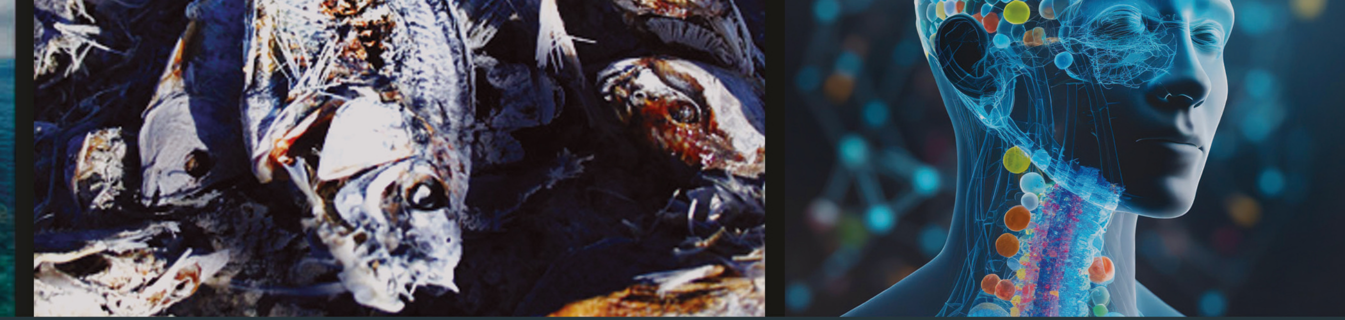
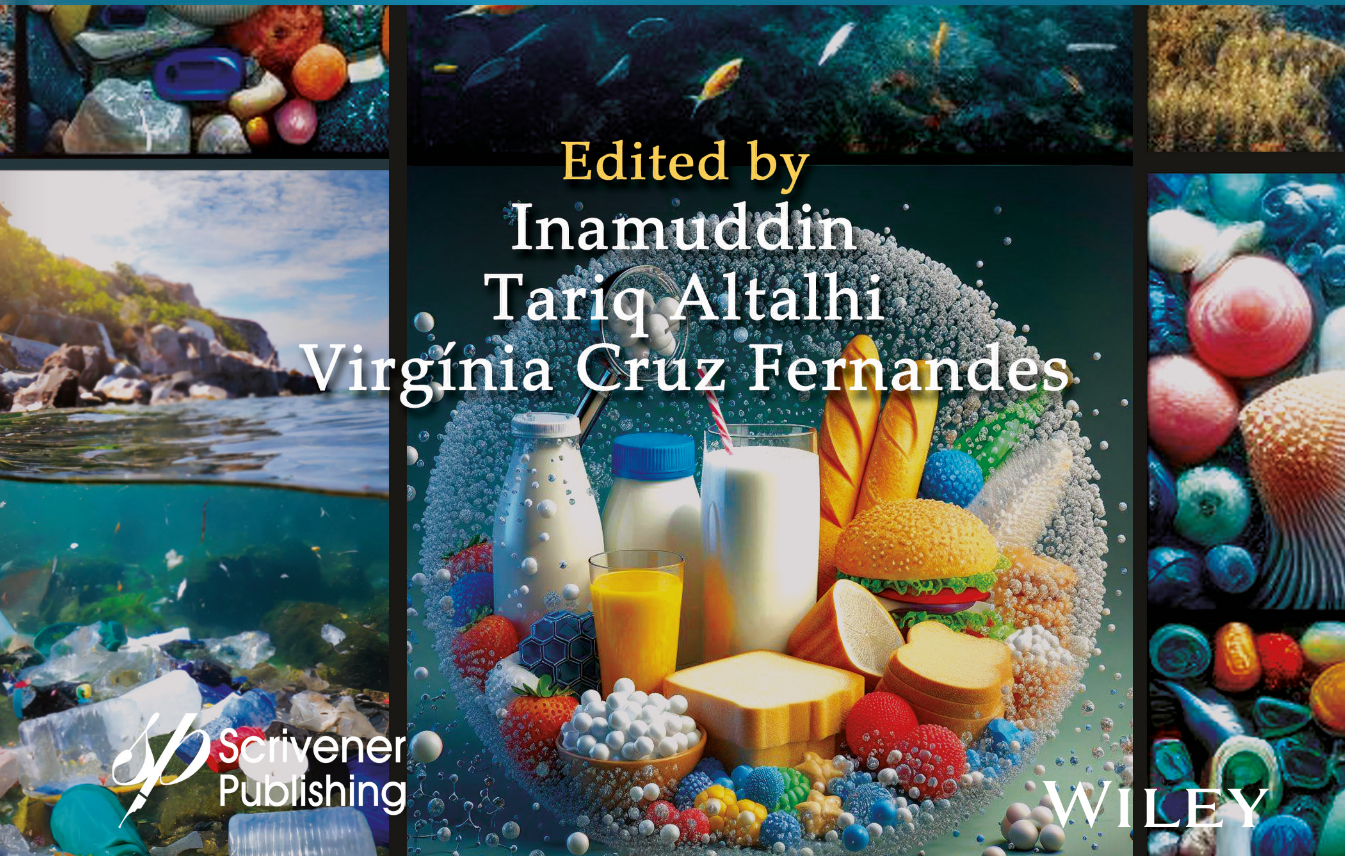


Toxic Effects of Micro and Nanoplastics

Environment, Food and Human Health



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Preface

Micro- and nanoplastics are the degradation products of large plastic compounds. These degraded polymers enter into the natural environment including air, water, and food, which leads to various significant threats to human health. The nature of these micro- and nanoplastics is persistent and consequently accumulates in the exposed person's body. Research into microplastics has shown that these particles accumulate in various human organs and impart detrimental effects on humans. To safeguard human health, analysis and remediation strategies are necessary.

This book provides a comprehensive overview on the source, distribution, life cycle assessment strategies, physico-chemical interactions, methods of analysis, toxicological investigation, and remediation strategies of micro- and nanoplastics. It is an invaluable resource for academics, researchers, post-doctoral and Ph.D. students, the polymer industry, environment agencies, food and beverage professionals, etc.

Chapter 1 explains the effect of natural processes that microplastics undergo in the environment (e.g., radiation, physical abrasion, chemical reactions, and biodegradation), which causes an increase in their ability to adsorb other pollutants and transport them. The chapter also outlines the analytical techniques used to evaluate the chemical and physical changes.

Chapter 2 presents life cycle analysis and its stages as applied to new materials called "biobased," which have emerged as an alternative to replace the use of plastics. The main focus of this chapter is to assess the environmental impacts of bioplastics versus petrochemical plastics and their sustainability.

Chapter 3 discusses micro- and nanoplastics as an invisible threat to human health. It reviews the various routes of exposure, the phenomenon of microplastics in nourishment and nutrients, and the impact of microplastics and nanoplastics on mammalian health and their effect on marine life.

Chapter 4 explains how the small plastic particles known as micro- and nanoplastics have become a significant environmental concern due to their widespread presence in various ecosystems. The toxic effects of these particles on the environment, food, and human health are a growing concern that requires more attention and action from governments, industries, and individuals. Reducing plastic waste and promoting the use of more sustainable alternatives can help mitigate this issue and protect our planet and health.

Chapter 5 discusses the probable sources of micro- and nanoplastics, and details their hazardous effects on different environments, including terrestrial, aqueous, atmosphere, wastewater treatment plants, and their resident organisms. It also explains the journey of these particles from their production source to their final destination.

Chapter 6 covers the routes through which micro- and nanoplastics can become part of our food and their possible toxic effects on human bodies and the food chain. Two primary ways that these plastic particles enter food products is through plastic food packaging or by being ingested by animals and absorbed into plants. This chapter explains how the side effects of MPs and NPs on human lives depend on numerous factors, such as plastic chemical functionality and biocompatibility, size, and amount of plastic ingested.

Chapter 7 discusses the microplastic, properties, types, and their impact on the environment in detail. Great attention is paid to various methods of eliminating microplastics. The chapter also includes goals and initiatives taken by the United Nations Sustainable Development Goal (SDG 14).

Chapter 8 analyzes the presence of micro- and nanoplastics in different types of beverages. It presents the classification of the analyzed beverages; the methods used for the quantification of micro- and nanoplastics; the characteristics of the particles; and their origin. Human exposure from the consumption of these products is also discussed.

Chapter 9 focuses on the effect of micro- and nanoplastics that end up in the terrestrial environment. It looks at their interaction with soil and plants while outlining their migration and accumulation inside the plant, and calculating their potential effect. The chapter also discusses the impact of micro- and nano plastics on terrestrial communities, including microbes and humans.

Chapter 10 addresses the presence of microplastics in personal care products (PCPs). The information is organized by three topics: the characterization of PM extracted from PCPs, their interactions with other substances, and toxicity. The chapter explains how the use of these products is alarming due to their wide use and risks to the environment.

Chapter 11 reveals how the various chemical compositions including plastics and microplastics are mixed into desired concentrations when manufacturing cosmetics. It discusses, too, the main sources of plastics and microplastics and their growth in India. The effect of cosmetics on human health is explained. Finally, alternative products to plastics and microplastics for use in cosmetics are listed.

Chapter 12 delves into the detrimental impact of micro- and nanoplastics on the human genome. The introduction of such particles into the ecosystem, and ultimately to the human body, is explained. This chapter presents an thorough toxicological analysis of these particles, shedding light on the urgent need for proactive measures to safeguard our ecosystem.

Chapter 13 discusses the generation, as well as the techniques for the measurement and identification, of micro- and nanoplastics. Various degradation methods are also discussed, as are the harmful effects of plastics, nanoplastics, and microplastics. Measures to avoid the production of plastics, nanoplastics, and microplastics are emphasized.

Chapter 14 details the source and hazardous effects of micro- and nanoplastics in marine environments. Additionally, it elaborates on the damages caused by the plastic pollution on air, water, and soil. Methods for decreasing microplastics in the environment are also discussed, along with the severance of microplastics from water, sediments, and marine microbial strains associated with degrading microplastics.

Chapter 15 reviews the advances and challenges in assessing the toxicity of micro- and nanoplastics (MPs and NPs) in human beings. An analysis of 85 research articles is also presented. Results show that in most cases there is a negative effect associated with MPs and NPs, but this chapter explains how methodology differences don't allow the establishment of cause-effect relationships.

Chapter 16 delves into the extensive impact of plasticizers and flame retardants on ecosystems and human health. The presence of plasticizers and flame retardants in various environments raises concerns about potential ecotoxicological effects. This chapter explains how bridging knowledge gaps and promoting safer alternatives are crucial to address the risks posed by these additives.

Chapter 17 details the invisible threat of micro- and nanoplastic materials on mankind and the environment. It discusses the harmful effects of inorganic and organic contaminants that are present in MPs and NPs. Inorganic contaminants primarily include heavy metals and pesticides. However, organic contaminants are persistent organic pollutants, and the impact of persistent organic pollutants and inorganic contaminants on the environment are presented in detail.

Chapter 18 compares the toxicity of microplastics, nanoplastics, and nanoparticles in the ecosystems. Smaller particles can penetrate organisms and tissues leading to more severe impacts. Their unique properties increase reactivity and oxidative stress, raising concerns about bioaccumulation and higher trophic levels. This chapter explains why urgent mitigation strategies are needed to protect ecosystems from these pervasive pollutants.

Chapter 19 discusses the occurrence and sources of micro- and nanoplastics and the pretreatments performed in the samples. Additionally, it thoroughly discusses several techniques that can be used to characterize, identify, and quantify them. Furthermore, this chapter presents a general overview of the advantages, disadvantages, and limitations of those techniques.

Chapter 20 presents new analytical approaches for the analysis of micro- and nanoplastics in the environment. Microscopic, spectroscopic, thermal, and electroanalytical techniques are commonly used for the analysis of MPs and NPs. The chapter describes the development of analytical techniques for monitoring plastic pollution based on single and combined methods.

Chapter 21 details various enzymes that are applied for the biodegradation of micro- and nanoplastics. In this chapter, the advantages of enzymatic approaches compared to conventional methods are presented. The mechanism of enzyme-catalyzed degradation of plastics is also discussed, as are some examples from biodegradation of synthetic polymers that use various enzymes.

Chapter 22 explains how the most common physical, chemical, and biological techniques work to remove micro- and nanoplastics. Some of the most relevant findings found in the literature for each technique are presented, as are the advantages and disadvantages of each type of removal technique.

Chapter 23 details the different materials used to remove the micro- and nanoplastics from the water. This chapter explains how to use sponge/aerogel materials, materials with metals, and biochar to remove MPs and NPs. Also, remediation methods that employ powder and granulated activated carbons are presented.

Chapter 24 details the toxicity and aftereffects of micro- and nanoplastics on the marine environment and its flora and fauna. The providence of MPs and NPS and their migration to the aquatic environment, along with an analysis of various micro/nanoplastics toxicity and the propensity towards environmental implications, is also presented.

We are deeply grateful to everyone who helped with this book and greatly appreciate the dedicated support and valuable assistance rendered by Martin Scrivener and the Scrivener Publishing team during its publication.

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Aging Process of Microplastics in the Environment

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Abstract

The presence of plastics in various ecosystems is an emerging worldwide environmental concern. Researchers have studied the interaction of microplastics (MPs) with other pollutants that are also present in the environment and have concluded that they act as vectors for pollution dispersion, transporting pollutants to different ecosystems, and being taken up by living organisms. The effects of natural processes that MPs undergo in the environment (UV radiation, physical abrasion, chemical reactions, and biodegradation) cause changes in their external surface, morphology, and chemical alterations that increase their ability to interact with other pollutants and transport them. Researchers have developed laboratory techniques to simulate the aging process of polymers and predict the behavior of MPs in real ecosystems. These reports highlight permanent physical and chemical changes in different properties of MPs, such as color, morphology, particle size, specific surface area, hydrophobicity, crystallinity, melting and glass transition temperature, surface groups, carbonyl index, and oxygen/carbon ratio. These properties have been measured using standard techniques (e.g., optical, fluorescence, and scanning electron microscopy, Fourier-transform infrared spectroscopy, Raman spectroscopy); however, emerging techniques are being explored (two-dimensional correlation spectroscopy and excitation–emission matrix-parallel factor analysis), where it is possible to detect the release products of the aging process.

Keywords: Advanced oxidation process, aged microplastic, biodegradation, emerging contaminants, mechanical stress, photooxidation, pristine microplastic

1.1 Introduction

Plastics are widely used to meet various societal needs. Advantages such as light weight, low cost, and long durability have led to their expanded use and application in fields such as healthcare, engineering, construction, agriculture, and high-performance apparel [1–4]. The distribution of plastic use in industries is estimated to be 4% is used in the electrical and electronics industry and construction, 6% for transportation, 12% for consumer and institutional

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products, 14% for textiles, 13% for other industries, and 43% for packing [5]. Apart from their applicability, their production can also have a great impact on the environment, as they can be manufactured with fossil fuels, which have a great impact on the carbon footprint, or with natural materials, such as cellulose [2, 3]. Biobased plastics have been researched in recent years and have proven to be an alternative to fossil plastics, as they are largely derived from biomass. However, they currently account for only 1%–2% of the annual production of plastics. Nevertheless, a study of the cradle-to-grave life cycle of biobased plastic should be conducted to balance the use of fossil versus biobased plastic [6, 7]. Despite these new alternatives, low-density polyethylene (LDPE), high-density polyethylene (HDPE), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polypropylene (PP), and polystyrene (PS) are the most commonly used polymers that are produced from fossil hydrocarbons [3, 8–10].

Plastics are adaptable and inexpensive, and plastic production between 2005 and 2017 was as high as in the last 50 years, showing a tendency to increase exponentially, posing a problem in the treatment and disposal of plastic waste [1]. In 2016, the entrance of 19 to 23 million t of plastics into the aquatic environment was estimated and it is predicted that 20–53 Mt/year will be released into aquatic systems by 2030 [11]. Researchers expect that double plastic production would be achieved by 2050, meaning that approximately 8 million tons of plastic waste will escape into the oceans [12]. Single-use plastics, such as bags and straws, represent approximately half of the plastic waste generated. During the COVID-19 pandemic, protective gear containing plastics (e.g., gloves and face masks) is often used by the population, increasing the amount of plastic waste [1, 12, 13]. Zhao *et al.* reported that 6,300 million tons of plastic waste was generated in 2015, of which only 9% was recycled, 12% was incinerated, and 79% was disposed of in landfills [2]. According to Williams *et al.*, of the plastic waste generated since 1950, 14% is incinerated, 40% is sent to landfills, and 14% is recycled. However, of this amount of recycled plastic only, 2% is optimally recycled, and the remaining 12% produces material with lower quality and functionality than the original, which is referred to as “downcycle” [12].

Based on this information and knowledge of the long life of plastics, humanity may face a worrying environmental problem in the coming years [14]. Governments around the world have introduced regulations to reduce the use of single-use plastics, namely imposing taxes on plastic bags and food packaging [1]. The incorrect disposal of plastics is a major problem of pollution, which may cause their entrance into the oceans [12, 15]. In recent years, researchers have explored plastic pollution from manufacture to final disposal, and the damage caused by plastic to ecosystems, but there is still a long way to go to understand how harmful their chronic presence may be to the environment.

MPs may have two types of sources: the primary source, which is considered a direct contributor, focused on the manufacturing of MPs in various industries, such as exfoliating cleansers, cosmetics, and toothpaste [14, 16]; and the secondary source, which is considered an indirect contributor to MPs, caused by the fragmentation of large plastic pieces into small ones, which can be promoted by photodegradation, mechanical or chemical action, or other weathering processes to which plastics are subjected to improper disposal in the environment [9, 16, 17].

Plastics are subjected to physical, chemical, and biological reactions over time, resulting in the desorption of smaller particles [8, 18]. Plastics can be classified based on their size as megaplastics (>50 cm), macroplastics (>5 to 50 cm), mesoplastics (≥5 mm to 5 cm), microplastics (≥1 μm to <5 mm), and nanoplastics (<1 μm) [14, 18, 19]. MPs have become the focus of research in recent years owing to their widespread presence in ecosystems, which is considered a threat to the environment, and consequently to human health. Microplastics (MPs) have been identified in freshwater [8, 10, 14, 16, 17, 20, 21], groundwater [8, 17, 20], snow [17], ice [17], sediments [8, 16, 17, 21, 22], soils [10, 17, 22–24], terrestrial and aquatic biota [10, 14, 24], air [17, 22, 25], foodstuffs (e.g., honey and salt), tap/bottled water [17, 22, 26], and biological samples (e.g., blood, human placenta, lung tissue) [27–29]. The ubiquity of MPs in the environment and their presence in consumer products, such as food or freshwater, leads to unrestrained consumption of MPs by humans [17]. Ingestion through direct consumption of contaminated products, inhalation of airborne contaminants with inhalable sizes of MPs and dermal contact between nanoplastics and the skin barrier are considered human exposure to MPs [22].

The biggest problem arises when researchers discover the ability of MPs to adsorb and transport various types of pollutants [9, 14, 23, 30–32]. Reports have shown that pollutants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), heavy metals, pesticides and antibiotics can be transported by MPs [10, 20, 30, 33–35]. Moreover, ecotoxicity studies show the hazardous effects of MPs taken up by earthworms, mussels, gobies, seabirds, turtles, seals, mammals, fish, reptiles, and plants [8, 14, 23, 36]. Depending on their exposure and susceptibility to MPs, they are considered potentially harmful to humans because of their high surface area, which can provoke cytotoxicity, oxidative stress, and translocation to other tissues [17, 22, 37]. Their persistence may also cause chronic inflammation with possible carcinogenic effects and immune or neurodegenerative diseases [22]. Recent studies have reported that MPs have been detected in human placenta, blood, and lung tissue [27–29], increasing the urgency to understand the behavior of MPs, including their interactions, and find solutions to minimize their impact on ecosystems, organisms, and human health.

Reducing plastic use is crucial to minimize this problem. Resolutions are being made regarding single-use plastics, and some countries have defined laws banning certain types of plastics. Resolutions such as taxing the production of single-use plastic (SUP) bags, charging for the use of SUP bags, assigning recycling targets to the manufacturer, and more radically, countries such as Jakarta have already banned the use of SUP bags completely, requiring the use of environmentally friendly bags [38]. The use of biodegradable plastics contributes to solving the plastic waste problem; however, suitable microorganisms must be present to ensure their degradation; otherwise, we will only address the problem [4]. It is crucial to harmonize policies, invest in alternative materials, and improve research on MPs, particularly in terms of ecotoxicity, namely the chronic effects on human life, which are still unknown. In addition, the focus should be on the pathways and interactions to find future solutions to minimize the impact of this problem.

1.2 Impact of MPs on the Environment

Recent studies have focused on the effects of MPs on the ecosystems where they are spread (air, terrestrial, and aquatic). As physical–chemical properties change due to the natural aging process, researchers have driven their studies on the behavior and ability of MPs to transport pollutants (e.g., PAHs, PCBs, pesticides, etc.) [10, 20, 30, 33, 34]. Adsorption and absorption constitute the sorption process and consist of the transfer of chemicals from liquids or gases to a solid, in this case MPs [39, 40]. The transfer of contaminants occurs due to interactions (van der Waals, ionic and steric forces, π–π interactions, and covalent bonds) with the surface of MPs, which is considered an adsorption process [39, 40]. Strong interactions between a low pollutant concentration and the surface of the adsorbent lead to adsorption. However, if the contaminant concentration is high, absorption occurs as soon as a large volume of pores is available to settle the pollutant molecules [39, 40]. Characteristics such as composition, size, shape, density, and chemical composition of MPs are key factors that promote the adsorption of MPs [40, 41], which may be changed by the aging processes that occur in MPs. However, environmental conditions (e.g., pH, temperature, salinity, and ionic strength) can also influence the adsorption process [42].

Studies have been carried out to predict the impact of the presence of MPs in different organisms, from aquatic (e.g., crabs and fish) to terrestrial (e.g., earthworms, nematodes, and mites) organisms. Although the responses differ according to the test organism, researchers have shown that MPs can cause hazardous effects (e.g., oxidative stress, cytotoxicity, and translocation to other tissues). Long-term contact and constant ingestion of MPs by organisms such as fish may cause effects along the food chain, leading to chronic inflammation (e.g., of the lungs) and increased risk of cancer, immune or neurodegenerative diseases, and metabolic disorders in humans [8, 22, 43, 44]. Furthermore, the harmful effects of MPs on other living organisms (plants and soil invertebrates) are of great concern [36].

Lei *et al*. investigated the effects of PS (diameter between 100 and 500 nm) on the survival rate, lifespan, motor behavior, movement-related neurons, and oxidative stress in *Caenorhabditis elegans*. After 3 days of contact, a decrease in the rate of survival, a large decrease in the organism length, and a decrease in the average life span of the nematodes were observed. In this study, it was also found that MPs can cause oxidative damage in nematodes, and the size of the particles affects their toxicity, which has far-reaching effects [43].

HDPE particles can transport chlorpyrifos (CPF), a commonly used pesticide. When this combination is in contact with mussels for 21 days, changes in the biological responses can be observed, which are greater than those induced by any stressor individually, according to the study by Fernándes *et al.* [31].

In a study performed by Bessa *et al*., 157 particles of MPs were detected, corresponding to 38 % of all fish, with 1.67 ± 0.27 (SD) MPs per fish, in three commercial fish species: sea bass (*Dicentrarchus labrax*), sea bream (*Diplodus vulgaris*), and flounder (*Platichthys flesus*). In addition, ecotoxicological studies need to be conducted to understand the risks to fish health and the consequences of consuming these fish in humans [20]. According to a review by Rakib *et al*., approximately 25 studies have reported various effects of MPs on different marine organisms, including ingestion, translocation, and respective impacts, reduction of the feed, oxidative stress or retention in the digestive tract, or even mortality of species [45].

1.3 Pristine and Aged Microplastics

MPs are widespread in the atmosphere and in terrestrial and aquatic systems. After their release, they are subjected to natural phenomena that lead to aging [46]. Ultraviolet (UV) radiation, physical abrasion, chemical oxidation, and biodegradation cause physical and chemical changes to the MPs [46, 47]. Exposure to UV radiation, known as photooxidation, leads to rapid degradation of the polymer in the environment, resulting in color changes and the appearance of cracks [48]. Although UV radiation is considered the main cause of aging of MPs, it is important to consider other phenomena that may play a role, such as mechanical stress or physical abrasion. Waves, tides, gravel, sand, stone, water flow, and other particles surrounding MPs can affect their physical properties and render them brittle. This aging process can result in changes in crystallinity, thermal hydrophilicity, and degree of polymerization [46, 49]. Chemical reactions may also occur, promoted by reactive oxygen species (ROS) [50, 51]. Photooxidation may occur because of a chemical reaction between MPs and ROS produced from natural organic matter (NOM), NO^{-3}, and CO_2^{-3}. In addition, after exposure to sunlight, pigments can produce ROS through a series of reactions that can oxidize the polymer [50–52]. Weathering phenomena, such as UV light, mechanical erosion, or chemical reactions, can play an important role in the life cycle of MP, as they cause changes in polymer properties.

The use of their aged in a natural environment was the better choice to study their interactions, but uncontrollable factors were associated with it. Therefore, researchers have focused on simulating the aging process in the natural environment of the laboratory, which although being more controlled may be less realistic. With constant changes in the environment and the emergence of new pollutants and possible new interactions, researchers have also focused on simulating environmental phenomena at the laboratory scale, such as photooxidation, mechanical stress, and chemical oxidation [53]. The development of these laboratory-scale aging tests is important for predicting and determining the behavior of aged MPs compared to pristine MPs, as the process of aging is very slow in the real environment [53]. According to Liu *et al.*, researchers are focusing on selecting the best laboratory technologies to increase the speed of the MP aging process. The most commonly used technology is light irradiation (66.7%), followed by chemical oxidation (16.7%), heat treatment, and microbial degradation (less than 26.6%) [52]. Despite the difficulty of the developed aging techniques, researchers have focused on understanding the significant changes in MPs after the aging process: physical changes, such as color changes, cracks on the surface of MP, or chemical changes, such as the differences between spectra from the Fourier-transform infrared spectroscopy (FTIR) and Raman analysis, or even changes in crystallinity, such as an increase in melting temperature. Table 1.1 summarizes the significant changes found in MPs after the aging process in the laboratory, with different changes showing the effects of aging processes. Understanding the behavior of MPs and their interactions can be complex, considering that mechanical agents, chemical, and biological reactions constantly occur in the environment. The change in properties has a significant impact on the adsorption behavior of MPs [54–57].

Adsorption studies were conducted with a focus on comparing the behavior of MPs in the pristine and aged states to understand the influence of altered properties. Zhang *et al.* studied the adsorption process of oxytetracycline in PS using purchased PS foams and aged PS foams made from plastic waste collected from coastal beaches. The influence of pH (between 2.0 and 10.0) and ionic strength (using sodium chloride, calcium chloride, and sodium sulfate) was tested to understand the effect on the adsorption process. The maximum adsorption capacity was observed at pH 5 for the beached PS samples, and stronger sorption of oxytetracycline in the MPs was observed in the presence of $CaCl_2$. Based on the equilibrium isotherms, it was found that aged PS had a higher adsorption capacity than pristine PS (1,520 $\mu g\ g^{-1}$ and 27,500 $\mu g\ g^{-1}$, respectively) [58]. Fan *et al.* simulated the aging behavior of PS and polylactic acid (PLA) in a natural environment, exposing the MPs in a

Table 1.1 Physical and chemical changes of MPs after suffering an aging process.

Property	Agent	Changes	References
Color	Photooxidation	Yellow, opacity	[49, 64, 66, 95–98]
Morphology	Photooxidation AOP Mechanical stress Biodegradation	Cracks, flakes, roughness, biofilm colonization	[56, 66, 95–97, 99–104]
Particle size	Photooxidation AOP Mechanical stress Biodegradation	Decrease	[49, 59, 86, 88, 89, 98]
SSA	Photooxidation AOP	Increase	[33, 53–55, 58, 67, 84, 105]
Contact angle	Photooxidation AOP	Decrease	[77, 99, 100, 105, 106]
Crystallinity	Photooxidation AOP	Increase Decrease	[33, 56, 74] [75, 100, 107]
Melting temperature	Photooxidation	Increase/Decrease	[59, 100, 103, 108]
Glass transition temperature	Photooxidation	Changeable	[59, 108–111]
Surface groups	Photooxidation AOP Mechanical stress Biodegradation	New peak/band formation	[67, 78, 79, 95, 103, 112, 113]
CI	Photooxidation AOP Mechanical stress Biodegradation	Increase	[50, 92, 100, 101, 106, 107]
O/C	Photooxidation AOP Mechanical stress Biodegradation	Increase	[53, 56, 84, 90, 98, 99, 106]
Adsorption capacity	Photooxidation AOP Mechanical stress Biodegradation	Increase	[47, 96, 101, 102, 106, 114, 115]