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Surface Chemical Analysis of Plastic Materials by X-Ray Photoelectron Spectroscopy: Understanding Weathering, Fragmentation and Contaminant Uptake in Marine Environments

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ABSTRACT

Plastics have become an integral part of modern life due to their durability and versatility. However, their extensive use and subsequent degradation into micro- and nanoplastics have raised significant environmental concerns, particularly in aquatic systems. The fragmentation of plastics, a process starting from their surfaces, not only alters their chemical composition but also facilitates the adsorption of various hazardous contaminants, posing further risks to living organisms. Despite extensive research efforts, predicting degradation behavior and subsequent contaminant interactions remain challenging due to the complex and dynamic nature of these processes. Current approaches emphasize the need for advanced surface characterization techniques to unravel these complexities. In this context, X-ray Photoelectron Spectroscopy (XPS) has emerged as a powerful tool, capable of providing detailed insights into surface chemical modifications. Motivated by these challenges and opportunities, this Perspective assesses the role of XPS applications to the study of the mechanisms related to plastic fragmentation/weathering and pollutant adsorption.

1 | Introduction

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is a powerful analytical technique widely used to examine the surface chemistry of materials [1–4]. It provides information on elemental composition, empirical formulas (excluding hydrogen), and the chemical and electronic states of atoms within the top 1–10 nm of the sample [1, 2]. When an X-ray beam irradiates a material's surface, electrons are emitted with characteristic kinetic energies [1]. Once corrected for the spectrometer work function, these values yield the binding energies used as an analytical signal to generate XPS spectra (Figure 1). During the photoelectric effect, photons with energy ($h\nu$) exceeding the atom binding energy ionize it, converting the excess energy into the kinetic energy (E_k) of ejected electrons. The electron binding energy (E_b) is determined from the difference between the ionized atom's final energy (E_f) and its initial energy (E_i) [2].

The number of detected electrons is proportional to the number of atoms of a given element present in the sample, even plastic (Figure 1).

While XPS excels at providing detailed surface information, its limited probing depth, due to the limited inelastic mean path of electrons in condensed matter, may not fully represent

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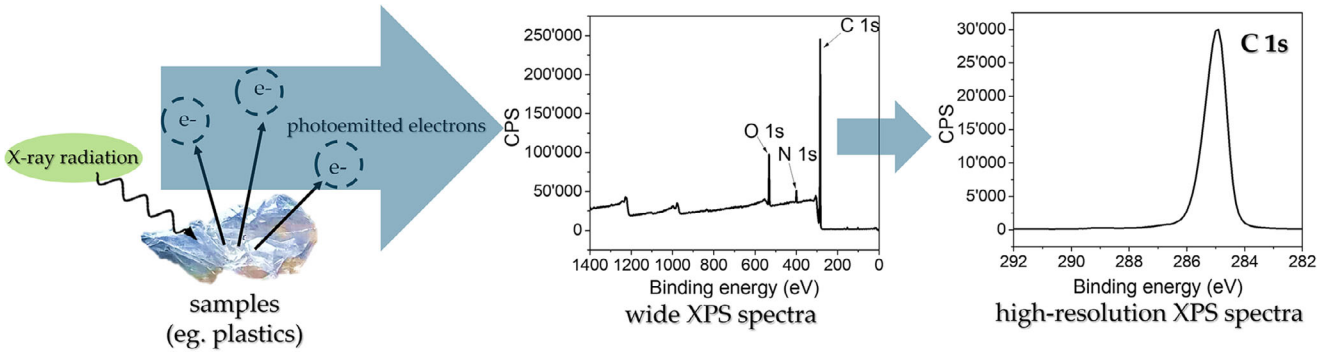


FIGURE 1 | Schematic representation of XPS analysis of plastic samples.

the bulk chemical composition—especially in heterogeneous or multilayered materials [5, 6]. However, this surface sensitivity represents an advantage when surface has a role in a process, opening peculiar applications in several fields, including environmental analyses. Since the surface is the primary interface between materials and surroundings, its analysis offers critical insights into the influence of biotic and abiotic factors on material transformation upon environmental exposure.

This surface-focused approach is especially valuable in studying the environmental fate of plastic materials, which are now recognized as priority pollutants due to their ubiquity, persistence, and limited biodegradability [7]. The wide use of plastics [8–13], combined with their limited end-of-life management, has contributed to an unprecedented environmental burden: since the onset of mass production in the late 1940s, it is estimated that approximately 8 billion tons of plastic have been produced globally, with around 6 billion tons ultimately discarded.

In the marine environment, macroplastics (MaPs, >5 mm) degrade into microplastics (MPs, <5 mm) and nanoplastics (NPs, 1 nm–1 μm) through processes such as physical abrasion, hydrolysis, oxidation, and photodegradation [14, 15]. These degradation processes not only facilitate the plastics dispersal but also promote the adsorption of hazardous substances due to the increased surface area. Consequently, plastics can adversely affect organisms at all levels of biological organization, from individual inflammation and altered gene expression to disruptions in food webs through bioaccumulation and biomagnification [16–18].

Understanding the dynamics of plastic degradation, fragmentation, and contaminant adsorption in the marine environment remains a major analytical challenge due to the multitude of influencing factors and the complexity of the underlying mechanisms. In this context, XPS offers a powerful means to investigate the surface-level transformations of plastic materials. Importantly, this emerging research direction benefits from a well-established foundation of XPS applications in polymer science, which can now be exploited to address these pressing environmental questions. In fact, XPS has long been employed for the post-synthetic characterization of plastics [19–23], and for assessing their chemical inertness and surface alterations following various physical, chemical, and biological stressors—including plasma-induced weathering [24–26], electric discharges [27], mechanical abrasion [28], exposure to high-energy radiation [29], hydrolysis [30], thermal treatments [31], biodeterioration [32–34], and UV radiation [35, 36].

In this Perspective, Authors critically examine the evolving role of XPS in elucidating environmentally significant processes affecting plastic materials. Specifically, plastic degradation in aquatic and marine settings is considered as they represent the environmental scenario more critically affected due to the water effect in driving polymer breakdown and in carrying plastics and their by-products. As a result, plastics are found throughout the oceans—from nearshore waters and offshore regions to subtropical gyres and even remote polar seas.

2 | Understanding the Plastic Degradation Process in Marine Environments: The Contribution of XPS Studies

Different initiation mechanisms have been proposed for plastic degradation in aquatic and marine environments [37–39, 15]. These pathways are strongly influenced by polymer chemistry and the presence of easily oxidizable functional groups. In general, plastics undergo photo oxidation [37, 38] in water under UV irradiation, which is part of the natural solar radiation via charge transfer complex (CTC) formation between the polymer and molecular oxygen:

$$RH + O_2 + h\upsilon = 2R^{\cdot} \quad (1)$$

Even though CTC absorption above 290 nm is weak, experimental evidence supports its role in generating radical species and hydrogen peroxide, which ultimately form oxygen containing moieties on polyolefins. A more widely acknowledged pathway involves surface hydroperoxides that absorb UV light and decompose into alkoxy and hydroxyl radicals:

$$ROOH + h\upsilon = RO^{\cdot} + OH^{\cdot} \quad (2)$$

Since UV A (315–400 nm) and UV B (280–315 nm) reach the Earth's surface, these bands—despite accounting for only 5 % of solar irradiance—carry sufficient energy to cleave polymer chains [40]. Photo-oxidation begins when chromophoric groups [41] absorb photons, possibly leading to C—H bond scission [40, 42]. The resulting radicals react with oxygen to form peroxy and hydroperoxy radicals, which subsequently generate new oxygen-containing groups that act as additional chromophores. These

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new chromophores enhance light absorption, thus accelerating further degradation [41] and establishing a positive feedback loop [14].

However, even polymers lacking classical chromophores (e.g., polyethylene, polypropylene) can undergo photo-oxidation, likely because trace oxygen containing groups—introduced during synthesis or by atmospheric exposure—serve as latent initiation sites. Despite these hypotheses [43, 30], the precise onset and evolution of photodegradation remain incompletely understood [14].

XPS has emerged as a valuable tool in this context due to its ability to detect subtle changes in surface composition and oxidation states, which can be conveniently used to elucidate degradation mechanisms and track surface chemical modifications in plastics over time. As an example, in the analysis of aged PE samples, XPS analysis revealed clear changes in plastics surface chemistry after the weathering process [44], particularly on C 1s signal (Figure 2 A (i)), revealing the progressive formation/increase of oxygen-containing functionalities such as hydroxyl, carbonyl, and carboxyl groups, consistent with oxidation and hydrolysis mechanisms typically associated with macroplastic degradation. Correspondingly, oxygen-containing moieties such as C—O and C═O are typically identified by fitting of the O 1s region at binding energies above 530 eV [45].

Nonetheless, one limitation in studying these processes is the common adoption of overly simplified approaches, such as the exclusive analysis of experimentally aged materials (e.g., via artificial weathering), without a critical comparison with plastics exposed to real environmental conditions. Validating laboratory findings against real-world samples is essential to truly understand how plastics behave in natural environments. Without this comparison, there is a risk of misinterpreting degradation patterns, missing key environmental factors that influence plastic aging. Only by integrating controlled experiments with real field studies is it possible to obtain a comprehensive picture of plastic transformation pathways. In this direction, our research group [46] recently investigated the chemical transformations occurring in polystyrene (PS) and polyethylene (PE)—two of the most abundant plastics in marine environments—upon artificial weathering through UV irradiation under simulated hydrodynamic conditions and directly comparing XPS results with what observed on real marine samples collected from Italian beaches. The XPS analysis revealed clear changes in plastics surface chemistry, particularly referring to C 1s signal, exhibiting an increase of oxygen-containing functionalities such as hydroxyl, carbonyl, and carboxyl groups (Figure 2 A (ii)), possibly correlated with oxidation and hydrolysis mechanisms typically associated with macroplastic degradation. Notably, the O/C atomic ratio increased significantly from 0.02 to 0.19 for PE (Figure 2 A (iii)) and from 0.01 to 0.24 for PS, confirming the oxidative character of the weathering process. Importantly, similar evidence about surface chemistry emerged from XPS analysis on samples collected from the marine environment, exhibiting the same oxidized components observed in artificially weathered plastics. This finding confirms that the agents simulated in the lab—water exposure, hydrodynamic stress, mechanical friction, and UV irradiation—also play a decisive role in driving degradation and fragmentation of plastics in natural settings.

Interestingly, similar surface chemistry was observed also on other polyolefins (e.g. polypropylene) artificially aged and collected from the marine environment confirming the occurrence of surface oxidation. This behavior may be attributed [47–50, 35] to the presence of pre-existing oxygen-containing functional groups introduced during manufacturing or due to environmental exposure which can act as chromophores, absorbing solar radiation and initiating degradation.

In thermoplastic materials like polystyrene, along with the increase of C 1s components between 286 and 290 eV with the aging process (Figure 2 B (i-iii)), the identification of π–π shake-up satellite in the XPS spectra can serve as additional markers for degradation studies. A decrease in its intensity has been indeed associated with the decomposition of phenyl rings and the concurrent formation of oxygenated degradation products [45, 46]. Similar trends have been confirmed using angle-resolved XPS (ARXPS), used to investigate chemical speciation as a function of sampling depth (up to ≈10 nm), which revealed that oxygen-containing functional groups are most abundant at the outermost surface and decrease with depth, further demonstrating that degradation is prominent at the polymer–environment interface [51].

Remarkably, the increased amount of carbonyl and hydroxyl functionalities evidenced by XPS analysis contribute to weaken the cohesive polymer network—lowering fracture toughness and promoting micro-crack initiation under mechanical stress—then leading to enhanced embrittlement and fragmentation. This self-reinforcing cycle [14], in which an increasingly oxidized and hydrolyzed surface becomes more susceptible to further degradation, ultimately results in the release of ever-smaller plastic particles into the environment [52, 53]. Such experimental evidence supports the proposed degradation pathways involving the incorporation of polar oxygen-containing groups at the surface [52, 53] (Figure 2C).

However, this trend is not universal across all polymer classes. For example, Kovacic et al. [54], investigated the aging of the polyester polyethylene terephthalate (PET) [58] by XPS observing a decrease in signal components ascribed to C—O—C/C—OH and O—C═O bonds, which was ascribed to ester-linkage scission and loss of terminal —OH and —COOH groups. Also, an increase in C═C and conjugated π–π signals emerged, which they attributed to decarboxylation and chain-scission processes yielding unsaturated fragments, which promote π–π stacking and radical-driven crosslinking, thereby raising the relative abundance of C—C bonds. In another work, Ioakeimidis, et al. [55] gained the same evidence by ATR-FTIR [59], showing an attenuation of the ester band at 1715 cm^{-1} and the appearance of new alkane (C—H) and alkyne ($C{\equiv}C$) bonds at 1435 and 620 cm^{-1}, respectively, after crosslinking processes.

In other words, different PET modifications have been documented by XPS upon artificial and environmental weathering mainly consisting in the progressive accumulation of hydroxyl, carbonyl, and carboxyl functionalities on PET surfaces—changes that correlate with increased embrittlement and fragmentation of the polymer matrix [56, 57].

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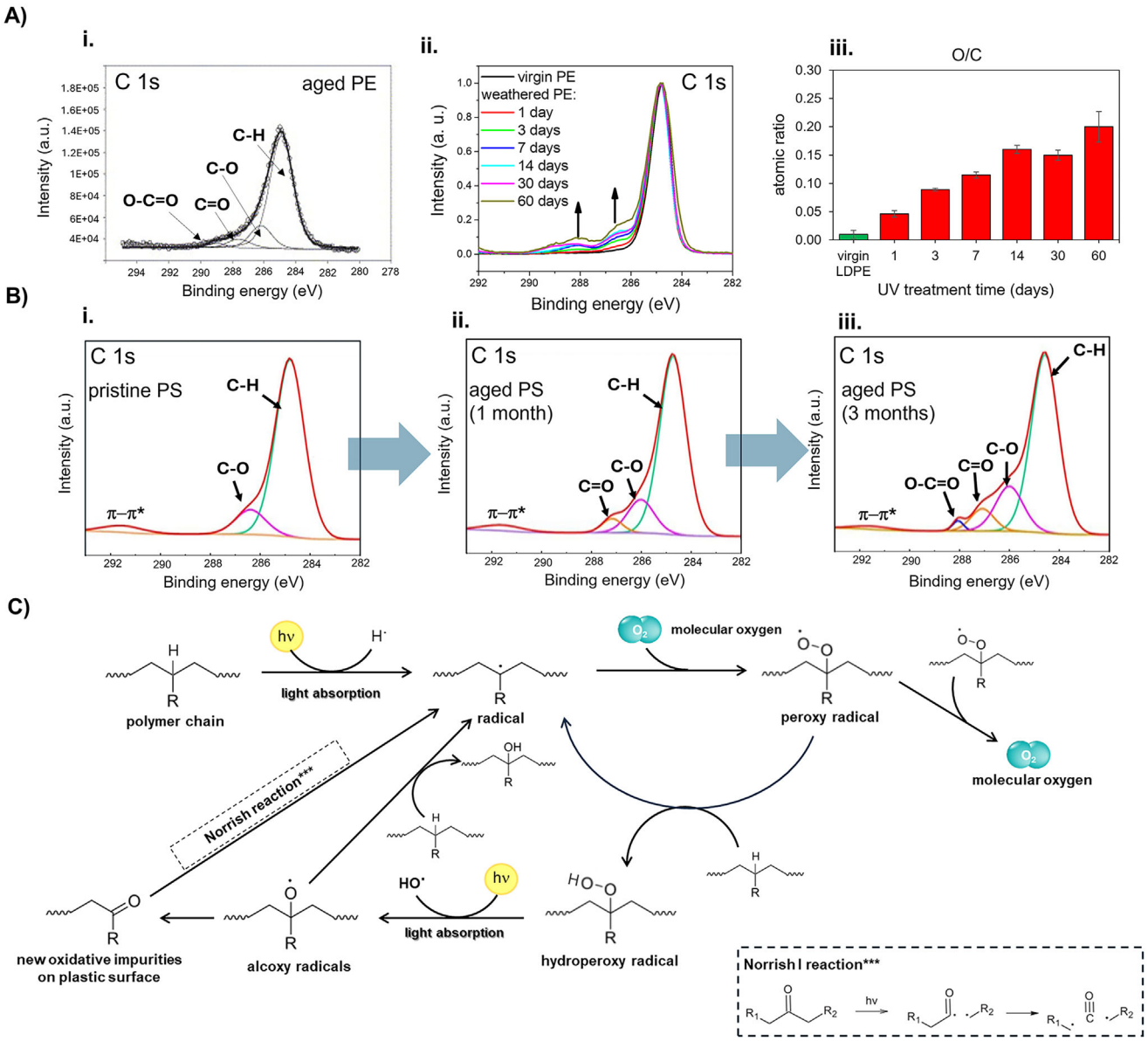


FIGURE 2 | A) High-resolution spectra: i) C 1s signal recorded for polyethylene (PE) after a UV-light mediated weathering process. Reproduced with permission [44]. Copyright 2004, Elsevier. ii) C 1s signal evolution during its aging. Adapted under the terms of the CC BY 4.0 license [46]. Copyright 2024, MDPI. iii) O/C atomic ratio calculated from XPS analysis of LDPE samples exposed to the artificial weathering process for different time intervals. Reproduced under the terms of the CC BY 4.0 license [46]. Copyright 2024, MDPI. B) High-resolution C 1s spectra recorded before (i) and after a weathering process of ii) one month and iii) three months on polystyrene (PS). Reproduced with permission [35]. Copyright 2020, Elsevier. C) Proposed photo-degradation mechanism of PE (R H) and PS (R = Ph). Reproduced under the terms of the CC BY 4.0 license [46]. Copyright 2024, MDPI.

This apparent discrepancy stems largely from the two-step nature of PET photodegradation [15, 58]. In the early stages, chain-scission reactions preferentially remove oxidized chain ends from the surface layer, yielding a transient drop in oxidized signal. With continued irradiation (especially under humid or oxidative atmospheres), secondary photo-oxidation dominates, generating new oxygenated groups and thus a net rise in oxidized functionalities. Both processes have been also confirmed by ATR-FTIR [15, 55, 56, 59]. Variations in UV radiation intensity, temperature, water content and polymer morphology are expected to modulate the balance between scission-driven removal and oxidation-driven formation of polar groups, reconciling both sets of observations.

Another significant contribution of XPS to studies on plastics degradation process can be found in evidence provided about bio-based plastics. Given the persistent issue of plastic dispersion in marine environments, increasing attention has been indeed directed toward the development of bio-based plastics as a strategy to reduce environmental impact. Biobased polymer blends have been proposed as eco-friendly alternatives to conventional plastics, aiming to mitigate plastic pollution [60]. However, the

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degradation behavior of these materials in marine conditions and their potential to generate microplastics remain poorly understood. Zhao et al. [61] investigated the formation of MPs and the changes in the physicochemical properties of three different bio-based polymer blends following photodegradation in seawater. Specifically, bio-based plastics were obtained by grafting conventional plastic materials (as polyethylene, PE, polypropylene, PP, and polystyrene, PS) with starch into the polymer matrix. Interestingly, the authors observed that starch-grafted plastics were more prone to fragmentation than their conventional counterparts. This enhanced fragmentation was attributed to preferential cleavage occurring at the starch functional groups embedded within the polymer network. XPS analysis revealed that, while in conventional plastics—especially PP—photooxidative degradation leads to a surface increase of oxygen-containing functional groups, the aging of the bio-based materials resulted in a reduction of oxygenated groups, as evidenced by a decrease in intensity of the C—O components in C 1s spectra. This reduction was attributed to the cleavage of ester bonds during UV exposure, suggesting that bio-based plastics may degrade more rapidly under environmental conditions, leading to an increased release of MPs. Importantly, XPS studies revealed that the resulting microplastics retain a core structure composed of PE, PP, or polystyrene (PS)— which are inherently persistent and non-biodegradable in the marine environment. These findings raise a critical concern regarding the design and use of bio-based plastics: while intended to be more sustainable, these materials may unintentionally accelerate the release of harmful microplastics. Therefore, future development of bio-based polymers should critically consider this aspect, foreseeing the structure of micro- and nanoplastics possibly formed during degradation, which are required to be biocompatible, readily oxidizable, and capable of undergoing complete mineralization under environmental conditions.

An interesting example of XPS application to the study of plastics environmental fate is provided by Pikuda et al. [62], who investigated the release of microplastics from disposable face masks, whose use and dispersion in the environment has exponentially increased with the COVID-19 pandemic [63, 64]. The study demonstrated that environmental factors such as mechanical abrasion and solar radiation—particularly in the UV range—trigger the release of microplastics from these masks. The authors observed that used masks tend to release PP microfibers more readily than unused ones, often carrying material originating from the inner backbone layers of the mask. Using XPS, they monitored Si 2p signal on microfibers, calculating the atomic Si/C ratio. Their findings revealed that microfibers released from used face masks exhibited a significantly higher silica content—over 240% greater—compared to microfibers from new masks. This result was attributed to the reduced structural integrity of used masks which facilitates increased PP particle release during environmental exposure. Furthermore, the microfibers from used masks exhibited increased surface roughness and a higher density of oxygen-containing functional groups, both of which enhance their susceptibility to further fragmentation once released into the environment. It is thus evident that the recent pandemic event has significantly contributed to the overall plastic load discharged into aquatic systems further increasing the uncontrolled microplastic pollution [63, 64].

3 | A Focus on Contaminants Adsorption Behavior on Plastic Materials Through XPS Investigations

The study of plastic surfaces by XPS can provide insightful information about their fate in the environment also investigating another crucial phenomenon they are exposed to, once dispersed in the environment, relying in the adsorption of contaminants, which makes plastics their vectors even for prolonged distances thus contributing to widespread contaminants dispersion in different environmental matrices. Plastics adsorb both inorganic and organic compounds and can concentrate them several orders of magnitude greater than the levels found in their surrounding environment, potentially leading to bioaccumulation and adverse biological effects [35, 65, 66]. On a larger scale, the ability of MPs to transport sorbed pollutants across ecosystems introduces new pathways for environmental contamination, posing long-term risks to biodiversity and ecosystem health. This underlines the importance of understanding not only the fate of plastics in the environment but also their role as vectors of chemical contaminants.

Given the relevance of this phenomenon, numerous studies have focused on the adsorption of both heavy metals and organic contaminants onto plastic surfaces. A growing body of evidence has demonstrated that the ability of plastics to act as contaminant carriers can be influenced by their environmental aging state, which in turn depends on their residence time and weathering in the environment. For instance, Herath et al. [67] compared the adsorption behavior of two chemically similar polymers, low-density polyethylene (LDPE) and high-density polyethylene (HDPE). They firstly found that the lower crystallinity of LDPE rendered it less photostable than the more linear, crystalline HDPE, with the presence of the O 1s peak in LDPE before photodegradation, attributed to intrinsic surface oxidation and the presence of stabilizers, fillers, or residual impurities introduced during manufacturing to enhance mechanical strength, durability, and thermal resistance. The higher amount of oxidized surface functionalities in LDPE—confirmed by detailed C 1s and O 1s spectral fitting—was found to significantly enhance its sorption capacity for heavy metals in stormwater, reaching surface loadings of 2526 $\mu g/m^2$ for Pb(II). These findings suggest that degraded plastic debris may act as more efficient carriers of contaminants from urban areas to nearby aquatic environments, potentially exacerbating local pollution levels.

In another work [68], Salehi et al. observed that the oxygen-containing functional groups formed on the LDPE surface upon environmental exposure, such as C—O, C═O, and (C═O)—O, acted to enhance its reactivity toward heavy metal ions. These moieties serve indeed as nucleation sites for $Pb(OH)_2$ deposition, significantly increasing heavy-metal binding compared to pristine LDPE (Figure 3). XPS survey spectra further confirm this effect: aged LDPE exhibits clear metal-related signals that are absent in the unweathered polymer (Figure 3). These findings hold relevance considering the growing use of plastic-based infrastructure for potable water distribution systems.

The concern raised by plastic interaction with metal ions evidently relies not only in their long-distance transport and

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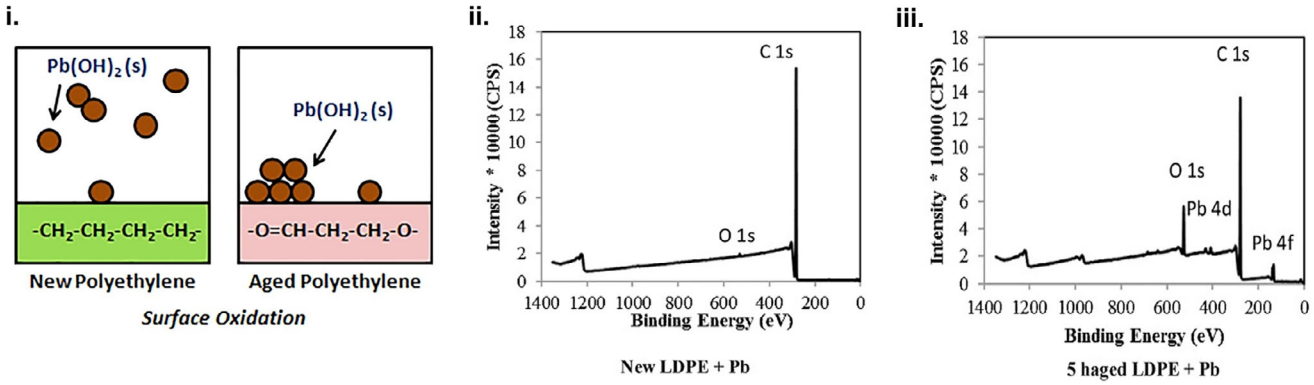


FIGURE 3 | i) Different adsorption behavior of Pb on pristine and weathered polyethylene. Wide XPS spectra recorded for ii) pristine and iii) aged polyethylene after exposure with $Pb(OH)_2$ solutions. Reproduced with permission [68]. Copyright 2018, Elsevier.

concentration, but also in desorption processes possibly occurring when plastics are exposed to different conditions (for example in terms of pH, ionic strength, competing ligands, etc) [67, 68]. For instance, under slightly acidic conditions, protonation of —COO^- groups weaken metals binding promoting their release. From a practical standpoint, water distribution and irrigation systems that utilize plastic components based on recycled materials—such as pipes, fittings, or filtration media—can become secondary sources of contamination [69, 70]. To mitigate this risk, it is advisable to implement screening protocols (e.g. surface analysis and batch desorption tests) to quantify both the adsorbed metal load and its possible release under expected operating conditions.

An increased susceptibility to contaminants adsorption on aged plastic surface has been proved by XPS studies also for organic species. In a recent study, Feng et al. [71] demonstrated that aged microplastics (MPs) can significantly influence oil transport dynamics in shoreline environments. The authors investigated the combined effects of seawater exposure and UV irradiation on plastic aging, using XPS to monitor surface chemical changes. The aging process was found to alter both physical and chemical properties of the MPs—namely, increasing hydrophilicity and crystallinity, reducing mean particle size and promoting the formation of new oxygen-containing functional groups (e.g., C—O and C═O), consistent with previous reports [46, 67, 68]. However, conclusions are drawn based on questionable O 1s peak fitting assigning the components at ≈532 and ≈530 eV to C—O and O—C═O, respectively [72], indirectly remarking the key role of rigorous fitting spectra procedures for accurate data interpretation [73, 74]. Nevertheless, the authors conclude that the observed surface modifications enhance oil retention on the microplastics, thereby influencing the behavior of oil within oil-contaminated beach resulting from pollution. Such findings suggest that microplastics may contribute to the redistribution of hydrophobic contaminants across coastal ecosystems, transporting them from sink areas to more distant sites, depending on the hydrodynamic conditions. With the emergence of new pollutant forms such as "*plastitar*"—resulting from the aggregation of oil derivatives (tar) with plastics (mainly of primary origin)—understanding the mechanisms driving their formation has become critically important [75]. Gaining insight into these dynamics is essential to prevent their widespread dissemination on a global scale.

Microplastics can also act as pollutant carriers without undergoing prior aging. In an innovative study, Chen et al. [76] investigated the adsorption behavior of various tetracyclines (TCs) onto pristine polyethylene (PE) microplastics in aqueous environments. Molecular dynamics simulations were employed to gain molecular-level insight into the adsorption mechanisms. Results showed that PE effectively adsorbs TCs through non-covalent interactions, displaying the highest affinity for chlortetracycline (CTC) and oxytetracycline (OTC), followed by tetracycline (TC). These findings were experimentally supported by XPS analyses conducted before and after exposure to TCs. Following adsorption, a marked increase of the C 1s signal was observed along with the appearance of the O 1s peak, confirming surface intrusion of TC molecules. The O 1s region was fitted into two peaks at 531.8 and 533.0 eV, corresponding to C = O and C-OH groups, consistent with the known TC chemical structure. Similar studies have reported the adsorption of other contaminants, including pharmaceuticals and personal care products, onto plastic surfaces [57, 65, 66]. Coupling computational chemistry with XPS experiments offers a powerful, complementary strategy as molecular-level simulations can predict adsorption sites, binding energies, and reaction pathways, which can be validated by XPS, thus allowing a deeper understanding of contaminant–polymer interactions to be achieved.

4 | Remaining Questions and Possible Future Advancements

X-ray photoelectron spectroscopy (XPS) is establishing itself as a crucial analytical technique for unraveling the complex surface chemistry of environmental plastics. Its sensitivity to the outermost 1–10 nm of material enables direct monitoring of photooxidation, hydrolysis, and contaminant adsorption processes that govern plastic degradation pathways. By monitoring and quantifying changes in elemental composition—most notably the stoichiometric O/C ratio—and resolving chemical states via high-resolution C 1s and O 1s spectra, researchers have gained critical insights into weathering pathways occurring on plastics, which are responsible for their fragmentation and, thus, for low-size (from micro- to nano-) plastics dispersion in the environment.

Comparative XPS studies on conventional polymers (PE, PS, PET) revealed different transformation pathways, while investi-

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gations of starch-grafted bio-based polymers demonstrate accelerated fragmentation at starch-rich sites, though the resulting microplastics still retain persistent PE, PP, or PS cores, underscoring the imperative for developing fully biodegradable plastics in next-generation materials. The adsorption of heavy metals and organic pollutants onto weathered and pristine microplastics has been also elucidated through XPS, underscoring plastics dual role as both pollutant concentrating agents and vectors.

Despite the unique contribution provided by XPS in explaining the interfacial chemistry, which plays a key role in determining plastics fate in the environment governing their degradation/fragmentation pathways, it presents some limitations, and some questions still remain unanswered.

While XPS is generally considered non-destructive, extended X-ray exposure can induce radiation damage [77]. Intrinsic limitations rely in the required operative conditions, especially in terms of vacuum requirements, which do not allow the direct investigation of plastics-water interface under realistic conditions. Additionally, the ultra-high vacuum environment can lead to the desorption of low-molecular-weight species, potentially altering native surface chemistry. Recent advancements in near-ambient pressure XPS (NAP-XPS) [78], also known as in situ XPS, have enabled measurements at pressures up to ≈10 mbar, facilitating the investigation of solid–gas, solid–liquid, and liquid–gas interfaces [79]. Nevertheless, its application to plastic surface analysis is still largely unexplored, possibly due to the advanced correction strategies [80] required for achieving an accurate spectra interpretation. In NAP-XPS in fact photoelectrons must traverse the gas phase before detection, where they undergo inelastic scattering with gas molecules [81] with subsequent attenuation of the primary signal, broadening of spectral features, and appearance of secondary background components with artificial energy loss features [81, 82]. Additional efforts are thus required from companies and manufacturers operating in the interfacial chemistry field to develop novel solutions for carrying out surface analysis at lower pressure without losing analytical information.

One underexplored aspect in the XPS study of plastics in the environment still concerns the investigation of *different* plastic materials collected from *different* real environments for a wide comparative investigation. This approach could cast light on weathering factors that accelerate or modify degradation in natural environments, possibly evidencing more susceptible plastics and more impactful environmental conditions. In this way, plastic production could be oriented accordingly, and higher-risk areas could be identified and, maybe, taken under more strict control. For such an approach, standardization of sampling and analytical protocols across laboratories would be required to ensure data comparability and build robust environmental baselines for regulatory and remediation efforts.

The accurate investigation of plastic degradation processes by XPS analysis evidently relies on spectral fitting procedures and critical data interpretation. Although it is widely demonstrated that XPS is employed to monitor modifications in the C 1s and O 1s core-level spectra, which are particularly sensitive to chemical alterations caused by aging processes toward the fragmentation, not rigorous XPS spectra fitting approaches can be found in the literature on the subject, along with controversial assignment of peak components, thus complicating a critical direct comparison across published studies. Looking forward, this analytical step could be supported by artificial intelligence (AI) tools, considering its increasing impact on modern research activity. Advances in spectral fitting—potentially driven by machine-learning algorithms—could streamline the interpretation of complex, overlapping signals, making XPS analysis more accessible to not highly expert users.

Similarly, tools for analyzing/predicting molecular interaction mechanisms could be beneficially integrated with XPS studies. Especially for plastics interaction with contaminants, the applications of density functional theory (DFT) and quantitative structure activity relationship (QSAR) modelling could identify functional moieties particularly reactive toward specific contaminants, with further XPS validation. Such integrated information could be then used for orienting the choice toward less reactive plastics, when possible, and as a basis for modifying plastics synthetic protocols with the introduction of additional components (ion exchangers, quenchers, …) possibly reducing plastic interaction with contaminants or, at least, limiting subsequent contaminants desorption.

XPS is a pivotal tool for characterizing environmental plastics, but the complexity of real-world weathering and adsorption processes demands a synergistic, multi-analytical approach. XPS coupling with bulk-sensitive techniques, such as attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) and Raman spectroscopy, can provide insights into chemical changes throughout the material [55, 83]. Pyrolysis coupled with gas chromatography–mass spectrometry (Py–GC–MS), widely used in plastics weathering studies [84], can facilitate the identification and quantification of polymeric materials based on their characteristic thermal degradation products [84]. Additionally, chemical analysis can be conveniently supported by morphological and mechanical characterizations.

In the Authors' opinion, an existing gap remains nowadays between the richness of analytical findings from XPS and applicative solutions adopted for plastic pollution remediation. For possibly reducing or eliminating such a void, qualitative and quantitative XPS data should be packaged in tailored, non-technical formats suitable for diverse audiences. In this way, for example, plastics manufactures could exploit the information for modifying the synthetic protocols accordingly (e.g., using targeted additives as ion-exchangers or radical scavengers) to slow degradation and avoid pollutant uptake. AI and data-science developers may embed XPS-derived descriptors (such as O/C ratios, functional-group densities, and binding-energy shifts) into predictive models and digital twins able to forecast polymer behavior under different environmental conditions.

Such an information package could also be customized for non-expert users, as local authorities, educators, and general public. Local authorities could benefit from concise policy briefs summarizing XPS studies to prioritize cleanup efforts and to regulate polymer grades for specific applications. Finally, simplified visualizations—infographics or interactive dashboards—could empower educators and the public to understand how surface chemistry drives microplastic fragmentation and pollutant transport.

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By bridging the gap between interface chemistry insights and real-world action, XPS data could directly inform materials science innovation, predictive modeling, policy decisions, and public engagement, transforming analytical knowledge into tangible strategies to mitigate plastic pollution.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The authors have nothing to report.

References

1. D. Briggs, *Surface Analysis of Polymers by XPS and Static SIMS* (Cambridge University Press, 1998), https://doi.org/10.1017/CBO9780511525261.

2. F. A. Stevie and C. L. Donley, "Introduction to X-Ray Photoelectron Spectroscopy," *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* 38 (2020): 063204, https://doi.org/10.1116/6.0000412/1024200.

3. G. Greczynski and L. Hultman, "A Step-by-Step Guide to Perform X-Ray Photoelectron Spectroscopy," *Journal of Applied Physics* 132, no. 1 (2022): 011101, https://doi.org/10.1063/5.0086359/2837063.

4. E. Mazzotta, S. Rella, A. Turco, et al., "XPS in Development of Chemical Sensors," *RSC Advances* 5 (2015): 83164–83186, https://doi.org/10.1039/C5RA14139G.

5. J. W. Pinder, G. H. Major, D. R. Baer, et al., "Avoiding Common Errors in X-Ray Photoelectron Spectroscopy Data Collection and Analysis, and Properly Reporting Instrument Parameters," *Applied Surface Science Advances* 19 (2024): 100534, https://doi.org/10.1016/J.APSADV.2023.100534.

6. D. R. Baer, K. Artyushkova, C. Richard Brundle, et al., "Practical Guides for X-Ray Photoelectron Spectroscopy: First Steps in Planning, Conducting, and Reporting XPS Measurements," *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* 37 (2019): 031401, https://doi.org/10.1116/1.5065501.

7. G. Binda, G. Kalčíková, I. J. Allan, et al., "Microplastic Aging Processes: Environmental Relevance and Analytical Implications," *TrAC Trends in Analytical Chemistry* 172 (2024): 117566, https://doi.org/10.1016/J.TRAC.2024.117566.

8. L. Desidery and M. Lanotte, "Polymers and Plastics: Types, Properties, and Manufacturing," *Plastic Waste for Sustainable Asphalt Roads* (Woodhead Publishing, 2022): 3–28, https://doi.org/10.1016/B978-0-323-85789-5.00001-0.

9. U. Kong, N. F. Mohammad Rawi, and G. S. Tay, "The Potential Applications of Reinforced Bioplastics in Various Industries: A Review," *Polymers* 15, no. 10 (2023): 2399, https://doi.org/10.3390/POLYM15102399.

10. M. K. Huda and I. Widiastuti, "Natural Fiber Reinforced Polymer in Automotive Application: A Systematic Literature Review," *Journal of Physics: Conference Series* 1808, no. 1 (2021): 012015, https://doi.org/10.1088/1742-6596/1808/1/012015.

11. F. Gagliani, T. Di Giulio, S. Grecchi, et al., "Green Synthesis of a Molecularly Imprinted Polymer Based on a Novel Thiophene-Derivative for Electrochemical Sensing," *Molecules* 29, no. 7 (2024): 1632, https://doi.org/10.3390/MOLECULES29071632.

12. T. Di Giulio, M. I. Asif, M. Corsi, et al., "Visible-Light Photo-Iniferter Polymerization of Molecularly Imprinted Polymers for Direct Integration with Nanotransducers," *Small Methods* 9 (2025): 2401315, https://doi.org/10.1002/SMTD.202401315.

13. T. Di Giulio, I. M. Asif, M. Corsi, et al., "A Molecularly Imprinted Polymer-Based Porous Silicon Optical Sensor for Quercetin Detection in Wines," *ACS Applied Materials & Interfaces* 17 (2025): 12663–12675, https://doi.org/10.1021/ACSAMI.4C21238/ASSET/IMAGES/LARGE/AM4C21238_0005.JPEG.

14. A. L. Andrady, P. W. Barnes, J. F. Bornman, et al., "Oxidation and Fragmentation of Plastics in a Changing Environment, from UV-Radiation to Biological Degradation," *Science of The Total Environment* 851 (2022): 158022, https://doi.org/10.1016/J.SCITOTENV.2022.158022.

15. B. Gewert, M. M. Plassmann, and M. Macleod, "Pathways for Degradation of Plastic Polymers Floating in the Marine Environment," *Environmental Science: Processes & Impacts* 17, no. 9 (2015): 1513–1521, https://doi.org/10.1039/C5EM00207A.

16. G. E. De Benedetto, S. Fraissinet, N. Tardio, et al., "Microplastics Determination and Quantification in Two Benthic Filter Feeders Sabella Spallanzanii, Polychaeta and Paraleucilla Magna, Porifera," *Heliyon* 10, no. 11 (2024): 31796, https://doi.org/10.1016/j.heliyon.2024.e31796.

17. S. Fraissinet, D. Arduini, A. Martines, et al., "Microplastics Uptake by Four Filter Feeders," *Journal of Marine Science and Engineering* 12, no. 6 (2024): 1000, https://doi.org/10.3390/JMSE12061000/S1.

18. S. Fraissinet, D. Arduini, A. Martines, et al., "Seasonal Occurrence and Distribution of Microplastics in Four Different Benthic Suspension Feeders from an Integrated Multi-Trophic Aquaculture (IMTA) Facility: A Bioremediation Perspective," *Marine Pollution Bulletin* 207 (2024): 116811, https://doi.org/10.1016/J.MARPOLBUL.2024.116811.

19. S. Rella, E. Mazzotta, A. Caroli, et al., "Investigation of Polydopamine Coatings by X-Ray Photoelectron Spectroscopy as an Effective Tool for Improving Biomolecule Conjugation," *Applied Surface Science* 447 (2018): 31–39, https://doi.org/10.1016/J.APSUSC.2018.03.057.

20. C. Malitesta, I. Losito, L. Sabbatini, et al., "New Findings on Polypyrrole Chemical Structure by XPS Coupled to Chemical Derivatization Labelling," *Journal of Electron Spectroscopy and Related Phenomena* 76 (1995): 629–634, https://doi.org/10.1016/0368-2048(95)02438-7.

21. C. Malitesta, M. R. Guascito, E. Mazzotta, et al., "X-Ray Photoelectron Spectroscopy Characterization of Electrosynthesized Poly(3-Thiophene Acetic Acid) and Its Application in Molecularly Imprinted Polymers for Atrazine," *Thin Solid Films* 518, no. 14 (2010): 3705–3709, https://doi.org/10.1016/J.TSF.2009.10.016.

22. I. Losito, C. Malitesta, I. De Bari, et al., "X-Ray Photoelectron Spectroscopy Characterization of Poly(2,3-Diaminophenazine) Films Electrosynthesised on Platinum," *Thin Solid Films* 473, no. 1 (2005): 104–113, https://doi.org/10.1016/J.TSF.2004.07.059.

23. C. Malitesta, I. Losito, and P. G. Zambonin, "Molecularly Imprinted Electrosynthesized Polymers: New Materials for Biomimetic Sensors," *Analytical Chemistry* 71, no. 7 (1999): 1366–1370, https://doi.org/10.1021/AC980674G/ASSET/IMAGES/LARGE/AC980674GF00005.JPEG.

24. J. S. Kong, D. J. Lee, and H. D. Kim, "Surface Modification of Low-Density Polyethylene (LDPE) Film and Improvement of Adhesion between Evaporated Copper Metal Film and LDPE," *Journal of Applied Polymer Science* 82, no. 7 (2001): 1677–1690, https://doi.org/10.1002/APP.2008.

25. J. H. Lee, K. Y. Rhee, Y. H. Lee, et al., "An Application of Plasma Treatment to Improve Shear and Bending Behavior of HDPE/Steel Composites," *Journal of the Korean Physical Society* 54, no. 3 (2009): 986–991, https://doi.org/10.3938/JKPS.54.986.

26. O. M. Ba, P. Marmey, K. Anselme, et al., "Surface Composition XPS Analysis of a Plasma Treated Polystyrene: Evolution over Long Storage Periods," *Colloids and Surfaces B: Biointerfaces* 145 (2016): 1–7, https://doi.org/10.1016/J.COLSURFB.2016.04.026.

14392054, 0, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/mame.202500280 by Elisabetta Mazzotta - Università Del Salento Ser Inf Biblior "La Stecca" , Wiley Online Library on [14/10/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

27. F. Clément, B. Held, N. Soulem, et al., "A Study on the Aging Process of Polystyrene Thin Films Treated under DC Pulsed Discharges Conditions in Oxygen and Argon-Oxygen Mixtures," *European Physical Journal* 21, no. 1 (2003): 59–66, https://doi.org/10.1051/EPJAP:2002102.

28. J. Gao, L. Wang, W. M. Wu, et al., "Microplastic Generation from Field-Collected Plastic Gauze: Unveiling the Aging Processes," *Journal of Hazardous Materials* 467 (2024): 133615, https://doi.org/10.1016/J.JHAZMAT.2024.133615.

29. S. Dorey, F. Gaston, S. R. A. Marque, et al., "XPS Analysis of PE and EVA Samples Irradiated at Different γ-Doses," *Applied Surface Science* 427 (2018): 966–972, https://doi.org/10.1016/J.APSUSC.2017.09.001.

30. S. Massey, A. Adnot, A. Rjeb, et al., "Action of Water in the Degradation of Low-Density Polyethylene Studied by X-Ray Photoelectron Spectroscopy," *Express Polymer Letters* 1 (2007): 506–511, https://doi.org/10.3144/EXPRESSPOLYMLETT.2007.72.

31. M. U. De La Orden, J. M. Montes, J. Martínez Urreaga, et al., "Thermo and Photo-Oxidation of Functionalized Metallocene High Density Polyethylene: Effect of Hydrophilic Groups," *Polymer Degradation and Stability* 111 (2015): 78–88, https://doi.org/10.1016/J.POLYMDEGRADSTAB.2014.10.023.

32. Y. Zhang, J. N. Pedersen, B. E. Eser, et al., "Biodegradation of Polyethylene and Polystyrene: From Microbial Deterioration to Enzyme Discovery," *Biotechnology Advances* 60 (2022): 107991, https://doi.org/10.1016/J.BIOTECHADV.2022.107991.

33. Z. Wang, X. Xin, X. Shi, et al., "A Polystyrene-Degrading Acinetobacter Bacterium Isolated from the Larvae of Tribolium Castaneum," *Science of The Total Environment* 726 (2020): 138564, https://doi.org/10.1016/J.SCITOTENV.2020.138564.

34. J. Yang, Y. Yang, W. M. Wu, et al., "Evidence of Polyethylene Biodegradation by Bacterial Strains from the Guts of Plastic-Eating Waxworms," *Environmental Science & Technology* 48, no. 23 (2014): 13776–13784, https://doi.org/10.1021/ES504038A/SUPPL_FILE/ES504038A_SI_001.PDF.

35. R. Mao, M. Lang, X. Yu, et al., "Aging Mechanism of Microplastics with UV Irradiation and Its Effects on the Adsorption of Heavy Metals," *Journal of Hazardous Materials* 393 (2020): 122515, https://doi.org/10.1016/J.JHAZMAT.2020.122515.

36. K. Zhu, H. Jia, S. Zhao, et al., "Formation of Environmentally Persistent Free Radicals on Microplastics under Light Irradiation," *Environmental Science & Technology* 53, no. 14 (2019): 8177–8186, https://doi.org/10.1021/ACS.EST.9B01474/ASSET/IMAGES/LARGE/ES-2019-01474J_0006.JPEG.

37. J. C. W. Chien, "On the Possible Initiation of Photooxidation by Charge-Transfer Excitation," *The Journal of Physical Chemistry* 69, no. 12 (1965): 4317–4325, https://doi.org/10.1021/j100782a040.

38. P. Gijsman, "Reply to "Comment on Oxygen Charge-transfer Complexes as Peroxidation Initiators in Polymers"," *Polymer Degradation and Stability* 60, no. 1 (1998): 217–219, https://doi.org/10.1016/S0141-3910(97)00079-7.

39. G. Grause, M. F. Chien, and C. Inoue, "Changes during the Weathering of Polyolefins," *Polymer Degradation and Stability* 181 (2020): 109364, https://doi.org/10.1016/J.POLYMDEGRADSTAB.2020.109364.

40. Y. K. Song, S. H. Hong, M. Jang, et al., "Combined Effects of UV Exposure Duration and Mechanical Abrasion on Microplastic Fragmentation by Polymer Type," *Environmental Science & Technology* 51, no. 8 (2017): 4368–4376, https://doi.org/10.1021/ACS.EST.6B06155/SUPPL_FILE/ES6B06155_SI_001.PDF.

41. P. Gijsman, G. Meijers, and G. Vitarelli, "Comparison of the UV-Degradation Chemistry of Polypropylene, Polyethylene, Polyamide 6 and Polybutylene Terephthalate," *Polymer Degradation and Stability* 65, no. 3 (1999): 433–441, https://doi.org/10.1016/S0141-3910(99)00033-6.

42. G. Binda, D. Spanu, D. Monticelli, et al., "Unfolding the Interaction between Microplastics and (Trace) Elements in Water: A Critical Review," *Water Research* 204 (2021): 117637, https://doi.org/10.1016/J.WATRES.2021.117637.

43. S. Massey, D. Roy, and A. Adnot, "Study of Natural Ageing of Polypropylene by X-Ray Photoelectron Spectroscopy," *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 208 (2003): 236–241, https://doi.org/10.1016/S0168-583X(03)00662-1.

44. N. M. Stark and L. M. Matuana, "Surface Chemistry Changes of Weathered HDPE/Wood-Flour Composites Studied by XPS and FTIR Spectroscopy," *Polymer Degradation and Stability* 86, no. 1 (2004): 1–9, https://doi.org/10.1016/J.POLYMDEGRADSTAB.2003.11.002.

45. G. Meera, I. M. Sasidharan Pillai, P. G. Reji, et al., "Coagulation Studies on Photodegraded and Photocatalytically Degraded Polystyrene Microplastics Using Polyaluminium Chloride," *Waste Management* 170 (2023): 329–340, https://doi.org/10.1016/J.WASMAN.2023.09.018.

46. T. Di Giulio, G. E. De Benedetto, N. Ditaranto, et al., "Insights into Plastic Degradation Processes in Marine Environment by X-Ray Photoelectron Spectroscopy Study," *International Journal of Molecular Sciences* 25, no. 10 (2024): 5060, https://doi.org/10.3390/IJMS25105060/S1.

47. Z. Huang, Q. Cui, X. Yang, et al., "An Evaluation Model to Predict Microplastics Generation from Polystyrene Foams and Experimental Verification," *Journal of Hazardous Materials* 446 (2023): 130673, https://doi.org/10.1016/J.JHAZMAT.2022.130673.

48. S. Liu, W. Huang, J. Yang, et al., "Formation of Environmentally Persistent Free Radicals on Microplastics under UV Irradiations," *Journal of Hazardous Materials* 453 (2023): 131277, https://doi.org/10.1016/J.JHAZMAT.2023.131277.

49. M. Ghanadi and L. P. Padhye, "Revealing the Long-Term Impact of Photodegradation and Fragmentation on HDPE in the Marine Environment: Origins of Microplastics and Dissolved Organics," *Journal of Hazardous Materials* 465 (2024): 133509, https://doi.org/10.1016/J.JHAZMAT.2024.133509.

50. K. Jarosz, A. Borek-Dorosz, M. Drozdek, et al., "Abiotic Weathering of Plastic: Experimental Contributions towards Understanding the Formation of Microplastics and Other Plastic Related Particulate Pollutants," *Science of The Total Environment* 917 (2024): 170533, https://doi.org/10.1016/J.SCITOTENV.2024.170533.

51. L. E. P. Real, In *Weathering of Polymers and Plastic Materials* (Springer Nature Switzerland, 2023), https://doi.org/10.1007/978-3-031-33285-2/COVER.

52. N. T. Dintcheva, F. P. La Mantia, and V. Malatesta, "Photo-Oxidation Behaviour of Polyethylene/Multi-Wall Carbon Nanotube Composite Films," *Polymer Degradation and Stability* 94, no. 2 (2009): 162–170, https://doi.org/10.1016/J.POLYMDEGRADSTAB.2008.11.012.

53. A. C. Albertsson, S. O. Andersson, and S. Karlsson, "The Mechanism of Biodegradation of Polyethylene," *Polymer Degradation and Stability* 18, no. 1 (1987): 73–87, https://doi.org/10.1016/0141-3910(87)90084-X.

54. M. Kovačić, A. Tomić, S. Tonković, et al., "Pristine and UV-Weathered PET Microplastics as Water Contaminants: Appraising the Potential of the Fenton Process for Effective Remediation," *Processes* 12 (2024): 844, https://doi.org/10.3390/PR12040844/S1.

55. C. Ioakeimidis, K. N. Fotopoulou, H. K. Karapanagioti, et al., "The Degradation Potential of PET Bottles in the Marine Environment: An ATR-FTIR Based Approach," *Scientific Reports* 6, no. 1 (2016): 1–8, https://doi.org/10.1038/srep23501.

56. M. Perraki, V. Skliros, P. Mecaj, et al., "Identification of Microplastics Using μ-Raman Spectroscopy in Surface and Groundwater Bodies of SE Attica, Greece," *Water* 16, (2024), 843, https://doi.org/10.3390/W16060843.

57. P. W. Chen, M. N. Hsiao, L. W. Xiao, et al., "Adsorption Behavior of Heavy Metals onto Microplastics Derived from Conventional and Biodegradable Commercial Plastic Products," *Science of The Total Environment* 951 (2024): 175537, https://doi.org/10.1016/J.SCITOTENV.2024.175537.

58. A. Chamas, H. Moon, J. Zheng, et al., "Degradation Rates of Plastics in the Environment," *ACS Sustainable Chemistry & Engineering* 8 (2020):

14392054, 0, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/mame.202500280 by Elisabetta Mazzotta - Università Del Salento Ser Inf Biblist "La Stecca" , Wiley Online Library on [14/10/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

3494–3511, https://doi.org/10.1021/ACSSUSCHEMENG.9B06635/ASSET/IMAGES/LARGE/SC9B06635_0009.JPEG.

59. S. Rostampour, R. Cook, S. S. Jhang, et al., "Changes in the Chemical Composition of Polyethylene Terephthalate under UV Radiation in Various Environmental Conditions," *Polymers* 16 (2024): 2249, https://doi.org/10.21203/RS.3.RS-4402725/V1.

60. S. Nizamuddin, A. J. Baloch, C. Chen, et al., "Bio-Bio-based Plastics, Biodegradable Plastics, and Compostable Plastics: Biodegradation Mechanism, Biodegradability Standards and Environmental Stratagem," *International Biodeterioration & Biodegradation* 195 (2024): 105887, https://doi.org/10.1016/J.IBIOD.2024.105887.

61. S. Zhao, L. Liu, C. Li, et al., "Photodegradation of Biobased Polymer Blends in Seawater: A Major Source of Microplastics in the Marine Environment," *Frontiers in Marine Science* 9 (2022): 1046179, https://doi.org/10.3389/FMARS.2022.1046179/BIBTEX.

62. O. Pikuda, M. Lapointe, O. S. Alimi, et al., "Fate of Microfibres from Single-Use Face Masks: Release to the Environment and Removal during Wastewater Treatment," *Journal of Hazardous Materials* 438 (2022): 129408, https://doi.org/10.1016/J.JHAZMAT.2022.129408.

63. L. Wang, S. Li, I. M. Ahmad, et al., "Global Face Mask Pollution: Threats to the Environment and Wildlife, and Potential Solutions," *Science of The Total Environment* 887 (2023): 164055, https://doi.org/10.1016/J.SCITOTENV.2023.164055.

64. J. Ammendolia, J. Saturno, A. L. Brooks, et al., "An Emerging Source of Plastic Pollution: Environmental Presence of Plastic Personal Protective Equipment (PPE) Debris Related to COVID-19 in a Metropolitan City," *Environmental Pollution* 269 (2021): 116160, https://doi.org/10.1016/J.ENVPOL.2020.116160.

65. Y. Guan, J. Gong, B. Song, et al., "The Effect of UV Exposure on Conventional and Degradable Microplastics Adsorption for Pb (II) in Sediment," *Chemosphere* 286 (2022): 131777, https://doi.org/10.1016/J.CHEMOSPHERE.2021.131777.

66. P. Liu, K. Lu, J. Li, et al., "Effect of Aging on Adsorption Behavior of Polystyrene Microplastics for Pharmaceuticals: Adsorption Mechanism and Role of Aging Intermediates," *Journal of Hazardous Materials* 384 (2020): 121193, https://doi.org/10.1016/J.JHAZMAT.2019.121193.

67. A. Herath and M. Salehi, "Studying the Combined Influence of Microplastics′ Intrinsic and Extrinsic Characteristics on Their Weathering Behavior and Heavy Metal Transport in Storm Runoff," *Environmental Pollution* 308 (2022): 119628, https://doi.org/10.1016/J.ENVPOL.2022.119628.

68. M. Salehi, C. T. Jafvert, J. A. Howarter, et al., "Investigation of the Factors That Influence Lead Accumulation onto Polyethylene: Implication for Potable Water Plumbing Pipes," *Journal of Hazardous Materials* 347 (2018): 242–251, https://doi.org/10.1016/J.JHAZMAT.2017.12.066.

69. M. Whitt, K. Vorst, W. Brown, et al., "Survey of Heavy Metal Contamination in Recycled Polyethylene Terephthalate Used for Food Packaging," *Journal of Plastic Film & Sheeting* 29, no. 2 (2013): 163–173, https://doi.org/10.1177/8756087912467028.

70. M. K. Eriksen, K. Pivnenko, M. E. Olsson, et al., "Contamination in Plastic Recycling: Influence of Metals on the Quality of Reprocessed Plastic," *Waste Management* 79 (2018): 595–606, https://doi.org/10.1016/J.WASMAN.2018.08.007.

71. Q. Feng, C. An, Z. Chen, et al., "Investigation into the Impact of Aged Microplastics on Oil Behavior in Shoreline Environments," *Journal of Hazardous Materials* 421 (2022): 126711, https://doi.org/10.1016/J.JHAZMAT.2021.126711.

72. G. Levi, O. Senneca, M. Causà, et al., "Probing the Chemical Nature of Surface Oxides during Coal Char Oxidation by High-Resolution XPS," *Carbon* 90 (2015): 181–196, https://doi.org/10.1016/J.CARBON.2015.04.003.

73. G. H. Major, V. Fernandez, N. Fairley, et al., "Guide to XPS Data Analysis: Applying Appropriate Constraints to Synthetic Peaks in XPS Peak Fitting," *Journal of Vacuum Science & Technology A* 40, no. 6 (2022): 063201, https://doi.org/10.1116/6.0001975/2844339.

74. D. R. Baer, G. E. McGuire, K. Artyushkova, et al., "Introduction to Topical Collection: Reproducibility Challenges and Solutions with a Focus on Guides to XPS Analysis," *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* 39 (2021): 021601, https://doi.org/10.1116/6.0000873/397281.

75. S. Fraissinet, E. Mancini, C. Funiati, et al., "New Plastitar Record for the Mediterranean Sea: Characterization of Plastics and Tar from the Salento Peninsula (Ionian Sea)," *Toxics* 13, no. 1 (2025): 13, https://doi.org/10.3390/TOXICS13010013/S1.

76. Y. Chen, J. Li, F. Wang, et al., "Adsorption of Tetracyclines onto Polyethylene Microplastics: A Combined Study of Experiment and Molecular Dynamics Simulation," *Chemosphere* 265 (2021): 129133, https://doi.org/10.1016/J.CHEMOSPHERE.2020.129133.

77. D. J. Morgan, "XPS Insights: Sample Degradation in X-Ray Photoelectron Spectroscopy," *Surface and Interface Analysis* 55, no. 5 (2023): 331–335, https://doi.org/10.1002/SIA.7205.

78. D. E. Starr, "A Brief Overview of the Principles of Ambient Pressure X-Ray Spectroscopies," *American Chemical Society* 1396 (2021): 1–17, https://doi.org/10.1021/BK-2021-1396.CH001/ASSET/IMAGES/LARGE/BK-2021-00356M_G020.JPEG.

79. D. N. G. Krishna and J. Philip, "Review on Surface-Characterization Applications of X-Ray Photoelectron Spectroscopy (XPS): Recent Developments and Challenges," *Applied Surface Science Advances* 12 (2022): 100332, https://doi.org/10.1016/J.APSADV.2022.100332.

80. S. Tougaard and M. Greiner, "Method to Correct Ambient Pressure XPS for the Distortion Caused by the Gas," *Applied Surface Science* 530 (2020): 147243, https://doi.org/10.1016/J.APSUSC.2020.147243.

81. H. Li, A. Jana, A. T. Garcia-Esparza, et al., "When Photoelectrons Meet Gas Molecules: Determining the Role of Inelastic Scattering in Ambient Pressure X-Ray Photoelectron Spectroscopy," *ACS Central Science* 11 (2024): 98–106, https://doi.org/10.1021/ACSCENTSCI.4C01841.

82. L. Pielsticker, R. Nicholls, S. Beeg, et al., "Inelastic Electron Scattering by the Gas Phase in near Ambient Pressure XPS Measurements," *Surface and Interface Analysis* 53, no. 7 (2021): 605–617, https://doi.org/10.1002/SIA.6947.

83. R. Anshari, M. Tsuboi, H. Sato, et al., "Raman and ATR-FTIR Unmask Crystallinity Changes and Carboxylate Group and Vinyl Group Accumulation in Natural Weathering Polypropylene Microplastics," *Scientific Reports* 15, no. 1 (2025): 1–15, https://doi.org/10.1038/s41598-025-85837-y.

84. N. M. Ainali, D. N. Bikiaris, and D. A. Lambropoulou, "Aging Effects on Low- and High-Density Polyethylene, Polypropylene and Polystyrene under UV Irradiation: An Insight into Decomposition Mechanism by Py-GC/MS for Microplastic Analysis," *Journal of Analytical and Applied Pyrolysis* 158 (2021): 105207, https://doi.org/10.1016/J.JAAP.2021.105207.

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