HIGH SCHOOL EDITION
Journal of Student Research

PET Microplastics and Grand Challenges: Effects on CNS and Detection/Degradation Methods

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ABSTRACT

Despite the growing production of plastics, there is a serious gap in knowledge on its effect on human health. Microplastics are damaging to locomotor behavior, the gut-brain axis, and other functions of the central nervous system. In this review, we look at the evolution of microplastic detection methods, adverse effects associated with exposure to Polyethylene Terephthalic microplastics, or PET-MP, and the potential of chemical recycling as an efficient and beneficial recycling process. We found that, although detection methods have improved in terms of accuracy, there is still much to be optimized, such as tedious processes, long detection times, and lack of versatility in microplastics that can be detected. We found that PET microplastics significantly increased spontaneous activity in *Drosophila Melanogaster* and negatively affected gut microbiota, which can potentially impair learning and memory. There are still major gaps in understanding the effect of PET microplastics on organisms, as most research is catered towards polyethylene microplastics. Lastly, we looked at the presence of PET-MP in terms of a Grand Challenge and looked at potential solutions for remediation. We found that methods such as glycolysis and hydrolysis, which use chemical agents to depolymerize PET-MP as a way of recycling, hold lots of potential for environmental remediation.

Introduction

The discovery of synthetic plastics in the early 1900s marked the beginning of the great commercial success of manufactured plastic (Chaudhry et al., 2021). Many factors such as their low cost, low density, versatility, and low thermal and electric conductivity made plastics extremely efficient for commercial use, causing a significant increase in plastic usage (Chaudhry et al., 2021). While revolutionary both to modern life and polymer research, there has been great concern over the growing production of plastic and its impact on the environment. The global market volume of plastics has increased dramatically in the past few decades, leading many environmentalists to be concerned about the range of effects of the pollutants (Padervand et al., 2020).

Microplastics are the product of erosion of bulk plastic (Matthews et al., 2021), smaller than 5 mm (Shamskhany et al., 2021), and can be obtained from any type of plastic, the seven main types being polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET), polystyrene (PS), polyurethane (PU), polyvinyl chloride (PVC), and polycarbonate (PC) (Kannan et al., 2021). Polyethylene terephthalate microplastics, or PET-MP, are commonly used to make textiles and packaging materials (Barredo et. al)(Shen et al., 2021). They are a linear thermoplastic polyester with great chemical inertia (ability to resist degradation against several influences) (Barredo et. al) and impact resistance, making PET-MP an optimal choice for water and carbonated beverage bottles (Shen et al., 2021). PET-MP is optimal for commercial purposes but poses an environmental threat. For example, due to their high chemical inertia and resistance to degradation, many PET-MP end up accumulating in aquatic environments for centuries (Shamskhany et al., 2021).

PET-MP is one of the most commonly used microplastics, accounting for almost 10% of plastic consumption in Europe, mostly recyclable plastic and beverage bottles (Shen et al., 2021). In a study of microplastics in human feces, PET-MP were the most prevalent types of microplastics found. Despite its well-documented exposure to biological systems, research on the effects of PET-MP on biological systems has been severely limited, with the majority of research focused on polystyrene and polyethylene microplastics (Shen et al., 2021). The biological toxicity of microplastics can be dependent on the type of microplastic making toxicological studies more difficult (Liu et al., 2021). Therefore, there is a significant need to elucidate our understanding of the effect of PET-MP on human health.

Current research demonstrates that exposure to a variety of microplastics may have adverse effects related to the nervous system in model organisms. Due to their size, MP can enter the digestive tract and infiltrate blood, liver, kidneys, and brain (Zhu et al., 2023), and cross the blood-brain barrier in zebrafish, subsequently causing a wide array of issues (Pitt et al., 2018). They have been proven to have a neurotoxic effect in Caenorhabditis elegans (Lei et al., 2018) that spans transgenerationally (Chen et al., 2021). They have also been shown to cause brain
damage and cognitive deficits during the exposure of microplastics to fetuses (Chen et al., 2021). The severity of these effects indicates a need for further research.

Due to concerns about animal welfare, safety, and costs, many researchers have been trading vertebrate models for alternate ones. One of these models is *Drosophila Melanogaster* (Dahleh et al., 2023). Sequencing of the genome of *Drosophila Melanogaster* shows 75% similarity with the genome of a human (Dahleh et al., 2023). *Drosophila Melanogaster* has the same basic physiological responses as mammals (Dahleh et al., 2023). Due to the high neuronal complexity of *Drosophila Melanogaste*r, it has become significant in research involving neurotoxicology as well.

However, while invertebrate models such as *Drosophila Melanogaster* are considered the superior models due to their high accuracy and predictability, there is a need to involve in-vitro models due to ethical and monetary considerations (Zink et al., 2020). Due to the advancements of in-vitro models, and the ability to limit interspecies variability through the use of human cells, in-vitro models have become a potential replacement for animal models (Zink et al., 2020).

With the rise of the concept of "Grand Challenges," or global challenges that demand research for resolution, there has been a rise in the need for collaboration between academia and industry (Välikangas et al., 2022). Due to the uprise of PET production, there has been a greater need for waste management, especially through means of recycling. Currently, there are four main methods of recovering or recycling: primary, secondary, tertiary, and quaternary recycling (Barredo et al., 2023). Primary recycling, also known as closed-loop recycling, consists of on-site recycling without the facilitation of chemicals or other materials (Bardoquillo et al., 2023). Secondary recycling, or mechanical recycling, consists of a series of mechanical processes such as grinding, sorting, and cleaning (Bardoquillo et al., 2023). Tertiary recycling, or chemical recycling, consists of depolymerizing polymers back to the initial raw monomers with the help of chemical reactions (Bardoquillo et al., 2023). Quaternary recycling, or incineration, involves the combustion of polymers (Bardoquillo et al., 2023).

Tertiary, or chemical recycling, is a method of recycling that interests many researchers due to its sustainability (Bardoquillo et al., 2023) and the potential to achieve "permanent recycling" (Barredo et al., 2023). Due to this potential, many researchers have sought to optimize chemical recycling methods. These methods include hydrolysis, glycolysis, methanolysis, and aminolysis (Barredo et al., 2023). However, many of these methods have issues regarding purity and costs (Bardoquillo et al., 2023).

First Area of Focus: A Review of Microplastic Detection Methods

The uprise in plastic production has subsequently led to an advancement of more accurate and effective detection methods, compared to archaic visual inspection methods, where microplastics are classified by direct observations (Ye et al., 2022). Proper detection methods are vital to understanding and determining the risks of MPs to human health and ecological environments (Kannan et al., 2021). They are also vital to efforts to understand the feasibility of reducing microplastic proposals. This makes methods of detecting microplastics an essential topic to fully understand and optimize (Huang et al., 2022).

Visual detection methods, are the most traditional and archaic of all methods, where microplastics are analyzed using microscopes or the bare eyes (Ye et al., 2022). This method is simple and cost-effective, but time-consuming and difficult, and only works efficiently when the microplastics are large enough (Huang et al., 2023). Therefore, more focus has been put on utilizing other methods. Chemical detection methods study the chemical properties of microplastics to classify microplastics, utilizing thermal analytical methods, which measure the relationship between physical properties and temperature of microplastics under specific temperature conditions, and vibration spectral methods, which detect and identify polymers in environment samples through specific absorption spectra (Huang et al., 2023) (Ye et al., 2022)

However, both thermal and vibration spectral methods have their advantages and disadvantages. For example, while thermal methods such as Pyrolysis gas chromatography–mass spectrometry (Pyr-GC–MS), thermal extraction desorption gas chromatography–mass spectrometry (TED-GC–MS), and differential scanning calorimetry (DSC) are all highly accurate, they are difficult to work with and are too easily affected by impurities in samples (Sorolla-Rosario et al., 2023). On the other hand, vibrational spectral methods such as Raman spectroscopy (Raman) and Fourier transform infrared spectroscopy (FTIR), are also quite accurate (Ye et al., 2022). However, Raman spectroscopy has a fairly long detection time, and the FTIR cannot identify microplastics larger than 20 μm (Araujo et al. 2018) Despite these major advancements and achievements, there is still a need for methods of quantitative determination of MPs to evolve.

Second Area of Focus

PET-MP Had a Neurotoxic Effect On Spontaneous Activity of Drosophila Melanogaster

Exposure to neurotoxic agents such as microplastics can cause many disruptions to the nervous system. One of these disruptions is locomotor behavior and spontaneous activity (Shen et al., 2021). Shen et al (2021) mixed Drosophila food with 1 g, 10 g, and 20 g PET-MPs at 2 μm, added into 60 μl ethanol and 60 μl H2O. They were fed for 6 days and placed in a Drosophila Activity Monitoring (DAM) system (Trikinetics) for spontaneous activity monitoring. The data collected showed that the 24 h total activity of female Drosophila with 1 g/L, 10 g/L, and 20 g/L increased by 20%, 25%, and 22% respectively, and the total activity of male Drosophila increased by 28%, 32%, and 43%. Experimental results showed that both male and female Drosophila have a significant increase in spontaneous activity after exposure to PET-MPs indicating alterations or damages to the central nervous system.

This increase in spontaneous activity is likely due to neuron damage caused by the PET-MP (Shen et al., 2021). Research has shown that, when exposed to PS-MP, Caenorhabditis elegans showed similar damage/activity (Shen et al., 2021). PS-MP was shown to cause damage to GABAergic and cholinergic neurons, which cause damage to the flies' ability to control motor ability (Shen et al., 2021). These results suggest that PET-MP microplastics have the potential to negatively affect motor and locomotor abilities in humans as well.

PET-MP Affected Human Gut Microbiota, Potentially Affecting Brain Development, Learning, And Memory

The gut microbiota is a diverse community of microorganisms that cohabit in the human colon and are responsible for many physiological functions such as the central nervous system, where it uses mechanisms involving nervous signaling (Fournier et al., 2023) (Martin et al., 2018). This phenomenon is called the microbiota gut-brain axis.

Some studies have shown that changes to gut microbiota have dramatically affected the central nervous system, human health, hippocampal neurogenesis, learning, and memory (Martin et al., 2018). Previous research shows that exposure to polystyrene microplastics causes deficits in learning and memory and that there likely is a correlation between these deficits and the microbiota gut-brain axis (Lee et al., 2022). Therefore, investigating PET-MP's potential risk on the gut microbiota is crucial to uncovering its effect on the central nervous system and neurological function.

Fournier et all sought to understand the relationship between microplastics and the gut-brain axis. A dosage of 0.166 g/intake was given 4-5 times using human colonic microbiota (Fournier et al., 2023). Results showed that exposure to PET-MP affected the composition of the microbiota, diversity of the human colonic microbiota, and bacterial counts of Bacteroides, Parabacteroides, and Alistipes, which are essential for healthy microbiota (Fournier et al., 2023). These results all suggest that the influence of PET-MP is largely negative on gut biota (Fournier et al., 2023, and that they might affect the central nervous system as well (Martin et al., 2018).

Third Area of Focus

Although current methods of recycling, mainly secondary recycling, play a significant role in recovering plastic waste, they are not sustainable (Teo et al., 2023). Plastics are unable to withstand many rounds of mechanical recycling, and lose value after each round of recycling, inevitably sentencing MPs to incineration or landfills, which pose environmental problems (Teo et al., 2023; Crippa et al., 2020). Chemical recycling, or the process of depolymerizing waste into its building blocks, is much more sustainable as plastics can be chemically degraded infinitely (Bardoquillo et al., 2023). Plastics that, under mechanical recycling, may have had an "end life," now have the opportunity to be broken down into pure monomers, then regenerated into new plastics or be used as raw materials used in the mass production of new compounds in the energy market (Teo et al., 2023). This makes chemical recycling an invaluable recycling method.

It is important to understand the synthesis and degradation patterns of PET in chemical recycling. PET is synthesized by performing condensation processes involving the two monomers, terephthalic acid (TPA) and ethylene glycol (EG), with a Fischer esterification creating a product of PET and water (Nisticò et al., 2020). Degradation processes, such as chemolysis, include breaking down the polymer using different degradation reagents (Padhan et al., 2019). Chemolysis is extremely versatile and has the opportunity to create many different byproducts, depending on the method used (Bardoquillo et al., 2023). These methods include glycolysis and hydrolysis (Crippa et al., 2020).

Glycolysis involves a transesterification reaction between PET and glycols, such as ethylene glycol, at high temperatures and pressures, creating byproducts of polyols such as BHET, or bis(hydroxyethyl) terephthalate, as well as TPA, EG (Padhan et al., 2019) (Ghosal et al., 2022). It is the simplest and oldest method of chemolysis, making this method one of the most commercially used (Crippa et al., 2020). Research done on glycolysis has shown that, despite efforts to optimize the process, glycolysis remains an extremely slow process that requires the use of catalysts to achieve complete depolymerization of PET, making catalyst-assisted glycolysis extremely popular amongst commercial and industrial spaces (Ghosal et al., 2022). Unfortunately, this has encouraged the use of metal salt-based catalysts, which can be toxic to the environment (Zangana et al., 2022). Therefore, efforts have been made to search for methods that can speed up the process of glycolysis while avoiding the use of toxic catalysts.

One of these methods includes using CaO activated carbon and microwave irradiation to lower the activation energy for the transesterification reactions during this process (Zangana et al., 2022). Results showed that by utilizing these conditions, they were able to crystallize BHET in approximately 3.5 minutes, which, to our knowledge, was the fastest process of glycolysis recorded (Zangana et al., 2022).

Hydrolysis involves a transesterification reaction between PET with water under different conditions, creating byproducts of TPA and EG (Padhan et al., 2019). These conditions include alkaline, acidic, and neutral conditions. Under neutral conditions, water with alkali metal acetates is used (Padhan et al., 2019). However, the low purity associated with neutral hydrolysis makes it a less desirable method for commercial use (Stanica-Ezeanu et al., 2021). Under an acidic condition, concentrated sulfuric acid is used to break apart the polymeric chains (Barredo et al., 2023) (Padhan et al., 2019). However, the lower temperature and pressure required for acidic hydrolysis results in slower degradative rates, making it less efficient (Barredo et al., 2023). Under an alkaline condition, aqueous solutions of NaOH or KOH at various concentrations are used to gain EG and disodium salt (Barredo et al., 2023). This method of hydrolysis is the most efficient and shows the most promise, as it produces byproducts with the greatest purity (Barredo et al., 2023). However, this process still requires phase transfer catalysts, and there is a gap in knowledge surrounding alternative methods of lowering activation energy (Barredo et al., 2023).

Conclusion

As we become more cognizant of the ubiquitous presence of microplastics, it is important for us to not only become aware of its effect on human health and other biological systems but to improve methods of recycling as an effort to solve the issue of ubiquitous exposure. Methods of detection currently have several limitations, ranging from effectiveness to efficiency. These limitations make it difficult to fully understand the risks of MPs to human health and ecological environments. There are also currently several gaps in knowledge surrounding PET-MP and its effect on human health. While methods of chemical recycling such as glycolysis and hydrolysis are viable, there is still much work to be done before these methods can be successful commercially. Understanding these limitations is vital to encourage solutions, and to truly view PET microplastics as a Grand Challenge.

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