Journal Pre-proof

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PII: S0734-9750(19)30201-0

DOI: https://doi.org/10.1016/j.biotechadv.2019.107501

Reference: JBA 107501

To appear in: *Biotechnology Advances*

Received date: 1 August 2019

Revised date: 17 December 2019

Accepted date: 19 December 2019

Please cite this article as: C. Sánchez, Fungal potential for the degradation of petroleum-based polymers: An overview of macro- and microplastics biodegradation, *Biotechnology Advances* (2019), https://doi.org/10.1016/j.biotechadv.2019.107501

FUNGAL POTENTIAL FOR THE DEGRADATION OF PETROLEUM-BASED POLYMERS: AN OVERVIEW OF MACRO- AND MICROPLASTICS BIODEGRADATION

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ABSTRACT

Petroleum-based plastic materials as pollutants raise concerns because of their impact on the global ecosystem and on animal and human health. There is an urgent need to remove plastic waste from the environment to overcome the environmental crisis of plastic pollution. This review describes the natural and unique ability of fungi to invade substrates by using enzymes that have the capacity to detoxify pollutants and are able to act on nonspecific substrates, the fungal ability to produce hydrophobins for surface coating to attach hyphae to hydrophobic substrates, and hyphal ability to penetrate three dimensional substrates. Fungal studies on macro- and microplastics biodegradation have shown that fungi are able to use these materials as the sole carbon and energy source. Further research is required on novel isolates from plastisphere ecosystems, on the use of molecular techniques to characterize plastic-degrading fungi and enhance enzymatic activity levels, and on the use of omics-based technologies to accelerate plastic waste biodegradation processes. The addition of pro-oxidants species (photosensitizers) and the reduction of biocides and antioxidant stabilizers used in the plastic manufacturing process should also be considered to promote biodegradation. Interdisciplinary research and innovative fungal strategies for plastic waste biodegradation, as well as ecofriendly manufacturing of petroleum-based plastics, may help to reduce the negative impacts of plastic waste pollution in the biosphere.

Keywords: Biodegradation, fungi, fungal enzymes, petroleum-based plastics.

1. INTRODUCTION

The market for petroleum-based plastic products has had a great expansion in industries such as the construction, automotive and packaging industries in the twentieth century (Lintsen et al., 2017). Plastic materials have been very successful due to their low cost and weight, as well as their versatility and durability, making them present in nearly every material used in human daily life (Andrady and Neal, 2009) (Table 1). The use of plastics has increased twenty fold since 1964, and it is expected to double by 2035 (Velis, 2014). It has been reported that the world's synthetic plastic production will be approximately 1800 million tons in 2050 (Gallo et al., 2018) and approximately 12,000 million metric tons of plastic waste will be in the environment by that year (Geyer et al., 2017; https://www.nature.com/articles/s41467-018-04565-2.pdf). Approximately 90% of the products made with plastic are used once and then discarded (https://www.nature.com/articles/s41467-018-04565-2.pdf). Therefore, the disposal of used plastic materials and plastic packaging materials has become a global concern due to their high recalcitrance resulting in their long persistence in the environment. It is estimated that the packaging sector constitutes 39.9% of the plastic market and approximately 42% of plastic waste within a city's solid waste comes only from packing materials, such as polyethylene (PE) (Table 1) (Biron, 2013; Narancic and O'Connor, 2017). Plastic pollution is spread throughout the world's oceans by prevailing winds and surface currents, with some of it ending up in the digestive system of marine animals, which finally affects human health (Eriksen et al., 2014; Quero and Luna, 2017). It has been estimated that almost 6.4 million tons of waste is introduced into marine environments annually (Agamuthu, 2018). In terms of the global composition of marine litter, plastics account for 62.31%. Plastics also contribute 49% of the litter composition in the seafloor and 81% on the sea surface (Litterbase; https://litterbase.awi.de/). Plastics are differentiated according to their structural arrangements, physical properties and applications. They can be homopolymers or heteropolymers if they are derived from identical or different (but often similar) types of monomers, respectively (Table 1). Plastics are classified on the basis of their properties and the chemical structure of the polymer's backbone and side chains in thermoplastics (uncrosslinked plastics, which are recyclable) and thermosets (or duroplastics) (contain a high density of chemical crosslinks, which are not recyclable) (Eyerer, 2010; http://www.ilocis.org/documents/chpt77e.htm) (Fig. 1). Manufacturing petroleum-based plastics requires crude oil and natural gas (two components of crude petroleum) as raw materials (Fig. 2). Several operations are performed to refine the crude oil, such as distillation, followed by cracking to provide the intermediates to form different polymers through polymerization and/or polycondensation reactions (Eyerer, 2010; http://www.ilocis.org/documents/chpt77e.htm). Processing plastics into end products requires the addition of some additives, which also cause environmental pollution. For example, some plastic additives, such as plasticizers (e.g., phthalates), flame retardants antioxidants (e.g., boric acid, brominated flame retardants), antioxidants and UV stabilizers (e.g., bisphenol A, butylated hydroxytoluene), heat stabilizers (e.g., cadmium and lead compounds), slip agents (e.g., fatty acid amides), curing agents (e.g., diaminodiphenylmethane), biocides (e.g., arsenic compounds), pigments (e.g., cadmium compounds) and others are incorporated into thermoplastics to achieve the desired final functional properties (Hahladakis et al., 2018) (Fig. 2). The most produced thermoplastics

are high and low density polyethylene (HDPE and LDPE) and polypropylene (PP) (the polyolefins), followed by polyvinyl chloride (PVC) and polystyrene (PS) (http://www.ilocis.org/documents/chpt77e.htm). Plastic pollution in landfills causes visual derogation of the landscape, contamination of soils with small plastic particles, and the release of greenhouse gases and hazardous chemicals (Mudgal, 2011; de Souza-Machado et al., 2018) (Table 1). In addition, the presence of microplastics and nanoplastics in the environment is growing rapidly due to the global ubiquity of macro-plastics and the technological developments of using new micro- and nanoplastic materials. These materials might have major chemical and physical impacts on the environment and human health because of their unique physiochemical micro- and nanoscale properties (Mattsson et al., 2015; Waring et al., 2018; Peiponen et al., 2019). Due to these concerns, there is a need to search for alternatives for cleaning up the environment. Bioremediation is considered the most desirable approach for eliminating many environmental pollutants. Bioremediation is an environmentally friendly and low-cost technology which can be undertaken on site since it involves natural processes (Das and Adholeya, 2012). In this sense, fungi have promising practical applications to remediate environments polluted by plastics using their powerful enzymes.

2. ABILITY OF FUNGI AS DEGRADERS OF COMPLEX POLYMERS

Fungi constitute a large and diverse kingdom of eukaryotic organisms morphologically classified as yeasts, filamentous fungi, or dimorphic fungi. These organisms can be saprotrophs (decomposing dead material), obligated or opportunistic organisms (decomposers, mutualists or pathogens) (Schmit and Mueller, 2007; Črešnar and Petrič, 2011). Fungi are found in different environments and some of them have evolved to adapt and grow even in terrestrial and marine environments under extreme conditions (Raghukumar, 2017). Most fungi are aerobic, but anaerobic fungi have been found in freshwater lakes, landfill sites and the rumen of herbivores (Ivarsson et al., 2016). Fungi have the capacity to extend through substrates in their search for nutriments with their filamentous network structure, exploring and growing in places that are more difficult to reach for other microorganisms. Filamentous fungi are the most commonly classified species of fungi to date. These organisms have developed an extraordinary ability to adapt to changing environments and to tolerate several types of pollutants. They are able to break down and use these pollutants to grow or to make their chemical components available to other microorganisms. As a consequence, filamentous fungi play a crucial role in the degradation and mineralization of diverse environmental pollutants by catalyzing important chemical reactions (Črešnar and Petrič, 2011). Fungi are heterotrophic organisms that feed by absorbing nutrients from outside their cells. They release digestive enzymes by exocytosis outside of their hyphae, which break down macro and organic molecules into smaller organic compound to absorb them back up, releasing CO_2 and H_2O under aerobic conditions (and CH_4 under anaerobic conditions) if mineralization of the substrate occurs (Pathak and Navneet, 2017) (Fig. 3). Fungi have various extraordinary strategies to counteract numerous complex compounds, some of them pollutant and toxic substances (Olicón-Hernández et al., 2017). These strategies include a powerful enzymatic system, the ability of adsorption and the production of natural biosurfactants (i.e., hydrophobins), which enable them to use polymers (i.e., plastics) as a source of

carbon and electrons, providing them with cellular materials and an energy source, respectively (Fig. 4).

2.1. Intracellular and extracellular enzymatic systems

Fungi have a machinery of unspecific enzymes able to catalyze diverse reaction mechanisms that make them highly convenient for pollutants degradation (e.g., petroleum-based polymers), which is possible due to their different mechanisms in combination with both their intracellular and extracellular enzymatic systems. The intracellular enzymatic system acts as an internal mechanism for detoxification and plays a major role in fungal adaptation (Jeon et al., 2016; Olicón-Hernández et al., 2017; Schwartz et al., 2018). This enzymatic system is mediated by the cytochrome P450 family (CYP) epoxidases (Phase I enzymes) and transferases (Phase II enzymes). Phase I and phase II enzymes include those enzymes involved in oxidation and conjugation reactions, respectively (Schwartz et al., 2018) (Fig. 4). CYP are a large family of enzymes and heme-containing monooxygenases (mainly) that are able to catalyze various enzymatic reactions (i.e. the metabolism of aliphatic, alicyclic, and aromatic molecules), resulting in epoxidation, hydroxylation, dealkylation, sulfoxidation, desulfuration, deamination, dehalogenation, and N-oxide reduction (Shin et al., 2018). Fungi possess more diverse CYP families than animals, plants, or bacteria (Shin et al., 2018). The evolutionary conserved (CYP51) and fungi-specific (CYP61 and CYP56) P450 enzymes are essential for primary metabolism, enabling the preservation of the hyphal wall integrity and the formation of the spore outer wall, respectively (Črešnar and Petrič, 2011). CYP isoforms are anchored in the membrane of the endoplasmic reticulum, having their active sites connected to both the cytosolic and membrane environments so they can accept substrates from both cellular surroundings (Šrejber et al., 2018). CYP contains three cofactors ($NADPH+H^+$, FAD and heme) and two enzymes (NADPH-CYP reductase and cytochrome P-450 hydrolase) (Fig. 4). Additionally, the extracellular enzymatic system consists of the hydrolytic system that produces hydrolases, which is responsible for polysaccharide degradation, and an extraordinary and unspecific oxidative system involved in the breakdown of complex structures (e.g., lignin degradation) (Sánchez, 2009). Hydroxylation can be considered a biotransformation approach for bioremediation processes since it increases the solubility of pollutants and therefore reduces the bioaccumulation potential (Olicón-Hernández et al., 2017). The unspecific oxidative system is formed mainly by nonspecific oxidoreductases, including enzymes such as class II peroxidases (manganese peroxidase, lignin peroxidase and versatile peroxidase), laccases, dye decolorizing peroxidases and unspecific peroxygenases. This oxidative system is able to oxidize a wide range of substrates and is a powerful tool for environmental cleaning. These enzymes transfer electrons from organic substrates to molecular oxygen (laccases) by oxidation-reduction reactions using H_2O_2 as an electron accepting co-substrate (class II peroxidases and dye peroxidases), or by epoxidation, aromatic peroxygenation and sulfoxidation, among others reactions (unspecific peroxygenases) (Karich et al., 2017). This enzymatic complex is produced mainly by wood-degrading fungi, such as basidiomycetes (Sánchez, 2009).

2.2. Fungal production of hydrophobins

Hydrophobins are surface hydrophobic proteins (70-350 amino acids in length) produced by fungi that contain eight cysteine residues and form four disulfide bridges in a conserved pattern (Wessels, 1996; Wösten and Scholtmeijer, 2015). These proteins are involved in the formation of aerial structures of filamentous fungi (such as hyphae, fruiting bodies, and spores) and in the attachment of hyphae to hydrophobic surfaces. However, the bacterial adhesion to the plastic surface depends on the physicochemical surface and bacterial properties rather than on biological processes (Artham et al. 2009; Urbanek et al., 2018). Lobelle and Cunliffe (2011) reported that bacteria can colonize plastic; however, there is no evidence of potential degradation during early attachment. Fungal hydrophobins self-assemble into amphipathic films (monolayers) on hydrophobic-hydrophilic interfaces (Wessels, 1996; Kulkarni et al., 2017; Wu et al., 2017). Based on their hydrophobic patterns, the morphology of the monolayers and their solubility in detergents, hydrophobins are divided in two classes. Class I hydrophobins are highly insoluble in aqueous solutions and form functional amyloid fibers organized in layers with rodlet morphology. Class II hydrophobins are soluble in aqueous dilutions of organic solvents and their monolayer lacks the rodlet morphology and is less stable (Wu et al., 2017). Several hydrophobins have been isolated from different fungi. Normally, each fungus contains a number of different hydrophobins (Table 2). These proteins represent an important tool for bioremediation purposes since they act as biosurfactants improving substrate mobility and they increase the bioavailability. It has been reported that the chemical structure of fungi biosurfactants involves, among other things, sophorolipids, glycolipids, protein-lipid/polysaccharide complexes, and glycolipoproteins (Olicón-Hernández et al., 2017). The extraordinary properties of hydrophobins (such as their strong adhesion, high surface activity and the formation of various self-assembled structures that are often highly insoluble) have allowed them to be used to promote the growth of cells on a hydrophobic surface for applications in medical implants. In fact, a hydrophobin coating can improve the growth and morphology of fibroblasts on a plastic surface (e.g., polystyrene, Teflon, etc.) (Hektor and Scholtmeijer 2005; Pistelli et al., 2017).

3. DEGRADATION PROCESS OF PETROLEUM-BASED POLYMERS BY FUNGI

3.1. Enzyme involved in the degradation of petroleum-based plastics

Fungal degradation of polymers such as PP, PVC, polyethylene terephthalate (PET), polyesters and microplastics has been studied (Table 3). Primarily ascomycetes, followed by basidiomycetes and zigomycetes, have been found to be able to degrade petroleum-based plastics (Table 3). Plastic biodegradation processes can be evaluated through microbial growth and/or changes in the polymer itself. Fungal growth can be assessed mainly by enzyme assays, biochemical oxygen demand, biomass production and carbon dioxide production under aerobic conditions. The effects of fungi on the physiochemical properties of plastics include changes in the crystallinity, molecular weight, tensile properties, extent of fragmentation and functional groups found on the plastic surface (Restrepo-Flórez et al., 2014). The main techniques used to follow these changes are: Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and x-ray photoelectron spectrometry (XPS). Fungal growth causes a decrease (consumption) of carbonyl groups from the original oxidation products (e.g., esters, lactones and ketones)

(Ammala et al., 2011). The biodegradation and biodeterioration (break down in properties) of plastics by fungi have been demonstrated by several researchers. However, the enzymes that are involved in the processes have been investigated in only a very few studies (Table 3). For example, El-Morsy et al. (2017) demonstrated the protease, esterase and lipase production in polyurethane biodegradation with *Monascus* sp. strains. Russell et al. (2011) reported enhanced serine hydrolase activity of *Pestalotiopsis microspore* when it was grown on polyester polyurethane (impranil) as its sole carbon source. In addition, the ascomycetes *Zalerion maritimum* and *Gloeophyllum trabeum* were reported as able to degrade microplastics (Krueger et al., 2015; Paço et al., 2017). Ameen et al. (2015) found that a consortium of ascomycete strains were able to degrade LDPE, showing laccase, manganese peroxidase (MnP) and lignin peroxidase (LiP) activities (Table 3). It has been suggested that fungal enzymes are able to decrease the length of PE chains and that once this occurs, a metabolic pathway for the degradation of PE can be proposed (Restrepo-Flórez et al., 2014). It has been reported that in general, fungi are better degraders of PE and polyurethane than bacteria (Prathak and Navneet, 2017; Muhonja et al., 2018). On the other hand, the enzymes involved in PET degradation are typical serine hydrolases such as cutinases (EC 3.1.1.74), carboxylesterases (EC 3.1.1.1) and lipases (EC 3.1.1.3) (Danso et al., 2019). Among the reported microbial polyester hydrolases, cutinases and their homologues have shown the greatest potential for PET hydrolysis (Kawai et al., 2019). Liebminger et al. (2007) isolated polyesterase from *Penicillium citrinum* able to hydrolyze PET pellets. Ronkvist et al. (2009) found that *Thermomyces* (formerly *Humicola*) *insolens* and *Fusarium solani* had catalytic activities of cutinase when low-crystallinity (7%) PET films were used as substrates (Table 3).

3.2. Biodegradation pathways

Figure 5 shows a hypothetical biodegradation pathway for PE by *Aspergillus terreus* under aerobic conditions, which was developed based on previously identified intermediate compounds by GC-MS after incubation of 30 d (Balasubramanian et al., 2014). The proposed PE biodegradation pathway would begin with the activation of a MnP, enzyme with enhanced activity during PE biodegradation (Ameen et al., 2015). The catalytic active site of MnP includes aspartate (Asp179), glutamate (GluS5 and GluS9), a heme propionate, and two water molecules (one of them is a free water molecule) (Sundaramoorthy et al., 1994). The heme propionate has 2 propionate groups, one of them bound to a water molecule and the other bound to Mn^{2+}. The catalytic activity of the MnP (heme MnP) would start from free radicals in acidic conditions with optimal activity at pH 5 (Chandra et al., 2017) (a). During this step, the hydrogen peroxide, an oxidizing agent added to the culture medium, would be homolytically cleaved, generating two hydroxyl free radicals which would bind to Fe^{2+} and the hydrogen water of the heme MnP, respectively, and releasing a water molecule (a). As a result, hydroxy-ferryl center free radical and porphyrin π-cation free radical could be formed, and hydrogen in the hydroxy-ferryl center free radical would bind to the nitrogen of the porphyrin π-cation free radical to stabilize the molecule (b). The oxygen radical of the oxy-ferryl center free radical would oxidize Fe^{2+} to Fe^{3+}, forming oxy-ferryl center. Additionally, a group propionate would bind to H^{+} of the hydroxyl group, oxidizing Mn^{2+} to Mn^{3+} and would form an oxy ferryl center-MnP free radical complex (c). PE would enter the active site of the heme MnP and the Mn free radical would react with PE, which would be broken down into small molecules, such

as dodecane free radical, ethyl free radicals, alkanes (e.g., dodecane, nonadecane, etc.), and ethanol (e). Ethanol would be oxidized into acetic acid (f), which would enter into the Krebs cycle (g). Dodecane free radical would enter the MnP catalytic site (h) and would be oxidized to dodecane (i). Alternatively, dodecane free radical and dodecane would be subsequently oxidized to dodecanol (j), dodecanal (k) and dodecanoic acid (l), which would react with an ethyl free radical to form tetradecanoic acid (m). Tetradecanoic acid would react with CoA to form tetradecanoyl CoA (n), which would undergo β-oxidation to form acetyl-CoA units which would enter into the Krebs (o) (White and Rusell, 1994; Sundaramarthy et al. 1994; Balasubramanian et al. 2014). The substrate-free MnP would then have an unoccupied substrate-binding site (p), attracting another substrate molecule for a new catalytic cycle (q). On the other hand, cutinases possess a catalytic triad that is composed of a serine (Ser), a histidine (His), and an aspartate (Asp) residue (Martínez et al., 1992; Danso et al., 2019). They can also contain several disulfide bonds formed by cysteine residues, which promote thermal stability and specific binding to PET (Danso et al., 2019). Figure 6 shows a PET hypothetical biodegradation pathway by a cutinase of *F. solani*. The catalytic active site of this cutinase includes; Ser 120, Asp 175 and His 188 (Martínez et al., 1992). The proposed PET biodegradation pathway would begin with the activation of two molecules of cutinase. The electrons from the oxygen of serine would react with the carbonyl group of PET (a), which would form a serine-terephatalate complex and two ether compounds (b). Alternatively, PET can be hydrolyzed by cutinase, which would be broken down into mono-(hydroxyethyl) terephthalate (MHET), bis-(hydroxyethyl) terephthalate (BHET), and terephthalic acid (TPA) (Han et al., 2017) (c). Oxygen of the ether compound would form a covalent bond with the hydrogen of histidine, which would undergo hydrolysis to form ethylene glycol (d). Ethylene glycol would be converted to a series of intermediates by oxidation to form glyoxylate, which would enter into the Krebs cycle (e). Serine-terephthalate complex and the Asp-His residue would be hydrolyzed using two water molecules (f). The oxygen from the serine would bind the hydrogen from the histidine (g) and two molecules of cutinase and TPA would be released (h). Cutinase molecules would begin a new catalytic cycle (i) and TPA would be hydrolyzed to cis-4,5-dihydroxycyclohexan-1(6),2-diene-1,4-dicarboxylate (j), which would form catechol by decarboxylation (k). Catechol would be hydrolyzed to 2-hydroxymuconate semialdehyde (l), which would then be oxidized to 2-oxopent-4-enoate (m). This last compound would be converted to a series of intermediates by hydrolysis to form pyruvate (n) which would enter into the Krebs cycle (e).

4. CONCLUDING REMARKS

It can be concluded that petroleum-based plastics are necessary in human life and represent an ever increasing market. The development of diverse industrial sectors (e.g., pharmaceutical) has resulted in the production of several plastic materials at micro and nano scale levels (microbeads and nanobeads). The pollution of macroplastics is an environmental crisis of great concern, but environmental pollution from micro and nano scale plastics is even more disturbing since it is possible to fight that what is visible but smaller plastics are a threat which cannot be seen. Therefore, there is an urgent need to provide an effective and harmless solution to plastic pollution. Several studies have been undertaken to determine the plastic biodegradation by fungi, however, very little is known

about the enzymes involved in the plastic biodegradation process and on the plastic biodegradation pathways. Fungi have a great potential for reducing the negative impacts of plastic pollution due to their specific characteristics, such as their enzymatic system with the capacity for pollutant detoxification and unspecificity of substrates, their ability to produce hydrophobin for surface coating to attach hyphae to hydrophobic substrates, and their cellular ability to penetrate three dimensional substrates. Future research should focus on novel isolates from plastisphere ecosystems (a new habitat that may host fungal strains able to use plastic polymers for growth), on the use of molecular tools to characterize plastic-degrading fungi and improve enzymatic activity levels, and on the use of omics technologies to accelerate plastic waste biodegradation processes. On the other hand, it is of crucial importance to balance the plastics formulation to promote plastic waste biodegradation; biocides and antioxidant stabilizers should be reduced or even eliminated (after all, 90% of the products made with plastic are used once and then discarded) and pro-oxidants (photo sensitizers) have to be incorporated into plastic manufacturing processes to promote biodegradation. Interdisciplinary investigations and innovative fungal strategies for plastic waste biodegradation, as well as ecofriendly manufacturing of petroleum-based plastics, may reduce plastic waste pollution and help to clean the biosphere.

ACKNOWLEDGEMENTS

The author thanks Dr. Ericka Santacruz-Juarez for her time and valuable help with Fig. 5 and Fig. 6. The work in C. Sánchez's lab has been supported by the Mexican Council for Science and Technology (CONACyT), current grant 1549 (Fronteras de la Ciencia).

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FIGURE LEGENDS

Fig. 1. Classification and structure of petroleum based plastics. Plastics are classified as thermoplastics and thermosets (duroplastics). Thermoplastics are uncrosslinked plastics that can be softened by the application of heat (which makes them recyclable materials). Duroplastics, or thermosetting materials, are polymers that contain a high density of chemical crosslinks, resulting in a close-meshed crosslinking of macromolecules (which are not possible to recycle).

Fig. 2. Schematic representation of the manufacturing of petroleum-based plastics with an example of a finished product. Manufacturing petroleum-based plastics requires crude oil and natural gas as raw materials. Several operations are performed to refine the crude oil, such as distillation, followed by cracking to provide intermediates to form different polymers (thermoplastics or thermosets) through polymerization and/or polycondensation reactions. Processing plastics into end products requires the addition of additives such as plasticizers, flame retardant antioxidants, antioxidants and UV stabilizers, heat stabilizers, curing agents, pigments, and others.

Fig. 3. General scheme of biodegradation of complex polymers (e.g., petroleum-based plastics) by a fungal cell (hypha). Fungi are heterotrophic organisms that feed by absorbing nutrients from outside their cells. In general, the hyphal structure can be organized into 4 zones: the apical growth zone, absorption zone, storage zone and senescence zone, each of them with a specific metabolic activity. Hyphae release digestive enzymes by exocytosis outside of hyphae, which break down macro and organic molecules into smaller organic compounds and absorb them back up, releasing CO_2 and H_2O (the mineralization of a substrate under aerobic conditions).

Fig. 4. Schematic representation of fungal mechanisms for the degradation of complex polymers (e.g., petroleum-based plastics). These fungal mechanisms include a powerful intracellular and extracellular enzymatic system, the ability of adsorption, and the production of natural biosurfactants (i.e., hydrophobins), which enable them to use complex polymers as a source of carbon and electrons to provide cellular materials and an energy source, respectively.

Fig. 5. A proposed catalytic cycle for the biodegradation of PE using the heme manganese peroxidase (heme MnP). The dashed line shows the compounds identified (acetic acid, dodecane, dodecanal and tetradecanoic acid) previously by GC-MS during PE biodegradation by *A. terreus* under aerobic conditions (Balasubramanian et al., 2014). The rest of the compounds shown in the biodegradation pathway were proposed based on previous reports (White and Rusell, 1994). The catalytic activity of the heme MnP starts from free radicals in acidic conditions. The PE hypothetical biodegradation pathway shows that MnP would eventually mineralize this polymer, generating a PE catalytic cycle.

Fig. 6. A proposed catalytic cycle for the biodegradation of PET using a cutinase of *F. solani*. The catalytic active site of this cutinase includes; Ser 120, Asp 175 and His 188 (Martínez et al., 1992). The proposed PET biodegradation pathway would begin with the activation of two molecules of cutinase by the electrons transfer from the hydrogen atom of histidine to the hydroxyl group of serine. The PET hypothetical biodegradation pathway shows that cutinase would eventually mineralize this polymer, generating a PET catalytic cycle.

Table 1. Characteristics of some petroleum-based plastics, their impact as waste, their greenhouse gas emissions, and their main applications.

Polymer type (common abbreviation)	Structure	R-group	Estimated plastic waste within municipal solid waste (%)	Global warming (Kg CO_2 eq/Kg)	Melting point (°C)	Volatile organic compounds	Application (examples)
Low density polyethylene (LDPE)	Homo-polymer	Hydrogen	23	5.04	105- 115	Unsaturated aliphatic hydrocarbons, aliphatic aldehydes	Packing: bags (e.g., for bread, frozen food, garbage), squeeze bottles, films, coating
High density polyethylene (HDPE)	Homo-polymer	Hydrogen	19	4.84	120- 130	Unsaturated aliphatic hydrocarbons, aliphatic aldehydes	Packing: shopping bags, bottles (milk, juice, shampoo, detergent, etc.), cereal-box lines
Polypropylene (PP)	Homo-polymer	Methyl	14	*	165	Unsaturated and saturated aliphatic hydrocarbons	Construction: pipes Packing: bags, trays, recycle bins Others: automotive battery cases, carpets, fabric material
Polyethylene terephthalate (PET)	Homo-polymer	Carbonyl and hydroxyl	10	4.93	280	Toluene, xylene, butylated hydroxytoluene	Packing: bottles, food wrappers Construction: pipes Other: microwave trays
Polystyrene (PS)	Homo-polymer	Phenyl	7	5.98	240	Styrene, ethylbenzene, methylstyrene Styrene, ethylbenzene, pentane	Construction: flooring, insulation boards and frames Others: hangers, pencil boxes, cups, cosmetics.
Polyvinyl chloride (PVC)	Homo-polymer	Chlorine	6	NA	115- 245	Chlorinate compounds, e.g., 1-chlorobutane, 1,1-dichloroacetone; plasticizers (frequently phthalic acid esters), (2-butoxy-ethoxy) ethanol, butoxyethanol, 2-ethyl-hexanol, phenol, alkyl	Packing: various containers and hard packing Construction: floors, pipes, panels, tubes, cables, binders Others: medical tubing and bags

						benzenes	
Polyamide (PA) (nylon)	Homo-polymer	Amide	*	7.64	190, 276	ε-caprolactam Cyclopentanone, hexamethylenediamine	Fiber manufacturing
Polyurethane (PU)	Hetero-polymer	Isocyanate and polyol	*	NA	400	Depending on the type (e.g., Carboxylic, ether and glycol ether, diisocyanates, hydrogen cyanide, aromatic amines, chlorinated phosphoric acid esters as flame protection agents)	Packing materials Others: fibers, foams, paints, coating

NA; Not available

*; 19%, including PA, PU and other plastics.

References: Gironi and Piemonte, 2011; Hidalgo-Ruíz et al., 2012; Avérous and Pollet, 2012; Babul et al., 2013; Biron, 2013; Curran and Strlič, 2015; Pathak and Navneet, 2017; Bodzay and Bánhegyi, 2016.

Table 2. Hydrophobins isolated from some ascomycetes and basidiomycetes.

Fungus	Fungal taxa	Hydrophobin	Class	Molecular weight (kDa)	Reference
Agaricus bisporus	Basidiomycota	ABH1	I	16	Lugones et al., 1996
		ABH3	I	19	Lugones et al., 1998
Aspergillus fumigatus	Ascomycota	Rod A	I	16	Paris et al., 2003
Claviceps fusiformis	Ascomycota	CFTH1	II	36.5	de Vries et al., 1999
Claviceps purpurea	Ascomycota	CPPH1	II	70	Mey et al., 2003
Coprinus cinereus	Basidiomycota	CoH1	I	10	Ásgeirsdóttir et al., 1997
Cryphonectria parasitica	Ascomycota	Cryparin	II	18.6	Carpenter et al., 1992
Dictyonema glabratum	Basidiomycota	DGH2	I	14	Trembley et al., 2002
Neurospora crassa	Ascomycota	EAS	I	7	Templeton et al., 1995
Ophiostoma Ulmi	Ascomycota	Cerato-ulmin	II	7.6	Yaguchi et al., 1993
Pleurotus ostreatus **var**. *florida*	Basidiomycota	Fbh-1	II	12	Peñas et al., 1998
Pleurotus ostreatus	Basidiomycota	POH1	I	15	Asgeirsddttir et al., 1998
Pleurotus ostreatus	Basidiomycota	POH2	I	20	Asgeirsddttir et al., 1998
Pleurotus ostreatus	Basidiomycota	POH3	I	10	Asgeirsddttir et al., 1998
Pleurotus ostreatus **var**. *florida*	Basidiomycota	Vmh1 and Vmh2	nd	9	Peñas et al., 2002
Pleurotus ostreatus **var**. *florida*	Basidiomycota	Vmh3	nd	17	Peñas et al., 2002
Trichoderma reseesi	Ascomycota	HFBI	II	7.5	Askolin et al., 2001; Kubicek et al., 2008;

Trichoderma reseesi	Ascomycota	HFBII and HFBIII	II	7.2	Neuhof et al., 2007; Kubicek et al., 2008
Tricholoma terreum	Basidiomycota	Hyd 1	II	23	Mankel et al., 2002
Xanthoria parietina and X. ectaneoides (a conglutinate)	Ascomycota (symbiotic phenotype of the lichen-forming ascomycetes)	XEH1	I	10	Scherrer et al., 2000
Schizophyllum commune	Basidiomycota	SC 1	I	13.5	Schuren and Wessels, 1990; Wessels, 1997
Schizophyllum commune	Basidiomycota	SC3	I	15	Schuren and Wessels, 1990; Wessels, 1997
Schizophyllum commune	Basidiomycota	SC 4	I	14.5	Schuren and Wessels, 1990; Wessels, 1997

Nd; not determined

Table 3. Current research on the biodegradation of petroleum-based plastics using fungi.

Test organism (group)	Plastic as substrate	Findings	References
Aspergillus terreus, Aspergillus sydowii (Ascomycete)	PE	Fungal strains were efficient at PE degradation based on weight loss and reduction in tensile strength after 60 d (FTIR and SEM were used).	Sangale et al., 2019
Chaetomium globosum (Ascomycetes)	PVC	PVC showed adhesion and growth of *C. globosum* fertile structures (perithecia) after 28 d.	Vivi et al., 2019
Trichoderma viride, Aspergillus nomius (Ascomycetes)	LDPE films	*T. viride* and *A. nomius* reduced the weight of LDPE films after 45 d of growth.	Munir et al., 2018
Aspergillus oryzae (Ascomycete)	LDPE sheets	LDPE sheets showed a weight reduction after 4 months.	Muhonja et al., 2018
Cladosporium cladosporioides, Xepiculopsis gramínea, Penicillium griseofulvum, Leptosphaeria sp. (Ascomycetes)	Polyester polyurethane (PPU)(assays carried out on Petri dishes with agar medium)	Growing cultures had a visible clearance zone ('halo') as a result of enzymatic plastic degradation (between 6-14 d of growth).	Brunner et al., 2018.
Monascus ruber, Monascus sanguineus and *Monascus* sp. (Ascomycetes)	PPU (dispersion; assays carried out on Petri dishes with agar medium)	*Monascus* sp. was the most efficient strain in PPU degradation. SEM micrographs showed complex formations between the PPU and hyphae (after 14 d). Protease, esterase, and lipase were detected.	El-Morsy et al., 2017
Penicillium oxalicum and Penicillium chrysogenum (Ascomycete)	HDPE and LDPE sheets	Morphological damages were observed on PE sheets after 60 d (SEM and FTIR spectroscopy were used).	Ojha et al., 2017
Zalerion maritimum (Ascomycete)	PE microplastics (Batch reactors)	This marine fungus was able to utilize PE microplastics, showing a decrease in both the size and mass of the pellets after 28 d (requiring minimum nutrients).	Paço et al., 2017
Aspergillus tubingensis (Ascomycete)	PPU film (liquid medium)	A PPU film was completely degraded into smaller pieces after 2 months (SEM and FTIR were used).	Khan et al., 2017
Fusarium oxysporum, Aspergillus fumigatus, Lasiodiplodia crassispora, Aspergillus niger, Penicillium sp. and *Trichoderma harzianum*.	LDPE (solid and liquid media), and PU sheets	*F. oxysporum* and *A. niger* had the greatest biodegradation efficiency of LDPE and PU after 90 d. Morphological damage and a halo around the growing culture on both LDPE and PU media were observed.	Raghavendra et al., 2016
Aspergillus niger, *Aspergillus flavus* (Ascomycetes)	LDPE granules and films	Reduction of 26% (with *A. niger*) and 16% (with *A. flavus*) in molecular weight for a period of 6 months.	Deepika and Jaya, 2015
Aspergillus	LDPE film	Strains were able to grow on LDPE.	Ameen et

caespitosus, Phialophora alba, Paecilomyces variotii, Aspergillus terreus, Alternaria alternate, Eupenicillium hirayamae (Ascomycete)		Biodegradation of the films was showed using SEM, CO_2 emission and enzymatic activity (Laccase, MnP and LiP), after 4 weeks. Their consortium had the highest enzymatic activity (MnP showed the greatest activity).	al., 2015
Gloeophyllum trabeum (Ascomycete)	Polystyrene Sulfonate (microplastic)	Up to 50% reduction in molecular mass within 20 days.	Krueger et al., 2015
Fusarium sp., *Penicillium* sp., *Aspergillus niger, Aspergillus japonicus* and *Aspergillus flavus*, *Mucor* sp. (Ascomycetes, Zygomycetes)	LDPE sheets	*A. japonicas, Fusarium* sp. and *A. flavus* degraded 36%, 32% and 30%, respectively, the rest of the strains degraded by approximately 20% in terms of weight loss (after 4 weeks).	Singh and Gupta 2014
Aspergillus sp., *Fusarium* sp. (Ascomycetes)	LDPE films	Decrease in weight of LDPE films was observed over a period of 60 d.	Das and Kumar, 2014
Aspergillus terreus (Ascomycete)	HDPE (i.e., UV-pretreated; collected from plastic waste dump yard)	The strain was found to be efficient in degrading HDPE by weight loss after 30 d (SEM, FTIR spectroscopy and GC-MS were used).	Balasubramanian et al., 2014
Penicillium sp. (Ascomycete)	PET powder and flakes	Structural and chemical changes were detected in the PET power and flakes after 4 weeks (SEM and FTIR spectral analysis were carried out).	Sepperumal et al., 2013
Aspergillus niger (ascomycete) (a mixed culture with *Lysinibacillus xylanilyticus*)	LDPE films	The percentages of biodegradation were 29% and 16% for the UV-irradiated and non-UV-irradiated LDPE films, respectively, after 126 d.	Esmaeili et al., 2013
Phanerochaete chrysosporium, Lentinus tigrinus, Aspergillus niger, Aspergillus sydowii	PVC films	A significant change in color and surface deterioration of PVC films were observed after 10 months.	Ali et al., 2013
Mucor hiemalis, Aspergillus versicolor, Aspergillus niger, Aspergillus flavus, Penicillium sp., Chaetomium globosum, Fusarium oxysporum, Fusarium solani, Phoma spp., Chrysonilia setophila (ascomycete, basidiomycetes, zigomycetes)	PE and PVC (plastic sheets)	The strains *A. flavus, F. oxysporum* and *Phoma* spp. were able to efficiently break down both plastics after 2 months (FTIR spectroscopy, SEM and CO_2 production were observed).	Sakhalkar and Mishra, 2013
Aspergillus versicolor, Aspergillus sp. (Ascomycete)	LDPE film	LDPE was degraded into CO_2. *A. versicolor* and *Aspergillus* sp evolved approximately 4 and 3.8 g/l of CO_2, respectively in a week.	Sindujaa et al., 2011
Pestalotiopsis microspora (and other endophytic fungi) (Ascomycete)	PPU (liquid medium with	*P. microspora* degraded PPU Impranil DLN after 16 d (clearance of the medium was observed).	Russell et al., 2011

	Impranil DLN as the sole carbon source)		
Penicillium funiculosum (Ascomycete)	PET films	Important chemical changes of polymeric chains were detected after 84 d (by FTIR spectroscopy and XPS analysis).	Nowak et al., 2011
Fusarium sp. (Ascomycete)	Polyamide 4 (nylon 4) film	Morphological damages were observed on the surface of nylon 4 films after 2 months (by SEM).	Tachibana et al., 2010
Aspergillus fumigatus, Aspergillus terreus, Fusarium solani (Ascomycete)	LDPE	*A. terreus* and *A. fumigatus* could utilize LDPE as a carbon source after 100 d (SEM and FTIR spectroscopy were used).	Zahra et al., 2010
Thermomyces (formerly Humicola) *insolens* (Ascomycete)	low-crystalline PET film	97% weight loss within 96 h of reaction at 70°C. Fungal cutinase degraded PET to TPA	Ronkvist et al., 2009
Fusarium solani (Ascomycete)	low-crystalline PET film	Fungal cutinase degraded PET to TPA	Ronkvist et al., 2009
Penicillium citrinum (Ascomycete)	PET pellets	Isolated polyesterase from *P. citrinum* can hydrolyze PET	Liebminger et al., 2007

Highlights

This review provides an overview of the current knowledge on fungal biodegradation of macro- and microplastics.

Fungi have a great potential for reducing the negative impact of plastic pollution due to their natural and unique ability to invade substrates.

Fungal bioremediation is an environment-friendly and efficient method able to remove plastic wastes.