1969). Later, regurgitation of plastics from adult specimens to chicks of Laysan albatrosses, causing intestinal obstruction and ulcerations in the gastrointestinal tract, was reported (Pettit et al. 1981). Marine animals can get entangled in ghost fishing gear or ingest plastic debris (Croxall et al. 1990; Cadée 2002; Gregory 2009; de Stephanis et al. 2013; Schuyler et al. 2014; Thiel et al. 2018). Ingestion of plastic leads to nutritional deficiencies and reduction of energy budgets in marine biota (Van Cauwenberghe et al. 2015; Watts et al. 2015). Dolphins (Hernandez-Gonzalez et al. 2018), other whales and turtles (Mascarenhas et al. 2004; Campani et al. 2013; Clukey et al. 2018), seals (Bravo

Rebolledo et al. 2013), various fish species (Boerger et al. 2010; Bucol et al. 2020), squids (Braid et al. 2012) and jellyfish (Iliff et al. 2020), among others, have ingested plastic either directly or possibly via trophic transfer. Furthermore, it has been proposed that smaller plastic particles are more detrimental to many organisms (Koelmans et al. 2015), which makes fragmentation and degradation of larger plastics into smaller micro and nanometre-sized plastics as well as the immediate release of such plastic size classes to the marine environment particularly problematic (Mattsson et al. 2017). Small microplastic particles and nanoplastics were enriched in filter feeders (von Moos et al. 2012; Van Cauwenberghe et al. 2015). Nanoplastics can be transferred in the food chain from algae through zooplankton to fish where these may cross the blood–brain barrier and cause behavioural disorders (Mattsson et al. 2017).

Plastics often contain chemical additives such as plasticizers, for enhancing polymer properties (Hahladakis et al. 2018). Some of these components act as endocrine disruptors, even at extremely low concentrations (Gallo et al. 2018; Galgani et al. 2019). Plastic additives can leach into the water, with the potential to contaminate soils, groundwater, rivers and the marine environment. Phthalates get released from PE bags and PVC cables, exposed to seawater (Paluselli et al. 2019). Polymers are lipophilic and absorb persistent organic pollutants (POP) to their surface where these compounds may become concentrated by a factor of 10^6 compared to the surrounding seawater (Mato et al. 2001). PE and PP, for example, were found to absorb higher amounts of polyaromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) in comparison to PVC and PET (Rochman et al. 2013). As a result of microplastic ingestion in worms and mussels, bioaccumulation of PAHs occurs, and adverse effects were reported (Browne et al. 2013; Avio et al. 2015). In addition, plastics can accumulate heavy metals (Holmes et al. 2012; Rochman et al. 2014), which, if released, can cause a diversity of toxic effects. PVC and PP particles absorbed more cadmium and lead than PE, PA and particulate organic matter (Gao et al. 2019). Micro-and nanoplastics have a high surface to volume ratio and, thus, can absorb relatively high amounts of hydrophobic contaminants. These plastic size classes are readily ingested by many organisms where the contaminants may be rereleased. However, the end effect depends on microplastic particle concentration in nature, the chemical equilibrium between water and plastics, species and microniches, such as gut systems (Diepens and Koelmans 2018; Menéndez-Pedriza and Jaumot 2020). Although plastics function as a potential transport vector for harmful compounds, it remains challenging to quantify the amounts released into biota, accumulation in the marine food web and their contribution in nature. In particular, if the same toxic compounds are present in the food, surrounding water and sediment, these may be incorporated from these compartments, too (Ziccardi et al. 2016).

5.3 Plastic Degradation

Plastics are typically designed for durability, which makes them a valuable material. However, the chemical structure of the primary polymer and admixture of additives make plastics rather resistant to degradation in the environment where they persist for elongated periods of time. This poses critical questions: How do plastics degrade? What is the contribution of abiotic and biotic factors? What is the rate of this process? What is the identity of degradation products? Plastic degradation is considered a process resulting in changes of polymer properties due to chemical, physical or biological forcing factors (Singh and Sharma 2008). It is generally believed that recalcitrant plastics are not biodegradable and can persist from 10 years to hundreds or perhaps even thousands of years in nature, to the extent of being the marker of 'Anthropocene' in the geological record (Corcoran et al. 2014; Zalasiewicz et al. 2016; Geyer et al. 2017; Joly and Coulis 2018; Krause et al. 2020). However, this argument is not substantially founded because hardly any data exists on the kinetics of plastic degradation in the marine realm, neither physicochemical nor biological. Laboratory simulations revealed HDPE to be more resistant to fragmentation when exposed to seawater in comparison to samples on beach sand in 6-month experiments (Kalogerakis et al. 2017). It thus seems that ocean plastic degradation might be slower than terrestrial plastic degradation, where higher rates of solar radiation and higher temperatures facilitate enhanced breakdown of plastics (Andrady and Neal 2009).

5.3.1 Abiotic Factors Influencing the Degradation of Plastic

In the marine environment, plastic fragments into smaller particles due to mechanical shear stress imposed by e.g. wave action, causing collision and embrittlement of the polymer structure (Barnes et al. 2009). In addition, fragmentation is accelerated by the weathering process (most notably, photooxidation, see below), which breaks chemical bonds, allowing oxygen incorporation into the chemical structure (Kalogerakis et al. 2017; Gewert et al. 2015; Wayman and Niemann 2021). Fragmentation of macroplastics results in large fragments as well as particles on the milli-, micro- and nanometre scale. In the ocean, small microplastic particles dominate in abundance, while nanoplastics have only been detected recently (Ter Halle et al. 2017), and their abundance and distribution in marine systems are unknown.

Plastic degradation is facilitated by UV radiation, causing photooxidation. Photooxidation is a multi-step process, resulting in changes in the chemical structure as well as in the physical appearance of the polymer. UV radiation causes chemical bonds to break, and the formation of free radicals, which may react further with the polymer. This chain reaction proceeds until stable products have been formed and typically involves incorporating oxygen in the carbon backbone. Moreover, UV-induced photooxidation causes the release of chain scission products from the polymer matrix, e.g. low-molecular-weight polymer fragments with carboxyl groups (Gewert et al. 2018), and hydrocarbon gases such as methane, ethylene, ethane and propylene (Royer et al. 2018). Nanoparticle formation due to UV irradiation has been reported from PS (Lambert and Wagner 2016). Furthermore, UV exposure causes dissolved organic carbon to leach from the plastics (Zhu et al. 2020; Romera-Castillo et al. 2018). Extrapolation to the global scale revealed that 23,600 metric tons of DOC might leach annually to the marine environment (Romera-Castillo et al. 2018). Due to variations in chemical structure, polymers react to mechanical and oxidative stress differently, with PE having higher dissociation energy in comparison to PP (Gewert et al. 2015; Min et al. 2020). PE is characterized as more susceptible for oxidative stress, possibly due to additives it contains, as heavily oxidized patches have been observed on otherwise intact plastics (Cooper and Corcoran 2010). The number of factors affecting the fate of plastics in natural environments can be considered 'unlimited', as the environment and the polymer itself can vary. Besides UV exposure, variables such as temperature, mechanical forces (wave action, wind), visible light and, potentially, microbial growth (Gu 2003; Artham et al. 2009; Gewert et al. 2015; Klein et al. 2018; Pickett 2018; Min et al. 2020) may affect the further fate of plastic in the environment.

5.3.2 The Potential for Microbially Mediated Plastic Degradation

Biodegradation is a biologically mediated process, whereby organisms convert complex compounds into simpler and smaller molecules or environmentally less hazardous ones.

In the marine environment, organic matter is both aerobic and anaerobically degraded by microbes. Aerobic biodegradation occurs at the sea surface, in the water column or oxic layers of sediments, while anaerobic biodegradation proceeds in deeper sediments or other anoxic (micro)niches. Aerobic biodegradation requires oxygen as an electron acceptor and commonly results in the production of the terminal oxidation end product CO_2. Anaerobic degradation processes, on the other hand, utilize alternative electron acceptors and may oxidize, reduce or disproportionate the organic matter substrate, yielding CO_2 and/or CH_4. Polymer biodegradation involves depolymerization, yielding oligomers and/or monomers and probably further degradation of such reaction intermediates to fuel catabolic and anabolic processes. Biodegradation may be incomplete, which is often referred to as 'biodeterioration' (which may also occur due to the combination of biotic and abiotic processes). However, both biodegradation and biodeterioration result in the loss of structural integrity of the polymer, which supports fragmentation and eventual breakdown.

Microorganisms can degrade, transform, convert and accumulate a wide variety of organic compounds. Polymers of biological origin such as chitin, cellulose, polyhydroxybutyrate and pullulan, for example, undergo rapid and complete mineralization in nature. Microbes and microbial consortia can also degrade complex hydrocarbons, such as petroleum and polycyclic aromatic hydrocarbons (Yakimov et al. 1998; Huy et al. 1999; McKew et al. 2007; Zhao et al. 2008; Zhou et al. 2008; Joutey et al. 2013; Kim et al. 2015), which chemically resemble some polyolefin-type plastics. In principle, plastic polymers could thus be potential substrates for microorganisms (Wayman and Niemann 2021). However, plastics are synthetic and, on an evolutionary time scale, a new substrate for microorganisms. Even though plastics hold chemical energy, it is unclear to which extent microbes can make use of these. Plastic polymers are structurally large and complex molecules. Microorganisms have developed strategies to break down large molecules extracellularly, which also appears to be the case for some plastics. The organisms secrete exoenzymes, which act on the plastic surface, releasing smaller scission products. These smaller molecules may then be degraded further extracellularly or taken up into the cells (see Sect. 5.5 for details).

Several microorganisms depolymerize/degrade specific plastics, for example *Rhodococcus ruber* (Gilan et al. 2004; Sivan et al. 2006; Mor and Sivan 2008; Yang et al. 2018), *Ideonella Sakaiensis* (Tanasupawat et al. 2016; Yoshida et al. 2016), *Brevibacillus borstelensis* (Hadad et al. 2005), several strains of *Pseudomonas* sp. (Ward et al. 2006; Ronkvist et al. 2009; Kyaw et al. 2012; Pramila et al. 2012), several strains of *Bacillus* sp. (Sudhakar et al. 2008; Harshvardhan and Jha 2013; Yang et al. 2014; Syranidou et al. 2017; Ingavale and Raut 2018; Novotný et al. 2018), *Zalerion maritimum* (Paço et al. 2017), *Penicillium simplicissimum* (Sowmya et al. 2015), *Penicillium citrinum* (Liebminger et al. 2009), *Fusarium solani* and *Fusarium oxysporum* (Nimchua et al. 2007) and also several strains of *Aspergillus* sp. (Pramila and Ramesh 2011; Esmaeili et al. 2013). However, less is known about the potential plastic biodegradation in the oceans, the involved microorganisms and metabolic pathways. The following sections address the most commonly applied techniques and methods to detect plastic degradation and identify responsible microorganisms.

5.4 Methods and Techniques Applied in the Assessment of Polymer Biodegradation

5.4.1 Methods to Evaluate Biodegradation

Monitoring alterations of polymers' physicochemical properties, including changes in crystallinity, molecular weight, the topography of samples and the functional groups, during experiments, is a common way to evaluate the involvement of microbes in plastic degradation. These may be specific strains or consortia of cultured microbes as well as natural communities. In contrast, the genesis of degradation products is less frequently measured. These are some of the most frequently used physicochemical methods:

1. One of the most common methods to evaluate biodegradation is measuring the gravimetric mass loss of plastics, i.e. monitoring plastic weight-changes exposed to natural or laboratory (cultures, microbial consortia or environmental communities) conditions. Marine isolated bacteria from pelagic coastal waters of the Arabian Sea were assayed for the ability to utilize polyethylene as the sole

carbon source (Harshvardhan and Jha 2013). Three of the strains identified as *Kocuria palustris* M16, *Bacillus pumilus* M27 and *Bacillus subtilis* H1584 caused a weight loss of the tested PE film of 1%, 1.5% and 1.75% after 30 days of incubation, respectively. Marine acclimated consortia (indigenous and bio augmented consortia) reduced the weight of PS films more efficiently than non-acclimated bacteria (Syranidou et al. 2017). *Penicillium oxalicum* NS4 and *Penicillium chrysogenum* NS10 strains reduced the weight of PE films by ~60% over 90 days period (Ojha et al. 2017). Environmental studies assessing gravimetric mass loss have been carried out in the water column, sand beds and sediments (Kalogerakis et al. 2017; Syranidou et al. 2017; Welden and Cowie 2017). Gravimetric measurements do not require extensive resources, but they lack accuracy to detect small mass changes (as is typically the case during exposure experiments). Determination of the polymer weight is complicated further by the fact that post-incubation treatment of plastic samples is necessary to remove biofilms and residues of organic matter, which bears the risk of accidentally altering the mass of the plastic itself. Finally, when this method is applied in natural conditions, it is imprecise to distinguish between abiotic (weathering, ageing and/or loss) and biotic (biofragmentation, biodegradation and/or biomineralization) degradation.

2. An alternative method to gravimetric measurements in assessing microbial degradation is to monitor weigh-average-molecular-weight (Mw) and weigh-number-molecular-weight (Mn). An increase in both Mw and Mn is related to the consumption of the low Mw of the polymer (see Sect. 5.5) and might also be related to crosslinking reactions of the carbon backbone. Shifts of the spectra towards high Mw and Mn have been reported in several studies (Albertsson et al. 1995, 1998; Kawai 1995; Erlandsson et al. 1998; Hakkarainen and Albertsson 2004; Koutny et al. 2006b; Yoon et al. 2012), including marine-related strains.
3. Atomic force microscopy (AFM) (Binnig et al. 1983), measurements offer quantitative and qualitative data on the surface topography and occurring changes, with high spatial resolution. Exposure of silicone rubber, polyurethane, polyester, syntactic foam, glass fibre reinforced polymer and carbon fibre reinforced plastic for 1 year in the water column increased surface roughness (Muthukumar et al. 2011). Similarly, an increase in roughness, development of cracks and grooves were monitored on HDPE and LDPE films after exposure to *Penicillium oxalicum* NS4 and *Penicillium chrysogenum* NS10 strains for 90 days (Ojha et al. 2017). Scanning electron microscopy (SEM) has been used to visualize physical deterioration of polymer surface (pits, cracks, grooves or other abnormalities on the plastic surface) as a function of exposure to the environment and/or microbes. Simultaneously, SEM allows visualization of adhering prokaryotes and eukaryotes (Zettler et al. 2013; Eich et al. 2015; Bryant et al. 2016; Paço et al. 2017; Dussud et al. 2018b; Delacuvellerie et al. 2019) (Fig. 5.4).
4. Fourier transformation infrared spectroscopy (FTIR) that can be coupled to attenuated total reflectance (ATR) is one of the most widely used technique for polymer identification and evaluation of degradation. FTIR allows molecular and

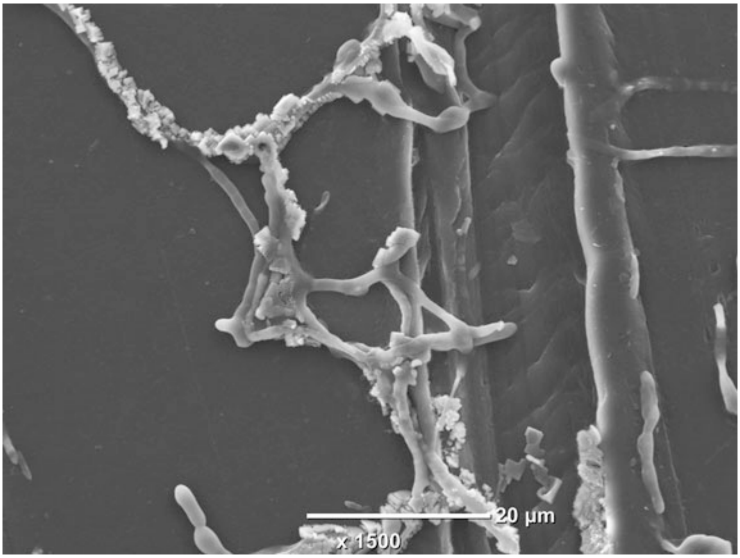


Fig. 5.4 SEM image of photo-oxidized PE, colonized by a marine fungus

structural characterization of the polymers, including plastics, copolymers and rubbers and their products (Bhargava et al. 1970; Chalmers 2006; Mecozzi et al. 2016). FTIR is mostly applied to detect oxidative damages on plastic polymers (Almond et al. 2020), by either abiotic or biotic factors. Degradation by microorganisms is monitored by the detection of specific peaks in the IR spectrum. The changes of carbonyl groups (as a result of UV oxidation or biodegradation) and the relative size of these peaks, described by the carbonyl index (peak intensity at 1850–1650 cm^{-1} in relation to the reference peak) (Almond et al. 2020), is routinely taken as a measure to determine the magnitude of degradation. It has become a standard method for identification of microplastics in sediments and the water column (Veerasingam et al. 2020). Examples of FTIR applications range from identification of polymers ingested by sea turtles (Jung et al. 2018) to the formation of carbonyl groups on PE exposed to seawater (Da Costa et al. 2018) and evaluation of the degradation of PET bottles in seawater (Ioakeimidis et al. 2016). Although FTIR can be applied to assess the biomass attachment to the polymers, revealing the presence of nucleic acids, lipids and protein content of the biomass (Paço et al. 2017), the same biomass signals may interfere with the absorption spectra of the polymer (Bonhomme et al. 2003).

Besides the above-mentioned methods, several other methods are applied to assess plastic degradation. Respirometric measurements evaluate the production of excess CO_2 and biomass variations when the polymer is the only available carbon source for microorganisms. Mechanical properties, such as tensile strength, crystallinity, hydrophobicity/hydrophilicity of the surface, are, as well, taken as a measure of degradation (Pegram and Andrady 1989). Labelled polymers (^{14}C) were used already in the 1970s, to demonstrate PE and PS degradation by fungal strains (Guillet et al. 1974; Albertsson 1978). Recently, isotopically labelled polymers were applied in the terrestrial realm to evaluate plastic-derived carbon assimilation into living cells (Zumstein et al. 2018). Similarly, labelled ^{13}C-polyethylene has been used to evaluate aquatic microbial biodegradation and eventually trace microbial-animal trophically transfer (Taipale et al. 2019). The combination of isotopically labelled polymers with molecular analyses to evaluate the mineralization (incorporation of labelled carbon into cells, nucleic acids or lipids, for example) are promising techniques to be explored.

Despite various evaluation methods to investigate plastic biodegradation, many lack rigor in fully confirming the initial depolymerization, assimilation and mineralization, and thus remain non-quantitative and inaccurate.

5.4.2 Colonization of Prokaryotes and Eukaryotes on Marine Plastic

Cultivation-independent studies often investigate microbial community composition by next-generation sequencing methodologies, mainly amplicon sequencing of the 16S rRNA (for prokaryotes) or the 18S rRNA gene (for eukaryotes). Only sparsely have eukaryotes been targeted by sequencing of the Internal Transcribed Spacer (ITS) region with specific primers (De Tender et al. 2017) or by metagenomic sequencing (Bryant et al. 2016; Pinnell and Turner 2019), to unravel which organisms adhere to the plastic surface. Applying next-generation sequencing for detecting unknown plastic degraders involves the premiss for substrate-driven selection of plastic degraders during colonization (i.e. that plastic surface will be colonized preferentially by plastic degraders). However, attachment to surfaces is a universal and fundamental trait of many microorganisms across the three domains of life, because life in a biofilm offers critical advantages (De Tender et al. 2015; Dang and Lovell 2016). In marine environments, any available surface will be colonized rapidly by microbes since forming assemblages and biofilms on a surface protects microbes from fluctuating environmental parameters such as UV radiation and predation (Eich et al. 2015). Thus, caution has to be taken when interpreting colonization data while trying to detect potential plastic degraders.

Biofouling is a multi-step process composed of priming the surface, attachment of early settlers, secretion of extracellular polymeric substances and the formation of mature biofilms (Flemming and Wingender 2010; Rummel et al. 2017). In a mature biofilm, microorganisms have proliferated, and secondary settlers are incorporated into the biofilm and may have replaced primary settlers. For plastic marine debris, the surrounding seawater provides the initial inoculum of microbial assemblages which can adhere to the polymer surface. Sequentially, the early colonizers influence the mature biofilm composition and dynamics (Dang and Lovell 2000; Dang et al. 2008). Microorganisms colonize submerged surfaces rapidly, including plastics

(Salta et al. 2013; Harrison et al. 2014). That raises the question if plastics host a specific microbial community when compared to seawater and other hard surfaces?

For plastics, it has been shown that the community of settlers and the surrounding seawater share a high degree of the same taxa; however, plastics harbour distinct and significantly different microbial assemblages (Bryant et al. 2016; De Tender et al. 2017; Kettner et al. 2017; Dussud et al. 2018b; Frère et al. 2018; Vaksmaa et al. 2021). A recent review suggests to refrain from using seawater as a control because free-living and biofilm communities differ (Wright et al. 2020a). Using hard/inert surfaces (PET, PHA and ceramics) during benthic incubations revealed that the degree of similarity between the settling communities is higher than the seawater inoculum (Pinnell and Turner 2019). Indeed, microbial communities on PS, PP and PE were different from the communities developed on glass and cellulose (Ogonowski et al. 2018). A specific bacterial community was detected on PVC, but communities were similar on glass, LDPE, HDPE and PP (Kirstein et al. 2019). The approach by Kirstein et al. was novel as it focussed on the tightly adhered community members, assuming that direct contact with plastic could indicate more relevance in the potential role in biodegrading the plastic. Specific microbial community on 'wild plastic' was found on PS in comparison to PE and PP (Frère et al. 2018). In contrast, no difference was observed in the microbial communities, which developed on PET bottles and glass slides exposed at different locations and during different seasons (Oberbeckmann et al. 2016). Microbial communities on plastic have been reported to be more distinct in the early stage of biofilm formation (Pinto et al. 2019). However, currently, the hypothesis that plastics harbour a distinct microbial community in comparison to other inert surfaces can be neither confirmed nor rejected (Wright et al. 2020a) particularly in mature biofilms that are highly diverse.

Another critical question is: what is the role of additives in polymers in structuring the microbial communities? The majority of studies focus on the polymer type as the determining factor for biofilm composition. However, plastics are rarely used in their pure form. Consumer plastics usually contain additives, yet only a few studies investigated the potential influence of additives on the microbial community composition. Differential microbial communities were observed on PVC compared to other tested polymers (Kirstein et al. 2019); however, the authors hypothesized that this might have been caused by PVC additives and not per se the polymer. To better understand microbial colonization dynamics on plastics, future research endeavours need to investigate early stage community succession, the role of polymer type and additive admixture, and weathering in determining microbial community composition and succession.

5.4.2.1 Prokaryotic Colonizers on Marine Plastic

The core members of microbial assemblages on plastic are seemingly the same taxa independent of geographical location and whether the sample has been in the water column or sediments. For example, *Flavobacteriaceae* and *Rhodobacteraceae* were detected on PET bottles (Oberbeckmann et al. 2016), on sheets and dolly ropes of PE (De Tender et al. 2017), PVC (Dang et al. 2008), PE and PP (Zettler et al. 2013) and on PE, PP and PS (Vaksmaa et al. 2021) based on 16S rRNA gene amplicon sequencing. Similar results for PE and PP were obtained by metagenomic sequencing (Bryant et al. 2016). Other commonly detected families are *Alteromonadaceae* (Bryant et al. 2016; Xu et al. 2019) and *Saprospiraceae* (Bryant et al. 2016; Oberbeckmann et al. 2018; Kirstein et al. 2019), *Hyphomonadaceae* (Zettler et al. 2013; Bryant et al. 2016; Dussud et al. 2018b; Oberbeckmann et al. 2018; Ogonowski et al. 2018), *Sphingomonadaceae* (Debroas et al. 2017; Oberbeckmann et al. 2018; Ogonowski et al. 2018) and *Vibrionaceae* (Zettler et al. 2013; De Tender et al. 2015; Frère et al. 2018). Nevertheless, the functioning of these commonly detected taxa (often termed the 'core community of the plastisphere') remains unresolved, and it is unclear if and in how far these organisms play a role in potential plastic degradation. Indeed, plastic can be colonized by opportunistic microbes for which life in a biofilm is advantageous. It seems that general microbial colonizers are often early colonizers, such as members of Rhodobacterales (Dang and Lovell 2000; Dang et al. 2008; Elifantz et al. 2013; Schlundt et al. 2020; Tu et al. 2020). Other commonly detected groups in biofilms such as *Saprospiraceae* and *Flavobacteriaceae* have a preference for an adhered lifestyle (DeLong et al. 1993; Fernández-Gómez et al. 2013).

Several studies have also detected hydrocarbon-degrading bacteria (HCB) in plastic-associated biofilms (Zettler et al. 2013; Oberbeckmann et al. 2016; Debroas et al. 2017; Dussud et al. 2018b; Pinto et al. 2019; Erni-Cassola et al. 2020; Vaksmaa et al. 2021). A comparison of 2229 datasets of 35 independently published investigations of biofilm communities on plastic polymers was conducted to reveal common taxa in these biofilms (Wright et al. 2020b). This overview study highlighted that often, a fraction of the plastic colonizers were hydrocarbon degraders, specifically Oceanospirillales and Alteromonadales. Obligate hydrocarbon-degrading bacteria were found on thermo-oxidatively weathered and non-weathered polyethylene after 2 days of exposure to coastal waters and constituted 5.8% and 3.7% of relative sequence abundance, which stands in stark contrast to glass controls where they constituted only 0.6% (Erni-Cassola et al. 2020). Similarly, hydrocarbon degraders (mainly *Erythrobacter*) were found to comprise 7.4% of amplicon reads of plastic-associated biofilms in comparison to 7.8% of organic particle-associated (>3μm), while a lower abundance of 4.7% was found free-living (Dussud et al. 2018b). In a seawater flow-through reactor, where, LDPE, PE with added pro-oxidant, thermally aged PE, polyester and poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) were exposed for 6 weeks, HCBs constituted 34% of the biofilm community on the polymers. Especially *Alcanivorax* sp., *Alteromonas* sp., *Marinobacter* sp. and *Oleiphilus messinensis* were abundant, forming >5% of the total OTUs in one sample (Dussud et al. 2018a).

Genomes of hydrocarbon degraders encode for mono- and dioxidases, hydrolases and peroxidases (Brzeszcz and Kaszycki 2018). These enzymes can break down long chain or complex hydrocarbon molecules, which resemble some polyolefin-type plastics. Hydrocarbon degraders are thus potential candidates to break down plastic polymers (Dussud et al. 2018b; Basili et al. 2020; Erni-Cassola et al. 2020), and they may rapidly colonize plastic surfaces, because they are common in marine environments where hydrocarbon compounds (e.g. oil) are available (Kimes et al. 2013; Joye et al. 2014; Beckmann et al. 2019).

The argument that a versatile hydrocarbon degrader might indeed be able to degrade plastic is further underscored by the ability of the HCB *Rhodococcus ruber* (strain C208), an actinomycete, to degrade PE, PP and PS. *Rhodococcus ruber* possesses the ability to facilitate degradation of both linear, branched polymers and PS, which contains aromatic styrenes (Mor and Sivan 2008). Upregulated pathways during PE degradation by *Rhodococcus ruber* were those that are also active during alkane degradation and β-oxidation of fatty acids (Gravouil et al. 2017). Santo et al. demonstrated the upregulation of laccase upon UV-treated PE exposure in *Rhodococcus ruber* C208, indicating the possible role in the oxidation of the PE. An extracellular isoform of the laccase of the copper-induced *R. ruber C208* cells reduced 20% the Mw of the PE (Santo et al. 2013). Among Rhodococci, the ability to degrade aliphatic, aromatic and polyaromatic hydrocarbons has been shown. The genome of *Rhodococcus ruber* strain IEGM 231 harbours 45 dioxygenases, 73 monooxygenases, 22 cytochromes P450 oxygenases and 285 dehydrogenases (Ivshina et al. 2014). *Rhodococcus ruber* YC-YT1 strain, isolated from plastic in coastal seawater, is able to degrade di-(2-ethylhexyl) phthalate, a plasticizer of polyvinyl chloride, into phthalate (Yang et al. 2018). *Rhodococcus* sp. was isolated from terrestrial and marine environments (Sorkhoh et al. 1990; Hackbusch et al. 2020). Hydrocarbon degraders may also be fuelled indirectly with plastic derived carbon. Photooxidation by UV radiation initiates chain scission and the formation of carbonyl groups (Gewert et al. 2018). Hence, HCB might utilize the released hydrocarbons or take advantage of partially oxidized polymers. Indeed, it was recently found that DOM released during plastic photooxidation can be utilized by microbes (Romera-Castillo et al. 2018; Zhu et al. 2020).

5.4.2.2 Eukaryotes as Plastic Colonizers and Degraders

Immersed plastic surfaces are subjected to biofouling, a process that entails that a succession of microorganisms and multicellular organisms from different trophic levels attach to plastic debris. Plastic polymers in the marine environment harbour a diverse eukaryotic community as has been validated by visual observations, microscopy together with amplicon and metagenomic sequencing. Metagenomic sequencing revealed that in some cases, sequencing reads assigned to eukaryotes are more abundant than those assigned to prokaryotes (Bryant et al. 2016). Twenty-seven eukaryotic species were identified by Nanopore minION sequencing as plastic specific on PE bags exposed for 1 month to the Mediterranean Sea (Davidov et al. 2020). Microscopy-based investigations found that diatoms are early plastic surface colonizers, but they are also present in more mature biofilms (Carson et al. 2013; Zettler et al. 2013; Eich et al. 2015). Algae were also found to adhere to marine plastic surfaces (Zettler et al. 2013; Oberbeckmann et al. 2014; Bryant et al. 2016; Dussud et al. 2018b). In brackish environments, different eukaryotes were found on PE and PS: Ulva, Trebouxiophyceae, ciliates, rotifers Adinetida and Ploimida, the nematodes Diplogasterida and Rhabditida, mollusk Caenogastropoda and crustacean Podocopida (Kettner et al. 2019). Plastic debris offers for eukaryotic invasive species a path to disperse (Kiessling et al. 2015).

In the marine realm, fungi are understudied in general and in particular for fungi–plastic interactions. Until now, more than 50 studies have investigated 16S rRNA genes related to prokaryote–plastic interaction, but only less than ten have addressed the fungal community in marine and brackish environments (Wright et al. 2020b). The taxonomic composition of fungi in a seafloor PE biofilm community was investigated in the harbour of Ostend in Belgium during long-term incubation over 44 weeks (De Tender et al. 2017). Biofilm formation occurred within a week of exposure. In contrast to previous studies, this study could not detect bacteria that are known to degrade plastics. On the other hand, it found the fungal strains *Cladosporium cladosporioides*, *Fusarium redolens* and *Mortierella alpine*, which were previously identified as PE degraders (Albertsson 1978; Bonhomme et al. 2003; Koutny et al. 2006b; Restrepo-Flórez et al. 2014). The fungal community composition on PE and PS has also been investigated in the Baltic Sea, the River Warnow and a wastewater treatment plant. The results revealed that fungal communities on microplastics were different when compared to communities in the surrounding water and on wood (Kettner et al. 2017). The taxonomic composition of plastic-associated fungi in surface waters of the Antarctic Peninsula and the western South Atlantic was compared by using several molecular markers; ITS2 and the V4 and V9 regions of the 18S rRNA gene. At both locations, PE, polyamide, PUR, PP and PS were colonized by fungi. Besides identification of *Aspergillus, Cladosporium*, *Wallemia, Chytridiomycota* and *Aphelidomycota*, as well as *Zoopagomycota* and *Mucoromycota* were identified, taxa previously detected in the marine environment, but so far not on plastics (Lacerda et al. 2020). Only a few marine isolates of fungi have been evaluated for their ability to colonize and degrade plastics. A marine fungus, *Zalerion maritimum*, was isolated and able to utilize PE (250μm to 1 mm particles) in a minimal growth medium, already within 7 days (Paço et al. 2017). Concerning the generally diverse enzymatic potential of fungi, it is valid to assume that there are more fungal species able to degrade plastics in the marine environment than previously thought. This hypothesis is further supported by the already diverse set of fungal strains retrieved from lacustrine and terrestrial environments that are seemingly able to degrade plastic. From freshwater environments, ~100 fungal isolates from floating plastic debris in Lake Zurich, Switzerland were obtained and evaluated for their ability to degrade plastics. Different species, including saprotrophic and plant pathogenic fungi, were isolated. Although none of the strains isolated from plastic appeared to degrade PE, *Cladosporium cladosporioides*, *Xepiculopsis graminea*, and *Penicillium griseofulvum* (saprotrophic fungi) and the *Leptosphaeria* sp. (plant pathogen) were able to degrade PUR (Brunner et al. 2018). Furthermore, *P. simplicissimum* YK, a soil fungus, was capable of degrading previously irradiated PE and using it as a carbon source (Yamada-Onodera et al. 2001). *Aspergillus flavus*, isolated from the gut of the wax moth *Galleria mellonella*, is able to degrade HDPE. However, the HDPE was UV irradiated for sterilization prior to the experiment (Zhang et al. 2020). Fungal strains isolated from endemic plants *Aspergillus* sp., *Paecilomyces lilacinus* and *Lasiodiplodia theobromae* were able to degrade gamma-irradiated LDPE as shown by the decrease in intrinsic viscosity and average molecular weight. However, only *Lasiodiplodia theobromae* was able to degrade irradiated polypropylene as well (Sheik et al. 2015).

5.5 Enzymatic Potential of Microbes

5.5.1 General Considerations

Enzymes are large biomolecules acting as biological catalysts for the numerous (bio)chemical reactions that sustain life (Gurung et al. 2013). They are present in cells of all living organisms, including eukaryotes and prokaryotes, and are crucial to maintaining the organism's metabolism as most essential biochemical reactions proceed very slowly or may not occur spontaneously when uncatalysed (Harris and Hopkinson 1976; Berg 2002; Robinson 2015; Sheel and Pant 2018). Thus, biochemical reactions and metabolic pathways depend upon enzymes to catalyse each step by lowering the reaction's activation energy or changing the mechanism (Berg 2002; Lucas et al. 2008; Blanco and Blanco 2017). Structurally, the vast majority of enzymes are proteins, often containing or requiring other components, e.g. inorganic elements such as minerals or metal ions (Fe^{2+}, Mn^{2+}, Zn^{2+}), non-protein organic compounds (e.g. vitamins) and other cofactors (Kamerlin and Warshel 2010). Microbial enzymes accomplish numerous functions, including breaking down large molecules extracellularly. Microbes can excrete depolymerizing exoenzymes, which produce smaller sub-products that can be assimilated and further metabolized intracellularly. Microbes attach to the substrate and form biofilms of commensal and/or syntrophic consortia to enhance extracellular degradation. Although many microorganisms can break down natural complex organic polymers, the enzymatic capability to catalyse depolymerization of synthetic polymers such as plastics is rare (Albertsson 1978; Albertsson et al. 1995; Yoshida et al. 2016). Debate persists whether microbial enzymes used to degrade complex natural polymers (e.g. cutin, a waxy compound coating leaves, containing ester-bonds as in PET) have had enough time to evolve and to adjust to equivalent functions on synthetic polymers. Biodegradation of plastics is described as slow and complex process (Albertsson 1980; Hakkarainen and Albertsson 2004). Although several microbes have been shown to facilitate the breakdown of plastics, the key enzymes and metabolic pathways involved in the degradation process are not well understood, and little knowledge exists on the degradation intermediates and if these are assimilated (Ru et al. 2020). Like other complex organic compounds, plastic degrading microbes would need to attack plastics extracellularly and (partially) depolymerize the complex and large molecule to compounds that could be utilized as carbon and energy source (Gu 2003).

Research on microbial plastic degradation in terrestrial environments gained momentum over the last decades (Gilan et al. 2004; Zhao et al. 2004; Hadad et al. 2005; Sabev et al. 2006; Matsumiya et al. 2010; Latorre et al. 2012; Rajandas et al. 2012; Ali et al. 2014; Yoshida et al. 2016; Gravouil et al. 2017; Wei and Zimmermann 2017a, b; Austin et al. 2018). However, considerably fewer studies have been carried out in marine environments (Pegram and Andrady 1989; Artham et al. 2009; Balasubramanian et al. 2010; Lobelle and Cunliffe 2011; Yoon et al. 2012; Harshvardhan and Jha 2013). The next sections address extracellular and intercellular biodegradation.

5.5.2 Extracellular Biodegradation

Early studies have shown that only molecules <600 Da can pass the cellular membrane (Haines and Alexander 1974; Decad and Nikaido 1976). As prokaryotes cannot perform exo- or endocytosis, molecular weight is a critical factor in biodegradation (Albertsson et al. 1995, 1998; Kawai 1995; Erlandsson et al. 1998; Gu 2003; Hakkarainen and Albertsson 2004; Koutny et al. 2006b). High molecular weight results in a sharp decrease in solubility, rendering plastics unfavourable for the microbial attack, and a decrease in molecular weight increases the biodegradability (Gu 2003). Microorganisms apply extracellular enzymes to initiate degradation, and these bind to the plastic and catalyse bond cleavage in a single or a series of reactions (Kopeček and Rejmanová 2019), such as oxidation, reduction, hydrolysis and deesterification. In marine and aquatic environments, it is thus fundamental for the organisms to attach to the plastic surface to use it most efficiently as a substrate, although other free-living microorganisms might utilize intermediate products that are released during the initial extracellular degradation steps.

Concurrent abiotic and biotic processes have been suggested to facilitate plastic degradation (Albertsson et al. 1987; Hakkarainen and Albertsson 2004). An initial step of e.g. photooxidation, introducing carbonyl groups to the polymer backbone would quasi activate it for further enzymatic degradation (Gewert et al. 2015; Romera-Castillo et al. 2018; Wayman and Niemann 2021). By weathering, mainly the plastic surface gets initially affected; i.e. <100μm in photooxidation processes (Ter Halle et al. 2016). Therefore, studies investigating microbial degradation of pre-treated plastics need to be interpreted carefully, and additional information on the pre-treatment process needs to be taken into account for the results to be comparable and reproducible.

Plastics with functional groups, like esters, amides, carbonates and urethanes, are more prone to microbial attack because equivalent functional groups are present in other natural compounds. These heteroatoms and functional groups allow for a faster bond cleavage via enzymatic hydrolysis (Min et al. 2020). While genes and enzymes involved in the microbial degradation of such plastic types have been better characterized (Ghosh et al. 2013; Wei and Zimmermann 2017b; Ru et al. 2020), knowledge on the degradation of plastics with no hydrolysable chemical bonds in their backbone such as PE, PP, PVC is scarce (Zheng et al. 2005; Singh and Sharma 2008; Wei and Zimmermann 2017b; Ru et al. 2020). The exoenzyme group of depolymerases are able to degrade the substrate into smaller molecules. Nevertheless, the critical depolymerases involved in plastic degradation and the resulting depolymerization products remain often unknown (Ru et al. 2020). For instance, in the case of PE, past studies have identified enzymes related to peroxidases, laccase and homologous sequences related to laccases/multicopper oxidases as potential candidates involved in biodegradation. Furthermore, a manganese peroxidase (MnP) has been found to decrease the tensile strength and average molecular weight of PE (Iiyoshi et al. 1998). Similarly, the combination of soybean peroxidase (SBP) and hydrogen peroxide can oxidize and diminish the surface hydrophobicity of PE film (Zhao et al. 2004). Generation of carbonyl groups in PE films by oxidation could be mediated by a laccase exoenzyme (Santo et al. 2013). Three homologous sequences related to laccases/multicopper oxidases were identified in the transcriptome of *Rhodococcus ruber*, although the genes encoding for those sequences were neither up- nor down-regulated in an experiment with PE as a sole carbon source (Gravouil et al. 2017). In addition, recombinants from three alkane hydroxylase genes (alkB, alkB1 and alkB2) of *Pseudomonas aeruginosa* E7 strain from a contaminated beach soil were able to degrade low-molecular-weight PE (Yoon et al. 2012; Jeon and Kim 2015, 2016a). *P. aeruginosa* can use a wide range of substrates as a carbon and energy source and is a common microbial community member in soil and water (Jeon and Kim 2016a). *P. aeruginosa* strains PAO1 and RR1 contain enzymes involved in the degradation of n-alkanes: 2 alkane monooxygenases, 2 rubredoxins and 1 rubredoxin reductase (Marín et al. 2003; Jeon and Kim 2016a). In the case of PS, only a hydroquinone peroxidase was able to depolymerize PS into low-molecular-weight products in the presence of non-aqueous medium (dichloromethane) (Nakamiya et al. 1997) (Table 5.1). To the best of our knowledge, there are no reports on enzymes that degrade PP, and potential biodegradation processes remain to be clarified (Arutchelvi et al. 2008; Ru et al. 2020). Biodegradation of PP is expected to be more challenging than PE due to the stable methyl group in every monomer (Arkatkar et al. 2009; Jeon and Kim 2016b). Biodegradation studies of PP have, therefore, mostly been carried out with pre-treated substrates (UV irradiation, thermo-oxidation, γ-irradiation) under laboratory conditions (Alariqi et al. 2006; Jeyakumar et al. 2013; Sheik et al. 2015). For instance, two bacterial isolates of *Bacillus* sp. and *Rhodococcus* sp. (strain 27 and strain 36, respectively) from mangrove environments were able to grow in aqueous synthetic media containing UV-radiated PP microplastics (Auta et al. 2018). However, neither the biodegradation of the untreated plastic nor the processes and metabolic enzymes involved in the weight loss were studied. In the case of polypropylene blends (Jeyakumar et al. 2013; Jain et al. 2018) and PP with prooxidants (Fontanella et al. 2013), it is difficult to discern if the recalcitrant plastic is degraded. To date, only a few studies have shown biodegradation of untreated PP (Arkatkar et al. 2009; Jeon and Kim 2016b). However, these promising reports of PP degradation were based on weight loss or on the increase of the average molecular weight. It needs to be further tested if this is the result of degradation of the long-chain PP polymer or other shorter-chain molecules that might have been present in the plastic, too.

Regarding polyamides, few studies have shown biodegradation of different types of nylons (Negoro et al. 1992; Gold and Alic 1993; Klun et al. 2003; Tomita et al. 2003a, b), but only one study investigated PA degradation by marine bacteria and found the formation of new functional groups in the polymermatrix (i.e. NHCHO, CH_3, $CONH_2$, CHO and COOH; Sudhakar et al. 2007). Interestingly, the authors observed a greater extent of PA degradation by the marine bacteria when compared

Table 5.1 Marine microorganisms and enzymes associated with plastic biodegradation

Polymer	Relevant enzymes/ microorganism	Sample source	Test culture/environmental conditions, carbon source and time of exposure in days (d)	Weight loss (%)	Reference
PE (LDPE and HDPE film, unpretreated/thermal pre-treatment)	*Bacillus sphaericus* Alt; *Bacillus cereus* BF20	Marine water (shallow oceanic water)	MSM + PE SCS/150–365 d	Un-PE: 2–10 therm-PE: 6.52–19	Sudhakar et al. (2008)
PE (LDPE film)	*Bacillus subtilis* H1584	Marine water	30 d	1.75	Harshvardhan and Jha (2013)
PE (Pellets)	*Zalerion maritimum*	Marine environment	28 d	–	Paço et al. (2017)
PE (LDPE film)	*Alcanivorax borkumensis*	Mediterranean Sea (macroplastics afloat and in sediments)	Medium (0.05% hexadecane) + PE/80 d	3.5	Delacuvellerie et al. (2019)
PE (LMWPE: Thermal decomposition of HDPE and LDPE)	*Pseudomonas* sp. E4/*alkane* *hydroxylase gene* (alkB)	Marine environment (contaminated beach soil with crude oil)	Recombinant *E. coli* BL21 with alkB gene + compost with PE/80 d	4.9, 10.3, 14.9 and 28.6^{a}	Yoon et al. (2012)
PE (LMWPE: Thermal decomposition of HDPE and LDPE)	*Pseudomonas aeruginosa* E7/*alkane* *Monooxygenase, rubredoxin* and *rubredoxin reductase* genes (alkB, rubA1, rubA2 and rubB)	Marine environment (contaminated beach soil with crude oil)	Recombinant *E. coli* DH5-a with different genes + compost with PE/80 d	40.8^{a}	Jeon and Kim (2015)
PE (LMWPE: Thermal decomposition of HDPE and LDPE)	*Pseudomonas aeruginosa* E7/*alkane* *Monooxygenase, rubredoxin* and *rubredoxin reductase* genes (*alkB1*, *alkB2*, *rubA1*, *rubA2* and *rubB*)	Marine environment (plastic polluted coastal)	Recombinant *E. coli* DH5-a with different genes + compost with PE/50 d	19.6–27.6^{a}	Jeon and Kim (2016b)

PVC (LDPE and HDPE films (20 min UV radiation))	*Bacillus* sp. AIIW2	Marine environment (contaminated beach soil with crude oil)	BH minimal medium + PVC/ 90 d	0.96–1	Kumari et al. (2019)
PP (UV pre-treated microplastics from grated/cut PP granules (9003-07-0, sigma Aldrich) and commercial	*Bacillus* sp. strain 27; *Rhodococcus* sp. strain 36	Marine environment (mangrove sediment)	BH medium + PP/40 d	4–6.4	Auta et al. (2018)
PP plastic materials)					
PVC (PVC film without plasticizers (20 min UV radiation))	*Bacillus* sp. AIIW2	Marine environment (plastic-polluted coastal)	BH minimal medium + PVC/ 90 d	0.26	Kumari et al. (2019)
PA (Nylon 6; Nylon 6,6)	*Bacillus cereus, Bacillus sphaericus, Vibrio furnisii* and *Brevundimonas vesicularis*	Marine water	MSM + SCS	2–7	Sudhakar et al. (2007)
Marine plastic debris	*Alcanivorax* sp. 24/genes encoding for 2 cytochrome P450, 3 alkane	Marine environment (high intertidal zone)	BH medium + polyhydroxybutyrate (PHB)	–	Zadjelovic et al. (2020)
	Monooxygenases AlkB, and 2 monooxygenase-related AlmA (enzymes involved in the degradation of long-chain alkanes)				

Mineral salt medium (MSM); sole carbon source (SCS); period of time in days (d); average molecular weight (Wm); Bushnell Haas (BH) medium

[a] Weight loss measured as a ratio of CO_2 consumption with and without PE assuming that all carbons in the PE are mineralized into CO_2

with soil microorganisms (Sudhakar et al. 2007). One study reported on a laccase-mediator system (LMS) and showed that a fungal laccase, a multicopper-containing enzyme, was able to degrade PA (Fujisawa et al. 2001).

In the case of PVC degradation, most studies have been performed with both PVC and plasticizers (Moriyama et al. 1993; Gumargalieva et al. 1999; Sabev et al. 2006; Latorre et al. 2012). PVC contains commonly high proportion of plasticizers (up to 50%). Two studies were carried out with PVC films in soil (Kırbaş et al. 1999; Ali et al. 2014) and one in the marine environment (Kumari et al. 2019); however, the degradation was evaluated based on weight loss. In the case of marine bacteria *Bacillus* sp. AIIW2 PVC, only a weight loss of 0.26% was observed in the pre-treated (UV radiated during 20 min) PVC films after 90 days (Kumari et al. 2019). Thus, the enzymes involved in the microbial degradation of this polymer are still unknown (Ru et al. 2020).

Several enzymes contribute to the degradation of polyurethanes, both with polyether and polyester backbones (Cregut et al. 2013; Peng et al. 2018; Magnin et al. 2020; Ru et al. 2020). PUs are presumed to be the most susceptible types of conventional plastics to biodegradation due to the presence of urethane bonds and other hydrolysable groups in their carbon backbone (≥ 2 functional groups per monomer; Fig. 5.2). Seven fungal strains were found to grow on the surface of solid polyester PU (Darby and Kaplan 1968). Two fungal strains, *Aspergillus niger* and *Cladosporium herbarium*, were able to grow in cultures with polyether foam as the sole nutrient source (Filip 1979). A *Staphylococcus* bacterial strain was able to grow on polyether in the absence of organic nutrients (Jansen et al. 1991). An esterase able to degrade polyester was purified from a fungal strain, *Curvularia senegalensis* (Crabbe et al. 1994), a protease was purified from *Pseudomonas fluorescens* (Howard and Blake 1998) and a lipase from *Bacillus subtilis* (Rowe and Howard 2002). Since then, other enzymes with the capacity to degrade PU have been reported (Akutsu et al. 1998; Allen et al. 1999; Matsumiya et al. 2010). Cutinases, esterases and lipases are able to attack carboxylic linkage bonds, whereas endopeptidase enzymes are able to cleavage amide bonds (Lucas et al. 2008). However, these enzymes were not found to degrade solid polyester substrates, such as PU film, foam, and elastomer (Schmidt et al. 2017; Ru et al. 2020). Although it has been claimed that some enzymes possess depolymerization activity for degrading (co)polyesters (Lucas et al. 2008), to date none have been reported to be able to degrade and cleave the urethane bonds in both polyester and polyether PU (Ru et al. 2020).

Several enzymes have been reported to degrade PET since reporting of the hydrolase (cutinase-like TfH) which could degrade up to 50% of the polymer's weight at 55 °C in 3 weeks (Müller et al. 2005). Another three cutinases from three different microorganisms were reported to degrade both low- and high-crystallinity PET (Ronkvist et al. 2009). Nevertheless, two of them should be ascribed to PET surface-modifying enzymes due to their low weight loss effect (Ru et al. 2020) and only cutinase HiC from *Humicola insolens* was found as an efficient hydrolase, causing a 97% reduction of the low-crystallinity PET film at 70 °C within 96 h. This enzyme, recently renamed as *Thermobifida fusca cutinase* (TfCut2), has been shown to reduce similar amounts of weight in PET films than previously reported, and up to 56.6% in postconsumer PET packages at 70 °C within 120 h (Wei et al. 2019). PET consists of repetitive units of polyethylene terephthalate and is mainly synthesized from terephthalic acid and ethylene glycol. To date, *Ideonella sakaiensis* 201-F6 is the most in-depth studied PET degrading organism along with *Thermobifida* sp. and *Thermomonospora* sp. (Kleeberg et al. 1998; Müller et al. 2005). *I. sakaiensis* grows on low crystalline PET as a major carbon and energy source by adhering to the surface and releasing exo-enzymes (Yoshida et al. 2016). Two novel enzymes were identified to catalyse the full reaction of degrading PET: PETase, a hydrolase belonging to the α/β-hydrolase superfamily which converts PET into mono (2-hydroxyethyl) terephthalic acid (MHET) and terephthalate (TPA). The second enzyme MHETase, a tannase, hydrolyses MHET into TPA and ethylene glycol (EG). PETase has features similar to cutinases and lipases (Austin et al. 2018). Potential PETases were investigated by metagenomic mining, which revealed that with respect to the utilized database, >500 candidates, divided over different bacterial phyla exist that could express a PETase. The candidate genes coding for PETase originating from marine environment belonged mainly to Bacteroidetes and in the terrestrial environment to Actinobacteria. The database searches identified possible PET hydrolase homologs in 31 marine metagenomes and 11 terrestrial ones. The cloning of PETase and latter enzyme activity assays revealed that both PET and polycaprolactone were hydrolysed (Danso et al. 2018). Based on the low occurrence of PETase in the analysed metagenomes, they hypothesized that PET hydrolysing enzymes evolved only recently. The bacterial strain *Ideonella sakaiensis* 201-F6 also encodes another enzyme (*Is*PETase), able to degrade lcPET films but at an ambient temperature (Yoshida et al. 2016). However, the efficiency of this IsPETase at mesophilic temperatures is markedly lower than that of TfCut2 at a thermophilic temperature (Wei and Zimmermann 2017a, b; Ru et al. 2020).

5.5.3 Intracellular Biodegradation

Once the plastic has been degraded to short-chain molecules, e.g. short oligomers, dimers and monomers, these can be assimilated, and potentially further degraded and finally mineralized to CO_2, H_2O or CH_4 (Gu 2003). Concerning enzyme specificity, polymer biodegradability probably depends on molecular physicochemical characteristics such as density, crystallinity and structural complexity and the presence of functional groups (Kawai 1995; Gu 2003; Mohan and Srivastava 2010; Alshehrei 2017). A fundamental aspect to consider in this biodegradation stage is the assimilation sizes of the polymers. However, the upper size limit for plastic molecules to undergo direct biodegradation is not well constrained. In the case of PE, it is suggested that the polymer with the average molecular weight lower than ~1000 Da could be considered as biodegradable (Kawai 1995). Later, it was reported that some microorganisms were able to degrade quite rapidly previously photooxidized molecules with higher molecular weight, raising the upper limit to ~2000 Da (Kawai et al. 1999). Nevertheless, it is unclear whether those molecules were broken down extracellularly before being assimilated or not. Concerning longer n-alkanes and saccharides, earlier studies indicated that most of the microorganisms do not seem to be able to consume aliphatic chains displaying a Mw over 600 Da (Haines and Alexander 1974). During an experiment with PE wax, a consortium of bacteria could degrade molecules that were > 1000 Da (Kawai et al. 2004). Lower-molecular-weight PE (1700 Mw) was biodegraded ~6 times faster than larger PE molecules (23,700 Mw) by *Pseudomonas* sp. E4, isolated from beach soil (Yoon et al. 2012). A mesophilic polypropylene degrading strain, *Stenotrophomonas panacihumi* PA3–2, was reported to degrade two low-molecular-weight PP types containing molecules with a broad chain length spectrum and one high-molecular-weight PP (Jeon and Kim 2016b). Increase in average molecular weight was observed during incubations, and the authors concluded that the lightest molecules were mostly degraded. A few isolated microorganisms have shown the ability to utilize untreated PE as the sole carbon source (Gilan et al. 2004; Sivan et al. 2006), which points to the capacity of these organisms to utilize polymers with higher molecular weights. It is not clear how large molecules might be directly assimilated. Some authors suggest the possibility of a certain effect of biosurfactants produced by microorganisms, being then able to enter the assimilation pathway known for longer alkanes (Koutny et al. 2006a). In a gene expression experiment with *R. ruber* growing on PE as a carbon source, the authors identified 19 putative transporters upregulated in at least one of the treatments supplemented with PE. Of them, nine belonged to the major facilitator superfamily (MFS) and five belonged to the ATP binding cassette (ABC) family (Gravouil et al. 2017). They also reported a gene encoding for a protein sharing a transport function and NADH dehydrogenase activity, suggesting that this protein could be involved in both the oxidation and the transport.

The controversy of the results from different studies reveals that probably the assimilation size varies between different microorganisms and is polymer dependent. However, to date, there are not sufficient studies on different polymers and diversity of microorganisms to further constrain molecular weight cut-offs impeding biodegradation, leaving several aspects of the biodegradation unclear. For instance, regarding the biodegradation of PE, it is necessary to characterize the biochemical functions of the oxidases or oxygenases, such as the enzymes encoded by the genes *alkB*, *alkB1* or *alkB2*. Future efforts are required to characterize specific depolymerases degrading plastics and the assimilation process. In future screening experiments, it is essential to characterize the ability of microbial strains to depolymerize the long-chain molecules of the different untreated polymer resins, as well as to identify the genes encoding for membrane transporters and their regulations through gene expression experiments.

5.6 Valorization and Applications

Several bacterial and fungal strains can degrade plastic polymers, with varying efficiency. Thus, utilization and marketing of microbial plastic degraders, purified plastic-degrading enzymes, and further optimizing these for biotechnological and possibly environmental (pollution mitigation) applications is a potential future market sector. Nevertheless, with a few exceptions (Son et al. 2020), research in this area is not advanced far enough and key organisms and enzymes firstly need to be identified.

A promising candidate for future biotechnological applications is the *Ideonella sakaiensis* 201-F6, able to degrade plastics and to grow on the plastic derived carbon. The enzymes PETase and MHETase, mediating PET degradation and resulting in the release of terephthalic acid and ethylene glycol (EG), have been characterized; however, PET degradation is a very slow process (Tanasupawat et al. 2016; Yoshida et al. 2016). In order to achieve PET degradation at higher rates, protein engineering of wild-type enzyme resulted in a PETase (IsPETaseS121E / D186H/S242T/N246D) that outperformed the natural PETase by 58-fold (Son et al. 2020). In this process, it was also possible to recover the released terephthalic acid, which could then serve as a base material for the new PET production. For the first time, a biotechnological application for degrading waste of conventional plastics and contributing to its recycling was demonstrated (Tournier et al. 2020). Conventionally recycled PET (i.e. remolded) has technical disadvantages such as loss of mechanical properties, and for some applications, the quality of conventionally recycled PET is too low. However, digesting PET and 'mining' for its monomer thus offers, in principle, the possibility for a truly circular PET economy.

Furthermore, TPA and EG can serve to produce, polyhydroxyalkanoates (PHA), which are useful compounds for biotechnological applications. In nature, a variety of microorganisms ranging from general sugar fermenters to methanotrophs produce PHAs as cellular carbon storage and energy source. PHAs can be produced by *Pseudomonas* species from TPA, as well as EG (Kenny et al. 2008, 2012; Franden et al. 2018). *Pseudomonas putida* has often been suggested as a candidate to serve PHA production, not only from TPA and EG but also from the styrene degradation product phenylacetic acid (PAA) (Ward et al. 2006; Nikodinovic-Runic et al. 2011). The degradation products, TPA and EG, could serve as substrates for the bioplastic industry, where PHAs, such as polyhydroxybutyrate, are produced. However, the primary degradation of waste polymers needs to be initiated. While the discoveries for PET are promising, similar knowledge of naturally occurring enzymes and the further advancements of these enzymes has not been achieved for other polymer types. Future research thus not only needs to determine if a particular polymer type is biodegradable and which key players mediate this process, it also needs to include in-depth investigations into gene expression in order to find potentially relevant genes encoding for enzymes that mediate depolymerization which then could be used for biotechnological applications.

To date, there is no applicability of plastic degraders to counteract plastic pollution in nature. One of the reasons is our lack of understanding of naturally occurring plastic degraders and their functioning, which provides the basis for creating biotechnological applications. Furthermore, both wild-type strains and engineered enzymes are ideally associated with high degradation efficiencies to serve industrial needs and yield utilizable compounds. In a second step, these organisms/enzymes would need to be cultivated/produced in large quantities. As tempting as it is to envision plastic bioremediation by microbes in nature (a quasi-biochemical clean-up solution), in situ bioremediation might be applicable solely where plastic pollution is highly concentrated and localized, e.g. in terrestrial landfills or in local hot spots of pollution as have been found in some bays. There, it appears possible to apply microbes/enzymes at sufficient quantities on a small spatial scale. In contrast, the expanse of the ocean, both horizontally and vertically, is genuinely enormous. Although plastics tend to accumulate in the subtropical gyres and enclosed basins, it would thus require an massive quantity of microbes/enzymes to reach all plastic pieces from the ocean surface to the (deep) sea bottom. Furthermore, the marine environment is in constant motion, which further complicates such applications. Alternatively, using microbes to prevent/fight marine plastic pollution could work ex situ by retrieving plastic from the ocean, and, e.g. to extract monomers after enzymatic digestion. Though speculative, it might be plausible to design large bioreactors with plastic degrading microbes that could degrade plastics in a similar fashion as organic matter and nutrients are removed in biological wastewater treatment systems at present.

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