



Impact of weathering on the chemical identification of microplastics from usual packaging polymers in the marine environment



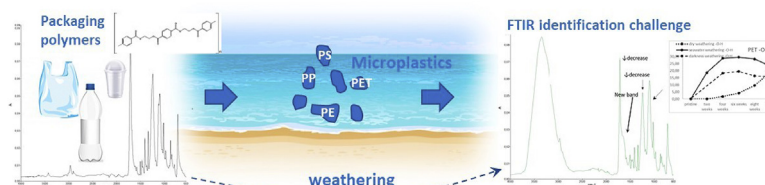
V. Fernández-González, J.M. Andrade-Garda, P. López-Mahía, S. Muniategui-Lorenzo*

Grupo Química Analítica Aplicada (QANAP), Instituto Universitario de Medio Ambiente (IUMA), Centro de Investigaciones Científicas Avanzadas (CICA), Universidad da Coruña, 15071A, Coruña, Spain

HIGHLIGHTS

- FTIR and SEM characterize weathering of common packaging polymers.
- Weathering modifies spectra so that IR identification gets difficult.
- Weathering implies non-linear, polymer-dependent processes.
- Inclusion of the spectra of weathered polymers in libraries is critical.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 7 August 2020

Received in revised form

22 October 2020

Accepted 1 November 2020

Available online 5 November 2020

Keywords:

Package polymers

Weathering

Microplastic

FTIR identification

Marine environment

ABSTRACT

Most of the plastics produced worldwide are finally disposed into the environment, most of them being one-use plastic packaging. Once released, plastics may undergo degradation through several agents, such as solar radiation, mechanical forces, and microbial action. Weathered plastics and microplastics (MPs) collected from the marine environment show considerable physical and chemical differences regarding their pristine counterparts; most notably on their surface, where spectrometric measurements are done. Hence, it is crucial to consider aging for their correct identification and quantification in environmental monitoring. Five of the most common polymers employed worldwide for packaging (LDPE, HDPE, PS, PP and PET) were weathered in a pilot-scale system simulating dry and marine conditions for more than 10 weeks. Aliquots were withdrawn periodically to monitor their weathering processes by means of infrared spectrometry and scanning electron microscopy; their spectra were compared and band ratios calculated. Results showed that an individual study of each polymer is necessary since degradation pathways and products depend on the polymer type. Moreover, including spectra of weathered polymers in the spectral libraries to obtain reliable identifications in microplastics pollution studies was critical.

© 2020 Elsevier B.V. All rights reserved.

1. Introduction

The world production of plastics surpassed the 320 million tons (Mt) level in 2016. Most of them are intended for packaging, being this sector the largest consumer of plastics (39.9%). Packing is dominated by polyethylene (PE) (29.8%) followed by polypropylene (PP) (19.3%), polyethylene terephthalate (PET) (7.4%) and polystyrene (PS) (6.7%). Together, they account for ≈60% of the plastic

demand in Europe [1]. As an unfortunate consequence of the ubiquitous use of plastics, the amount of packaging waste is growing in European countries. For instance, the total domestic production of packaging waste in Spain has increased from 5.8 Mt in 1997 to 7.2 Mt in 2016, with similar trends in other UE countries [2]. Consequently, these materials largely contribute to the generation of litter and it is estimated that between 5 and 13 Mt leak into the World's oceans every year [3,4].

Microplastics (MPs) appear in the environment both as manufactured microplastics (primary microplastics) and as a result of the

* Corresponding author.

E-mail address: soledad.muniategui@udc.es (S. Muniategui-Lorenzo).

continuous weathering of plastic litter, which yields progressively smaller plastic fragments (secondary microplastics). MPs are defined as any synthetic solid particle or polymeric matrix, with regular or irregular shape and with size ranging from 1 μm to 5 mm, of either primary or secondary manufacturing origin, which are insoluble in water [5].

Nowadays, it is well known that weathered MPs differ significantly from their pristine counterparts, mainly on their physico-chemical properties (e.g., size, color, crystallinity, mechanical properties and oxygen-containing groups) [6]. This is so because, once released to the environment, plastics and MPs may undergo degradation through several agents, such as solar radiation, mechanical forces, and microbial action [4]. Degradation of plastic polymers can proceed by either abiotic or biotic pathways. In general, the former precedes the latter, and is initiated thermally, hydrolytically, or by UV-light when released in the environment [3]. However, not all degradation pathways are effective on all polymer types.

It is worth understanding how plastics and the environmental conditions interact. Plastics degrade because of this interaction and usually their surface properties change accordingly, resulting in the creation of new functional groups or modification of existing ones. Then, plastics continue interacting with the environment and biota, which in turn modify also the surface, thus yielding a dynamic situation with ever-continuous changes [7]. It was shown, for example, that weathering of MPs promotes their ingestion by marine zooplankton [8,9] or mussels [10]. Besides altering the uptake, aging of MPs can influence its behavior in the water column and subsequent bioavailability through e.g. increased sinking rates or facilitating aggregation [8].

Many analytical techniques are available nowadays to characterize MPs although they can yield inconsistent results, somehow because MPs may contain copolymers and additives [11]. In particular the large diversity of the latter, as well as their different photooxidation and biodegradation routes, make the accurate identification of MPs pretty challenging [12]. The most frequent analytical techniques to identify and/or quantify MPs are based in spectrometry, microscopy and/or thermal analysis, being the most common approach the use of Fourier transform infrared spectrometry in the medium range (FTIR or mid-IR) [13]. It offers a simple, efficient, cost-effective, reagent-free and non-destructive way to identify and to distinguish polymers [14]. As IR spectral signatures relate to characteristic chemical moieties, some of which vary during weathering, this technique is a suitable tool to understand how aging affects the surface and chemical structure of MPs and therefore their interactions with the environment.

It is worth noting that the unequivocal identification of the type of polymer is usually not possible. Some reports described the misidentification of approximately 20% of the particles initially considered as microplastics by visual observation, which were subsequently identified as aluminium silicate from coal ash using scanning electron microscopy (SEM). In other works, 32% of visually counted microplastic particles below 100 μm were not confirmed as microplastics after micro-Raman measurements and up to 70% of particles had been erroneously identified as microplastics as confirmed after FTIR analysis [4]. Another relevant misidentification cause is the lack of comprehensive spectra of weathered plastics in the common databases. Weathering-related changes in the IR spectra difficult the correct match of the spectra of the particles when they are compared to most commercial IR polymer libraries.

The focus of this work is to characterize the weathering of the most abundant plastics found in the environment: the packaging materials. To this aim, pristine polymers of PE, PP, PS and PET were weathered under controlled, standardized conditions simulating

the natural ones (oceanic and shoreline conditions) and their changes were monitored using ATR (attenuated total reflectance)-FTIR and SEM. Then, selected band ratios were calculated to monitor and study their behavior. In the literature, few works tackled the environmental weathering of microplastics. Some of them presented theoretical works [3,6], others used simulated weathering conditions [15,16], and others studied the effects of weathering on MPs found in the environment [7,17,18].

Nevertheless, to the best of our knowledge this is the first time a study focused on a systematic characterization of the effects of weathering under controlled simulated environmental conditions, on the IR spectra of microplastics of the five polymers most widely used for packaging. This study is expected to contribute to improve the identification and quantification of MPs and, therefore, to help achieving more reliable analytical data on the occurrence and fate of microplastics in the marine environment.

2. Materials and methods

2.1. Instrumentation

FTIR measurements were done using a 400 FT-IR/FT-NIR PerkinElmer Spectrometer (4000–650 cm^{-1} , 4 cm^{-1} nominal resolution, Beer-Norton strong apodization, 50 scans per spectrum, background-, depth-penetration- and baseline-corrected) equipped with a horizontal one-bounce diamond crystal (Miracle ATR, Pike). An ad-hoc polymer library was generated for the identification and comparison of polymer particles.

SEM microscopy was done by means of a JEOL JSM 6400 device, after coating the MPs surfaces with a layer of gold. Because the surface textures of the weathered plastic pellets and powder grains are heterogeneous, visualization was repeated at different surface sites and at different grains. Comparisons among the surface textures of virgin and weathered MPs were done.

2.2. Sample description

The pristine materials (pellets and powder) were developed within the framework of the BASEMAN project (EU JPI Oceans Program), which considered the nine most frequent polymers found in the environment. They were provided by the Universität of Bayreuth (Germany) in two forms: powder (average size ca. 300 μm) and pellets (average size ca. 3 mm). HDPE (high density polyethylene) was from LyondellBasell, commercial name Lupolen 4261 AG UV, density and melting temperature were 0.945 g cm^{-3} and 130 °C. LDPE (low density polyethylene) was from Lyondell-Basell, commercial name Lupolen 1800P, density and melting temperature were 0.918 g cm^{-3} and 105 °C. PET (Polyethylene Terephthalate) was from Neogroup, commercial name Neopet 80, melting temperature was 248 °C. PP (polypropylene) was from Borealis, commercial name HL508FB, melting temperature 158 °C. PS (polystyrene) was from INEOS Styrolution, commercial name, Styrolution PS 158 N/L, density 1.04 g cm^{-3} .

Aliquots of each form of each plastic were weathered for 10 weeks in a low-cost pilot system under standardized, controlled conditions simulating both marine and dry conditions (the system was designed to simulate solar irradiation at medium latitude). More specific and comprehensive details can be found elsewhere [19].

Briefly, for marine weathering simulation 750 mL of seawater, 100 mL of siliceous sand and 10 g of powder or 20 g of pellets were placed into 1 L Pyrex cylinders with constant aeration and agitation and were exposed to two HQI-TS 2510W/NDL metal-halide bulbs in zenital and ground level positions (illumination: 12,200 lumen/m^2 , irradiance on air $60 \times 10^{-2} \text{ W/m}^2$, on seawater $25 \times 10^{-2} \text{ W/m}^2$). In

addition, weathering in dry conditions was carried out using 10 g powder or 20 g pellets in 12 cm diameter Petri dishes exposed to the same system. The content of each Petri dish was mixed every day and the locations of the dishes were interchanged each three days. This kind of weathering was made to simulate weathering under dry conditions (i.e., at the highest top location of beaches). Control samples were also considered (pellets and powder submerged in seawater at dark) and they were sampled with the same periodicity.

Aliquots were drawn weekly from the weathering system and measured by ATR-FTIR and SEM. The surface of the pellets and powder grains is very heterogeneous, so 5 pellets and 3 aliquots of grains of each polymer were measured and their spectra averaged. The variability associated to the measurement of the pellets was higher for seawater conditions, as expected because of the faster evolution suffered by the pellets in those conditions. On the contrary, the reproducibility of the powder measurement was lower

than 5% (RSD). This has been indicated along the index graphs (see supplementary material and explanations below). To simplify the explanations, only the results corresponding to the odd samples (i.e., a sample per fortnight) will be presented here.

3. Results and discussion

Three major IR spectral regions reflecting weathering-related changes were identified in previous researches: hydroxyl groups (broad peaks from 3100 to 3700 cm^{-1} , centered at 3300–3400 cm^{-1}), alkenes, or carbon double bonds (1600–1680 cm^{-1}), and carbonyl groups (1690–1810 cm^{-1} , centered at 1715 cm^{-1}) [6,15,17,20]. Fig. 1 shows that in general these bands become modified also in the present study for the five polymers. Relevant differences are seen quite easily between the pristine and weathered spectra for the different weathering setups and they are resumed schematically in Table 1. These weathering trends have been also observed in marine samples

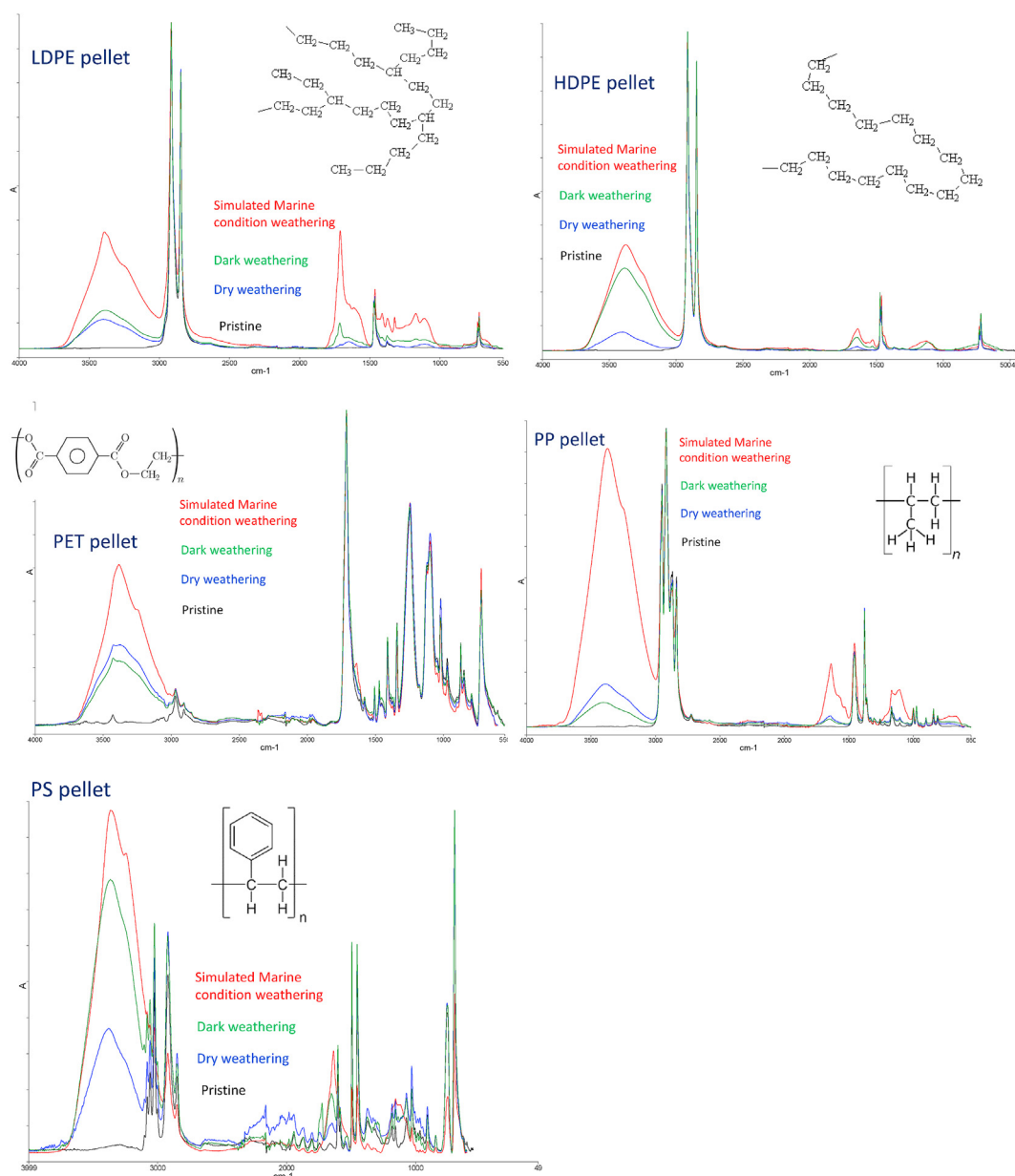


Fig. 1. General overview of the ATR-FTIR spectra of the pristine and weathered polymers.

Table 1
Main changes in the mid-IR bands of the weathered polymers (N = new band). The arrows indicate the increasing/decreasing behavior of the band with aging.

Bonds (cm ⁻¹)	-OH (polymeric alcohols, water, intramolecular bridges,-COOH ...)		-C=O carbo xylic acid		-C=C		C=C conjugated		C=O ketones		-CH ₂ bending		Carbo xylic acid		Aldehydes -O-CO-CH ₃		Carbo xylic acid		Acetate		Alkane		Secondary alcohols, ketones,		Aromatic compounds		alkanes/ alkenes		Aromatic compounds	
	3370	3240	1710	1640–1630	1600	1530	1460	1440	1410	1368	1320	1245	1170	1100	750	730	720	690												
LDPE	↑N	↑N	↑N	↑N	↑N	↑	↑	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	
HDPE	↑N	↑N	↑N	↑N	↑N	↑N	↑	↑	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	↑N	
PET	↑N	↑N	↓	↑N	↑N	↑N	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	
PP	↑N	↑N	↑N	↑N	↑N	↑N	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	
PS	↑N	↑N	↑N	↑N	↑N	↑N	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	

collected in coastal sites, as is exemplified in Fig. 2.

In addition, several common band ratios (indices) related to the hydroxyl, carbon-oxygen, and carbonyl functional groups were calculated as the ratio of the maximum absorbance value for the characteristic spectral band relative to the value of a reference peak. For the latter 2920 cm⁻¹ was selected as it changed very little with weathering, which agrees with previous reports [15].

In the next sections, the results for each polymer will be displayed –along with complementary information in the supplementary material– and, finally, some general conclusions will be reported.

3.1. Low and high density polyethylene (LDPE and HDPE)

Exceptional thermal and chemical properties combined with excellent processability make PE one of the most extensively used synthetic polymers. Indeed it is frequently reported as the most common polymer found in the marine environment [17,21–27]. The weathering of PE is known to have a strong damaging effect on its chemical and mechanical properties [28]. Physical features like color, shape, surface texture, and other visual characteristics that may contribute to visually distinguishing MPs from other particles, as it was done frequently to separate them from other components of the sample [4], change highly with weathering. One of the most common forms of the polymer, HDPE, contains linear chains with minimal branching while another common form, LDPE, is highly branched. Increasing branching reduces PE density, with HDPE and LDPE showing densities ranging 0.94–0.97 g cm⁻³ and 0.90–0.94 g cm⁻³, respectively [14]. Its low density, that allows its separation from the marine matrices by current flotation with NaCl, and its characteristic bands in the FTIR spectra, makes this kind of plastic easily identifiable.

The IR spectra of LDPE and HDPE can be distinguished thanks to the presence of the branched methyl groups (in LDPE) yielding a peak at 1377 cm⁻¹ [14,15]. Nevertheless, their spectra evolve differently, especially in the 1800–600 cm⁻¹ region (Fig. 3), thus complicating their identification. For LDPE new bands at 1780–1710, 1410, 1320 and 1170 cm⁻¹ appeared as weathering progressed which were not present (or less defined) in HDPE. However, bands at 1646 and 1526 cm⁻¹ were only seen (or well defined) in HDPE. This indicates that both PE types have different aging pathways. These absorption bands suggest that more than one oxidation product is formed during PE degradation.

Ketones, carboxylic acids, and carbon-carbon double bonds are the three major functional groups that appear during PE photo-degradation, being the formation of carbonyl and vinyl groups a direct indication of main chain scission [3]. This can be seen in Fig. 3, where the main changes are the formation of new bands at 3370, 1710, 1640, 1170 and 1100 cm⁻¹, which correspond to the formation of those groups. Those bands broaden as weathering advance, so that they clearly transform the spectrum of pristine PE. These results agree with previous works [3,15,29–32].

The evolution of the indices mentioned at the onset of this section were also different for LDPE and HDPE (see supplementary material, SM1 and SM2, pellets and powder respectively). The weathering processes seem faster and more pronounced for LDPE despite a general increase in all calculated indices for both types of PE can be seen. For LDPE, there is a remarkable different evolution between the marine conditions and the dry or darkness (control) treatment. This points towards more pronounced chemical changes for MPs weathered under marine conditions. Such a difference is not so noticeable for HDPE, whose indices evolve more or less similarly through all types of aging. Dry aging appear as the slowest and smoothest process for both types of PE. This evolution coincides with previous reports where it was found that the stability

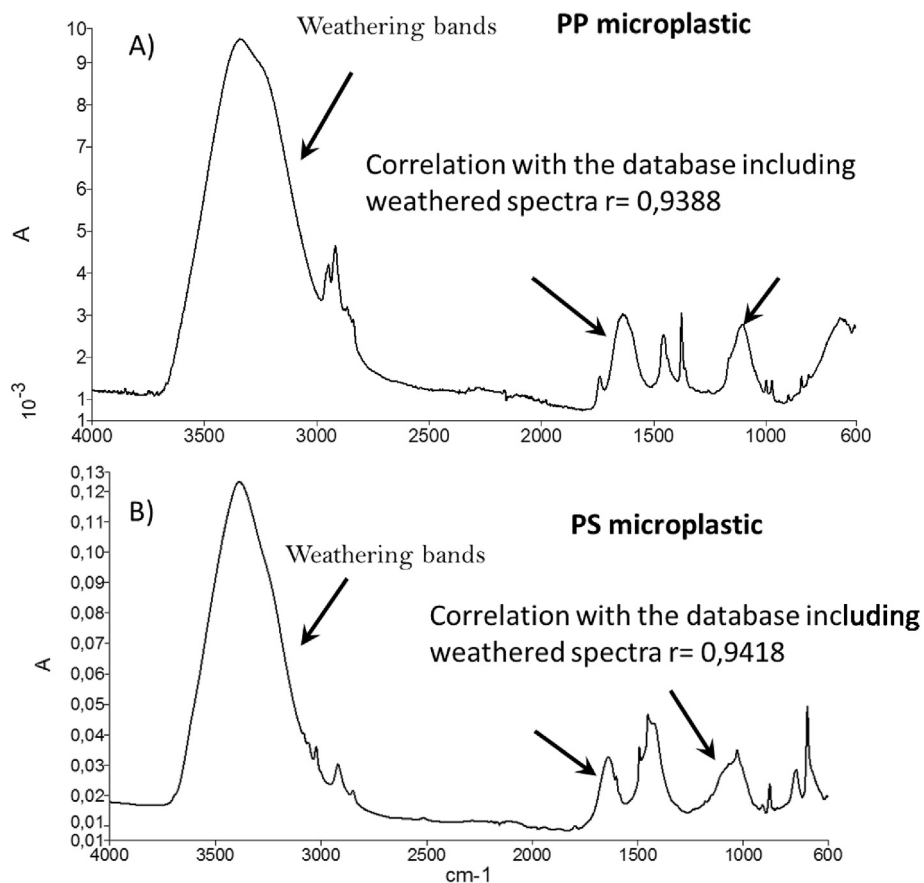


Fig. 2. Spectrum of PP (A) and PS (B) microplastics encountered in coastal sites samples. When the library without weathered spectra was used to identify the MPs, no match was found.

against oxidation was higher for HDPE than for LDPE [29].

It is worth noting that the indices do not have a steady behavior, as it is the case for the other polymers. This can be explained in different ways. It may be due, for example, to the formation of volatile compounds that would expose a part of the polymers that has not been exposed before. Another possibility is that as the plastic gets more brittle with aging, it breaks and exposes the newer, less weathered plastic from its interior [15]. Also, the numerous fractures and holes formed during aging expose the pristine parts of the MPs. In any case, this highlights the fact that estimating the time the plastic was in the environment using the infrared spectrum is very complicated and unreliable due to the multiple factors involved on aging. It is also noteworthy that this study is based on the polymers developed for the BASEMAN project, which incorporated minimum amounts of additives, as they might inhibit the effects of aging if they were present.

SEM images of HDPE and LDPE powder and pellets are shown in supplementary material, figures SM3 and SM4. For HDPE powder, in which the surface of the pristine polymer is very rough, holes and fractures are observed in the aged powder. In addition, the profile of the surface changes as it becomes flatter and smoother, probably due to mechanical degradation. It is also observed that some salt crystals grown in the holes formed at the powder grains weathered in marine conditions. A lot of cracks, fractures and crystalline formations are observed in the surface of weathered HDPE pellets.

With regard to LDPE, weathered powder shows clear surface changes associated mainly to flakes formation, especially during marine weathering (see SM4). For powder aged under dry

conditions the roughness of the surface increased. For pellets submerged in seawater the surface appears plenty of crystalline formations and their roughness increases. For pellets weathered under dry conditions the main change observed is the formation of flakes (SM4).

3.2. Polypropylene (PP)

PP is an attractive material for packaging due to its low cost, high tensile strength, glossy and versatility [33]. It is less stable than PE because every other carbon atom in the backbone is a tertiary carbon that is more prone to abiotic attack than the secondary carbons found in PE [3]. PP photodegradation leads to a molecular weight reduction and the formation of new functional moieties, especially carbonyl groups ($1150\text{--}1850\text{ cm}^{-1}$), hydroperoxides (3370 and 3240 cm^{-1}) and alkanes like pentane, 2-methyl-1-pentene and 2,4-dimethyl-1-heptene [3]. Most of these features are seen in the IR spectra of weathered PP, as it is exemplified in Fig. 4. The spectrum of the aged PP shows strong differences with the pristine one, most notably at 3370 and 3240 cm^{-1} (hydroxyl groups), 1640 cm^{-1} (C=O and C=C bonds), 1530 cm^{-1} (C=O ketones), 1440 cm^{-1} (carboxylic acids), 1140 cm^{-1} (alkanes), 1100 cm^{-1} (C-O bond) and 720 cm^{-1} (CH_2). This coincides fully with previous researches [15,34] and pellets collected in the marine environment (Fig. 2). Note that the entire $1550\text{--}1810\text{ cm}^{-1}$ range was referred to as the “carbonyl groups”, because of the strong overlap of several C=O containing functional groups here.

The hydroxyl, carbon-oxygen bonds and carbonyl group indices were calculated in the same way as for PE. Their profiles show

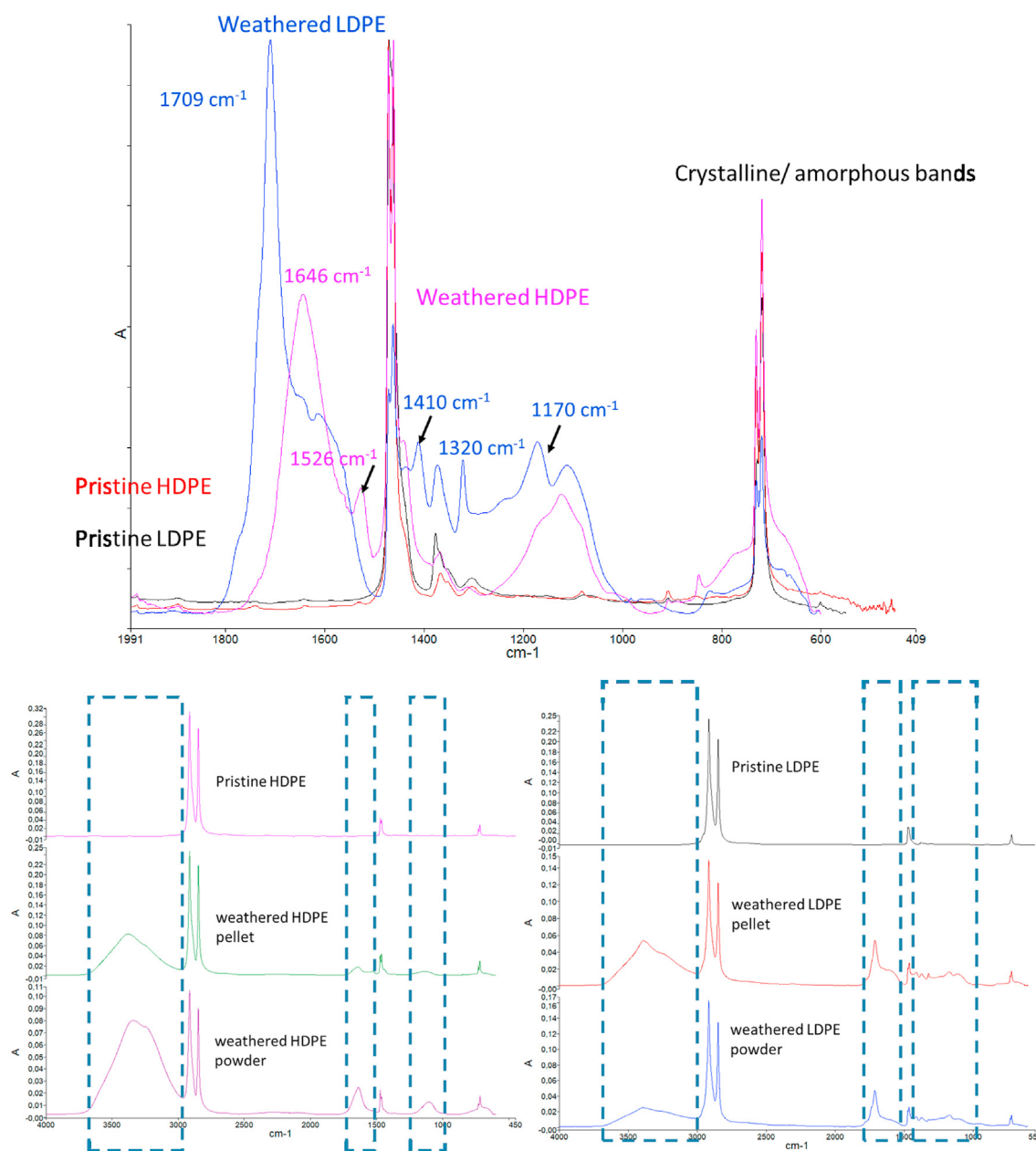


Fig. 3. ATR-FTIR spectral differences between weathered LDPE and HDPE (continues in next page). A) Superimposed overall spectra. B) Stacked view of selected spectra and regions of weathering bands.

(SM5) that the most extensive weathering for PP occurs under marine conditions, especially for pellets. For PP in powder form, the three aging processes lead to very similar profiles, being dry aging the slowest one.

For pellets, the three indices show similar temporal patterns, with increases up to the fourth-sixth week and, then, a sudden decrease and a final rise (SM5). This agrees with reports that stated that PP photo-oxidation produces significant amounts of low molecular-weight products that can migrate from the polymeric matrix to the atmosphere surrounding the material. Acetic acid was identified as the most abundant product of these low molecular-weight compounds [35]. These previous studies allow us to hypothesize that the acetic acid formed during the first stages of weathering gets trapped in the polymer somehow, where it accumulates and participates in the absorption band of the carbonyl

groups. The remaining acetic acid migrates and evaporates toward water or the gas phase. As a consequence, part of the carbonyl groups formed during aging may not be detected when measuring the polymer.

SEM images of weathered PP (SM6) revealed a lot of cracks, fractures and holes, where crystalline formations were formed. Although the surface of pristine PP is already rough due to the fabrication procedure, roughness increased with weathering. The surface of PP pellets aged during 10 weeks in dry conditions showed evidences of stretching and tearing, instead of the “clean” fractures that can be observed in pellets weathered at marine conditions. Pellets and powder weathered under marine conditions presented multiple crystalline formations grown onto their surface, likely increasing the size and number of cracks and holes.

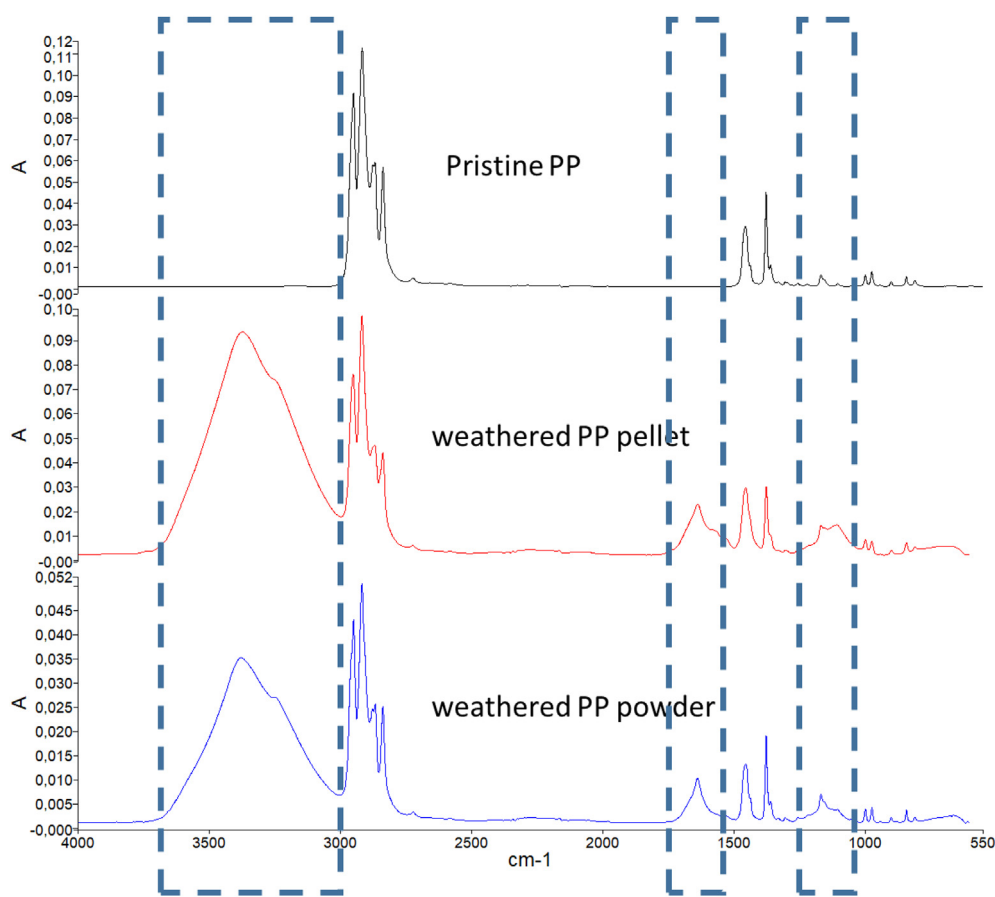


Fig. 4. Comparison of the ATR-FTIR spectra of pristine and weathered PP (pellets and powder) under simulated marine conditions.

3.3. Polystyrene (PS)

Polystyrene, one of the most important materials in the modern plastic industry, is used worldwide because of its excellent physical properties and low-cost. When polystyrene is subjected to UV irradiation in the presence of air, it undergoes a rapid yellowing and a gradual embrittlement [36]. Since it is mainly used for manufacturing of single-use products, a large portion of post-consumer production ends up into landfills or into oceans and remains there for several hundred years due to their resilience to degradation [37]. PS has various photodegradation mechanisms, due to its large UV absorption and subsequent formation of more stable tertiary carbon radicals. Photodegradation of PS is initiated by the absorption of UV radiation by the aromatic ring [38].

The IR spectra of weathered PS indicates (Table 1 and Fig. 5) the reduction of several bands and the appearance of several new ones. Some of them overlap in the fingerprint region so that the identification of weathered PS particles found in the environment becomes difficult. From our experience, ca. 70% of the PS particles identified in our laboratory became missed or unidentified with standard commercial databases. A homemade polymer database including spectra of weathered PS (and other polymers) allowed the correct identification of the particles in our samples (Fig. 2).

The main changes observed in the spectra of weathered PS correspond to (Fig. 5) the formation of new bands at 3360–3240 cm^{-1} (hydroxyl group), 1640 cm^{-1} (C=C or C=O groups) and $\approx 1100 \text{ cm}^{-1}$ (C-O bonds).

The three indices studied in this paper, indicate that the degradation rate of PS pellets under simulated marine conditions is remarkably higher than under dry or dark (control) weathering

(SM7). The indices have the same trend. Initially, they increase fast, especially for pellets under marine conditions, and after the first fortnight they decrease. This can be due to successive formation and loss of volatile compounds (styrene, such as dimer and trimer, benzene, ethylbenzene, methylstyrene, phenol, benzyl alcohol, benzaldehyde, ketones (acetophenone) and benzoic acid), originated in the weathering process and to new cross-linking [3,36]. Another possibility, mentioned above for PE, is that the weathered surface of PS breaks and exposes the newer, less weathered inside [15]. Dry and darkness weathering processes were much slower than marine conditions and both maintain an upward trend.

SEM images (SM8) showed that marine weathering was more aggressive than the others. In effect, the weathered surface presented many holes, cracks, fractures and flakes along with some crystalline formations. This contrasts to pristine PS, which shows only some marks from the manufacture process (in the powder form). When PS weathered in dry conditions, flakes and elongations as fine filaments were visible in the aged surface. It seems that the surface degradation is larger in the powder form than in pellets.

3.4. Polyethylene terephthalate (PET)

The aromatic ring coupled with the short aliphatic chain makes PET a stiffer molecule than other aliphatic polymers, such as polyolefins or polyamide. The lack of segmental mobility in the polymer chains results in relatively high thermal stability [39]. The overall spectral profile of weathered PET is not too different from pristine PET, being its identification by IR still relatively simple. Despite new weak bands relative to formation/cleavage of bonds can be seen in the weathered spectra, the main bands that

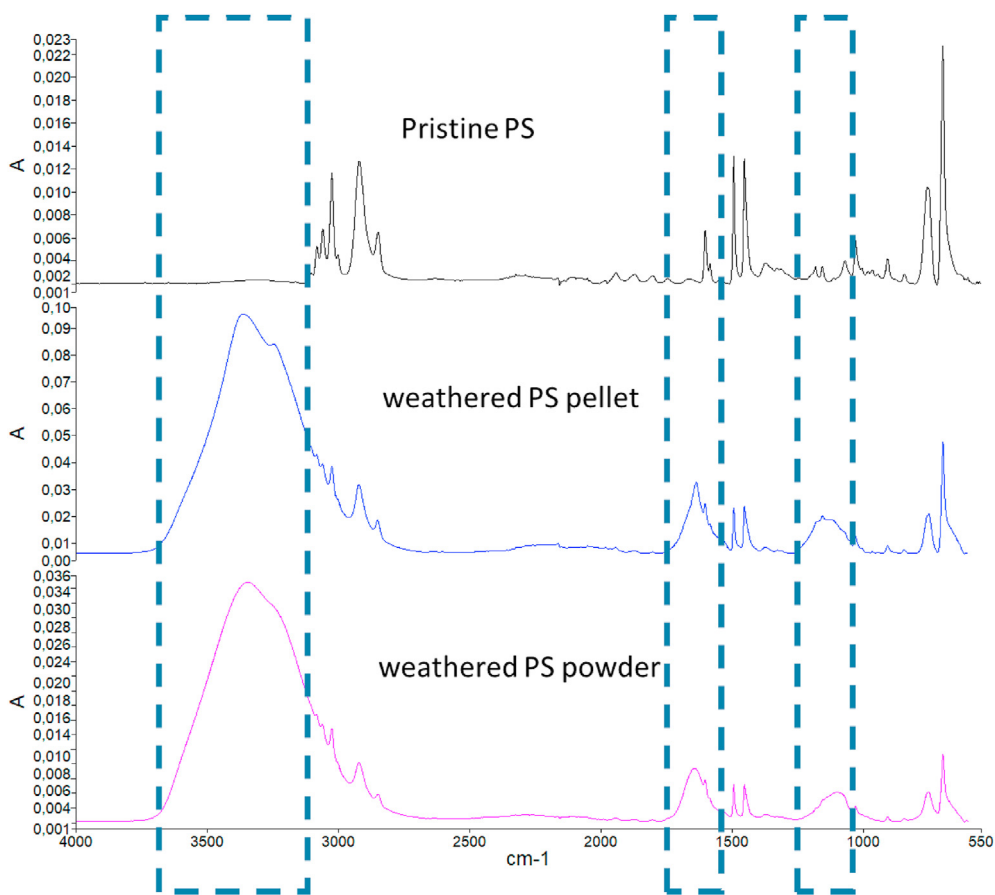


Fig. 5. Comparison of the ATR-FTIR spectra of pristine and weathered PS (pellets and powder) under simulated marine conditions.

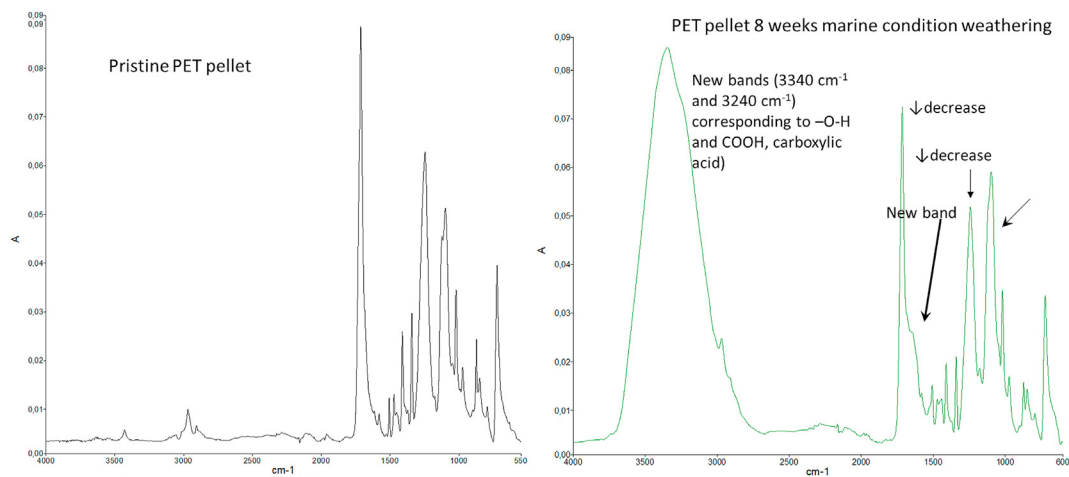


Fig. 6. Comparison of the ATR-FTIR spectra of pristine and weathered PET (pellets), under simulated marine conditions.

characterize this polymer in the fingerprint region ($1500 - 500 \text{ cm}^{-1}$) remain almost unchanged (although some of them showed different intensities). Therefore, the IR spectra of weathered PET gets still good matches when compared against usual databases.

PET photodegradation results in both hydroxyl and carboxylic end-groups along with carbon monoxide and carbon dioxide [3,7,40]. This explains the development of a new spectral band at 1680 cm^{-1} linked to C=C and carboxylic acids in benzene rings (Fig. 6) and the rising trend of the carbonyl index (SM9).

The hydroxyl and C=O indices for pellets and powder show a rising trend (SM9). The weathering of PET powder in marine conditions (and also the control samples) presents fluctuating values for the indices while dry weathering has a more progressive and homogeneous rising evolution. Again, the reason could be that due to weathering, the most eroded, aged surface breaks and less aged inner parts become exposed [15]. The –C–O index remains essentially stable with aging or with only slight reductions, for all weathering setups.

The SEM images (SM10) revealed that the surface of non-

degraded PET MPs was quite smooth, without cracks, holes and free of major noticeable characteristics. Only pristine powder presents a slightly rough surface, likely due to the mechanical forces required during its production. The most evident changes were observed for PET weathered under marine conditions, as the IR spectra and related indices put forward. Hence, it seems that this setup yields the most weathered MPs. In effect, the surface of those samples became rough, with fractures, cracks, cavities and holes, as well as some crystalline formations embedded in the surface. On the contrary, dry weathering produced almost no relevant visible effects on the surfaces.

4. Conclusions

It was seen that microplastics underwent weathering once released in the environment. Chemical changes occur mostly at their surface thus making their identification by FTIR challenging. These alterations must be taken into account when FTIR is used to identify the polymers and to monitor their aging. Remarkably, new spectral bands due to chemical changes can overlap with the most characteristic identification ones. In general, spectral indices are not adequate to quantify the aging time of plastics because their behaviours are not linear.

LDPE and HDPE evolve differently, especially in the fingerprint region. New bands appear for LDPE which are not present (or less defined) in HDPE. However, bands at 1646 and 1526 cm^{-1} are only seen (or well defined) for HDPE. The new bands broaden as weathering advances and clearly transform the spectrum of pristine PE. Weathering is more intense under marine conditions (although such a difference was not so noticeable for HDPE).

Aged PP shows strong differences with the pristine counterpart, more remarkable for pellets under marine conditions.

Weathered PS presents new overlapping spectral bands in the fingerprint region so that its identification becomes difficult. Weathering is more noticeable under simulated marine conditions.

Weathered PET remains rather simple to identify because its spectral shape is not too different from pristine PET.

Hence, it is concluded that the evolution of each studied polymer has to be considered independently and that the incorporation of weathered spectra of the polymers within the searching databases is necessary to get a reliable chemical identification of the microplastics.

CRediT authorship contribution statement

V. Fernández-González: Data curation, Formal analysis, Investigation, Methodology, Writing - original draft. **J.M. Andrade-Garda:** Data curation, Investigation, Methodology, Supervision, Writing - review & editing. **P. López-Mahía:** Conceptualization, Methodology, Supervision, Resources, Writing - review & editing. **S. Muniategui-Lorenzo:** Conceptualization, Investigation, Methodology, Project administration, Resources, Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported through the JPI-Oceans BASEMAN project, by the Spanish Ministry of Economy and Competitiveness -partially financed by the European Regional Development Fund

program- (PCIN-2015-170-CO2-01), JPI_Oceans 2019 MicroplastiX project (PCI2020-112145) by the Spanish Ministry of Science and Innovation. and RISBIOPLAS project (CHEMPLAS, PID2019-108857RB-C3/AEI/10.13039/501100011033), by the Spanish Ministry of Science and Innovation. The Program 'Consolidación e Estructuración de Unidades de Investigación Competitiva' of the Galician Government (Xunta de Galicia) is also acknowledged (ED431C 2017/28).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.aca.2020.11.002>.

References

- [1] PlasticEurope, Plastics-the facts 2019. https://www.plasticseurope.org/Application/Files/9715/7129/9584/FINAL_web_version_Plastics_the_facts2019_14102019.Pdf, 2019.
- [2] A. Bala, J. Laso, R. Abejón, M. Margallo, P. Fullana-i-Palmer, R. Aldaco, Environmental assessment of the food packaging waste management system in Spain: understanding the present to improve the future, *Sci. Total Environ.* 702 (2020), 134603, <https://doi.org/10.1016/j.scitotenv.2019.134603>.
- [3] B. Gewert, M.M. Plassmann, M. MacLeod, Pathways for degradation of plastic polymers floating in the marine environment, *Environ. Sci. Impacts* 17 (2015) 1513–1521, <https://doi.org/10.1039/c5em00207a>.
- [4] A.B. Silva, A.S. Bastos, C.I.L.L. Justino, J.P.J.P. da Costa, A.C. Duarte, T.A.P.P. Rocha-Santos, Microplastics in the environment: challenges in analytical chemistry -A review, *Anal. Chim. Acta* 1017 (2018) 1–19, <https://doi.org/10.1016/j.aca.2018.02.043>.
- [5] J.P.G.L. Frias, R. Nash, Microplastics, Finding a consensus on the definition, *Mar. Pollut. Bull.* 138 (2019) 145–147, <https://doi.org/10.1016/j.marpolbul.2018.11.022>.
- [6] P. Liu, X. Zhan, X. Wu, J. Li, H. Wang, S. Gao, Effect of weathering on environmental behavior of microplastics: properties, sorption and potential risks, *Chemosphere* 242 (2020) 125193, <https://doi.org/10.1016/j.chemosphere.2019.125193>.
- [7] K.N. Fotopoulou, H.K. Karapanagioti, Degradation of various plastics in the environment, in: H. Takada, H.K. Karapanagioti (Eds.), *Hazard. Chem. Assoc. With Plast. Mar. Environ.*, Springer I, 2019, pp. 71–92.
- [8] R.J.E. Vroom, A.A. Koelmans, E. Besseling, C. Halsband, Aging of microplastics promotes their ingestion by marine zooplankton, *Environ. Pollut.* 231 (2017) 987–996, <https://doi.org/10.1016/j.envpol.2017.08.088>.
- [9] Z.L.R. Botterell, N. Beaumont, T. Dorrington, M. Steinke, R.C. Thompson, P.K. Lindeque, Bioavailability and effects of microplastics on marine zooplankton: a review, *Environ. Pollut.* 245 (2019) 98–110, <https://doi.org/10.1016/j.envpol.2018.10.065>.
- [10] I.L.N. Brate, M. Blazquez, S.J. Brooks, K. V Thomas, Weathering impacts the uptake of polyethylene microparticles from toothpaste in Mediterranean mussels (*M. galloprovincialis*), *Sci. Total Environ.* 626 (2018) 1310–1318, <https://doi.org/10.1016/j.scitotenv.2018.01.141>.
- [11] E. Hendrickson, E.C. Minor, K. Schreiner, Microplastic abundance and composition in western lake superior as determined via microscopy, pyr-GC/MS, and FTIR, *Environ. Sci. Technol.* 52 (2018) 1787–1796.
- [12] N.L. Fahrenfeld, G. Arbuckle-Keil, N.N. Beni, S.L. Bartelt-Hunt, N. Naderi Beni, S.L. Bartelt-Hunt, Source tracking microplastics in the freshwater environment, *Trac. Trends Anal. Chem.* 112 (2019) 248–254, <https://doi.org/10.1016/j.trac.2018.11.030>.
- [13] R. Peñalver, N. Arroyo-Manzanares, I. López-García, M. Hernández-Córdoba, An overview of microplastics characterization by thermal analysis, *Chemosphere* 242 (2020), 125170, <https://doi.org/10.1016/j.chemosphere.2019.125170>.
- [14] M.R. Jung, F.D. Horgen, S.V. Orski, V. Rodriguez C, K.L. Beers, G.H. Balazs, T.T. Jones, T.M. Work, K.C. Brignac, S.J. Royer, K.D. Hyrenbach, B.A. Jensen, J.M. Lynch, Validation of ATR FT-IR to identify polymers of plastic marine debris, including those ingested by marine organisms, *Mar. Pollut. Bull.* 127 (2018) 704–716, <https://doi.org/10.1016/j.marpolbul.2017.12.061>.
- [15] J. Brandon, M. Goldstein, M.D. Ohman, Long-term aging and degradation of microplastic particles: comparing in situ oceanic and experimental weathering patterns, *Mar. Pollut. Bull.* 110 (2016) 299–308, <https://doi.org/10.1016/j.marpolbul.2016.06.048>.
- [16] R. Lenz, K. Enders, C.A. Stedmon, D.M.A.A. MacKenzie, T. Gissel Nielsen, T.G. Nielsen, A critical assessment of visual identification of marine microplastic using Raman spectroscopy for analysis improvement, *Mar. Pollut. Bull.* 15 (2015) 82–91, <https://doi.org/10.1016/j.marpolbul.2015.09.026>.
- [17] N. Sathish, I. Jeyasanta, J. Patterson, Abundance, characteristics and surface degradation features of microplastics in beach sediments of five coastal areas in Tamil Nadu, India, *Mar. Pollut. Bull.* 142 (2019) 112–118.
- [18] A. ter Halle, L. Ladirat, M. Martignac, A.F. Mingotaud, O. Boyron, E. Perez, To what extent are microplastics from the open ocean weathered? *Environ.*

- Pollut. 227 (2017) 167–174, <https://doi.org/10.1016/j.envpol.2017.04.051>.
- [19] J. Andrade, V. Fernández-González, P. López-Mahía, S. Muniategui, A low-cost system to simulate environmental microplastic weathering, *Mar. Pollut. Bull.* 149 (2019), <https://doi.org/10.1016/j.marpolbul.2019.110663>.
- [20] K.N. Fotopoulou, H.K. Karapanagioti, Surface properties of beached plastic pellets, *Mar. Environ. Res.* 81 (2012) 70–77, <https://doi.org/10.1016/j.marenvres.2012.08.010>.
- [21] J. Tibbetts, S. Krause, I. Lynch, G.H.S. Smith, Abundance, distribution, and drivers of microplastic contamination in urban river environments, *Water* 10 (2018), <https://doi.org/10.3390/w10111597>.
- [22] W.P. de Haan, A. Sanchez-Vidal, M. Canals, D. Amblas, A. Ayma, A. Calafat, M. Cerda-Domenech, R. Pedrosa-Pamies, X. Rayo, A. Rumin-Caparros, J. Tomer, N.S.S. Party, Floating microplastics and aggregate formation in the western mediterranean sea, *Mar. Pollut. Bull.* 140 (2019) 523–535, <https://doi.org/10.1016/j.marpolbul.2019.01.053>.
- [23] A. Gomiero, K. Birger Oysaed, T. Agustsson, N. van Hoytema, T. van Thiel, F. Grati, First record of characterization, concentration and distribution of microplastics in coastal sediments of an urban fjord in south west Norway using a thermal degradation method, *Chemosphere* 227 (2019) 705–714.
- [24] D. Rose, M. Webber, Characterization of microplastics in the surface waters of Kingston Harbour, *Sci. Total Environ.* 664 (2019) 753–760, <https://doi.org/10.1016/j.scitotenv.2019.01.319>.
- [25] M. Tiwari, T.D. Rathod, P.Y. Ajmal, R.C. Bhangare, S.K. Sahu, Distribution and characterization of microplastics in beach sand from three different Indian coastal environments, *Mar. Pollut. Bull.* 140 (2019) 262–273, <https://doi.org/10.1016/j.marpolbul.2019.01.055>.
- [26] Z. Pan, H. Guo, H. Chen, S. Wang, X. Sun, Q. Zou, Y. Zhang, H. Lin, S. Cai, J. Huang, Microplastics in the northwestern pacific: abundance, distribution, and characteristics, *Sci. Total Environ.* 650 (2019) 1913–1922, <https://doi.org/10.1016/j.scitotenv.2018.09.244>.
- [27] C. Zerì, A. Adamopoulou, D.B. Varezic, T. Fortibuoni, M.K. Virsek, A. Krzan, M. Mandic, C. Mazziotti, A. Palatinus, M. Peterlin, M. Prvan, F. Ronchi, J. Siljic, P. Tutman, T. Vlachogianni, Floating plastics in Adriatic waters (Mediterranean Sea): from the macro- to the micro-scale, *Mar. Pollut. Bull.* 136 (2018) 341–350, <https://doi.org/10.1016/j.marpolbul.2018.09.016>.
- [28] S.G. Hirsch, B. Barel, D. Shpasser, E. Segal, O.M. Gazit, Correlating chemical and physical changes of photo-oxidized low-density polyethylene to the activation energy of water release, *Polym. Test.* 64 (2017) 194–199, <https://doi.org/10.1016/j.polymertesting.2017.10.005>.
- [29] J. V. Gulmine, P.R. Janissek, H.M. Heise, L. Akcelrud, Degradation profile of polyethylene after artificial accelerated weathering, *Polym. Degrad. Stabil.* 79 (2003) 385–397, [https://doi.org/10.1016/s0141-3910\(02\)00338-5](https://doi.org/10.1016/s0141-3910(02)00338-5).
- [30] S.M. Mitroka, T.D. Smiley, J.M. Tanko, A.M. Dietrich, Reaction mechanism for oxidation and degradation of high density polyethylene in chlorinated water, *Polym. Degrad. Stabil.* 98 (2013) 1369–1377, <https://doi.org/10.1016/j.polymdegradstab.2013.03.020>.
- [31] L. Lin, L.-Z.Z. Zuo, J.-P.P. Peng, L.-Q.Q. Cai, L. Fok, Y. Yan, H.-X.X. Li, X.-R.R. Xu, Occurrence and distribution of microplastics in an urban river: a case study in the Pearl River along Guangzhou City, China, *Sci. Total Environ.* 644 (2018) 375–381, <https://doi.org/10.1016/j.scitotenv.2018.06.327>.
- [32] R. Satoto, W.S. Subowo, R. Yusiasih, Y. Takane, Y. Watanabe, T. Hatakeyama, Weathering of high-density polyethylene in different latitudes, *Polym. Degrad. Stabil.* 56 (1997) 275–279, [https://doi.org/10.1016/s0141-3910\(96\)00213-3](https://doi.org/10.1016/s0141-3910(96)00213-3).
- [33] K. Rajakumar, V. Sarasvathy, A. Thamarai Chelvan, R. Chitra, C.T. Vijayakumar, A.T. Chelvan, R. Chitra, C.T. Vijayakumar, Natural weathering studies of polypropylene, *J. Polym. Environ.* 17 (2009) 191–202, <https://doi.org/10.1007/s10924-009-0138-7>.
- [34] A. ter Halle, L. Ladirat, M. Martignac, A.F. Mingotaud, O. Boyron, E. Perez, To what extent are microplastics from the open ocean weathered? *Environ. Pollut.* 227 (2017) 167–174, <https://doi.org/10.1016/j.envpol.2017.04.051>.
- [35] C. Rouillon, P.O. Bussiere, E. Desnoux, S. Collin, C. Vial, S. Therias, J.L. Gardette, Is carbonyl index a quantitative probe to monitor polypropylene photodegradation? *Polym. Degrad. Stabil.* 128 (2016) 200–208, <https://doi.org/10.1016/j.polymdegradstab.2015.12.011>.
- [36] E. Yousif, R. Haddad, Photodegradation and photostabilization of polymers, especially polystyrene: review, *SpringerPlus* 2 (2013), <https://doi.org/10.1186/2193-1801-2-398>.
- [37] E. Syranidou, K. Karkanorachaki, F. Amorotti, M. Franchini, E. Repouskou, M. Kaliva, M. Vamvakaki, B. Kolvenbach, F. Fava, P.F.X. Corvini, N. Kalogerakis, Biodegradation of weathered polystyrene films in seawater microcosms, *Sci. Rep.* 7 (2017) 1–12, <https://doi.org/10.1038/s41598-017-18366-y>.
- [38] W.R. Waldman, M.A. De Paoli, Photodegradation of polypropylene/poly-styrene blends: styrene-butadiene-styrene compatibilisation effect, *Polym. Degrad. Stabil.* 93 (2008) 273–280, <https://doi.org/10.1016/j.polymdegradstab.2007.09.003>.
- [39] S. Venkatachalam, S.G. Nayak, J.V. Labde, P.R. Gharal, K. Rao, A.K. Kelkar, Degradation and Recyclability of Poly(Ethylene Terephthalate), *IntechOpen*, 2012, <https://doi.org/10.5772/48612>.
- [40] A. Gok, C.L. Fagerholm, R.H. French, L.S. Bruckman, Temporal evolution and pathway models of poly(ethylene-terephthalate) degradation under multi-factor accelerated weathering exposures, *PLoS One* 14 (2019) 1–23, <https://doi.org/10.1371/journal.pone.0212258>.