Research in Marine Sciences
Volume 9-Issue 3- 2024
Pages 559-582

A review paper

Microplastics in marine environments: occurrence and degradation mechanisms

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Received: 2024-08-16 *Accepted: 2024-09-23*

Abstract

The aquatic ecosystem faces significant threats from microplastic (MP) contamination, a global environmental concern of growing magnitude. Plastic pollution presents a substantial challenge, underscored by empirical data. Nevertheless, efforts to mitigate microplastic pollution have faced significant challenges in achieving effective removal. Microplastics, owing to their small size, exhibit heightened absorption capacities within biological cells and possess a vast surface area. Their hydrophobic nature attracts co-contaminants, facilitating their infiltration into living organisms. With a persistent presence in the environment, microplastics traverse the food chain, ultimately reaching humans as the ultimate consumers. The destiny and mobility of microplastics in the environment remain uncertain. Understanding and regulating the environmental behavior of microplastics are crucial to devising effective solutions for microplastic pollution. While initial studies have explored the distribution of microplastics in aquatic settings, a comprehensive inquiry into their environmental behaviors and degradation mechanisms in marine ecosystems is urgently needed. This review provides a thorough overview of recent research on microplastics, encompassing their origins and dissemination in marine environments. It focuses on advancing our understanding of the degradation mechanisms of microplastics in marine settings.

Keywords: Microplastics; Marine environment; Degradation; Plastic pollution; Contamination.

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1. Introduction

In colloquial language, "plastic" commonly denotes a category of organic polymers characterized by relatively high molecular weights. These elongated chains of polymers, originating from human-made industrial processes, play indispensable roles in daily existence. Exhibiting versatility, resilience, portability, and commercial value, plastic constituents have catalyzed a global surge in their production and utilization (Chandra *et al*., 2020; Wu *et al*., 2010). Plastic waste pervades numerous ecosystems, exerting diverse adverse effects on wildlife upon interaction. Such unintended consequences have spurred inquiries into the management of plastic refuse and its enduring ecological ramifications.

While the escalating utilization of plastics does indeed impact the environment, the simplistic "more plastic, more pollution" paradigm overlooks a host of nuanced issues. Most plastics exhibit remarkable resistance to decomposition, even with variations in composition and the inclusion of additives like plasticizers and pigments.

Anthropogenic activities stand out as one among various factors exerting sustained stresses on coastal and marine ecosystems. These stressors encompass pollution and environmental degradation, with the accumulation of refuse and sundry debris due to unsustainable development practices emerging as a paramount human-induced peril to shorelines (Tekman *et al*., 2023). The bulk of mixed-material detritus (MP waste) finds its way into the sea, with a meager fraction reaching land through sediment transport, buried shore detritus, and ingestion by marine organisms. This enduring presence in aquatic environments stems from plastics' recalcitrance to degradation in water, contrasting starkly with other waste materials like rubber, glass, metals, organic matter, textiles, wood, smoking/firework remnants, medical/personal hygiene items, and paper. Larger plastic entities degrade into microplastics, ranging from 0.001 to 5 mm, through assorted processes encompassing physical, chemical, and biogeochemical transformations (Chandra *et al*., 2020; Scalenghe, 2018; Andrady, 2011). Consequently, this review furnishes a comprehensive overview of the mechanisms governing the degradation of microplastic pollutants, alongside their origins, dissemination, and circulation within marine settings.

2. Characterization of microplastics

Characterizing and scrutinizing microplastics entails two primary approaches: physical and chemical. Chemical characterization centers on the elemental composition of microplastics, while physical characterization delves into their dimensions, shapes, and hues (Sun *et al*., 2019).

2.1. Characterization of physical properties

2.1.1 Shapes

In the environmental milieu, microplastics exhibit a diverse array of shapes and sizes (Rocha-Santos and Duarte, 2017). Notably, common forms include spheres, beads, fibers,

pellets, foam, films, fragments, and flakes, as outlined by Hidalgo-Ruz *et al*. (2012). The morphology of microplastics varies based on factors such as their initial configuration, the pace of surface disintegration, and the duration of environmental residence. Sharp-edged microplastics may signify recent introduction into the ecosystem, while those with smoother contours might have endured longer (Hidalgo-Ruz *et al.*, 2012; Rocha-Santos and Duarte, 2017). The dimensions of microplastic fibers can fluctuate between 0.01% and 0.05% (Cole, 2016). Notably, discerning whether a particle is a fiber can pose challenges in the realm of microplastics, given that fibers undergo chemical and mechanical degradation, causing their length to diminish until width and length align closely.

According to Bergmann *et al.* (2019), microplastics manifest in a spectrum of colors, encompassing hues like orange, red, brown, off-white, tan, blue, green, yellow, grey, and white, among others. Blue and red emerge as the most prevalent colors for fibers (Hidalgo-Ruz *et al*., 2012). Leveraging color can aid in tracing potential sources of plastic detritus and contaminations during sample preparation (Hartmann *et al*., 2019; Rocha-Santos and Duarte, 2017). White products are typically linked to polyethylene, while transparent and translucent items are often attributed to polypropylene (Rocha-Santos and Duarte, 2017). However, inferring a plastic particle's shape or origin solely based on color proves challenging. Notably, lighter colors tend to be more conspicuous upon visual inspection (Rochman *et al*., 2019). Microplastics can undergo discoloration due to weathering and sample handling, especially with oxidative digestion methods such as H_2O_2, necessitating caution in reporting and interpreting findings (Allen *et al*., 2019).

In the visual examination of samples for microplastics, color analysis serves as a pivotal tool. Given their diminutive size and frequent weathering, spectral or chemical identification holds particular significance for these microscale entities (Zhang *et al*., 2020). Researchers predominantly employ stereomicroscopy to explore the physical attributes of microplastics, although this method possesses limitations, notably in automation and polymer differentiation (Sun *et al.*, 2019). Additionally, it's crucial to acknowledge that plastics undergo various physical and chemical alterations, notably when immersed in saltwater over extended durations.

2.1.2 Capacity

The size of microplastic particles, as emphasized by Besseling *et al*. (2017) and Hüffer *et al*. (2017), fundamentally influences their interactions with biota and eventual environmental distribution. Analysis techniques typically dictate the size boundaries of microplastics (Hartmann *et al.*, 2019). While extensive studies on microplastics often overlook measurements of film and foam particle sizes, a study in the Pyrenees revealed film diameters ranging from 50-200μm, notably larger than prevalent fragment sizes (Allen *et al*., 2019). Noteworthy, Bergmann *et al.* (2019) suggested a decrease in microplastic particle quantity as their sizes increase.

3. Categorization of microplastics

For the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP, 2015), plastic is defined as "a synthetic water-insoluble polymer,

typically of petrochemical origin, that can be molded on heating and manipulated into a variety of shapes designed to be maintained during use." This categorization encompasses polypropylene, polyethylene, and all thermoplastics and thermosets.

3.1. Categorization based on dimensions

The study of microplastics has garnered substantial attention since their initial academic discourse. While the dimensions of microplastics were among the initial characteristics under scrutiny, Thompson *et al*. (2019) did not specify a minimum size threshold for classifying a plastic particle as a microplastic. Notably, there exist size distinctions between microplastics (small plastic particles) and macroplastics (larger visible debris pieces), as delineated by various researchers. This distinction proves pivotal, as it differentiates minute macroplastics from microplastics; the former can be identified through straightforward methods owing to their larger physical dimensions, while the latter typically necessitate optical instruments for fragment characterization (Costa *et al.,* 2010). Despite the scholarly focus on plastic waste since the 1980s, there has been limited attention given to differentiating between microplastics and macroplastics (Claessens *et al.,* 2011; Gregory, 1983).

The collection, characterization, and quantification of microplastics in the environment pose significant challenges. Over the past decade, a scientific consensus has been endeavoring to establish a size criterion for plastic waste (Malankowska *et al.,* 2021) (Table1).

Table 1. Microplastic Size Criteria as Per Scholarly Literature

References	Size criteria
(Graham and Thompson, 2009)	< 10mm
(Ryan *et al*., 2009)	< 2 mm
(Costa *et al*., 2010)	< 1 mm
(Andrady, 2011)	0.06–0.5 mm
(Eriksen *et al*., 2014)	>0.2 mm
(Law and Thompson, 2014)	<5mm
(Horton *et al*., 2018)	<5mm
(Auta *et al*., 2017)	<5mm
(Hale *et al*., 2020)	<5mm

In a recent plastic definitions framework proposed by a consortium of global scientists (Hartmann *et al*., 2019), which considers biological impacts, endpoints, and various interdisciplinary concerns, the magnitude of the litter issue does not reign as the primary determinant (Welden and Lusher, 2020). Owing to scant literature reports, tasks like assessing the impacts of microplastics on human health and the environment or defining precise size standards for these particles pose challenges (Malankowska *et al*., 2021) that has been summarized in Table 1.

3.2. Organization based on place of origin

The categorization of microplastics into primary or secondary is guided by specific criteria (Figure1).

Principal microplastics

Primary microplastics refer to particles intentionally added to products. These include items like scrubbing brushes commonly found in beauty products such as face cleansers, cosmetics, and air blasting media. Other primary microplastics encompass plastic pellets and pharmaceutical carriers. Auta *et al*. (2017) lists various cosmetics containing microplastics, including eye shadows, peelings, baby products, makeup bases, deodorants, bubble bath lotions, hair colorants, insect repellents, mascara, shaving cream, blush powders, sunscreens, and nail polish.

Despite discussions in North American literature regarding microplastics and their presence in specific industries, a comprehensive assessment of primary microplastic generation remains lacking. In 2017, based on available data on microplastic production and environmental occurrence, the EPA compiled expert opinions in a report. However, businesses are still obligated to provide estimates of their output. Initial estimates by the International Union for Conservation of Nature (IUCN) indicate a significant introduction of primary microplastics into American seas and oceans. The European Union generates approximately 240,000 metric tons of primary microplastics annually, a figure mirrored by the United States (Boucher and Friot, 2017).

In 2018, reports from Kentin and Kaarto highlighted that numerous countries, including several in Europe, have banned the use of microplastics in cosmetics and toiletries since 2016, a measure also adopted by South Korea.

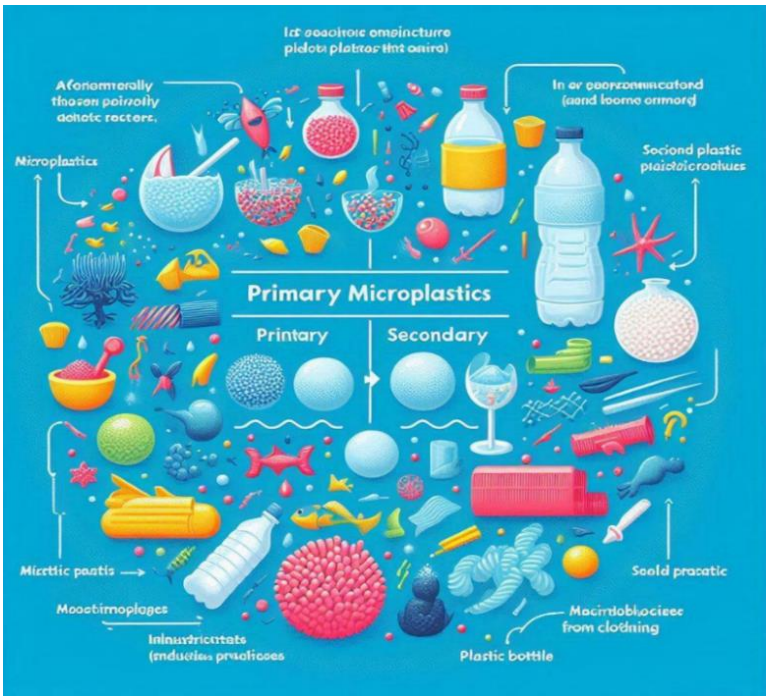


Figure 1. Classification of plastic litter according to origin (By author)

Intervening microplastics

Secondary microplastics are defined as "microlitter resulting from the physical, biological, and chemical degradation of larger plastic debris" according to Cole *et al*. (2011). A fundamental step in comprehending the behavior and fate of microplastics in the ocean involves understanding the four primary processes of polymer degradation: hydrolysis, heat oxidative degradation, photo-oxidative degradation, and biodegradation (Andrady, 2011). As polymers degrade, their average molecular weight decreases, leading to the fragmentation of plastic pieces into brittle or powdery forms.

Plastic degradation commonly occurs in beaches and oceans, where environmental conditions are harsher compared to land and inland waterways. Factors such as sand presence, increased oxygen concentration, wind-driven scrubbing, erosion, corrosion, and intense UV radiation contribute to noticeable degradation on beaches (Cole *et al*., 2011). Offshore, plastic waste is exposed to UV radiation and high oxygen levels.

However, when submerged in water, the impact of UV radiation is reduced due to lower water temperatures and oxygen levels in saltwater compared to open-air beach environments (Malankowska *et al*., 2021). According to Figure 2, global plastic production in 2015 comprised 36.3% polyethylene (16.3% HDPE and 20% HDL), 21.0% polypropylene, 11.8% PVC, 10.2% PET, 8.2% PU, 7.6% PS, and 4.9% other polymers.

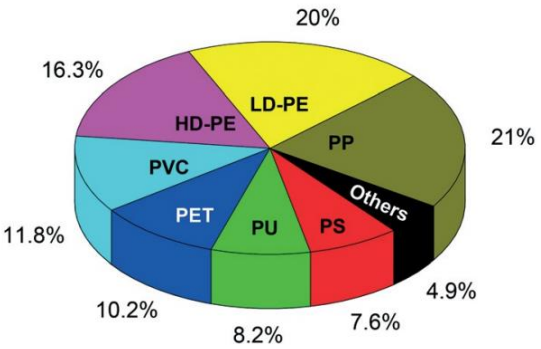


Figure 2. Global distribution of plastic fragment production (Malankowska *et al*., 2021)

4. The origin of microplastics in marine environments

Understanding the origins of microplastics is crucial for enhancing our knowledge of their fate and impact on marine ecosystems. The literature on industrial plastics (GESAMP, 2015) suggests that the global issue of aquatic debris began with the rapid growth of the plastics industry in the mid-1950s. Classification of plastic sources based on their movement through the economy using the concept of producer and consumer responsibility for a product's lifecycle is referenced by GESAMP (2015) and Tang *et al*. (2020).

4.1. Sources located on land

Figure 3 illustrates that since most human activities occur on land, the majority of plastic waste, including microplastics, is directly disposed of on soil. Research by Kershaw *et al*.

(2011) indicates that a significant portion of oceanic microplastics originates from land-based sources. Various human activities such as cooking, cleaning, gardening, outdoor recreation, illegal dumping, and poor waste management contribute to this issue (Boucher and Friot, 2017). Both natural and anthropogenic factors significantly influence the quantity and distribution of microplastics, with environmental factors often having a more pronounced impact than human activities.

Microplastics accumulate in locations like beaches, landfills, sediments, and seawater due to activities such as fishing and tourism (Pirsaheb *et al.*, 2020; Auta *et al.*, 2017). Industries such as laundry, textiles, cosmetics, and personal care products, particularly those containing microbeads, are major contributors to microplastic pollution in aquatic environments, as noted by Napper *et al.* (2015). Rillig and Bonkowski (2018) found that toothpaste and face cleansers with exfoliants released 94,500 microbeads into the environment. Xanthos and Walker (2017) attribute a significant portion of microplastics to human activities such as toothpaste use, aquaculture, tourism, and wastewater discharges from both industrial and household sources.

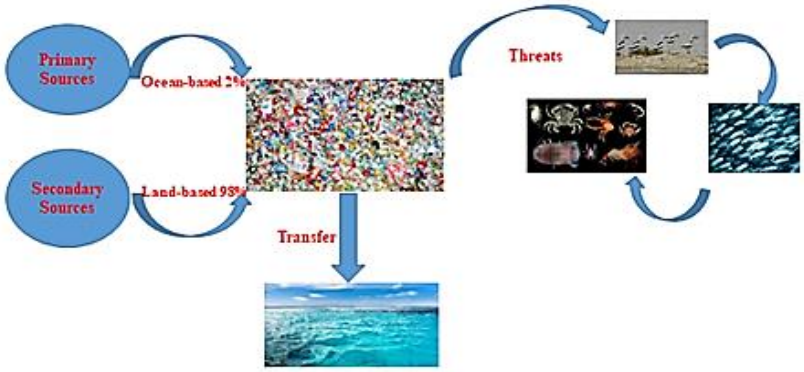


Figure 3. Sources and transfer of MPs marine environment (By author)

4.2. Resources found in the ocean

Coastal water currents play a significant role in transporting plastic debris from beaches to the ocean. The trash from activities like fishing, including discarded monofilament and nylon nets, often ends up floating on the ocean's surface and is carried away by currents (Cole *et al.*, 2011). The accumulation of plastic waste in marine and coastal environments can be attributed to various marine-related factors such as commercial fishing, navigation, shellfish/fish farming, and waste disposal practices. Studies have highlighted the substantial contribution of offshore fishing and aquaculture to marine plastic pollution. Improper disposal of plastic waste during transportation, whether on land or at sea, is another factor leading to the direct or indirect flow of plastic debris into the ocean, often linked to mismanagement of plastic packaging (Woodall *et al*. 2014; Cole *et al*., 2011).

5. Small plastic debris in the oceans

Plastic waste originating from land can find its way into oceans through three main pathways: wind, soil, and water, that the water is the most significant route (Zhang *et al*., 2016). Once microplastics, either alone or mixed with larger plastic pieces, enter the water, they can travel both horizontally and vertically, influenced by various factors. These factors

include microplastic properties such as density, surface charge, hydrophobicity, chemical composition, and size (Alimi *et al*., 2018), coastal characteristics like gravel, coastal vegetation, and bedrock, oceanic processes such as wind, waves, tides, water currents, thermohaline gradients, and geostrophic circulation, and human activities like fishing, urban development, and tourism (Arat, 2024).

Biological interactions such as ingestion by marine organisms and biofouling are additional factors affecting the movement and distribution of microplastics in marine environments (Zhang *et al.*, 2017). Research has primarily focused on microplastic pollution in major oceans including the Pacific, Arctic, Atlantic, and Indian oceans, with findings suggesting widespread presence of microplastics at varying concentrations (Table 2). Human activities significantly contribute to microplastic pollution in oceans, with certain regions showing higher microplastic abundance compared to others, as indicated by studies like Peng *et al.* (2020).

The rapid increase in the toxicity of microplastics in oceans is a concerning aspect of microplastic contamination. Studies have shown a significant rise in microplastic concentrations over the years, indicating the growing impact of human activities on marine environments. The movement of microplastics in oceans is influenced by factors like density, leading to horizontal or vertical transport, with marine organisms playing a role in the dispersal of microplastics to distant locations (Peng *et al*., 2020; Lusher *et al*., 2015).

6. Microplastic degradation in the marine environment

The degradation of microplastics in aquatic environments presents a fascinating realm where polymer science meets environmental chemistry. Polymer engineers have delved deeply into the realm of plastic polymers' deterioration, focusing on the nuanced concept of "degradation," which signifies the loss of a polymer's inherent characteristics (Yousif and Haddad, 2013). While environmental chemists are captivated by the intricate chemical processes leading to breakdown, the characteristics and potential hazards of chemicals released during polymer degradation often take a back seat in their studies (Gewert *et al*., 2015). In the ethereal dance of weathering conditions encountered by environmental plastics, not all degradation mechanisms treat all polymers equally. Microplastic deterioration, a captivating subject in numerous referenced studies, has spurred contemplation on how established findings can shed light on the plight of floating plastics adrift in the ocean. A tapestry of mild weather, gentle sunshine, and the play of diverse solar radiations envelops these plastics, shaping their fate on the water's surface.

The saga of abiotic degradation unfurls under the orchestration of moderate temperatures, oxygen's embrace, and the tender caress of sunshine (Gewert *et al*., 2015). Hydrolysis, a noble ally, stands ready to confront certain polymeric polymers. Synthetic polymers, bastions of stability in the face of environmental tumult, exhibit a reluctance towards degradation, leading to extended sojourns within the environment. Biotic or abiotic categorizations of synthetic polymers hinge on the interplay of physical, chemical, and biological forces guiding their gradual transformation into smaller molecular entities.

Table 2. Occurrence of microplastics in seawater in different regions in the world

Location	Concentration	Unit	Reference
Madu-Ganga estuary, Sri Lanka	40.06 -1.84	items/m^3	(Praboda, *et al.*, 2020)
Black Sea	7.3	items/L	(Georgieva *et al.*, 2023)
Northwestern Pacific	640-42000	items/km^2	(Pan *et al.*, 2019)
Marmara Sea	18.68	items/m^3	(Erkan *et al.*, 2021)
Guanabara Bay, Rio de Janeiro, Brazil	1.4–21.3	items/m^3	(Olivatto *et al*., 2019)
Western Pacific	0.02-0.1	items/m^3	(Liu *et al*., 2021)
Antarctic Peninsula	755-3524	items/km^2	(Lacerda *et al*., 2019)
Eastern Indian Ocean	0.01-4.53	items/m^3	(Li *et al*., 2021)
Northwestern Pacific from Fremantle to Hobart, Australia	0.13 ± 0.11	items/m^3	(Mu *et al*., 2019)
Seto Island Sea	53.82	items/L	(Jiang *et al*., 2020)
Jiaozhou Bay, China	20-120	items/km^2	(Zheng *et al*., 2019)
Bohai Bay, China	650.0-2700.0 and 540.0-1550.0	items/km^2	(Wu *et al.*, 2019)
Hong Kong, China	3.973	items/m^3	(Cheung *et al*., 2019)
Kingston Harbour,Jamaica	0-5.73	items/m^3	(Rose and Webber, 2019)
Coast of South Korea	1051	items/m^3	(Song *et al*., 2018)
NorthYellow Sea,China (Asia)	545 ± 282	items/m^3	(Zhu *et al*., 2018)
Arctic Central Basin	0.7	items/m^3	(La Daana *et al*., 2018)
Gulf of Lion, Mediterranean sea, France	112,000	items/km^2	(Schmidt *et al*., 2018)
Coastal waters of western Mediterranean sea, Tuscany, Italy	69,161± 83,244 0.26 ± 0.33	items/km^2 items/m^3	(Baini *et al*., 2018)
Arabian Gulf	4.38 ×10^4-1.46 ×106	items/m^3	(Abayomi *et al*., 2017)
Turkish coastal waters, Mediterranean Sea	16,339 -520,213	item/km^2	(Güven *et al*., 2017)
Gulf of Mexico, Louisiana	5.0–18.4	items/m^3	(Di Mauro *et al*., 2017)
Ross Sea (Antarctica)	0.0032-1.18	items/m^3	(Cincinelli *et al*., 2017)
Bohai Sea, China	0.33	items /km^2	(Zhang *et al*., 2017)
Levantine coast of Turkey, Mediterranean Sea	1,067,120	items/km^2	(Gündougdu, 2017)
Slovenian part, Northern Adriatic	406 ×103	items / m^3	(Gajšt *et al*., 2016)
Jinhae Bay, South Korea	88	items /L	(Song *et al*., 2015)
South-eastern coastline of South Africa	257.9-1215	items /m^3	(Nel and Froneman, 2015)
Suruga Bay,Tokyo Bay, Ise Bay, Seto Inland Sea (Asia)	0.03–0.075	items /m^3	(Isobe *et al*., 2015)
Southwest and south of Svalbard, Norway	0.34 ± 0.31	items /m^3	(Lusher *et al*., 2015)
Whole Mediterranean Sea	243,853	items/km^2	(Cózar *et al*., 2015)
French-Belgian-Dutch coastline	0.4	parts/L	(Van Cauwenberghe *et al*., 2015)

Venturing into the realm of microplastic breakdown methodologies (Section 7), the long-term behavioral trajectory of polymers in vital industrial domains has been meticulously chronicled, with a focus on the degradation of industrial plastic products (Zhou *et al*., 2021; Zhou *et al*., 2014). Investigations have probed the biodegradability of products, their resilience against elemental ravages, and the emergence of microplastics through chemical, mechanical, and biological degradation pathways.

The transformation of macroplastic detritus into microplastic fragments raises concerns of ecological perturbations, potentially disrupting the delicate threads of the food chain (Besseling *et al.,* 2019). A burgeoning presence of plastic particles in aquatic realms threatens clarity, diminishing the light that sustains myriad life forms. Microplastics' intrusion into beach and benthic sediment may alter the behavior and fitness of bioturbators, while beachgoers might witness shifts in nesting habits as sands warm under the burden of microplastics (Beckwith and Fuentes, 2018).

The alchemy of microplastics' breakdown unfolds through a symphony of physical, chemical, and biological approaches, with chemical photodegradation emerging as a favored protagonist among researchers for its efficiency in dismantling microplastics with relative ease.

In the grand narrative of plastic deterioration, the interplay of living organisms and inanimate forces can sculpt the destiny of plastics. Abiotic degradation, catalyzed by the silent touch of air, water, light, and temperature, often precedes the embrace of biodegradation, a testament to plastics' limited bioavailability (Andrady, 2015).

7. Abiotic degradation of plastics

7.1. Physical Wear and Tear

When examining the degradation of plastics in water, a primary focus lies on mechanical breakdown processes. Research by Yoshioka *et al*. (2008) highlights how the characteristics of polymers can evolve, becoming more brittle over time due to environmental influences such as chemical or photo-degradation of additives. Organic components like shell fragments, wood particles, and silt contribute to this process. Conversely, human-made structures such as seawalls, groynes, and vehicles fall into the category of anthropogenic influences. The impacts of fluctuating temperatures and wet/dry cycles on the mechanical degradation of plastics are also a subject of exploration.

As plastics traverse diverse habitats, they undergo relentless abrasion, gradually breaking down into minute particles through static friction. This breakdown yields plastic particles ranging from 1 to 5,000 micrometers in size. Even at the microplastic scale, physical degradation persists, potentially leading to the formation of nanoplastics - structures composed of even smaller particles. The properties of nanoplastics may diverge from those of their macroscopic or microscopic predecessors. Figure 4 illustrates how reduced particle size and increased surface area due to physical deterioration enhance reactivity, accelerating the degradation process.

Distinct surface patterns like conchoidal fractures and grooves, indicative of mechanical weathering, are observable through scanning electron microscopy (SEM) investigations (Liu *et al*. 2019a; Zhou *et al*. 2018; Wang *et al*. 2017). Coastal regions often exhibit similar patterns in natural sedimentary quartz grains, a consequence of frequent grain-to-grain interactions (Vos *et al*. 2014). Hence, beaches serve as prime locations for microplastic abrasion (Corcoran *et al*. 2009).

Both sunlight exposure and mechanical stresses expedite the weathering process, as demonstrated in an experimental study by Kalogerakis *et al.* (2017) using PE films in artificial beach and offshore settings. In another method, plastic strips enclosed in sand-filled bottles were rotated continuously for 24 hours, resulting in the creation of microscopic plastic particles equivalent to around fourteen percent of the plastic's original weight. These findings underscore the capacity of mechanical abrasion to degrade polymers to a certain extent.

In a study by Song *et al*. (2017), a simulated beach environment was utilized to observe the reaction of microplastics to mechanical abrasion and ultraviolet radiation. The researchers noted varying degrees of mechanical degradation among different polymer types, with polypropylene (PP) and polyethylene (PE) showing minimal dissolution due to mechanical weathering. Conversely, expanded polystyrene (EPS) underwent fragmentation solely through friction. In aquatic environments, microplastics can undergo mechanical degradation when subjected to shear stress pressures, as demonstrated by Enfrin *et al*. (2019) through the application of mechanical stirring, pumping, and ultrasonic irradiation on polyethylene (PE) microbeads used in facial cleansers.

The benefits of physical degradation include cost-effectiveness, rapid reaction times, and ease of implementation. However, its application scope is limited, and the degradation impact may be intensified. Typically used in conjunction with other methods, physical pyrolysis has proven effective in removing microplastics from wastewater and sludge. Further research is needed to delve into the physical degradation process, the crucial environmental factors at play, microplastics degradation via co-pyrolysis, as well as the similarities and disparities among various microplastics. These investigations could serve as the cornerstone for future assessments of degradation processes.

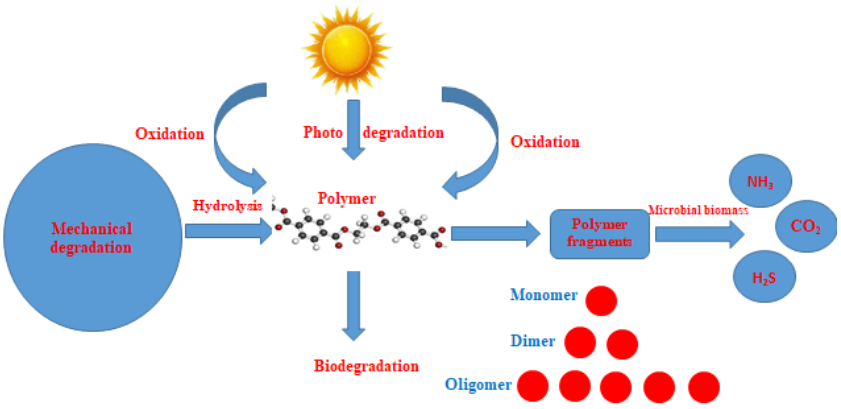


Figure 4. Pathways of Microplastic Degradation in Aquatic Environments

7.2. Chemical Degradation of Plastics

Within the intricate dance of synthetic polymers in aquatic realms, chemical degradation emerges as a crucial player, orchestrating transformations that sculpt the fate of these resilient materials. The thermal breakdown of synthetic polymers finds its wings clipped in the cool embrace of freshwaters, where the tepid temperatures fail to kindle the flames of chemical reactions (Gewert *et al*., 2015). However, nature's alchemy weaves a tale of molecular metamorphosis through the twin forces of photooxidation and chemical oxidation, each polymer type bearing its own unique pathway to dissolution.

As photons from the sun caress the polymers, initiating free radical-mediated reactions, the stage is set for a nuanced interplay of molecular disintegration. Photooxidation, a swift protagonist, wields its power with finesse, driving the degradation process at a vigorous pace. Yet, the quantity of antioxidants nestled within the polymer's matrix plays a pivotal role, dictating the cadence of its demise.

In the aqueous realm, where plastics find solace in the embrace of waters, a tale of contrasting fates unfolds. Polystyrene (PS) and polyethylene (PE), basking near the water's surface, succumb more swiftly to the ravages of degradation compared to their brethren immersed partially or entirely beneath the waves. Here, the diminished light intensity in the water column serves as a mitigating force, tempering the fervor of photooxidative onslaught.

The ocean, a vast repository of plastic detritus, harbors a haunting reality - these polymers, once ensnared, linger for centuries, if not eons, a testament to humanity's enduring legacy. Yet, the enigmatic depths of deep sediments pose a conundrum, where the confluence of limited oxygen and light shrouds the fate of microplastics in mystery, beckoning for further exploration (Rogers *et al*., 2020).

The chemical realm extends its reach beyond the sun's caress, delving into the realm of air pollutants that cast their shadow upon plastics. Ozone, sulfur dioxide, nitrogen dioxide, and volatile organic compounds emerge as formidable adversaries, capable of instigating direct assaults on plastics or catalyzing their degradation through radical-forming photochemical reactions (Crawford and Quinn, 2017).

pH and salinity emerge as the custodians of plastic fate in aqueous domains, with hydrolyzable plastics like polyamides (PA) poised on a precipice in the presence of acidic or basic hydroxides, where degradation looms as a distinct possibility. These chemical influencers not only sculpt the fate of microplastics but also mold their surface properties, influencing their behavior in aqueous realms and their interactions with other contaminants (Liu *et al*., 2019b).

In the hidden world of sediment communities, where microbial populations reign supreme, the interplay between redox conditions and community composition dances to an intricate rhythm (Jørgensen, 2019). Germs, nestled on microplastics, glean electrons from their synthetic hosts and surrounding organic matter in an anoxic milieu, a symbiotic exchange

that hints at the potential for biodegradation of microplastics in oxygen-depleted sediments (Rogers *et al*., 2020).

As the curtains draw close on the chemical saga of plastic degradation, the symphony of thermal degradation unfurls its final act. Plastics, vulnerable to thermo-oxidative reactions under the fiery gaze of high temperatures, bear witness to a transformative journey where molecular bonds fracture, radicals roam free, and the alchemy of heat yields a tapestry of scission and growth (Crawford and Quinn, 2017).

In the crucible of chemical degradation, plastics navigate a labyrinth of reactions, each unveiling a facet of their demise. From ozone-induced breakdown to the intricate dance of carbonyl compounds and ether formation, the saga of plastic degradation unfolds, a testament to the intricate interplay between polymers and their chemical milieu.

The dichotomy of carbon-carbon backbone and heteroatoms in microplastics paints a canvas of diversity, with PE, PP, PS, and PVC standing as stalwarts of the carbon realm, while PET and PU bear the mark of heteroatoms in their molecular tapestry, each carving a unique path towards dissolution.

In the grand tapestry of plastic degradation, chemical forces emerge as a potent sculptor, etching the destiny of synthetic polymers with finesse and fury, a testament to the enduring dance of nature's alchemy upon the creations of human ingenuity.

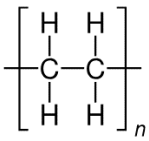
7.3. Abiotic degradation pathways of PP, PS, and PE in aerobic environments

In the realm of abiotic degradation pathways for polypropylene (PP), polystyrene (PS), and polyethylene (PE) within aerobic environments, the process of photo-initiated oxidative breakdown stands out as the most efficient (Gewert *et al*., 2015).

The degradation route can be segmented into three distinct stages: initiation, propagation, and termination (Andrady, 2011). Initiation, triggered by light or heat, disrupts chemical bonds in the primary polymer chain, giving rise to free radicals. The presence of unsaturated chromophoric groups, which absorb light energy, is essential for the initiation of photochemical reactions within the polymers. Notably, the absence of unsaturated double bonds in the backbone renders photo-initiated breakdown unlikely in PP and PE polymers.

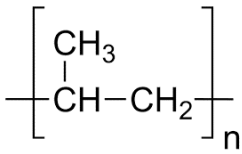
Nevertheless, photo-initiated breakdown may still occur due to external pollutants or structural irregularities integrated into the macromolecular structure. When ultraviolet radiation severs carbon-hydrogen bonds within the polymer backbone, it engenders free radicals. These radicals subsequently evolve into peroxy radicals through interactions with oxygen as the degradation process progresses. Alongside hydroperoxides, autoxidation emerges as a byproduct of intricate radical mechanisms. Chain scission and crosslinking are imperative for propagation, leading to oxidation-induced branching, crosslinking, and the formation of oxygen-containing functional groups, alongside spontaneous chain scission and end-chain scission. Olefins, aldehydes, and ketones are anticipated to be particularly vulnerable to photocatalyzed degradation due to their unsaturated double bonds, emerging as products of radical termination reactions (Gewert *et al*., 2015).

7.3.1 Polyethylene (PE)



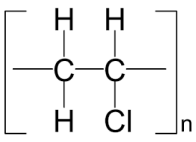
In the context of polyethylene (PE), the absence of chromophores in water renders photodegradation unfeasible. However, imperfections or contaminants within the polymer's structure can act as chromophores upon exposure to environmental elements (Fairbrother *et al.*, 2019). Carbonyl groups embedded in the PE backbone possess the capability to serve as chromophores. Radical generation, end-vinyl group and ketone group formation via Norrish Type I and II reactions are instrumental in breaking the primary polymer chain (Karlsson and Albertsson, 2002). Free radicals transition into peroxide molecules through hydrogen abstraction, leading to the creation of peroxy radicals upon interaction with oxygen. The ensuing cascade is catalyzed by macro-alkoxy and hydroxyl radicals, generated upon peroxide dissociation. The reaction sequence may result in polymer chain scission, cross-linking, and the production of alcohols, esters, ketones, carboxylic acids, and aldehydes.

7.3.2 Polypropylene (PP)



In the realm of polymer stability, polyethylene's secondary carbons exhibit greater resistance to abiotic assaults compared to the tertiary carbons present in polypropylene's backbone, rendering the latter more stable. Mirroring polyethylene, the reaction mechanisms at play remain consistent. However, polypropylene's stability is relatively lower due to the presence of tertiary carbons, which are more susceptible to oxidative attacks by oxygen. The photodegradation processes of PP and PE share similarities, where impurities like chromophores within polypropylene enable the generation of radicals upon exposure to UV radiation, subsequently leading to biodegradation. The formation of degradation products with reduced molecular weight typically results from radical-mediated events, inducing random chain scission and cross-linking (He *et al*., 2019; Su *et al*., 2019).

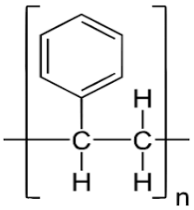
7.3.3 Poly (vinyl chloride) (PVC)



Upon exposure to ultraviolet light, polyvinyl chloride (PVC) undergoes rapid dehydrochlorination and conjugated unsaturation sequences. The likelihood of photodegradation increases within unsaturated C=C double bonds due to their diminished

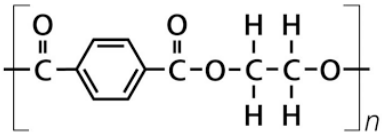
stability. Analogous to PE and PP, PVC can absorb UV radiation and generate free radicals owing to impurity-induced chromophores. Free radicals, in turn, facilitated by hydroperoxides, cleave the double bonds in the backbone chain, yielding smaller degradation products (Yang *et al*., 2022). Recent studies unveiled a novel environmental degradation process for PVC involving the oxidation of polyene structures into ketones and alcohols by O_2 and OH• radicals (Wang *et al*., 2020). Notably, halogens, especially chlorine, augment the resistance of substances to biodegradation in aerobic environments. Biodegradation, is anticipated to succeed abiotic breakdown, leading to dechlorination of the polymers. Various metal compounds, including organotin and lead, serve as stabilizers for PVC, with concern mounting over the long-term ecological impact of semivolatile organotin compounds found in PVC products (Gewert *et al*., 2015).

7.3.4 Polystyrene (PS)



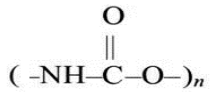
An aromatic ring within polystyrene becomes excited and transitions into a triple state upon exposure to ultraviolet radiation, rendering the material susceptible to photodegradation. The excited benzene's Triplet energy can either facilitate the dissolution of the phenyl group or be transferred to adjacent C-H or C-C bonds. In an oxygen-deficient setting, a polystyryl radical emerges following the rupture of a C-H bond. Upon the introduction of oxygen, the polystyryl radical evolves into a peroxy radical, subsequently engaging with surrounding polystyrene molecules. Through mechanisms involving chain scission and cross-linking, the synthesis of carbonyl compounds, alkenes, and styrene monomers transpires (Kumar *et al*., 2020; Dris *et al*., 2017).

7.3.5 Poly Ethylene Terephthalate (PET)



Within water, hydrolytic breakdown of poly ethylene terephthalate (PET) involves the reversal of an esterification step, a common occurrence even though the process is sluggish at room temperature. This hydrolysis generates functional groups such as alcohols and carboxylic acids. Since the rate of hydrolysis differs depending on whether the condition is acidic or basic, PET hydrolysis is an autocatalytic process when carboxylic end groups are produced (Gewert *et al*., 2015).

7.3.6 Polyurethane (PU)



The ester bond within polyurethane (PU) is predominantly hydrolyzed during degradation. While urea and urethane bonds can also undergo hydrolysis, their degradation rate is comparatively lower. Under acidic conditions, the formation of carboxylic acid end groups is expedited, propelling hydrolysis as an autocatalytic process.

While fungal biodegradation of PU is well-established, bacterial degradation and polyurethanase-mediated breakdown are also plausible. Products derived from polyurethane primarily comprise polyol segments disintegrated by urethane linkages. Notably, polyether PU segments exhibit greater resistance to microbial degradation compared to polyester PU segments, which are more susceptible to microbial breakdown (Gewert *et al*., 2015).

8. Microbial degradation of plastics in marine environments

In the intricate realm of microbial degradation of plastics within marine environments, the interplay of environmental variables across vertical gradients influences microbial communities and the biodegradation of microplastics (Rogers *et al*., 2020). However, the precise mechanisms governing how microbes in anoxic settings either preserve or decompose microplastics remain shrouded in mystery.

Research on plastic breakdown in aquatic realms is scant, yet emerging studies hint at the capability of oceanic microbes to biodegrade diverse plastic types, sparking interest due to the global ramifications of plastic waste. Biodegradation, lauded for its cost-effectiveness and eco-friendliness, involves a convergence of environmental factors orchestrating the intricate degradation processes of resilient plastics in marine settings.

The initial phase of microbial biodegradation of microplastics involves the breakdown of polymers into oligomers, dimers, and monomers. Subsequently, polymers are fragmented into smaller particles from their larger structures. Bacteria, as elucidated by Blair Espinoza (2019), possess the ability to mineralize contaminants, converting microplastics into carbon dioxide through enzymatic actions, as depicted in Figure 2. Bacterial colonization of plastic surfaces gives rise to plastispheres, microbial biofilms marking the onset of biodegradation.

Microbes engaged in plastic degradation are just one subset within the diverse plastisphere microbial community (Kirstein *et al*., 2019). These microbial cohorts assist in polymer breakdown by fostering biofilm formation within marine ecosystems (Urbanek *et al*., 2018), reducing the buoyancy and hydrophobicity of microplastics. Notably, the bacterium Rhodococcus ruber infiltrates mature biofilms, generating intricate mushroom-like structures (Niu *et al*., 2021).

To render plastic polymers more amenable to degradation, microbes secrete an array of enzymes such as manganese peroxides, esterases, laccase, lipase, and lignin peroxides. These enzymes catalyze the conversion of polymers into functional groups like alcohols or carbonyls, enhancing microbial accessibility and promoting degradation (Shahnawaz *et al*., 2019; Taniguchi *et al*., 2019). Extracellular hydrolases interact with plastic surfaces, fragmenting them into smaller molecules, including poly (3-hydroxybutyrate), esterases, lipases, and depolymerizes. Enzymes in microbial degradation processes facilitate chain cleavage by targeting vulnerable bonds within plastic structures, albeit confined to surface degradation due to their size, potentially leading to eventual cracking.

A simplified polymer conversion ensues through assimilation within the biological fragmentation process, where enzymes weaken the carbon backbone, breaking down polymers into oligomers, dimers, and monomers. Enzymatic depolymerization augments microbial biomass, yielding carbon-rich monomers readily consumed by microorganisms. Evidence supports the involvement of peroxidases, laccases, oxidases, and amidases in plastic degradation (Niu *et al*., 2021). Intracellular enzymes continue the breakdown through oxidation and the tricarboxylic acid (TCA) cycle post-bio-fragmentation, culminating in mineralization as plastics disintegrate, releasing CO_2, H_2O, and CH_4.

The intricate dynamics between bacterial colonization surface area and biofilm formation were explored by Fleming *et al*. (2017). Attachment mechanisms such as biofouling, penetration into polymer structures, hydration, plasticizer breakdown, and polymer backbone degradation influence microplastic biofilm formation, potentially expediting biodegradation due to the high surface area-to-volume ratio of microplastic particles. Successful plastic-degrading microbes must possess appropriate enzymes, metabolic pathways, and conducive environmental conditions encompassing temperature, salinity, moisture, and pH levels. The chemical bonds and physical properties of microplastics play pivotal roles in microbial adhesion, while the polymer structure's branching and polymerization degrees should not impede biological reactions. The enzymatic degradation rate is influenced by polymers' amorphous versus crystalline regions, with polyhydroxyalkanoates (PHA) depolymerase enzymes primarily targeting amorphous chains before eroding crystalline structures (Shabbir *et al*., 2020).

9. Conclusions and future perspectives

The precarious state of both marine and terrestrial ecosystems due to the pervasive presence of microplastics underscores the urgency of understanding their origins, dispersion, and breakdown mechanisms, particularly within marine environments. Through an extensive review of existing literature, it becomes evident that the degradation of plastics involves intricate processes influenced by biotic and abiotic factors, encompassing chemical, physical, and biological responses. Ultraviolet light emerges as a key driver of degradation, prompting the development of cutting-edge methodologies to elucidate the degradation pathways of plastics. In natural environments, oxidation and chain cleavage transform polymer plastics, yielding degradation byproducts with modified physicochemical and mechanical attributes that can be metabolized and mineralized by bacterial communities.

Biological decomposition stands out as a promising avenue for microplastic removal. However, the sheer diversity of microbial species in the wild poses challenges in identifying effective microorganisms capable of degrading microplastics. Addressing this issue necessitates innovative research to enhance our understanding of microplastic-degrading microbes and optimize their synergistic interactions to bolster degradation efficiency, thus surmounting current limitations in microplastic remediation strategies.

Future investigations should prioritize identifying critical environmental parameters and plastic characteristics that influence degradation processes. Such insights are pivotal for predictive modeling of plastic fate in diverse ecosystems and the formulation of strategies to mitigate plastic pollution. Moreover, intensified research efforts focusing on the production and degradation dynamics of microplastics, including nanoplastics, are imperative to comprehensively evaluate their ecological hazards and environmental repercussions. By delving deeper into these realms, we can proactively safeguard our ecosystems from the perils of microplastic contamination and pave the way for sustainable environmental stewardship.

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