



The effects of weathering-induced degradation of polymers in the microplastic study involving reduction of organic matter[☆]

Maria Clara Lessa Belone^{*}, Marika Kokko, Essi Sarlin

Faculty of Engineering and Natural Sciences, Tampere University, PO Box 589, FI-33014, Finland

ARTICLE INFO

Keywords:

Sewage sludge
Chemical digestion
Microplastics
Polymer weathering

ABSTRACT

The analysis of microplastics in complex environmental samples requires the use of chemicals to reduce the organic matrix. This procedure should be evaluated in terms of the preservation of the microplastic's integrity, typically done with pristine reference microplastics. However, real microplastics are most likely degraded due to weathering, so pristine reference microplastics might not depict the appropriateness of the process. This study performed a purification process using sodium dodecyl sulfate and hydrogen peroxide on sewage sludge containing LLDPE, HDPE, PP, PS, PET, PA66 and SBR samples exposed to simulated environmental weathering. The degradation of the polymers was assessed by analyzing surface morphology, mass variation, and mechanical, thermal and chemical properties. Comparison with pristine polymers revealed that the purification process can lead to more detrimental effects if the polymers are weathered. After the purification process, some important observations were: 1) LLDPE, PP and SBR surfaces had cracks in the weathered samples that were not observed in the pristine samples, 2) weathered LLDPE, PP and PA66 experienced greater mass loss than pristine, 3) the fragmentation propensity of weathered LLDPE, HDPE, PP, PS and SBR increased compared to pristine samples and 4) the main characteristic peaks in FTIR spectrum could be identified and used for chemical identification of most polymers for pristine and weathered samples. Based on the findings of this study, when analyzing the efficiency and adequacy of a purification process with methods based on surface morphology, mass variation and particle counting indicators, it is recommended to consider the differences that potentially arise between pristine and weathered microplastics, especially for polyolefins (PEs and PP).

1. Introduction

The use of plastics in countless applications has resulted in the exponential growth of global plastics production since the 1950s. For most plastics, natural decomposition occurs at an extremely low rate and the mineralization of the polymer chains requires 30–1000 years (Delaney, 2013; Chamas et al., 2020). Meanwhile, during the service life and if discarded into the environment, the surrounding conditions – biotic and abiotic – promote the weathering of plastics. Biotic conditions refer to the colonization of the plastic's surface with bacteria, fungi and algae, which are able to secrete enzymes that cause depolymerization (Yuan et al., 2020). Abiotic conditions include the presence of light, heat, moisture and oxygen, which trigger hydrolytic, photolytic and oxidative reactions (Klein et al., 2018). According to Chamas et al. (2020), weathering is typically initiated abiotically.

Weathering leads to the alteration of the plastics' physicochemical

properties (Sun et al., 2020). At the molecular level, weathering can result in the formation of reaction byproducts, chain scission, a decrease in molecular weight, a change in chemical functionality and the chains' state of order (Ehrenstein & Pongratz, 2013). Visually, the changes can be manifested by variation in color, the formation of cracks and, ultimately, fragmentation (Chamas et al., 2020). Therefore, under continuous exposure to environmental stresses, secondary microplastics (MPs) are eventually created (Lechthaler et al., 2020). Secondary MPs are classified as plastics measuring less than 5 mm that originates from the fragmentation of macroplastics. Lassen et al. (2015) have suggested that the fragmentation of macroplastics contributes more significantly to the abundance of MPs in the environment than the emissions of primary MPs, which are those already produced at a micrometer scale (<5 mm).

A significant quantity of MPs ends up in wastewater treatment plants (WWTP), thus considerable attention has been given to these facilities (Ziajahromi et al., 2016; Conley et al., 2019; Gatidou et al., 2019; Sun

[☆] This paper has been recommended for acceptance by Eddy Y. Zeng.

^{*} Corresponding author.

E-mail addresses: clara.lessabelone@tuni.fi (M.C. Lessa Belone), marika.kokko@tuni.fi (M. Kokko), essi.sarlin@tuni.fi (E. Sarlin).

et al., 2019; Xu et al., 2021). Domestic, commercial and industrial wastewaters as well as the urban runoff (storm and melt water) transport secondary MPs to the WWTP (Pankkonen, 2020; Rasmussen et al., 2021). When the wastewater reaches the facility, the treatment often starts with screening and grit removal. The process continues with a primary settling followed by activated sludge process and secondary settling. The sedimentation of solids and biomass in the primary and secondary settling forms the sewage sludge. The WWTP may utilize tertiary treatment and/or disinfection steps for the purified wastewater. Most of the MPs accumulate in the sewage sludge (Talvitie et al., 2017; Vollertsen & Hansen, 2017; Rasmussen et al., 2021). Studies have shown that polyethylene (PE) and polypropylene (PP) are the most abundant polymer type in the sewage sludge (Hatinoğlu & Sanin, 2021; Rasmussen et al., 2021; Li et al., 2022). The same studies also mention the occurrence of polyamide (PA), polystyrene (PS), polyethylene terephthalate (PET), polyvinyl chloride (PVC).

In MP research, it is a common practice to expose environmental samples, especially ones rich in organic matter like sewage sludge, to a purification process (i.e., chemical digestion) in order to reduce the organic matrix that could hinder the identification and analysis of MPs. For that, reference MPs have been used and a vast number of methods have been developed for different environmental samples, varying, e.g., by purification agents, duration and temperature (Nuelle et al., 2014; Löder et al., 2017; Karami et al., 2017; Hurley et al., 2018; Prata et al., 2019a; Yan et al., 2019; Zarfl, 2019; Duan et al., 2020; Li et al., 2020). Nevertheless, there is consensus that an appropriate purification process must eliminate as much of the matrix as possible while maintaining the integrity of the MPs (von Friesen et al., 2019).

In our previous study (Lessa Belone et al., 2021), the effects of the purification process developed for sewage sludge were assessed on pristine polymers. This approach is suitable to evaluate the behavior of primary MPs and secondary MPs with minor degradation (e.g., textiles washed for the first time) because it can be considered that they reach the sewage sludge chemically intact and close to their original state. This is due to the fact that the plastics' degradation is mostly absent during the transport of the wastewater to the WWTP (Dris et al., 2018). However, this is not the case for secondary MPs in general, because they have already been weathered before entering the WWTP (GESAMP, 2016).

To the best of our knowledge, few studies have evaluated the integrity of weathered plastics after being subjected to the purification process before MP analysis. In von Friesen et al. (2019), the effect of their digestion process (pancreatic enzymes, overnight, 37.5 °C for MPs in bivalve tissue) was assessed on low density polyethylene (LDPE), expanded PS and PP collected from a sea. There was no comparison between weathered and pristine plastics, and it was concluded that the digestion process did not affect the plastics significantly, as they could be identified without issue. Prata et al. (2019a) analyzed high-density polyethylene (HDPE), PE, PP, expanded PS and cellulose acetate (CA) collected from a beach before and after different purification processes (potassium hydroxide and hydrogen peroxide (H₂O₂) with an iron catalyst, 1 h, at room temperature and 50 °C for MPs in algae, driftwood and seagull). With the exception of CA, no visual changes, significant weight variation or impairment of identification were observed in the weathered plastics. However, they reported some differences in the carbonyl index (CI, an indicator of the degradation extent) after the purification process when the pristine and weathered pairs were compared. However, in these studies, the purification process was performed in samples without the organic matrix.

The exclusion of the matrix could have resulted in misleading conclusions because the oxidation of the matrix may have some effects on the plastics (Lessa Belone et al., 2021). For example, the increase in the temperature when using H₂O₂ intensifies the deterioration of some plastics (Munno et al., 2018; Lessa Belone et al., 2021). Moreover, because weathered samples were arbitrarily collected from the environment, it is uncertain for how long they were exposed to the external conditions, which makes analysis reproducibility and comparability

challenging. Despite not reflecting the actual processes, performing a simulated environmental weathering test in the laboratory is more suitable for the fundamental study of weathering (Sun et al., 2020).

In the present study, degradation during a purification process with H₂O₂ was studied for weathered polymers in sewage sludge. The purpose to test weathered samples is to create a more realistic approach in relation to secondary MPs. Also, to evaluate if the purification process has a more adverse effect on weathered MP samples than on pristine ones. For that, a simulated environmental weathering test was performed to simulate abiotic weathering prior purification process. The surface characteristics, chemical alterations, thermal properties, and mechanical properties of weathered plastics before and after the purification process were monitored and compared with the results of the pristine plastics discussed in our previous study (Lessa Belone et al., 2021).

2. Materials and methods

2.1. Sewage sludge source

Viinikanlahti WWTP (Tampere, Finland) was the source of the thickened sewage sludge. The sewage sludge production at the facility is approximately 63 m³/day (Karaila et al., 2019). The total solid (TS) and volatile solid (VS) contents were 4.5% and 2.2%, respectively.

2.2. Polymer samples

Polymer samples were cut from 1 mm thick sheets of linear low-density polyethylene (LLDPE, FB4230, Borealis, Austria), HDPE (CG9620, Borealis, Austria), PP (HC205TF D, Borealis, Austria), PS (143E, Basf, Germany), PET (RAMAPET R182, Indorama, Indonesia), polyamide 66 (PA66, Zytel 101F NC010, DuPont, United States) and styrene butadiene rubber (SBR, Etra standard SBR, Etra, Finland).

The samples were prepared according to Lessa Belone et al. (2021). For tensile tests, there were seven parallel dog bone samples (35 mm overall length, 12 mm gauge length and 2 mm gauge width) for LLDPE, HDPE, PP and SBR and ten rectangular parallel samples (35 mm overall length, 17 mm gauge length and 2 mm gauge width) for PS, PA66 and PET. Rectangular samples were used for brittle polymers to avoid breakage during cutting. Additionally, for each polymer there were three parallel quadrangular 10 mm × 10 mm samples for the other tests.

2.3. Simulated environmental weathering

Simulated environmental weathering was performed in a Q-SUN Xe-3 xenon arc chamber (Q-Lab, United States) accelerated weathering tester. The test was based on the ASTM D2565 standard and had two alternating cycles. The first cycle consisted of 102 min of UV light, an uninsulated black panel temperature of 63 °C and irradiance of 390 mW/m² at 340 nm. The wavelength is in the ultraviolet range, which is the radiation in sunlight that is effective on the Earth's surface and the main cause of degradation on plastics (Ehrenstein & Pongratz, 2013). The second cycle consisted of 18 min of darkness and water spray. The total testing time was 840 h, so the samples were irradiated with a total UV dose (irradiance × exposure time in seconds) of approximately 1000 kJ/m². The selected test time, which corresponds approximately to 0.5–1 year of UV radiation in different globe locations, can lead to the release of small secondary MPs particles (Svedin, 2020). Moreover, the test time is within the range being used in other MPs studies (Alimi et al., 2022). Halfway through the test, the samples were flipped, so both sides could be exposed to the test conditions. Before and after the weathering, the samples were dried for 24 h at 50 °C.

In this study, the pristine and weathered samples were denominated as V and W, respectively. Moreover, the pristine and weathered samples after the purification process were denominated as V + P and W + P, respectively.

2.4. Purification process

The purification process adopted was the one developed in Lessa Belone et al. (2021). First, the sewage sludge was vacuum filtered using a Millipore stainless-steel filter (Merk, United States) with a 125 μm mesh size. The mesh size was selected to avoid too quick clogging, and it is within the size range already used in the literature on MP sampling and detection (Prata et al., 2019b).

Then, 15.5 g of the sludge sample (wet weight) and 20 ml of sodium dodecyl sulfate 3% w/w (SDS, Acros Organics, United States) were mixed and incubated at 50 °C for 24h. Subsequently, the solution was filtered, and the retained material added to 20 ml of H₂O₂ 30% (Merck, United States) and incubated at 40 °C for 3 days. Then, the solution was again filtered, and 10 ml of H₂O₂ 30% was added to the retained material and incubated at 40 °C for 24h. Between each step, filtration was done using the same filter. At the end of the purification process, the samples were dried for 24 h at 50 °C.

2.5. Analytical methods

The verification of the weight variation of the three parallel quadrangular samples of each polymer was done using a laboratory balance with four significant digits. The true initial mass before weathering, true mass after weathering and true final mass after the purification process were obtained.

The surface after weathering and after the purification process was analyzed with a stereo microscope MZ 7.5 (Leica, Germany) and scanning electron microscope (SEM) JSM-IT500 (Jeol, Japan). For the SEM analysis, the samples were coated with a carbon layer to make them conductive.

The mechanical behavior under tension was studied using an Instron 5967 device (Instron, United States). The samples were conditioned at 23 °C and 60% relative humidity for at least 24 h before the test. Tests were performed at a crosshead speed of 10 mm/min for SBR and 2 mm/min for the other polymers until failure. For each polymer type, 7 to 10 samples were tested. Note that, compared to Lessa Belone et al. (2021), the crosshead speed was decreased for LLDPE, HDPE and SBR, which could have some effect on the results. The adjustment was necessary because these polymers became more brittle and the speed used in Lessa Belone et al. (2021) was not practical as the samples were fracturing straight after the beginning of the test.

The thermal stability under an inert nitrogen atmosphere was determined in triplicate after weathering and after the purification process by thermogravimetric analysis (TGA) using the TG 209 F3 Tarsus (Netzsch, Germany). The temperature range was 30–600 °C and the heating rate was 20 °C/min.

The chemical functional groups in the samples after weathering and after the purification process were characterized by Fourier transform infrared spectroscopy (FTIR) using a Spectrum One spectrometer (PerkinElmer, United States) equipped with an attenuated total reflectance sample holder. The aim was to check whether the polymer grades could still be identifiable after the purification process based on their identity peaks. The scanning range was 650–4000 cm^{-1} and the resolution was 4 cm^{-1} . Measurements were done in triplicate. The CI was calculated according to Lessa Belone et al. (2021), but with the following change in reference peaks: 720 cm^{-1} for LLDPE (Almond et al., 2020) and 973 cm^{-1} for PP (Ruoko, 2012). The new selection was done because there was a distortion of the reference peaks after exposition to the simulated weathering, which made them inadequate for the estimation of the CI. Moreover, for comparison, because of new reference peaks and different FTIR device from Lessa Belone et al. (2021) were used, the spectra and CI of V and V + P were obtained again.

3. Results and discussion

3.1. Surface characteristics

In the stereomicroscope images, for LLDPE and PP (Supplementary Material, Figures S1–S2), the even V and V + P surfaces were replaced by perceptible cracks in the W and W + P samples. Weathering on semi-crystalline polymers causes embrittlement via chain scission, leading to crack formation (Wang et al., 2021). The SEM study (Fig. 1) revealed that cracks developed during the weathering of LLDPE and PP, and further cracking was observed after the purification process (W + P). Tang et al. (2019) observed that cracks emerged in their PP samples after photooxidation. According to Enfrin et al. (2020), cracks play a determinant role in MP fragmentation, and therefore both weathering and purification will accelerate the fragmentation of LLDPE and PP compared to pristine materials. No significant changes were observed on the HDPE surface due to the weathering or purification process (Figure S5), evidencing its better stability against oxidation (Fernández-González et al., 2021).

Visual inspection revealed the yellowing of W PS and W + P PS. This is a typical outcome of PS photooxidation, which occurs due to the chromophore creation (Ehrenstein & Pongratz, 2013). Environmental weathering has been shown to cause microcracking of PS (Meides et al., 2021; Ding et al., 2020) but it was not observed after the weathering procedure used in this study. Instead, a smoothening of the grooves originated from the sheet production happened (Fig. 1). In the case of W + P PS, the surface presented some nicked shapes and pitting (Fig. 1).

The W PA66 surface showed signs of erosion, and the accumulation of debris on the surface is probably from the breakage of the sample during weathering (Fig. 1 and S3). Naik et al. (2020) noticed similar behaviour in PA6 subjected to artificial weathering. On the other hand, in W + P PA66, these features disappeared and a smooth surface with cracks was noticed. The state of the W + P PA66 surface could indicate that the original surface layer of the sample got weakened and was detached. The inherent propensity of PA66 to absorb a significant amount of water enhances oxidative reactions in its surface (Naik et al., 2020). Therefore, during the purification process, this could have led to the release of material of the surface that had already suffered morphology changes due to weathering.

The V, V + P, W and W + P SBR surfaces in Fig. 1 and S4 show that weathering was very detrimental to the rubber. It was noticed cracking on the W SBR surface but no loss of fillers, while in W + P, the cracks were more pronounced and the surface got rougher due to the loss of fillers. In the literature, the crack formation on SBR is known to be an outcome of UV irradiation, since an increase of surface crosslinking leads to shrinkage (Noriman and Ismail, 2012). This is an indication that the fragmentation of SBR is more probable during purification if the sample is weathered.

For PET, no significant changes of the surface features were visible due to the weathering or the purification process (Figure S5). The observation accords with those of Wang et al. (1998), who noted that UV exposure was not able to microcrack thin PET films.

3.2. Mass variation

Fig. 2 shows the mass variation of V + P and W + P (separated into mass variation after weathering and after the purification process). According to Chamas et al. (2020), the measurement of mass changes is the simplest and most direct way to assess bond cleavage. Based on this, it can be assumed that all the polymers suffered some degree of bond cleavage caused by the weathering and purification process. The mass changes can also be attributed to the loss of small molecular components, such as plasticizers, during the purification process. For some polymers, weathering affected the mass more than the purification process. That was the case for PP, which is known to produce significant amounts of volatile products during UV exposure that can migrate from

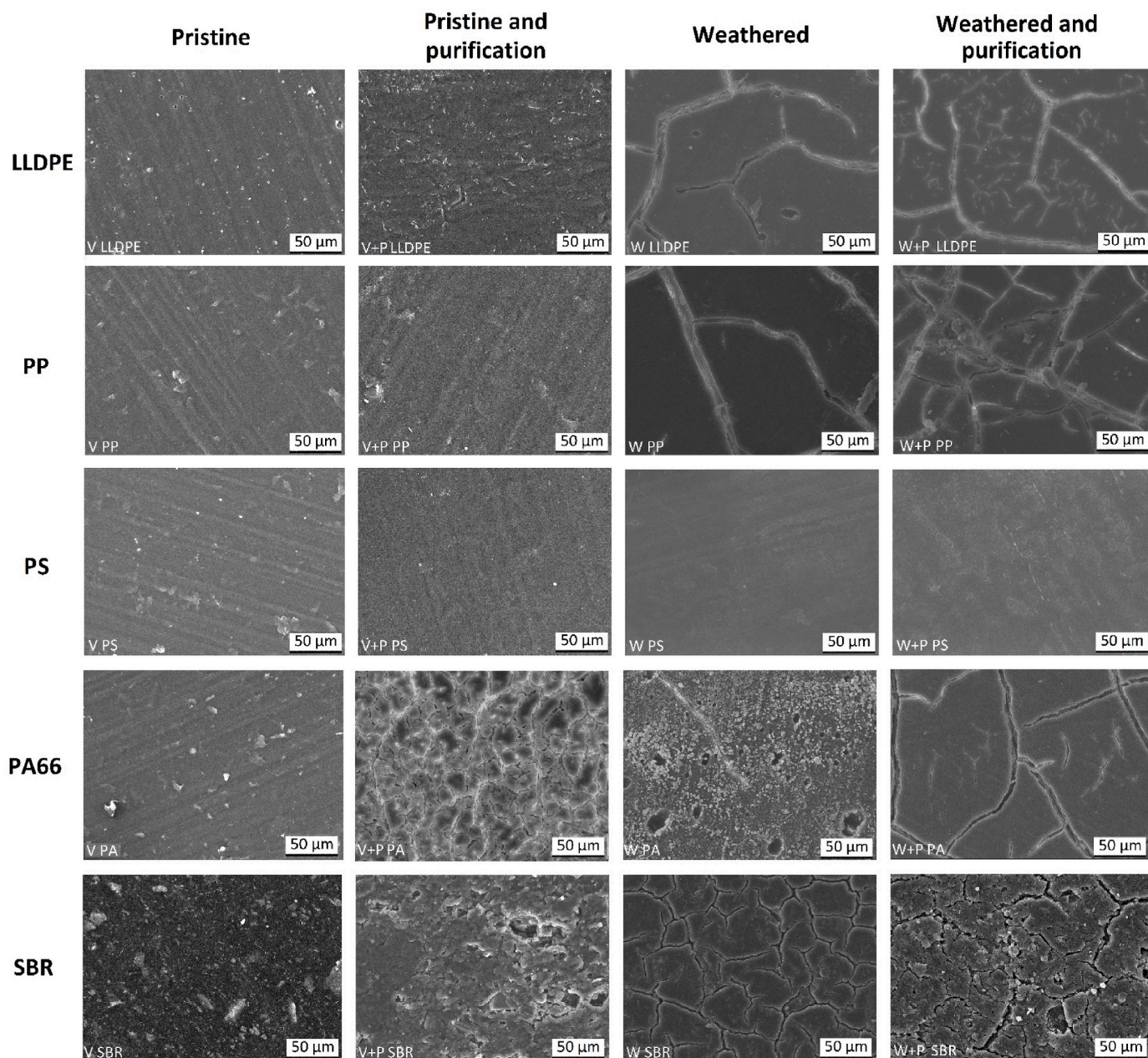


Fig. 1. SEM images of polymer surfaces before and after the weathering and purification process. The SEM images for HDPE and PET are shown in the Supplementary Material.

the polymer matrix to the surroundings (Rouillon et al., 2016). For others (LLDPE and PA66), the purification process was more detrimental. In the case of PA66, the significant mass loss concurs with the assumption of surface layer loss that was made based on the SEM studies.

As seen in Fig. 2, there was a mass loss for all weathered polymers after the purification process, and, except for SBR, it was more pronounced than the mass variations detected in V + P. Besides the mass variations regarding the effects of the purification process, the W + P samples could have also experienced the migration of products formed during weathering into the solution. Note that for W + P, the Δ mass was obtained by subtracting the true mass after weathering from the true final mass after the purification process.

3.3. Mechanical properties

The tensile strength, tensile strain, modulus and toughness of V, V + P, W and W + P samples are presented in Table 1. Additionally, Figures S6 to S12 show the representative tensile curves of the samples. After weathering, the mechanical properties of all polymers were compromised. It is known that UV irradiation is an essential factor for the loss of mechanical properties and the fragmentation propensity of polymers. This is mainly due to the embrittlement that polymers typically undergo during the early stages of photooxidation and the generation of cracks on the surface (Wang et al., 2021).

As seen in Figures S6 and S7, the V and V + P LLDPE and HDPE behave in a ductile manner, while the W and W + P samples behave in a brittle manner, as the specimens failed within the purely elastic part of the stress-strain curve. The increase in the modulus of LLDPE and HDPE after UV exposure can be related to post-crystallization on the surface

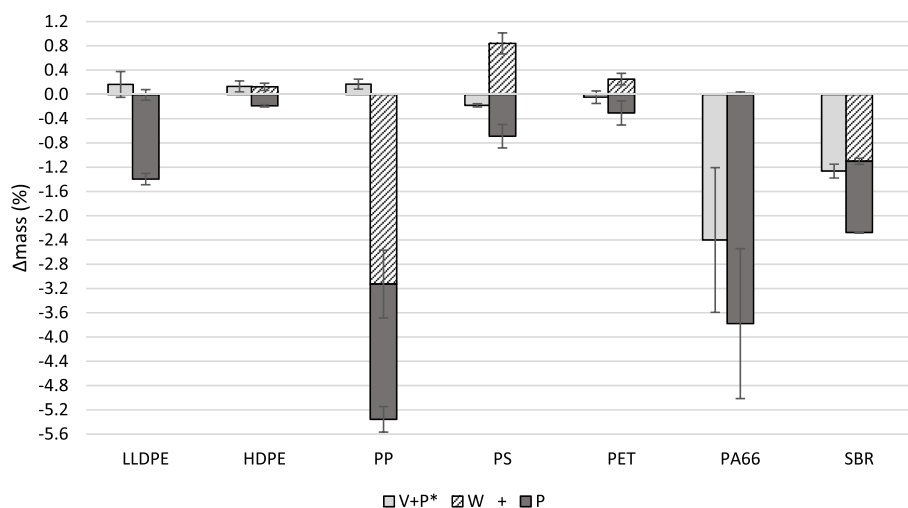


Fig. 2. The mass variation of pristine samples after the purification process (V + P), after weathering (W), and the weathered samples after the purification process (W + P). *Data obtained from Lessa Belone et al. (2021)

(Ehrenstein and Pongratz, 2013). This causes stress build-up between the surface and bulk region, which leads to the crack formation observed in LLDPE. On HDPE, the ultimate result of stress build-up might not have been reached since the surface was visually unaffected by cracks. Toughness, considered as the ability to resist fracture, seemed not to be affected by the purification process, while weathering caused its reduction.

For PET, it can be considered that the reduction of tensile stress was somewhat more pronounced from W to W + P than from V to V + P. This can be attributed to the fact that the simulated weathering had already deteriorated the mechanical properties of the samples, accelerating the degradation during purification. This is a consequence of the great contribution of photooxidation to PET's molecular chain scission (Bell, 2015). Chain scission leads to the higher free volume and propensity for water and oxygen penetration. This causes local concentration of stress that, under tension, leads to the formation of microvoids, facilitating the crack propagation (Al-Azzawi, 2015). In the case of V and V + P, the overall effect of the purification process on PET's mechanical properties was small.

During the purification process, the plasticizing effect of water on PA66's structure led to a decrease in modulus and an increase in elongation at break and toughness due to higher chain mobility (Ksouri et al., 2017). The elongation at break of PA66 increased 113% when comparing W to W + P which was higher than when comparing V to V + P (75%). From this, we assume there was more ingress of water in W + P PA66 than in V + P PA66. The TGA data corroborates this assumption considering that the amount of bonded water in W + P was almost twice the amount in V + P.

For SBR, the percentual increase in modulus was higher from V to V + P than from W to W + P indicating that the degraded surface layer of weathered SBR has protected the sample from further oxidation during purification. It has been reported that the barrier against oxygen is improved with the increase of the surface's crosslink density (Shahriari et al., 2019). Therefore, this protection could have been achieved in W SBR as a result of crosslinking caused by photooxidation.

The tensile test on W and W + P PP and PS samples were not successful, as the specimens were too brittle to be handled and positioned in the instrument. Under weathering, the ultimate strength and elongation at break of PP decrease rapidly, since its structure has multiple tertiary carbons that are more susceptible to scission than secondary or primary carbons (Ehrenstein & Pongratz, 2013). In the case of PS, Meides et al. (2021) reported that, above 200 h of simulated environmental weathering, a simultaneous growth of chain defects considerably embrittles PS.

3.4. Surface chemistry

The FTIR spectra are presented in the Supplementary Material (Figure S13 to S19). Both the simulated environmental weathering and purification process can induce polymer degradation. As expected, the spectra show that the intensity of both hydroxyl (-OH) and carbonyl groups (-C=O), which were used as markers of polymer degradation, increased when comparing W samples to V samples. It is known that the photophysical and photochemical effects of UV radiation, the oxidative effects of atmospheric oxygen and the hydrolytic effects of water are able to induce the formation of aldehydes, ketones, esters, carboxylic acids and peroxides on the polymer's surface (Feldman, 2002; Rouillon et al., 2016; Fernández-González et al., 2021). In this study, however, the focus was to evaluate the effects of the purification process and not of the weathering on the FTIR spectra.

It was noticed that degradation due weathering did not play a significant role on the chemical identification by FTIR of the polymers after purification process. Comparing with V, for W + P for HDPE, PS, PET, and PA66, no significant changes in the spectra were caused by the purification process. For LLDPE and PP, the V and W spectra have clear differences, in terms of peak appearance, position, intensity and broadening. However, after the purification process, the W + P spectra returned to resemble the V spectra. This could possibly be attributed to the removal of the degraded layer from weathering, which is in line with the mass loss experienced by these polymers after the purification process (Fig. 2). Peaks assigned to -C=O around 1650 cm^{-1} and 1700 cm^{-1} for LLDPE and PP, respectively, were the most important changes that remained.

It could be expected that the CI, as an indicator of the degree of oxidation of the polymer's surface, would have the tendency to increase when comparing W to W + P. However, this was observed only for some materials (Table 2). This may be due to the surface embrittlement with oxidation causing erosion and the exposure of the new and less weathered surface layer (Rouillon et al., 2016; Fernández-González et al., 2021) or, in the case of SBR, due to the degradation resistance caused by surface crosslinking.

Regarding SBR, similarly to Lessa Belone et al. (2021), the FTIR results had some contradictions if compared with the literature. The decrease of the absorption peaks related to the double bonds, which can be correlated with the formation of crosslinking (Mertz et al., 2012), was not evident based on the data. However, the other indications, such as the increase in modulus, suggested increased crosslink density.

Table 1
Mechanical properties of V, V + P, W and W + P samples. * Data obtained from Lessa Belone et al. (2021).

Polymer		Tensile strength (MPa)	Tensile strain (mm/mm)	Modulus (MPa)	Toughness (J/m ³)
LLDPE	V	28 ± 1.3*	11 ± 0.46*	194 ± 6.15	169 ± 11.5
	V + P	26 ± 2.5*	10 ± 0.89*	179 ± 5.31	160 ± 20.3
	W	6.2 ± 1.1	0.03 ± 0.01	296 ± 21.9	0.13 ± 0.050
	W + P	7.8 ± 0.60	0.04 ± 0.01	320 ± 23.0	0.19 ± 0.050
HDPE	V	32 ± 0.96*	14 ± 0.44	847 ± 45.5	280 ± 17.0
	V + P	34 ± 0.99*	4.9 ± 0.88	906 ± 24.0	90 ± 13
	W	10 ± 2.4	0.01 ± 0.00	895 ± 126	0.09 ± 0.04
	W + P	19 ± 1.1	0.02 ± 0.00	1342 ± 130.2	0.23 ± 0.040
PP	V	39 ± 2.9*	0.10 ± 0.01*	952 ± 88.8	5.0 ± 0.93
	V + P	40 ± 1.3*	0.10 ± 0.01*	947 ± 85.8	4.9 ± 1.5
	W	n.a.	n.a.	n.a.	n.a.
	W + P	n.a.	n.a.	n.a.	n.a.
PS	V	31 ± 1.7*	0.02 ± 0.00*	1653 ± 165.6	0.37 ± 0.030
	V + P	29 ± 2.4*	0.02 ± 0.00*	1552 ± 68.74	0.38 ± 0.030
	W	n.a.	n.a.	n.a.	n.a.
	W + P	n.a.	n.a.	n.a.	n.a.
PET	V	67 ± 2.0*	0.09 ± 0.02*	1345 ± 153.3	3.4 ± 1.0
	V + P	64 ± 2.4*	0.07 ± 0.00*	1318 ± 18.45	3.0 ± 0.17
	W	33 ± 8.3	0.03 ± 0.01	1249 ± 262.3	0.52 ± 0.22
	W + P	25 ± 4.1	0.02 ± 0.00	1210 ± 197.0	0.32 ± 0.050
PA66	V	58 ± 10*	0.16 ± 0.050*	783 ± 201	6.5 ± 2.7
	V + P	41 ± 2.8*	0.28 ± 0.040*	352 ± 15.6	8.9 ± 2.2
	W	41 ± 4.3	0.08 ± 0.02	818 ± 142	2.0 ± 0.71
	W + P	44 ± 10	0.17 ± 0.050	493 ± 60.5	5.5 ± 2.6
SBR	V	5.5 ± 2.0*	1.9 ± 0.16*	5.3 ± 1.7	4.8 ± 0.26
	V + P	2.3 ± 0.080*	0.73 ± 0.040*	7.4 ± 0.27	1.5 ± 0.12
	W	3.9 ± 0.38	0.96 ± 0.090	8.2 ± 0.80	2.4 ± 0.47
	W + P	2.7 ± 0.27	0.62 ± 0.050	8.9 ± 0.62	1.3 ± 0.20

Table 2
Carbonyl index of W and W + P samples.

Carbonyl index - CI		
Polymer	W	W + P
LLDPE	1.133 ± 0.003	1.266 ± 0.040
HDPE	1.082 ± 0.001	1.080 ± 0.014
PP	1.018 ± 0.011	1.008 ± 0.003
PS	1.014 ± 0.007	1.018 ± 0.007
PET	0.977 ± 0.003	0.965 ± 0.028
PA66	1.106 ± 0.002	1.032 ± 0.002
SBR	1.875 ± 0.298	1.860 ± 0.192

3.5. Thermal properties

The onset temperatures at which the polymer samples start to thermally degrade are presented in Figure S20. As expected, the onset temperature decreased for most of the polymers after weathering, except

for SBR, where it increased from 342 °C (V) to 346 °C (W), likely due to the surface's crosslinking. The most pronounced decrease was for PP and PA66, declining from 453 °C (V) to 434 °C (W) and from 427 °C (V) to 410 °C (W), respectively.

The purification process did not cause a significant change in the thermal stability of any weathered polymer sample (less than 5 °C from W to W + P). It was also noticed that for W and W + P, PP presented TGA curves with two mass-loss steps, in contrast to the single mass-loss step for V and V + P. The additional mass-loss step appeared between 160 and 180 °C and can be associated with the evaporation of water trapped inside the free volume of the PP's amorphous sections, as also identified for PA66 (de Jesus Silva et al., 2020; Lessa Belone et al., 2021).

3.6. Relevance of the results for microplastic research involving reduction of the organic matrix

Photodegradation initiated by UV radiation and oxygen is the most important abiotic degradation pathway that plastics undergo in the environment, and it has significant potential to change their physico-chemical properties (Duan et al., 2021; Alimi et al., 2022). So, considering the likely presence of weathered MPs in different environmental matrices, this study brings valuable information not only for sewage sludge but in the case of other organic-rich matrices as well.

As seen in Table 3, the findings of this study agree with Alimi et al. (2022); the focus of MP research on only pristine polymers in most of the current studies can lead to misleading results. In the following paragraphs, different indicators used in MP research are discussed together with their sensitivity to polymer degradation.

The surface morphology might appear unchanged or slightly changed in pristine reference MPs after the purification process. Therefore, one can argue that the purification process is adequate to reduce organic matter without damaging MPs. However, the resistance of polymers to the chemicals in the process can likely be decreased if they are weathered, as clearly seen in the case of LLDPE and PP. Similarly, the mass variation that may seem insignificant for pristine reference MPs can also present a noticeable change for weathered MPs, as in the case of LLDPE, PP and PA66. Therefore, the use of pristine reference MPs could lead to an underestimation in mass loss and a wrong indication that the purification process is gentle to certain MPs. Therefore, if surface morphology and/or mass variation are indicators adopted in the study of MPs, the validity of the results will very likely depend on the polymer state (pristine or weathered) and the interpretation of the results should be made in a conservative way.

The fragmentation tendency (based on the mechanical properties) can directly interfere in the particle counting, which is a common indicator to evaluate the MPs extraction efficiency. In the case of LLDPE and HDPE, the ductile-to-brittle transition is a condition that would enable the fragmentation of MPs. It was also evident that PP and PS MPs exposed to UV radiation would have a significant propensity to fragment during the purification process. So, this study shows that depending on how the purification process is designed, weathered reference MPs can potentially suffer breakage. This could lead to a higher chance of overestimation in particle counting, compromising the method validation based on this indicator.

To the best of our knowledge, there are no studies that have used TGA analysis on purification process validation. This is strongly impaired by the overlapping decomposition temperatures of the polymers with the organic matter. Further, if the thermal stability of the reference MPs is an indicator to be used to validate a purification process, this study shows that both the pristine and weathered samples did not have their thermal stability significantly compromised, although other clear indicators of degradation due to the purification process were observed.

Identification of polymer grades of pristine or weathered MPs with FTIR was not compromised by the applied purification process with the exception of the SBR. This is because despite any alterations to the

Table 3

Changes in the properties of the pristine and weathered samples after the purification process. * Data obtained from Lessa Belone et al. (2021).

	LLDPE	HDPE	PP	PS	PET	PA66	SBR
Surface deterioration							
○ = no significant changes	V to V + P	○	○	○	○	●●●	●
● = no cracks but holes and debris on the surface	W to W + P	●●	○	●●●	●	●●	●●●
●● = fragmented domains with large areas (> 1000 μm ²)* and small cracks within the domains							
●●● = fragmented domains with small areas (≤ 1000 μm ²)* debris on the surface might be present							
*Determination of the area on Supplementary Material							
Mass variation							
○ ≤ 0.5%	V to V + P*	○	○	○	○	●●	●●
● ≤ 1%	W to W + P	●●	○	●●	●	●●●	●●
●● ≤ 2.5%							
●●● > 2.5%							
Tensile strength							
○ ≤ 10%	V to V + P*	○	○	○	●	●●	●●
● ≤ 30%	V to W	●●●	●●●	n.a.	n.	●●	●
●● ≤ 50%	W to W + P	●	●●	n.a.	a.	●	●
●●● > 50%					n.		
n.a. = tensile test not possible to be performed					a.		
Thermal stability (TGA onset temperature)							
○ ≤ 5 °C	V to V + P*	○	○	○	○	●●	○
● ≤ 10 °C	W to W + P	○	○	○	○	○	○
●● > 10 °C							
CI							
○ ≤ 1%	V to V + P	●	●	○	○	●●	○
● ≤ 10%	W to W + P	●●	○	○	○	●	○
●● ≤ 20%							
●●● > 20%							

spectra, the V + P and W + P samples could still be recognized by comparison with the spectra from the pristine polymers, as they clearly contained the most important peaks for identification. Therefore, it is believed that validation methods for the purification process based on the chemical identification indicator probably would not yield radically different results if the reference MPs were pristine or weathered. However, if FTIR is used to identify from real MP samples whether the MPs are primary or secondary MPs, the changes in FTIR spectra indicating degradation would be relevant. For this kind of analysis, the purification process might lead to false results, as the spectra of purified samples could not be unambiguously linked with pristine or weathered MP. Therefore, other supporting methods should be applied to analyze this kind of studies.

4. Conclusions

Different characterization methods were used to study the effects of a purification process on the physicochemical properties of artificially weathered polymers (LLDPE, HDPE, PP, PS, PET, PA66, SBR). The purification process was developed for the study of MPs in sewage sludge, and it used SDS and H₂O₂ to reduce the organic matter of the matrix. It was evaluated if the purification process was more severe on weathered than on pristine samples. Based on the results, weathering can have a significant impact on the MPs' characterization after the purification process in terms of the preservation of the MPs. It could be noted that the extent of the physicochemical changes depends on the material. Thus, depending on the polymer type and the analysis methods, it is advisable to consider weathered MPs in the development of a purification process, as the use of pristine plastics will not fully reveal the adequacy of the process. It is especially recommended to be careful regarding results related to surface morphology, mass variation and particle counting, principally for polyolefins (PEs and PP), as they are the most often found MPs.

Author contributions

MCLB, MK, ES, Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project

administration, Supervision, Validation, Writing - original draft, 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.

Data availability

Data will be made available on request.

Acknowledgements

This work was supported by the Finnish Cultural Foundation. We thank Viinikanlahti wastewater treatment plant for providing the sewage sludge and Tampere Microscopy Center for the use of the SEM. We also thank, doctoral researchers Pauli Hakala, for helping with the weathering device, and Elina Yli-Rantala, for the revision and comments that contributed for the improvement of the manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2022.119669>.

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