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海洋中微塑料的老化机理及老化后环境行为研究进展

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摘要: 暴露于海洋环境中的塑料聚合物受海浪破碎、紫外照射和微生物降解等作用后, 会逐渐形成小粒径的微塑料(<5 mm, microplastics, MPs), 引起海洋生态风险。本文总结了海洋中 MPs 的类型和来源、老化过程、机理和影响因素, 以及 MPs 老化后理化性质和环境行为的变化。MPs 在海洋中的老化机理主要包括: 机械破碎、光降解、热降解、水解和生物降解等, 同时 MPs 的自身性质(粒径、形状、官能团、结晶度和添加剂等)和海洋环境条件(紫外辐射、温度和氧化还原状态等)会影响老化过程。老化后 MPs 的理化性质与原始 MPs 存在显著差异, 如表面形貌、颜色、粒径、官能团、结晶度、亲疏水性和吸附性能等; MPs 老化过程中还伴着增塑剂、阻燃剂和双酚 A 等添加剂的释放。老化过程也会影响 MPs 对海水中污染物(重金属、有机污染物等)的吸附, 可能会使 MPs 成为污染物的富集体, 进而对海洋生物造成更大的危害。此外富集污染物的 MPs 可能会通过食物链进入人体, 对人类健康造成危害。

关键词: 微塑料; 老化机理; 环境行为; 影响因素

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Research Progress on Aging Mechanism and Environmental Behavior of Marine Microplastics

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Abstract: Plastics of small particle size (<5 mm, microplastics, MPs) can be formed *via* wave action, ultraviolet (UV) irradiation, microbial degradation, etc., which will cause marine ecological risks. This review has summarized types, sources, the aging process, mechanism, and the main influence factors of MPs, as well as variations in physi-

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cal and chemical properties and environmental behavior of aged MPs. Aging mechanisms of MPs mainly involved mechanical crushing, photodegradation, pyrolysis, hydrolysis, biodegradation, etc., which can be affected by their properties (particle size, shape, functional group, crystallinity, additives, etc.) and environmental conditions in marine (UV irradiation, temperature, redox state, etc.). Physicochemical properties of aged MPs are significantly different from original MPs such as the surface morphology, color, particle size, functional groups, crystallinity, hydrophilicity, and adsorption performance. Meanwhile, the aging process of MPs is accompanied by the release of plasticizers, flame retardants, bisphenol A and other additives. The aging process may influence the adsorption performance of MPs for pollutants (heavy metals, organic pollutants, etc.) in seawater. Additionally, aged MPs may become an accumulation group of pollutants (heavy metals, organic pollutants, etc.) resulting in a greater threat to marine organisms. MPs enriched with pollutants may enter the human body through the food chain, causing a serious threat to human health.

Keywords: microplastic; aging mechanism; environmental behavior; influence factor

塑料已广泛应用于各类生产及生活用品中,然而,由于废弃塑料的回收利用效率不高且对塑料垃圾的管理不善,目前全球有近 79% 的塑料废弃物进入海洋环境^[1]。若不采取相关强制处理措施,到 2030 年预计每年将有 9 000 万 t 塑料垃圾进入水生生态系统^[2]。进入环境的塑料垃圾在一系列环境作用下(如紫外照射、海浪破碎和微生物降解等)会降解破碎成小粒径的颗粒,其中 <5 mm 的颗粒塑料被定义为微塑料(microplastics, MPs)。研究表明,从赤道到两极,从表层海水到深海沉积物,从海岸到开放海域,在各类海洋生态系统中都检测到了 MPs^[3]。由于 MPs 体积小、吸附能力强、持久性高,易被不同营养级的海洋生物直接摄食^[4],如底栖动物、浮游动物、鱼类和海洋哺乳动物等,MPs 并进入体内,对生物的生长发育、繁殖能力及行为特征产生影响^[5]。除此之外,MPs 在海洋环境中的累积会限制海洋生物泵的效率从而影响碳循环^[6],并通过抑制微生物的硝化和反硝化过程来影响氮循环^[7]。目前海洋系统中 MPs 的污染已经引起广泛关注,评估海洋中 MPs 的生态风险对海洋生态系统的健康及可持续发展至关重要。

受光照、风浪的机械磨损、热解、水解和生物降解等环境条件的综合作用,海洋中 MPs 会发生老化降解,导致其形态、结构及理化性质发生变化,进而影响 MPs 在海洋中的环境行为。如海洋中老化后的 MPs 更容易释放添加剂,且老化后的 MPs 更容易吸附环境中的有机污染物、重金属、病原体以及抗生素抗性基因等物质^[8],导致 MPs 表面的污染物浓度显著高于周围环境^[9]。这些富集污染物的 MPs 进入海洋生物体内后,在消化系统的作用下会将表面的

污染物析出,进一步进入血液循环系统中,由此产生更大的危害^[10]。海洋生物体内无法降解或排出体外的部分 MPs 会随食物链传递,最终进入人体并影响人类健康^[11]。因此,本文总结了 MPs 在海洋中的老化过程、机理及影响其老化的主要因素,MPs 老化后自身理化性质的改变,以及老化后 MPs 的环境行为,为深入了解老化后 MPs 的环境风险提供理论依据(图 1)。

1 塑料结构及海洋中 MPs 来源 (Plastic structure and source of MPs in marine)

塑料是通过加聚或缩聚反应聚合而成的高分子化合物,按分子结构可分为 2 种类型:一种是热塑性塑料,线型结构,硬度和脆性小,可重复生产。另一种为热固性塑料,体型结构,硬度和脆性大,无法重新塑造^[12]。每种塑料具有不同的结构,目前应用最广泛是聚丙烯(PP)和聚乙烯(PE),其中大部分用于制造柔韧的薄膜和包装材料,还有汽车零件、管道和家庭用品,据统计 2019 年全球 PP 和 PE 的产量占全部塑料产量的近 50%(表 1)^[13-14]。

海洋环境中的微塑料按照其来源可分为初级 MPs 和次级 MPs,初级 MPs 是用作工业材料、个人护理和清洁产品添加剂的粒径 <5 mm 的塑料碎片^[15],次级 MPs 来源于大块塑料在环境中老化破碎,其中海洋中次级 MPs 占主要地位^[16]。除了环境作用,人类的活动也会产生大量 MPs,例如海洋水产养殖^[17]、港口航运^[18]、污水处理排放^[19]和海边旅游业^[20]等,其中养殖设施老化及污水处理厂污水排放是海洋中 MPs 的主要来源^[21]。进入海洋环境的 MPs 由于自身密度的不同,分别存在于沉积物中、悬浮在水中或漂浮在水面上,因此在海洋中检出

MPs 的种类可能取决于采样深度。有研究报告了海洋中各种 MPs 的积累,沉积物中检出了聚酰胺(PA)、聚氯乙烯(PVC)和聚对苯二甲酸乙二醇酯(PET)等密度高于海水的 MPs,也有较低密度的 MPs,如聚苯乙烯(PS)、高密度聚乙烯(HDPE)、低密度聚乙烯(LDPE)、PP 和聚氨基酯树脂(PUR)等以海洋漂浮形式被检出^[22-23]。而且,在海洋生物中也发现了发泡聚苯乙烯(EPS)、PP 和 PE^[24]。还有研究调查了全球海洋中 MPs 的丰度,例如地中海北部和中西部的 MPs 丰度分别为 0.116 颗粒·m⁻³ 和 1.25 颗粒·m⁻³^[25-26],在大西洋中调查到的 MPs 丰度为 1.15 颗粒·m⁻³^[27],在韩国的半封闭海湾和近岸地区,MPs 丰度甚至达到了 2 000 颗粒·m⁻³^[28]。海洋环境中 MPs 来源广泛、种类复杂且数量庞大,不同种类 MPs 的老化降解过程、老化后自身结构和性质的改变以及对周围环境的影响都存在差异性,关注 MPs 在海洋环境中的老化过程及其影响至关重要。

2 海洋环境中 MPs 的老化机理 (Aging mechanism of MPs in marine)

2.1 光降解

光降解是 MPs 在海洋中老化的主要过程,MPs 在可见光和紫外线的照射下会发生降解,其中紫外照射对 MPs 的降解效果尤为明显^[29]。在 MPs 光降解的老化过程中,290 ~ 400 nm 波长的紫外线起主要作用(299 ~ 412 kJ·mol⁻¹),可以破坏塑料的 C—C 键(284 ~ 368 kJ·mol⁻¹)和 C—H 键(381 ~ 410 kJ·mol⁻¹)^[30]。该过程一般可分为 3 个阶段^[31]:首先是起始反应阶段,聚合物中的不饱和键或生色团吸收光能引发聚合物产生初始自由基,虽然 PE 和 PP 的主链上没有不饱和双键,但老化过程中掺入大分子结构中的少量外部杂质或自身结构异常可以在一定程度上诱发光降解;然后是传播过程,初始反应生成的大分子自由基易与氧分子发生加成反应,生成高分子过氧自由基、氢过氧化物,还会发生更复杂的自

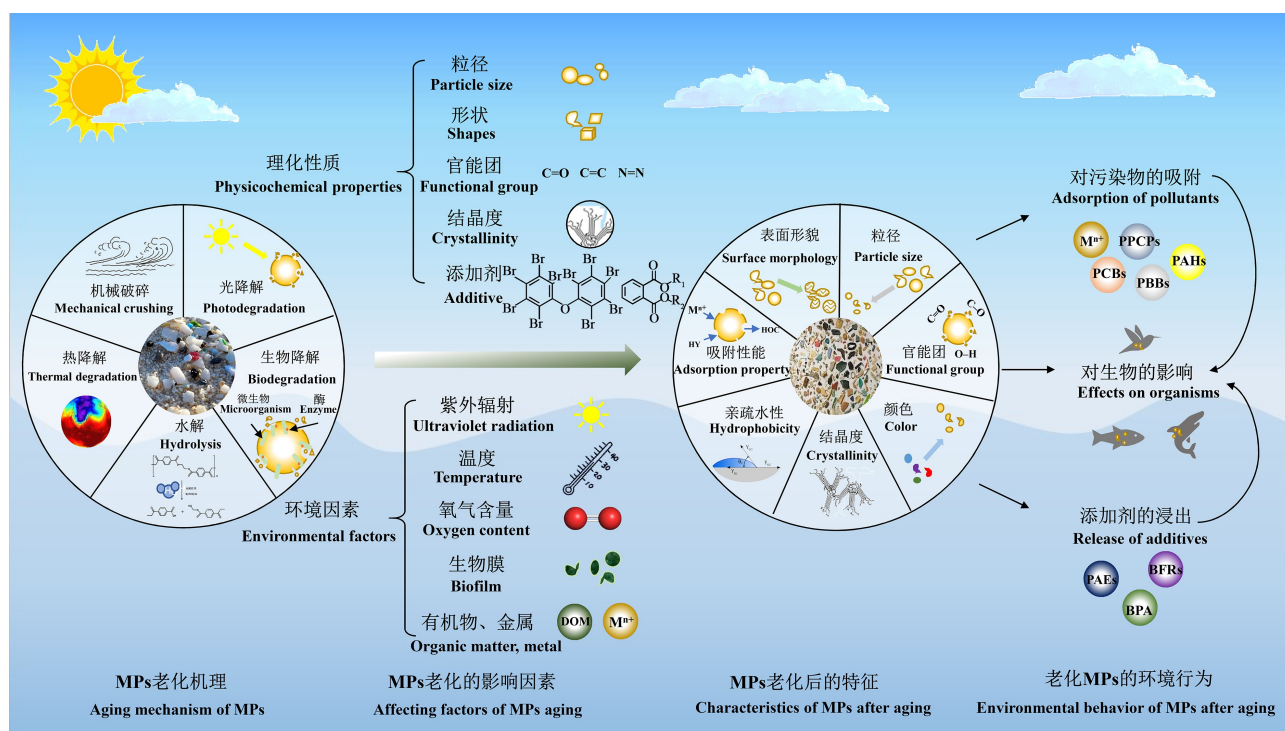


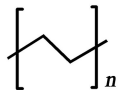
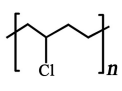
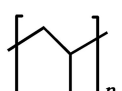
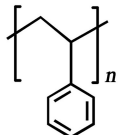
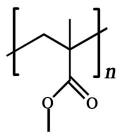
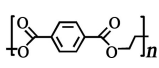
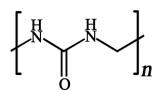
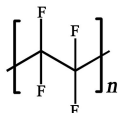
图1 微塑料(MPs)在海洋中的老化过程、机理和影响因素及 MPs 老化后自身理化性质的改变和环境行为

注:DOM、Mⁿ⁺、PAEs、BFRs、BPA、PPCPs、PAHs、PBBs 和 PCBs 分别表示溶解性有机物、金属离子、邻苯二甲酸酯、溴化阻燃剂、双酚 A、药品和个人护理用品、多环芳烃、多溴联苯和多氯联苯。

Fig. 1 The aging process, mechanism and the main affecting factors of microplastics (MPs), and the physicochemical properties variation and the environmental behavior of MPs after aging in marine

Note: DOM, Mⁿ⁺, PAEs, BFRs, BPA, PPCPs, PAHs, PBBs and PCBs stand for dissolved organic matter, metal ion, phthalic acid esters, brominated flame retardants, bisphenol A, pharmaceuticals and personal care products, polycyclic aromatic hydrocarbons, polybrominated biphenyls, and polychlorinated biphenyls, respectively.

表 1 常见塑料的部分理化性质
Table 1 Physicochemical properties of common plastics

名称 Name	缩写 Abbreviation	分子结构 Molecular structure	分子式 Molecular formula	密度/(g·cm ⁻³) Density/(g·cm ⁻³)	老化变化 Changes after aging	2019 年全球 产量/万 t ^[13] Global production in 2019/(10 ⁴ t) ^[13]
聚乙烯 Polyethylene	PE			0.910 ~ 0.976		
高密度聚乙烯 High density polyethylene	HDPE		(CH ₂ —CH ₂) _n	0.940 ~ 0.976	表面粗糙, 出现空洞 ^[14] The surface becomes rough, and holes appear ^[14]	10 966
低密度聚乙烯 Low density polyethylene	LDPE			0.910 ~ 0.925		
氯化聚乙烯 Chlorinated polyethylene	CPE		(CH ₂ —CHCl—CH ₂ —CH ₂) _n	1.22 (25 °C)		
聚丙烯 Polypropylene	PP		(CH ₃ —CH—CH ₂) _n	0.85 ~ 0.91	变色、变脆, 表面粗糙 ^[14] Discoloration, embrittlement, and the surface becomes rough ^[14]	7 139
聚氯乙烯 Polyvinyl chloride	PVC		(CH ₂ —CHCl) _n	1.16 ~ 1.35		3 680
聚苯乙烯 Polystyrene	PS		(C ₈ H ₈) _n	1.04 ~ 1.08	变黄 Yellowing	2 282
聚甲基丙烯酸甲酯 Poly(methyl methacrylate)	PMMA		[CH ₂ C(CH ₃)(COOCH ₃)] _n	1.16 ~ 1.20		
聚对苯二甲 酸乙二醇酯 Poly(ethylene terephthalate)	PET		(CO ₂ C ₆ H ₄ COOCH ₂ CH ₂ O ₂) _n	1.32 ~ 1.37	变色, 表面粗糙 Discoloration, and the surface becomes rough	2 907
聚氨酯树脂 Polyurethane resin	PUR			1.03 ~ 1.5		2 907
聚四氟乙烯 Polytetrafluoroethylene	PTFE		(CF ₂ —CF ₂) _n	2.10 ~ 2.30	变脆 Embrittlement	

由基反应并导致自氧化。含氧基团的增多会导致聚合物发生断链(摩尔质量减少)和交联作用,同时产生各种被氧化的官能团。最终为链终止反应阶段,自由基之间相互结合生成惰性产物,自由基反应结束。据报道,海水的折射率降低了光线强度从而降低了光氧化速率^[32],因此大量的 MPs 会在水生环境中滞留几十年或数百年。不同类型结构的 MPs 引发光降解的因素有所差异,例如,仅由碳原子构成主链的 PE、PP 和 PS 等 MPs,在有氧条件下由于氧化和断链,发生分支、交联和含氧官能团的形成(醛基、羰基等),而这些含氧官能团存在不饱和双键,使其更易受光催化引发老化降解,PET 等含有碳及杂原子的 MPs 更易通过水解将酯键断裂,再进一步进行光降解^[33]。

2.2 机械破碎

在剪切力和拉伸力的作用下,MPs 在海洋中会发生机械破碎从而脆化并进一步破碎成更小的颗粒,整个过程会持续至颗粒破碎到纳米尺寸,即纳米塑料^[34]。Enfrin 等^[35]发现水中剪切力主要通过裂纹扩展和破碎机制导致纳米塑料的生成。在破碎过程中,MPs 表面出现划痕和裂纹,粒径减小,表面积增加,从而增大环境接触面,并加速其降解。同时 MPs 在紫外线照射下,可以加快其机械破碎的速率,有研究发现,与未经过老化的 PP 小球相比,紫外老化后的小球在 2 个月的机械磨损下 MPs 颗粒增多了 600 倍^[36]。机械破碎是初始的 MPs 老化阶段,在此过程中不仅改变了 MPs 的原始表面形貌和结构,也加速了随后其他老化阶段的进行。

2.3 热降解和水解

在有氧的情况下,MPs 能与自然环境中的活性氧发生反应,也可与其他氧化剂相互作用以引起化学氧化^[37]。MPs 的热降解是高温克服键解离能的结果^[38],其所吸收的能量一旦超过化学键的解离能,就会发生弱位点的随机断裂和侧链分解,从而加速了 MPs 的老化。有研究在不同温度下对 MPs 进行降解^[39],结果表明与仅含碳主链的 MPs 相比,主链中含杂原子的 MPs 热稳定性较好,但这类 MPs 在海洋环境中易受水解影响发生裂解^[40]。一般来说含有酯基的 MPs 通过水解生成相应的羧酸和醇类,如图 2 所示,在海洋环境中 PET 易受水解的影响引起酯链的断裂,形成羧酸端基和乙烯端基^[41]。

2.4 生物降解

在海洋环境中,生物作用对 MPs 的老化降解起着不可或缺的作用^[42]。MPs 既可作为载体为微生物

的附着和生长提供支持,还可作为碳源为微生物构建生态位。而微生物则可通过胞内或胞外解聚酶对 MPs 进行降解,现已鉴定出许多降解 MPs 的微生物菌株^[43]。生物降解过程如图 3 所示,首先微生物与 MPs 接触后附着并定殖于 MPs 表面,随后 MPs 在微生物胞外酶的作用下破碎并发生解聚反应,形成较小的聚合物单元(单体、低聚体),释放添加剂^[44]。这些小分子聚合物可以被微生物吸收代谢,通过矿化过程最终生成无机产物,最后将这些产物可用作碳源和能源^[45]。在自然环境中,微生物之间的共生和协同作用在 MPs 生物降解中起着重要作用。例如,一种微生物产生的代谢产物可被另一种微生物用作底物,从而降低毒性代谢产物对 MPs 降解菌的影响^[46]。此外,海洋中的大型动物摄食 MPs 后,在消化系统的作用下会将其缓慢分解成小粒径 MPs 排出体外。在海洋环境中,大多数塑料不溶于水且许多是合成聚合物,如 PE、PP、PS 和 PET,降解十分缓慢甚至根本无法降解,这些聚合物的降解需结合生物和非生物的降解途径实现。

3 MPs 老化过程的影响因素 (Influencing factors of MPs aging process)

3.1 MPs 理化性质的影响

MPs 的老化往往受到自身理化性质的影响,例如粒径、形状、种类(官能团)、结晶度和添加剂等。研究发现,在 PVC 的光老化实验中,其老化速率与粒径呈负相关关系^[47]。但对于粒径<500 nm 的半结晶 PE MPs,小粒径反而具有更紧密的骨架结构,表现出较低的热降解率^[48]。MPs 的形状也会影响老化过程,相关研究发现在海洋环境中扁平的 MPs 通常有一个面易被老化^[49]。

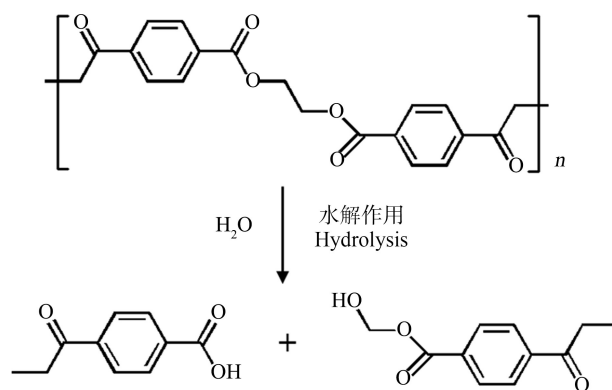


图 2 聚对苯二甲酸乙二醇酯 (PET) 的水解^[33]

Fig. 2 Hydrolysis of poly(ethylene terephthalate) (PET)^[33]

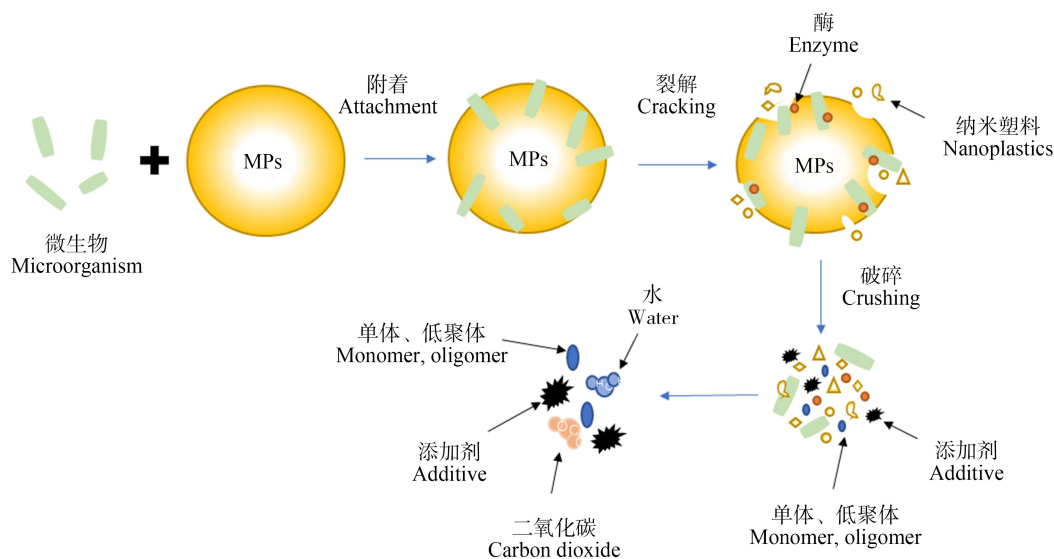


图 3 MPs 的微生物降解途径

Fig. 3 Degradation pathway of MPs by microorganisms

不同结构特点和化学组成的 MPs 光降解和生物降解的速率和效果存在差异。含有发光团(如 $C=C$, $C=O$, $N=N$ 等)的 MPs 具有更强的光敏度^[50], 光降解速率通常较快。例如, PP 和 EPS 在光照作用下出现裂隙的时间比 PE 缩短 3 倍; 聚合物化学组成会影响生物降解过程中酶的作用, 如芳香族对苯二甲酸酯单元会限制链的移动, 使得酶对骨架酯键的水解速率较低, 导致 PET MPs 相比其他 MPs 更难生物降解^[51]。MPs 的结晶度对其老化也存在影响, 研究表明 MPs 的降解主要发生在其表面非结晶的部分, 这主要是由于此部分氧渗透率较高所致。此外, 与非晶态 MPs 相比, 结晶度高的 MPs 具有有限的破碎区域。在非晶态 MPs 中, 裂纹扩展、链断裂和机械断裂优先发生^[52]。此外, 老化 MPs 释放的添加剂也会促进其降解。Khaled 等^[53]研究发现溴代阻燃剂在光照下释放的 Br^- 会加剧 PS 的断链反应。

因此, MPs 的粒径减小导致表面积增加, 含有更多发光团会增加 MPs 的光敏感性, 低的结晶度使得 MPs 具有更高的氧渗透率, 添加剂的释放会加速氧化等, 以上因素都会加剧 MPs 在海洋环境中的老化降解。

3.2 海洋环境的影响

除了塑料自身因素外, 紫外辐射强度、温度、水中盐度、酸碱性、氧化还原状态和微生物生长情况等环境条件对 MPs 的老化也具有重要影响。Ranjan

和 Goel^[54]发现 MPs 的老化程度与紫外辐射强度和时间呈正相关, 而与水中盐度呈负相关。高温可以通过降低 MPs 的拉伸性及其化学键断裂所需能量加速 MPs 的老化^[55], 同时还会破坏 MPs 的表面力学性能, 加速 MPs 内部分子的运动, 促进添加剂和单体的释放^[56]。海洋环境中的氧化还原状态还会影响 MPs 的光降解和生物降解过程。例如, PVC MPs 在氧化条件下的脱氯率相比无氧化条件提高 1.8 倍 ~ 2.8 倍。氧气可改变微生物的代谢途径, 以氧为电子受体更有利于 MPs 的生物降解^[57]。MPs 可作为生物膜的载体, 生物膜分泌的酶和粘液物质不仅会改变 MPs 的结构, 还可增加 MPs 质量使其沉积, 从而阻碍其光降解、机械破碎及热降解^[46]。除上述因素外, 水中其他化学成分也会影响 MPs 的老化降解, 如表面附着的有机物会减少紫外线对 MPs 表面的渗透及颗粒物的摩擦^[36], 而重金属的存在会加剧 PET 的降解速率^[58], 铜离子存在时 PP 的氧化降解速率也会成百倍增加^[59]。因此, 紫外辐射时间、辐射强度以及温度和氧气含量的增加会加速 MPs 老化, 而水中盐度、有机污染物含量的上升, 以及 MPs 表面形成的生物膜则会阻碍 MPs 的老化。

4 老化后 MPs 的特征 (Characteristics of MPs after aging)

4.1 老化后 MPs 表面形貌、粒径和颜色的变化

老化前后 MPs 的物理形态差异主要体现在表

面形貌、粒径和颜色上。其中,最显著的即为表面形貌的变化。在风浪的剪切力和海边沙粒的磨损力作用下,MPs 表面会产生划痕和裂纹^[60]。紫外光照射使 C—C 和 C—H 键从聚合物主链上解离,导致聚合物表面脆化,进而出现裂缝和孔隙^[61]。裂缝和空腔的形成是由于去除光降解副产品、表面无定形含量的重组以及晶体分数的增加导致表面层收缩。高结晶度会减少光的穿透距离,因此 MPs 老化后的氧化产物常出现在距离顶部 100 μm 处,同时老化 MPs 表层会生成纳米级颗粒物^[50]。相应地,由于 MPs 表面出现裂纹、内部发生脆化导致 MPs 破碎,老化后 MPs 粒径较小^[62]。颜色的变化也是塑料老化降解的表征之一,大多数 MPs 会因氧化作用由白色或半透明变为橙色和黄色,这可能是由于聚合物中热稳定剂如酚类抗氧化剂等,在光解时会氧化成醌类化合物等黄色产物所致^[63]。

4.2 老化后 MPs 官能团和结晶度的变化

MPs 在老化过程中常表现出羰基、羟基等含氧官能团数量增多、结晶度增加的特点。MPs 表面在机械摩擦、化学氧化和生物侵蚀的共同作用下,会产生羟基、羧基、醛基、酯基和酮基等含氧官能团。随着 MPs 老化的进行,其表面的含氧官能团数量逐渐增加。不同的环境条件和塑料类型会影响 MPs 老化后的官能团变化。PS 在空气环境中可以吸收足够的紫外光产生断键,优先形成羰基,在水环境中由于氢原子过量和对紫外光的利用率小于空气环境,酚羟基优先生成^[64]。还有研究发现,不同于 PS,老化后的 PVC 表面还生成了乙烯基酯^[37]。此外,MPs 的老化往往还伴随着结晶度的增加,而结晶度也是判断 MPs 老化情况的一个重要指标^[65]。Müller 等^[66]发现由于氧化断链的结晶过程以及随后重排为有序结构导致 PP 和 PS 的结晶度在老化后增加了约 50%。这是由于老化会优先降解塑料的无定形部分,从而增加结晶部分的占比^[67],同时 MPs 断链产生的短链聚合物在水中的高流动性加速了老化后期的再结晶过程^[52]。

4.3 老化后 MPs 亲疏水性和吸附性能的变化

老化后 MPs 的比表面积、含氧官能团和氢键的变化会影响 MPs 的亲疏水性和吸附性能。老化后 MPs 可以通过离子络合、氢键和静电相互作用促进重金属和过渡金属等潜在有毒元素的吸附。相关吸附动力学实验表明,老化后的 PE MPs 对金属离子的吸附速率大于原始的 PE,这是由于老化后的 PE

更易从金属离子中获得正电荷使表面电荷平衡^[68]。另一方面,在老化过程中产生的含氧基团与周围的水分子形成氢键会增加 MPs 的亲水性,进而增强其对亲水性有机污染物(HYs)的吸附,而 MPs 老化后疏水相互作用力的降低,会导致其对疏水有机化合物(HOCs)的吸附系数和吸附位点的减少^[69]。

由此可见,老化后 MPs 具有表面粗糙、亲水性增加、金属和 HYs 的吸附能力增强、HOCs 的吸附能力减弱等特点,并引发环境交互性发生改变。这对于评价各种污染物的吸附能力和生态效应具有重要的环境意义,可深入研究以确定老化后 MPs 在海洋环境中的行为影响。

5 老化后 MPs 的环境行为 (Environmental behavior of MPs after aging)

5.1 老化后 MPs 对污染物的吸附

海洋中 MPs 的老化增加了其表面积和亲水性,因此老化后 MPs 对亲水性污染物的吸附作用增强,包括吸附无机和有机污染物以及与其他共存固体组分的同聚体和异聚体^[70]。这些老化 MPs 吸附的环境行为将进一步影响 MPs 向生物体的迁移和生物利用度^[71]。总结了 MPs 老化前后对金属和有机污染物(多环芳烃、多氯联苯、抗生素和阻燃剂等)吸附的研究,结果如表 2 所示。在实验室研究和现场调查中均验证了 MPs 可吸附多种金属(包括 Ag、Cd、Co、Cr、Cu、Hg、Ni、Pb 和 Zn)^[72]。此外,Wang 等^[73]的研究表明,增加 MPs 的老化时间(紫外线辐射,200 ~ 500 h)可以提高 MPs 对 Cu^{2+} 和 Zn^{2+} 的吸附能力。老化 MPs 表面的氢键和静电相互作用对亲水性有机污染物的吸附起主要作用,包括常用的药品和个人护理产品(PPCPs)及多环芳烃(PAHs)。与原始 MPs 相比,紫外老化后的 MPs 对抗生素的最大吸附量增加了 1.2 倍 ~ 2.2 倍^[74]。

此外老化 MPs 对 HOCs 的吸附能力有所下降,如 UV 老化后的 PS MPs 对 2,2',4,4'-四溴二苯醚(BDE-47)的平衡吸附容量是原始 PS 平衡吸附容量的 50%^[65]。

5.2 老化后 MPs 中添加剂的浸出

在生产塑料制品过程中,化学添加剂可赋予塑料不同的使用价值,如增塑剂可提高柔韧性、阻燃剂可增强难燃性等。由于塑料分子和添加剂分子之间不存在共价化合物,因此 MPs 在老化时会会在海水中浸出这些物质。迄今为止,研究报告了包括邻苯二甲酸酯(PAEs)、溴代阻燃剂(BFRs)、双酚 A(BPA)和金

表 2 老化前后 MPs 对金属和有机污染物的吸附
Table 2 Adsorption of metal and organic pollutants by MPs before and after aging

污染物类型 Type of pollutant	名称 Name	MPs 类型 Type of MPs	实验条件 Experimental condition				吸附特征 Adsorption characteristics	参考文献 Reference
			MPs 粒径 Particle size of MPs	污染物浓度 Pollutant concentration	环境条件 Environmental condition			
					老化前 Before aging	老化后 After aging		
金属 Metal	Ag、Cd、Co、Cr、 Cu、Hg、Ni、Pb、Zn	PE	2 ~ 6 mm	2 ~ 20 $\mu\text{g}\cdot\text{L}^{-1}$	河水	岸边自然老化; 吸附 7 h	吸附常数增大 2 ~ 3 个数量级	[68]
					River water pH = 4 ~ 10	Natural aging by the riverbank; adsorption for 7 h	Adorption constant increases by 2 ~ 3 orders of magnitude	
	Cd	PS	400 nm	0.1 ~ 2 $\text{mg}\cdot\text{L}^{-1}$	模拟水环境 Simulated micro-cosmos system pH = 4	H ₂ O ₂ 和 Fenton 试剂老化 1 ~ 7 d; 吸附 0 ~ 48 h	Cd ²⁺ 的吸附量增加	[75]
						Aging for 1 ~ 7 d by H ₂ O ₂ and Fenton reagent; adsorption for 0 ~ 48 h	The adsorptive capacity of Cd ²⁺ improved	
有机污染物 Organic pollutants	3,3',4,4'-四氯联苯 (PCB77) 3,3',4,4'-tetrachlorobiphenyl (PCB77)	PP	0.18 ~ 5 mm	1 $\text{mg}\cdot\text{L}^{-1}$	饮用水	臭氧老化 2 ~ 10 h; 吸附 25 h	Cu ²⁺ 、Mn ²⁺ 、Pb ²⁺ 和 Zn ²⁺ 的吸附量增加	[76]
					Drinking water pH = 5.5 ~ 10.5	Aging by ozone for 2 ~ 10 h; adsorption for 25 h	The adsorptive capacity of Cu ²⁺ , Mn ²⁺ , Pb ²⁺ and Zn ²⁺ improved	
	芘(PYR) Pyrene (PYR)	PE, PS, PVC	100 ~ 150 μm	0 ~ 100 $\mu\text{g}\cdot\text{L}^{-1}$	纯水和海水	吸附 25 h	吸附容量随着粒径和温度的降低而增加	[77]
					Pure water and seawater	Adsorption for 25 h	The adsorptive capacity increases with decreasing particle size and temperature	
有机污染物 Organic pollutants	磺胺甲恶唑(SMX) Sulfamethoxazole (SMX)	PE, PS, PVC	100 ~ 150 μm	0 ~ 100 $\mu\text{g}\cdot\text{L}^{-1}$	人工淡水	吸附 48 h	PE 对 Pyr 的吸附性最高, 其次是 PS 和 PVC	[78]
					Artificial freshwater pH = 7	Adsorption for 48 h	PE has the strongest adsorption capacity for Pyr, followed by PS and PVC	
有机污染物 Organic pollutants	磺胺甲恶唑(SMX) Sulfamethoxazole (SMX)	PE	150 μm	0.2 ~ 5 $\text{mg}\cdot\text{L}^{-1}$	纯水	吸附 72 h	最大吸附容量可达 105 $\mu\text{g}\cdot\text{g}^{-1}$, 且不受 pH 值和盐度显著影响	[79]
					Pure water pH = 2 ~ 12, 25 $^{\circ}\text{C}$	Adsorption for 72 h	The maximum adsorption capacity reach 105 $\mu\text{g}\cdot\text{g}^{-1}$, and it was not affected by pH and salinity	

续表2

污染物类型 Type of pollutant	名称 Name	MPs 类型 Type of MPs	实验条件 Experimental condition				吸附特征 Adsorption characteristics	参考文献 Reference
			MPs 粒径 Particle size of MPs	污染物浓度 Pollutant concentration	环境条件 Environmental condition			
					老化和吸附方式 Aging and adsorption methods			
	六溴环十二烷 (HB-CDs)、三-(2,3-二溴丙基)异氰脲酸酯(TBC)	PP	0.45 ~ 0.85 mm	1 mg·L ⁻¹	模拟海水 Simulated seawater	吸附 24 h Adsorption for 24 h	PP 对 TBC 的吸附能力远高于 HBCDs, 吸附容量随着粒径减小而增加, 随温度和盐度升高先增加后减小 The adsorption capacity of PP for TBC is much higher than that for HBCDs; the adsorption capacity increases with decreasing particle size, and increases first and then decreases with increasing temperature and salinity	[80]
有机污染物 Organic pollutants	环丙沙星(CIP)	PS, PVC	75 μm	2 ~ 25 mg·L ⁻¹	纯水	紫外老化 96 h, 吸附 48 h	老化 PS 和 PVC 的吸附能力提高 123.3% 和 20.4% 以上	[37]
	Ciprofloxacin (CIP)				Pure water pH = 3 ~ 11	UV aging for 96 h, adsorption for 72 h	The adsorption capacity of PS and PVC increased by 123.3% and 20.4% after aging	
	17β-雌二醇(E2)	LDPE, HDPE, PP, PS, PC, PVC, PA, PMMA	75 ~ 250 μm	100 μg·L ⁻¹	去离子水、模拟海水和真实海水	吸附 120 h Adsorption for 120 h	各种 MPs 对 E2 的吸附能力依次为 PA>HD/LLD-PE>PP>LD/MD-PE>PS>PC>PMMA>PVC	[81]
	Estradiol-17 beta (E2)				Deionized water, simulated seawater and seawater	The adsorption capacity of various MPs for E2: PA>HD/LLD-PE>PP>LD/MD-PE>PS>PC>PMMA>PVC		

属元素以及其他有机化合物在内的各种添加剂的浸出^[82]。有研究表明,邻苯二甲酸二异丁酯(DiBP)和邻苯二甲酸二丁酯(DBP)是PE袋中释放的主要PAEs,且光和细菌暴露下PVC释放的PAEs总量增加了5倍^[83]。PS光解后会释放水溶性的带有芳香烃的溴化污染物及溴乙烷、二溴甲烷和溴仿等气态产物^[53]。同时,由于MPs的老化发生的断链反应释放了小分子量和低沸点的聚合物到海洋环境中^[84],多项研究表明在海洋环境中检测到了 $\text{ng}\cdot\text{g}^{-1}$ 至 $\text{mg}\cdot\text{g}^{-1}$ 浓度范围的PS单体、二聚体和三聚体^[85]。

5.3 老化后MPs对海洋生物的毒性效应

海洋生物摄入MPs后会产生饱食的假象,损伤消化系统,减少营养吸收。同时MPs进入生物体内后难以排除体外,会引发幼体畸形,抑制生长和繁殖,并改变生态行为^[86]。而老化后MPs对生物会产生更严重的威胁。首先,由于MPs老化后的大小、形状和表面粗糙度改变,生物体摄入MPs的方式和数量也随之改变^[87]。颗粒越小的MPs越有可能被不同营养级的生物摄入,并进入器官和组织中^[88]。有学者研究了斑马鱼对不同大小PS MPs的吸收和组织积累,发现直径为5 μm 的PS在鱼鳃、肝脏和肠道中积累,粒径为20 μm 的PS颗粒仅在鳃和肠道中积累,这表明越小的MPs越容易被生物体摄取。其次,MPs老化后表面会产生许多纳米级塑料,摄入老化后的MPs很可能会给生物体造成更大的损伤。有研究发现扇贝摄入纳米级PS后,在肾脏、性腺及肌肉中均检出该物质的存在,说明纳米级塑料可能会直接跨上皮细胞、细胞膜或通过血细胞吸收转运到循环系统^[89]。老化MPs进入海洋生物体内后会促进有毒添加剂和表面吸附的重金属、有机污染物的释放,危害海洋生物。有研究通过模拟肠道条件说明MPs吸附的污染物及其本身的化学添加剂都可能解析到体内,例如海鸟摄入MPs后,其表面上的有害金属、多溴联苯醚(PBDEs)、BPA和PAEs等污染物会造成重大风险^[90]。在此基础上,Rochman等^[91]还发现鱼类在摄食此类MPs后会改变鱼类的基因表达,从遗传水平上对海洋生物产生影响。同时由于MPs表面吸附的有害污染物在食物链中的生物利用度增加,一些有机污染物可能最终进入人体并产生危害^[92]。综合看来,老化后的MPs不仅会造成生物体的物理损伤,还会像一颗包裹有害物质的药丸,对生物体有巨大的潜在危害。

6 展望(Prospects)

(1)目前关于海洋环境中MPs聚合物的降解机理的研究很少,且大都来源于实验室研究推断。实际环境中影响因素较为复杂,因此需要在更接近海洋环境的条件下或直接在海洋环境中对MPs的反应途径和潜在老化产物进行进一步研究。

(2)MPs在海洋环境中的老化降解速率受多种因素影响,目前研究大多集中于实验室条件下,研究单一或2种联合作用下的老化速率,难以估计实际环境中塑料老化降解速率和持续时间,因此需要进一步考虑各种环境因素和MPs的类型,以实验模拟真实环境中MPs的老化过程。

(3)由于海洋中污染物都是共存的,而目前关于老化MPs对污染物的吸附研究多集中在单一污染物上,因此需要更加系统地研究MPs在老化前后对多种污染物的竞争和协同吸附关系。

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