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Mechanisms of Synthesised Polyvinylchloride Biodegradation by Microorganisms and Insects

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Abstract: *Degradation of plastic polymers takes decades, making them a serious global issue due to their non-biodegradable solid waste status. Comparing biodegradation to other degrading processes, it is the most efficient and optimal approach for plastic decomposition due to its non-polluting mechanism, eco-friendliness, and affordability. The biodegradation of synthetic plastic is a gradual process that is aided by ambient conditions and naturally occurring microbial species. By secreting enzymes that break down plastics, bacteria and fungus contribute significantly to the biodegradation of plastics. High molecular weight polymers are broken down into low molecular weight polymers by the enzyme's oxidation or hydrolysis, which produces functional groups that increase the hydrophilicity of the polymer. For this reason, plastics deteriorate in a couple of days. This study presents the most recent research on the different types of fungi and bacteria that break down polyvinyl chloride (PVC), as well as the roles played by insects and the mechanism underlying the process.*

Keywords: Biodegradation, Polyvinyl chloride (PVC, Bacteria, Fungi, insects, degrading enzymes

1. INTRODUCTION

A thermoplastic that is applicable in household implements, pipes, furniture, upholstery, disposable products like food, and pharmaceutical packaging, including medical devices, is known as polyvinyl chloride (PVC) (Giacomucci, Raddadi, Soccio, Lotti, & Fava, 2020). As a result of high demand based on its properties, a huge amount of this plastic material is generated. An estimated 6.3 billion tons of plastic have been manufactured since the start of widespread utilization, with seventy-nine percent of the waste going to landfills. This could result in 2.41 million plastic tons of waste ending up in the ocean each year (Lebreton et al., 2017).

The design of the plastic is to last because plastic wastes are persistent materials that pass through physical changes due to environmental conditions, resulting in microplastics, a condition known as tiny fragments that are currently discovered in remote, sparsely as well as densely populated areas (Bergmann *et al*., 2019). In every day activity, synthetic plastics are widely utilized by many companies, with a total annual global production of more than three hundred and fifty-nine million in 2018 (Plastics Europe, 2019).

On the basis of the demand for polymers in Europe, one of the six widely used plastics is polyvinyl chloride (PVC). The percentage presence reveals 29.7 percent of polyethylene (PE), 19.3 percent of polypropylene (PP), 10 percent of PVC, 7.9 percent of polyurethane (PUR), 7.7 percent of polyethylene terephthalate (PET), and 6.4% of polystyrene (PS) (PlasticsEurope, 2019). Phthalate esters are the additives that are commonly found in plasticized polyvinyl chloride (PVC), and these additives play important roles in improving the mechanical characteristics of the plastic, which is also responsible for close to fifty percent of its total weight (Ru *et al*., 2020).

Presently, phthalates are known as causatives of disruption of endocrine with the effects regarded as genotoxic. Other compositions like heavy metals and atoms of chlorine are also important environmental problems with respect to the deterioration of PVC in the environment and disposal of the landfill (Siciska *et al*., 2021). Generally, rigid PVC is made up of plasticizers with less than ten percent (w/w), whereas flexible PVC can make up approximately seventy percent (Wikipedia, 2020). For decades, PET and PS have been major environmental issues, and up to date, approximately six thousand three hundred million metric tons have been produced (Geyer *et al*., 2017).

Moreover, each year, residues from rubber contribute solid wastes worth millions of tons (Abelkheir *et al*., 2019a, 2019b). When exposed to sunlight, heat, and radiation from UVB, there is a reduction and weakening of polyvinyl chloride (PVC) physicochemical properties, while there is also a slow rate of natural degradation process compared to the rate of production demand across the globe

(Tang *et al*., 2018). There is also the presence of microplastics (MPs) in polyvinyl chloride (PVC) (Guo *et al*., 2020; O'Connor *et al*., 2019). The presence and persistence of nanoplastics in the environment can be attributed to the embrittlement and microcracking on plastic surfaces caused by weathering (Wang *et al*., 2021).

In the process of degradation of PVC, three reactions or stages are involved: depolymerization, or polymer chains breaking down; oxidized intermediate formation; and intermediate mineralization to form CO_2, H_2O, and Cl-. Depolymerization is the first and most useful reaction. The current review evaluates the roles of bacteria, fungi, insects, and microbial enzymes in polyvinyl chloride biodegradation (PVC).

2. Polyvinyl Chloride (PVC) Biodegradation by Bacteria

With strong depolymerizing activity against PVC additives relative to the PVC polymer chains, Pseudomonas citronellolis and Bacillus flexus have been found to biodegrade PVC film (Giacomucci et al., 2019). The dense biofilm that these strains have been found to grow on the plastic film's surface causes the mean molecular weight of the PVC film to drop. Dense biofilm growth and a drop in mean molecular weight (Mn) are two indicators of polymer chain biodegradation (Syranidou et al., 2017; Ahmed et al., 2018). Low molecular weight polymers are the result of exocellular enzymes being released into the culture medium, which hydrolyze the polymers both inside and at the ends of rigid chains.

Vinyl chloride monomers have been reported to be used by Pseudomonas putida strain AJ as a carbon source for growth (Verce et al., 2000). Because of the potential for the development of environmentally unfavorable degradation products including chlorine, the composting and biodegradation processes of polyvinyl chloride (PVC) remain controversial.

3. Fungi Degradation of Polyvinyl Chloride (PVC)

In certain rural areas, incinerating wastes is still a common practice for getting rid of wastes. However, when waste containing polyvinyl chloride (PVC) is heated, it releases various dangerous substances like hydrogen chloride, CO, free ions, and free radical molecules (Vivi, Martins-Franchetti, & Attili-Angis, 2019). There have been studies that demonstrate that fungi and bacteria can break down PVC, despite the material's resistance to biodegradation (Raddadi & Fava, 2019).

Due to their low specificity for breaking down organic compounds, ubiquity, rapid mycelial network spread, and ability to thrive at low pH levels, fungi seem to be a promising alternative (Pardo-Rodrguez et al., 2021). Additionally, fungi have the ability to create hydrophobins, which give them the ability to colonize hydrophobic substrates and bind to them, marking the beginning of the substrates' breakdown (Sánchez, 2020).

A few fungal species that have demonstrated the degradation of polyvinyl chloride (PVC) include Aureobasidium pullulans (Webb et al., 2020), Cochliobolus sp. (Sumathi et al., 2016), Phanerochaete chrysosporium, Aspergillus niger (Ali et al., 2014), Penicillium funiculosum ATCC 9644, Trichoderma viride ATCC 13631, Paecilomyces variotii CBS 62866, Aspergillus niger (ATCC6275) (Whitney 1996), and Chaetomium globosum (ATCC 16021) (Vivi et al., 2018). Some fungi that resembled yeast, such as Kluyveromyces spp. and Rhodotorula aurantiaca, have also been shown to have the ability to degrade polyvinyl chloride (Srikanth et al., 2022).

There are not many published research in the scientific literature about fungi's ability to break down polyvinyl chloride (PVC). In their study, Pleurotus sp., Poliporus versicolor, and Phanerochaete chrysosporium were found to degrade PVC at rates of 19.32% and 82.15%, respectively, whereas the latter two species demonstrated percentages of less than 13.17%. Kirbas, Güner, and Keskin (1999) examined these three fungal species' effects on PVC degradation.

Conversely, Phanerochaete chrysosporium, Lentinus tigrinus, Aspergillus niger, and Aspergillus sydowii were used by Ali et al. (2014) to examine the degradation of polyvinyl chloride (PVC) films. They discovered color changes and deterioration in the films that were analyzed. Furthermore, they discovered that all of the fungi under investigation had increased in biomass, indicating that the fungi were using polyvinyl chloride (PVC) as a carbon source.

Last but not least, Sumathi, Viswanath, Lakshmi, and SaiGopal (2016) separated the fungus Cochliobolus sp. from soils contaminated with plastic waste and examined how the fungus's laccase enzyme broke down low molecular weight polyvinyl chloride (PVC). They found that PVC exposed to the fungus deteriorated noticeably faster than untreated PVC.

4. Degradation of Polyvinyl Chloride (PVC) By Insects

Tenebrio molitor, also known as yellow mealworms, Tenebrio obscurus, also known as black mealworms, and Zophobas atratus, also known as superworms, or Zophobas morio, also known as yellow mealworms, have all been documented to be present throughout the past 10 years. Due to its exceptional capacity to biodegrade polystyrene and LDPE (Peng et al., 2019; Yang et al., 2018a, 2018b), consume PVC tubing (Bozek et al., 2017), and break down PVC plastic powders (Wu et al., T. molitor is a commercially available animal feed that has the potential to be a sustainable substitute for food protein for human consumption (Borremans et al., 2020).

The larvae possess an innate capacity to convert several polystyrene compounds into carbon dioxide by the action of intestinal bacteria (Yang et al., 2018b). Larvae broke down mixed polyethylene and polystyrene foam, and two bacterial genera—Citrobacter sp. and Kosakonia sp.—were connected to the biodegradation of polyethylene and polystyrene (Brandon et al., 2018). According to

Aboelkheir et al. (2019a), T. molitor larvae can also biodegrade tire crumb and vulcanized styrene-butadiene rubber (SBR) based on reduced cross-link degree, FTIR analysis, heat analysis, XRD patterns, and SEM observation.

It has been reported that Tenebrio obscurus larvae (dark mealworms), a different member of the Tenebrio genus, can also biodegrade polystyrene using the same gut microbe-dependent mechanism (Peng et al., 2019). Additionally, polystyrene and polyethylene degradation candidates have been extended to Zophobas atratus larvae (superworms) (Peng et al., 2020).

In a study conducted by Bo zek et al. (2017), the amount of polyvinyl chloride (PVC) consumed by T. molitor utilizing PVC medical tubing—which often contains a high amount of plasticizer—was found to result in a 3% mass reduction as opposed to 9% of polystyrene foam. Although biodegradation of PVC was not confirmed, their data showed encouraging signals of it. T. molitor larvae from three sources that were fed solely polyvinyl chloride (PVC) powder were evaluated by Wu et al. (2019). The results demonstrated considerable alterations in the Mn and Mw of the residual polymers in the frass, as well as changes in the FTIR spectra, suggesting the possibility of biodegradation. However, the depolymerization patterns and mineralization of PVC in *T. molitor* larvae as well as response of gut microbiome to PVC diet remain unknown based on the previous studies.

Although only 2.9% of the polyvinyl chloride was converted to chloride by T. molitor larvae, it was discovered that the larvae could quickly depolymerize and biodegrade polyvinyl chloride materials into organic chlorinated intermediates. Like the findings for PS breakdown by T. molitor larvae, depolymerization stopped when gut microorganisms were reduced with the antibiotic gentamicin, suggesting gut-microbial dependency.

5. Enzymatic Mechanisms Involved In Plastic Biodegradation by Fungi

A component of the biodegradation mechanism is the activity of microbial enzymes on plastic surfaces. Growing on the plastic film as a substrate and source of nourishment, microorganisms like fungi and bacteria cling to it and inactivate the enzymes. Consequently, the polymers progressively depolymerize, and the mineralization process compiles the degradation, yielding H2O (water), CO2 (carbon dioxide), and CH2 (methane) as the final products (Montazer et al., 2019). By employing enzymes that cleanse contaminants, fungi can infiltrate substrates. Hydrophobins, which are employed to coat hyphae on hydrophobic substrates, are examples of surface-active proteins that fungi can also manufacture. Since they proliferate and pierce the polymer solids, much fungus can induce tiny-scale swelling and bursting (Griffin, 1980).

Certain fungi use both extracellular and intracellular enzymatic systems to break down polymers. Fungal adaptability depends on the intracellular enzymatic system, which also serves as an internal detoxifying mechanism (Schwartz et al., 2018; Shin et al., 2018). The cytochrome P450 family (CYP), which involves oxidation and conjugation processes, is mediated by Phase I enzyme epoxidase and Phase II enzyme transferases. A class of heme-containing monooxygenases known as the Cytochrome P450 family catalyzes a range of enzymatic processes (Shin et al., 2018).

Enzymes such as cytochrome P450 are crucial for primary metabolism because they safeguard the integrity of the hyphal wall and aid in the development of the outer wall of the spore. In order for CYP isoforms to be able to absorb substrate from both the cytosolic and membrane environments, they are anchored in the endoplasmic reticulum membrane (rejber et al., 2018). NADPH: CYP reductase and cytochrome P-450 hydrolase are the two enzymes that make up CYP, together with three cofactors (H+, FAD, heme, and NADPH+).

The two main components of the extracellular enzymatic system are the hydrolytic system, which generates hydrolases involved in the breakdown of polysaccharides, and the unspecific oxidative system, which breaks down complex compounds like lignin (Srikanth et al., 2022). Many different substrates can be oxidized by the unspecific oxidative system. It is primarily produced by enzymes known as class II peroxidases, which include lignin peroxidase, versatile peroxidase, and manganese peroxidase, laccases, and unspecific peroxygenases (Srikanth et al., 2022). via employing H2O2 as an electron-accepting co-substrate in oxidation-reduction processes, or via epoxidation, aromatic preoxygenation, and sulfoxidation, these enzymes transfer electrons from organic substrates to molecular oxygen (laccases) (Karich et al., 2017).

Based on Srikanth et al. (2022) wood-degrading fungi, basidiomycetes are the main producers of this enzyme complex. Numerous environmental conditions, including temperature, pH, and moisture content, can affect the way fungus behave on plastic surfaces. Temperature also plays a significant role in this biodegradation process; polymers with a high melting point take longer to degrade than polymers with a low melting point. The activation of fungi requires sufficient moisture, while enzyme action on plastic polymers requires an appropriate pH environment (Srikanth et al., 2022).

6. CONCLUSIONS

Fungi's ability to biodegrade plastics can aid in reducing the issue of plastic pollution, which has a significant impact on living things. Plastic pollution research is currently focusing on the biodegradation of plastic polymers as one of its main approaches. The review offers significant insights into the diverse range of bacteria, fungi, and insects that participate in the degradation of various plastic polymers, as well as the particular enzymes that are produced by these microorganisms and play a role in the biodegradation process.

In order to combat environmental plastic pollution, a fresh field of research has focused on the biodegradation of petroleum-derived polymers. This review has covered the microbes and enzymes that have been shown to biodegrade these artificial polymers. Numerous strains of Bacillus and pseudomonas have been shown to partially decompose a variety of petro-plastics, including polyvinyl chloride (PVC), and to break down complex, resistant substances such polyaromatic hydrocarbons. Polyvinyl chloride polymers have also been found to be depolymerized by microorganisms found in the intestines of insects.

Gaining more knowledge about the genes and/or gene products (enzymes) that hydrolyze high molecular weight polymers of petroleum-plastics could help us comprehend the molecular mechanisms that underlie biodegradation. Investigating the digestive enzymes in the gut microorganisms of plastic-degrading invertebrates may also provide new avenues for plastic degradation, especially with regard to persistent non-hydrolyzable polymers.

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