



Degradation of common polymers in sewage sludge purification process developed for microplastic analysis[☆]

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ABSTRACT

To enable and/or facilitate analysis of microplastics from environmental samples, a purification process is required to reduce the organic matter content. The development of such process has as one main concern, besides achieving efficient organic matter reduction, the preservation of the microplastics. In this study, a three-step method for sewage sludge purification was proposed employing sodium dodecyl sulfate and hydrogen peroxide. The effects of the purification method on seven polymers (LLDPE, HDPE, PP, PS, PET, PA66 and SBR) were evaluated in terms of mass change, surface characteristics, mechanical properties, thermal properties and functional groups change. It was also assessed how the polymers were affected by the purification chemicals without the presence of sewage sludge. The purification process led to changes in all tested plastics, but in different intensities. LLDPE, HDPE, PP, PS and PET did not suffer considerable degradation. PET was more affected by hydrolysis than oxidation. On the other hand, the integrities of PA66 and SBR were noticeably affected. The effects of the purification process were considered to be due to the plasticizer behavior of water and oxidation on PA66 and loss of filler and oxidation on SBR. For both polymers there was a reduction on the tensile strength of around 50–60% after the purification, indicating they could be prone to fragmentate into smaller pieces along the process. After purification, PA66 also started to decompose at a temperature around 10 °C lower comparing to virgin samples. Except for SBR, the presence of sewage sludge and its oxidation was more harmful to the polymers than the purification chemicals without the presence of sewage sludge. This study serves as an evaluation of the effects of the purification process on the degradation of microplastics and a methodology for such assessment when designing a purification process.

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1. Introduction

Microplastics (MPs) are plastic particles smaller than 5 mm (Löder et al., 2017). Once released in the environment, they are a persistent and complex waste due to their size, variety and broad range of properties. They have been detected in marine (Gewert et al., 2015; Guo and Wang 2019), freshwater (Mendonza and Balcer 2019; Sun et al., 2019) and terrestrial environments (Li et al., 2019; Hou et al., 2021). For these reasons research on this field has gained attention in the recent years.

Municipal wastewater directed to the wastewater treatment plants (WWTP) is constituted of washing, bathing and flushing

water coming from domestic and business sources and can also include storm waters and water coming from industrial sources (Sun et al., 2019). Municipal wastewater is a noticeable source of MP waste. In the WWTP, up to 99% of MPs is retained in the sewage sludge (Magnusson and Norén 2014), while some are retained already in sieving or grit removal and some released together with the treated water at the end of the process (Carr et al., 2016; Talvitie 2018). Due to the high nutrient content of sewage sludge, its further use as fertilizer should be considered, but simultaneously its safety, regarding e.g. MPs contamination, should be verified.

For the analysis of the MPs from environmental samples, it is necessary to minimize the organic matter content, i.e. the matrix. Otherwise, it can interfere with the detection and characterization of MPs (Hurley et al., 2018; Prata et al., 2019). The matrix reduction process is referred as digestion or sample purification. In the sewage sludge, the matrix is a complex viscous solid composed of organic and inorganic components, microorganisms and other contaminants that can bind together. Also, the sludge has affinity

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for most polymer surfaces, so MPs can end up being covered with the sludge, complicating the purification (Hurley et al., 2018; Zarfl 2019; Zhang and Chen 2019).

The purification of environmental samples can be very challenging (Prata et al., 2019). The process should be as effective as possible to reduce the matrix but, concomitantly, should preserve the initial characteristics of the MPs, avoiding their extensive degradation or even destruction. A common approach employed is oxidative digestion with hydrogen peroxide (H_2O_2). H_2O_2 has been used in different solution strengths (10–35%), at different temperatures (room temperature to 100 °C) and for different time spans (1 h–1 week) (Zafli 2019).

Some authors have detected some effects of the digestion on the tested polymers, while others have not noticed any significant effects. Nuelle et al. (2014) observed that their purification process (sediment samples, 35% H_2O_2 , 1 week, room temperature) caused changes in polyamide (PA), polypropylene (PP), polyethylene terephthalate (PET) and linear low-density polyethylene (LLDPE). However, they considered the evaluation of the treatment effects on the MPs samples insufficient, since it was based only on visual inspection using optical microscope and on the determination of the surface area using an image-processing program. In the purification process of Karami et al. (2017) (fish tissue samples, 35% H_2O_2 , 96 h, different temperatures between room temperature to 60 °C), PET suffered discoloration and polyamide 66 (PA66) was destroyed. Their evaluation method was based on sample topography using scanning electron microscopy (SEM) and molecular alterations characterized by Raman spectroscopy.

Prata et al. (2019) have reported no significant effect of their treatment (algae, driftwood and seagull samples, 30% H_2O_2 , 1 and 6 h, room temperature, 25 and 50 °C) on low-density polyethylene (LDPE), high density polyethylene (HDPE), PP, polystyrene (PS), expanded polystyrene, PET, polyvinyl chloride (PVC), cellulose acetate and PA. Their findings were based on mass verification and Fourier transform infrared (FTIR) spectroscopy. Also, Duan et al. (2020) have reported that their treatment (mangrove sediment samples, 30% H_2O_2 , 11 h, 70 and 100 °C) did not cause significant damage on PET, PS, PE, PVC, PA and PP based on FTIR spectroscopy.

There is still a lack of studies that combine broader range of characterization methods to assess the effects of H_2O_2 treatments on polymers in terms of mass variation, surface analysis, chemical changes, mechanical and thermal properties. This information is needed to eliminate the effects of purification process when analyzing the nature of microplastics. Moreover, only Li et al. (2020) has focused on the effects of their purification process on the MPs in sewage sludge. They proposed the use of quantitative indicators to understand these effects by evaluating the adsorption potential of MPs to cadmium. Nonetheless, this qualitative method lacks a more direct approach and employs a toxic material.

This study presents versatile characterization of different virgin polymer films subjected to a H_2O_2 purification process of sewage sludge. Moreover, it evaluates how polymer samples were affected by solely the chemicals of the process and by the presence of the sewage sludge in the purification process.

2. Materials and methods

2.1. Origin of the sewage sludge

The sewage sludge was collected from Viinikanlahti wastewater treatment plant in Tampere, Finland. This facility has the following unit processes: sieving, grit removal, primary sedimentation, activated sludge process and secondary sedimentation. Phosphorous is precipitated at the WWTP with ferric sulfate that is added before the grit removal and after the primary sedimentation. The average

daily flow rate to the WWTP is around 70 000 m³/d. The sewage sludge was collected in a plastic canister before the thickening of the sewage sludge using a valve connected to a pipe. No precautions were taken to avoid contamination with other microplastics. Once collected, sewage sludge was stored at 4 °C.

2.2. Polymer samples

Seven polymers were selected: LLDPE (FB4230, Borealis, Austria), HDPE (CG9620, Borealis, Austria), PP (HC205TF D, Borealis, Austria), PS (143 E, Basf, Germany), PET (RAMAPET R182, Indorama, Indonesia), PA66 (Zytel 101 F N C010, DuPont, United States) and styrene butadiene rubber (SBR, Etra standard SBR, Etra, Finland). They were selected based on their high occurrence in the environment and on their use in previous studies (Lares et al., 2018; Sun et al., 2019; Birch et al., 2020). Their monomer, structure type and applications are presented in Table S1.

To produce the samples, pellets of LLDPE, HDPE, PP, PS, PET and PA66 were pressed to form 1 mm thickness sheets using a hot press. The SBR sheet of 1 mm thickness was kindly provided by Etra. The thickness was selected as it fits in the definition of MPs and, so, in terms of diffusion, the samples could be considered similar to MPs. Samples exposed to the sewage sludge and purification chemicals were cut from these sheets. For the tensile tests, LLDPE, HDPE, PP and SBR specimens were produced in dog bone shape with 35 mm overall length, 12 mm gauge length and 2 mm gauge width. PS, PA66 and PET were too brittle to be precisely cut with the dog bone shape cutter, so specimens were cut in rectangular shape with 35 mm overall length, 17 mm gauge length and 2 mm gauge width. For the other analysis, three parallel 10 mm × 10 mm samples were cut. By varying the shape of the samples, the identification of a specific sample was ensured after digestion (Fig. S2).

2.3. Digestion of the solid matrix

The sewage sludge was first vacuum filtered on a 125 µm Millipore stainless-steel screen (Merck, United States). For each digestion trial, 1.5 g of the sludge sample (wet weight) taken from the filter was used.

The purification process was done in three steps. First, 20 ml of sodium dodecyl sulfate solution (SDS, 3% w/w, Acros Organics, United States), was added for 24 h at 50 °C. It was expected to help macerate some of the organic matter, increasing the surface area and improving digestion efficiency (Löder et al., 2017). Then, digestion with hydrogen peroxide 30% (H_2O_2 , Merck, United States) was divided in two phases: 20 ml of H_2O_2 at 40 °C for 3 days and 10 ml H_2O_2 at 40 °C for 24 h. It was hypothesized that at the first stage small solids will degrade and large solids will decompose into smaller pieces and at the second stage the remaining solids will be digested. This was adopted by Yan et al. (2020) on the purification of high organic matter content samples. Between each step, sample was filtered on the 125 µm Millipore stainless steel screen and washed with distilled water.

2.4. Effect of the purification process on the polymer samples

The polymer samples were introduced in the purification process both without the sewage sludge as a control test to study the effect of only the chemicals on polymers, and with the sewage sludge as the actual purification process (Fig. S1). Different polymer types were introduced in separate beakers. After the control tests and the purification processes, samples were dried at 50 °C for 24 h.

2.5. Physicochemical analysis of the polymer samples

Weight variation of each polymer was determined during and after the control and the purification tests for the three parallel samples. The measurements were performed using a laboratory balance of four significant digits. To obtain the true initial mass, samples were first dried in oven at 50 °C for 24 h. During the immersion in the digestion solution (denominated as wet stage), the samples were dried using a lint-free cloth and weighted in intervals of 2 h. The registration of the mass in the wet stage was necessary to evaluate the possible mass losses or liquid absorption that the polymers could suffer. To obtain the true final mass, the samples were dried in oven at 50 °C for 24 h. After the weight variation measurements, the samples were used for other characterization methods.

The surface characteristics of the samples before and after the control test and the purification process were observed using the stereo microscope MZ 7.5 (Leica, Germany) equipped with a 5 megapixels DFC420 digital camera (Leica, Germany). They were also examined using the SEM JSM-IT500 (Jeol, Japan) under acceleration voltage of 20 kV. Before imaging, samples were coated with a thin carbon layer to guarantee the conductivity.

Quasistatic tensile tests with the Instron 5967 universal testing machine (Instron, United States) were conducted on the polymers before and after the experiments. In total, five to seven parallel samples were used for each polymer. Before testing, the samples were conditioned at 23 °C and 60% humidity for at least 24 h. After immersion and before conditioning the samples were first dried at 50 °C for 24 h. A load cell of 200 N was used and samples were tested at a constant crosshead speed (2 or 50 mm/min). The slower crosshead speed was used for brittle PS, PET and PA66 samples in order to record appropriately the changes on the material.

Thermal stability was measured with the TG 209 F3 Tarsus (Netzsch, Germany) in a temperature range of 30–600 °C, heating rate of 20 °C min⁻¹ and nitrogen atmosphere. The phase transition temperatures and enthalpy changes were determined for the polymer samples that presented significant change of thermal stability on TGA. Measurements were performed by differential scanning calorimetry (DSC) using the DSC 214 Polyma thermal analyzer (Netzsch, Germany) in a temperature range dependent on the polymer, heating rate of 10 °C min⁻¹ and nitrogen atmosphere.

To determine the chemical structural changes that could be introduced in the polymers, FTIR was performed using Tensor 27 spectrometer (Bruker Optics, United States) equipped with a GladiATR Attenuated Total Reflectance (ATR) sample holder (PIKE Technologies, United States). The samples were scanned from 600

to 4000 cm⁻¹, 4 cm⁻¹ resolution and 30 scans. Before the FTIR measurement and after immersion, samples were dried in oven at 50 °C for 24 h. Additionally, to ensure similar conditions and comparability, all samples were kept at 23 °C and 60% humidity for at least 24 h before the FTIR analysis.

The carbonyl index (CI) was calculated to evaluate the integrity of the samples according to Prata et al. (2019). The intensity of the carbonyl peak in the region between 1600 and 1800 cm⁻¹ was divided by the intensity of a reference peak (1471 cm⁻¹ for LLDPE and HDPE, 1458 cm⁻¹ for PP, 1452 cm⁻¹ for PS, 1504 cm⁻¹ for PET and 1464 cm⁻¹ for PA66). The reference peak is considered to remain unchanged during the degradation process. According to Guo et al. (2014), the degradation of SBR is more likely to occur on the polybutadiene portion, therefore, it is expected that the polystyrene portion will remain almost invariable after degradation. Based on that, the peak at 720 cm⁻¹ was selected as the reference for SBR.

3. Results

3.1. Mass variation

The difference between initial and final true mass of LLDPE, HDPE, PP, PS and PET samples was less than 0.4% and 0.2% for control test and purification process (Fig. S3), respectively, and can be attributed to experimental errors rather than real changes in mass. In addition, these polymer samples did not exhibit significant variation of wet mass (Table S2).

On the other hand, PA66 and SBR presented variation of mass more than 5% during both control test and purification process (Fig. 1). SDS had similar effect regardless to the presence of sludge but a difference occurred during the first H₂O₂ digestion step. For SBR, mass gain rate was 0.42% h⁻¹ for control test and 0.21% h⁻¹ for purification process. For PA66, there was a mass gain rate of 0.27% h⁻¹ without the use of sewage sludge but a mass loss rate of 0.09% h⁻¹ when sewage sludge was added. During the second H₂O₂ digestion step, just a slight mass variation was noticed for both PA66 and SBR.

3.2. Surface characteristics

The optical microscopy revealed no significant change on the surface of the polymers, except for PA66 and SBR. It was noticed that for PA66, comparing to the virgin polymer, the surface got opaquer and rougher after the control test, and this got even more pronounced after the purification process. For the SBR, erosion and

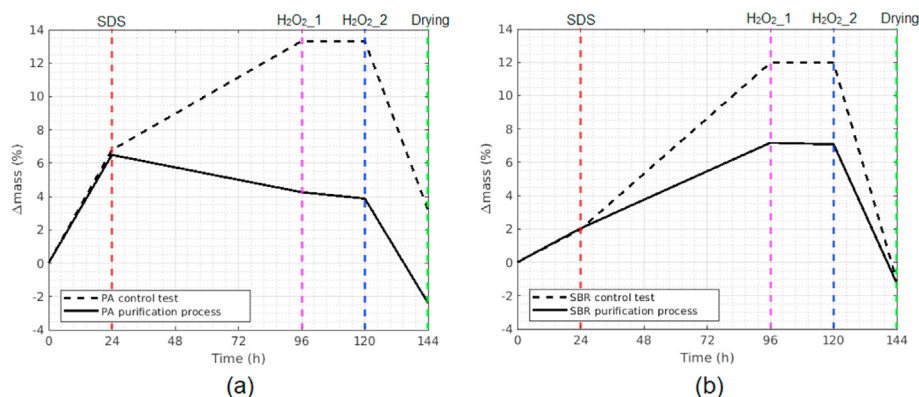


Fig. 1. Mass variation of PA66 (a) and SBR (b) during control test and purification process. The vertical dashed lines indicate the end of the SDS treatment, end of the first H₂O₂ treatment, end of the second H₂O₂ treatment and the end of drying step.

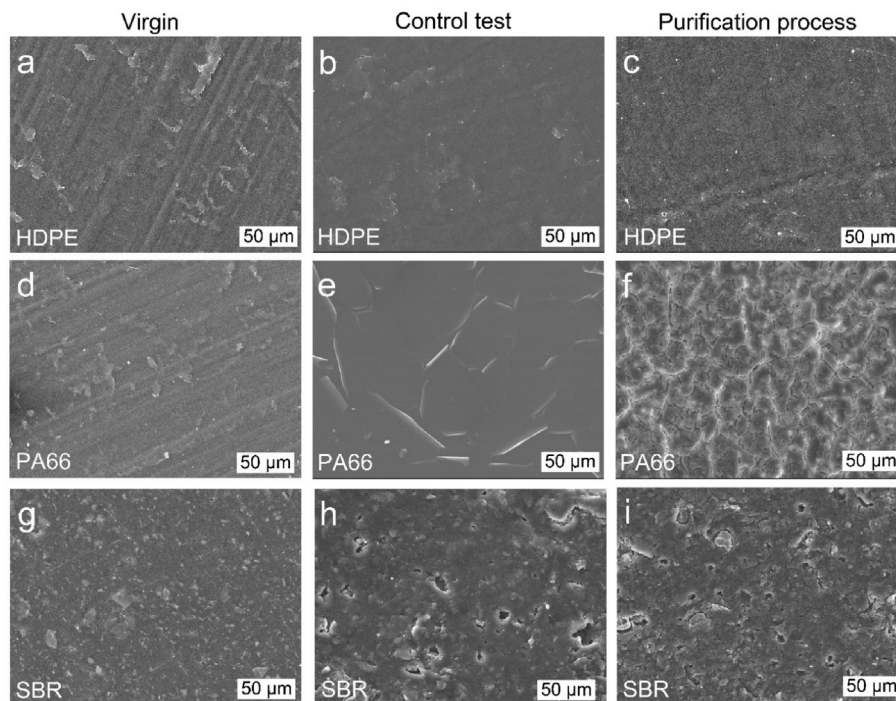


Fig. 2. SEM images of the surface of HDPE, PA66 and SBR before and after control test and purification process.

pitting were visible after both control test and purification process (Fig. S4). The control test seemed to be more aggressive to certain areas of the SBR surface (Fig. S4 (b)) supporting the mass variation observations while material loss from the surface seemed to happen more uniformly along the surface in the case of the purification process (Fig. S4 (c)).

Although not visible with optical microscope, SEM revealed that LLDPE, HDPE and PP also suffered some surface changes after control test and purification process. Virgin polyolefins (LLDPE, HDPE and PP) samples had parallel grooves on the surface that can be associated to the production process of the sheets. After the control test and purification process, these grooves appeared to be smoother in the case of PP and disappeared in the case of LLDPE and HDPE (Fig. 2 (a) to (c)). PA66 surface was extensively impacted by the purification process. While after the control test the surface lost its grooves and suffered slight peeling restricted to a thin layer of the surface, after the purification process it was completely dominated by surface cracking (Fig. 2 (e) and (f)). For PET, the surface quality was not satisfactory to draw plausible observations in terms of surface changes.

3.3. Tensile properties

Both control test and purification process led to a pronounced change in mechanical properties of PA66 and SBR. Comparing to the virgin polymer, there was a reduction in tensile strength of approximately 20% and 55% after the control test and 29% and 58% after the purification process for PA66 and SBR, respectively (Table S3). For PA66, the elongation at break (i.e. how much the material can be stretched before it breaks) increased by 62% and 75% after the control test and purification process, respectively, while for SBR it considerably decreased by 80% and 62%, respectively.

The tensile strength slightly increased after the control test for LLDPE, HDPE and PP, if compared to the virgin polymer. For PS, it can be considered that the variation of mechanical properties is

negligible. Finally, for PET, both tensile strength and elongation at break were slightly and similarly reduced after the control test and purification process.

3.4. Thermal properties

Table S4 shows the temperature at which the decomposition of the studied polymers before and after control test and purification process started (onset temperature). The onset temperature indicates the temperature limit in which the polymer is thermally stable. Any changes in the polymer structure, including the effects of degradation, can potentially change the thermal stability. Most of the studied polymers (LLDPE, HDPE, PP, PS and PET) did not have their thermal stability significantly affected by the control test and purification process. For those polymers, TGA curve presented a single mass loss step associated to their thermal degradation. All TGA curves can be found in Fig. S5.

However, in the case of PA66, comparing to the virgin polymer, the thermal stability considerably dropped after the purification process and the decomposition began 12 °C lower than that of the virgin polymer (Table S4). Moreover, both control test and purification process curves exhibited an initial small mass loss step around 180 °C associated to the evaporation of physisorbed water molecules that bonded with the amide groups in the polymer chains during immersion (Baena et al., 2018).

For SBR, the control test impacted the thermal stability the most. If compared with the onset temperature of the virgin polymer, it dropped by 7 °C. The mass loss of SBR is considered to happen in two steps. First one occurred below 300 °C and is related to the evaporation of volatile compounds. The second mass loss step is associated to the degradation of the polymer content of SBR.

The DSC curves of PA66 and SBR revealed some changes in the phase transitions. After the control test and purification process, the glass transition temperature of PA66 dropped approximately 3 and 4 °C, respectively (54.8 °C for virgin, 52.1 °C after the control test and 51.2 °C after the purification process). In addition, a

reduction on the melting temperature (263.4 °C for virgin PA66, 261.3 °C after the control test and 259.4 °C after the purification process) was observed. In the case of SBR, the glass transition temperature increased after the control test (−47.7 °C) and the purification process (−49.7 °C), if compared to the virgin polymer (−50.1 °C).

3.5. Surface chemistry

The FTIR spectrum of each virgin polymer was similar to the typical spectra found in literature in terms of assignment of the main peaks, although there were some controversies regarding to SBR. The assignment of those peaks is presented in Table S5. In the case of SBR, clear differences in terms of peak intensity or peak position could be pointed when comparing the spectra before and after control test and purification process (Fig. S6). However, for other polymers the spectra were very similar with the virgin samples.

The CI values obtained for the polymers are presented in Table S6. The carbonyl groups are amongst the most prevalent products when polymers suffer chemical degradation (Ehrenstein and Pongratz 2013), based on the changes on CI, all the polymers experienced some degradation after the control test and/or the purification process. For some polymers, changes were small that could be related to experimental errors, for others, it was significant. Moreover, in some case, differently from what was expected, there was a reduction on the CI values compared with the ones for virgin polymers.

4. Discussion

4.1. Activity of hydrogen peroxide

The H₂O₂ decomposes slowly in water if there is no elevation of temperature, catalysts or other components that can react with it (Pędzwiatr et al., 2018). The peroxide bond is very vulnerable and breaks evenly producing two hydroxyl radicals (OH[•]) (Woodard and Curran 2006). If the solution contains only H₂O₂ and water, the recombination of these radicals results in water and oxygen gas (O₂). When other compounds are present, the radicals can oxidize these other components in the solution (Woodard and Curran 2006), which, in this study, are the matrix of the sewage sludge (e.g. lipids, proteins and carbohydrates) and the polymer samples.

During the purification process, an increase in temperature of the system was noticed that was absent during the control test. This is attributed to the oxidation of the sewage sludge, indicating that it was more easily attacked by H₂O₂ than the polymer samples. The increase in temperature due to this exothermic reaction can potentially lead to enhanced H₂O₂ decomposition, radical formation and oxidation (Petri et al., 2011) and therefore a more severe environment than in the control test.

4.2. Effects of purification process on LLDPE, HDPE, PP and PS

In general, LLDPE, HDPE, PP and PS exhibit good resistance to water and detergents (Ehrenstein and Pongratz 2013) and, therefore, during the SDS treatment step, no damage was expected to happen which was also supported by the weight variation data. Below 60 °C, LLDPE and HDPE have been classified to have limited resistance to H₂O₂, while PP and PS have excellent resistance (Ehrenstein and Pongratz 2013), which is attributed to their resistance to oxidative agents. It could be assumed that, even with the heat generation during the exothermic oxidation of the sewage sludge, the temperature was not excessively higher than 40 °C. Based on the results, the thermo-oxidative degradation of these

polymers in the control test and the purification process were limited to a thin outer layer of the materials. It led to the observed surface ablation, smoothing and small or insignificant increase of CI. The small increase in tensile strength (except for LLDPE after the purification process in which tensile strength slightly decreased) can be associated with chain scission caused by degradation which resulted in chemi-crystallization on the surface (Guo and Wang 2019). Additionally, from the TGA and FTIR results, it can be concluded that these polymers did not suffer significant changes in their chemical structure.

4.3. Effects of purification process on PET

It has been stated that in water, hydrolytic degradation is the predominant degradation mechanism of PET, occurring much faster than thermo-oxidative degradation in a wide temperature range (room temperature to 120 °C) (Venkatachalam et al., 2012; Gewert et al., 2015; Arhant et al., 2019). PET is susceptible to hydrolysis due to the presence of ester bonds on its structure leading to chain scission (Al-Azzawi 2015; Arhant et al., 2019). However, hydrolysis should be significant only at temperatures above 100 °C (Al-Azzawi 2015), which is far from the maximum temperature we considered the samples were exposed to in this study. Hydrolytic degradation is assumed to cause the slight decrease in the tensile strength observed after control test and purification process of PET in this study. The chain scission hypothesis was supported by the observed variations in the FTIR peaks and CI values. For example, the peak in the region of 3430 cm^{−1} related to OH end groups slightly increased comparing to the virgin polymers because of the effects of hydrolysis. Also, the peaks between 2800 and 3000 cm^{−1} related to C–H vibrations slightly increased. This can be attributed to the decreasing of chain length caused by chain scission, which led to a growth in the number of terminal ethylene glycol groups (Sammon et al., 2000). Arhant et al. (2019) have shown that the hydrolysis rate of PET increases with the increase in temperature. Hence, this likely explains that changes in properties of PET, i.e. tensile strength, CI and peak intensity, after the purification process were slightly more noticeable than after the control test. However, as for the previous polymers, the effects of degradation were limited to the surface and therefore the overall effect was small.

4.4. Effects of purification process on PA66

PA66 exhibits a good resistance to detergents (Ehrenstein and Pongratz 2013), therefore, in the SDS step, only the presence of water could cause any effect on PA66. Gonçalves et al. (2007) have suggested that when exposed to water, the main mechanism of degradation of PA66 is thermo-oxidation. According to the authors, in a temperature range of 25–90 °C and 100 h immersion time in water, amide hydrolysis does not play a significant role in the degradation. Nevertheless, the water absorption into PA66 structure enables diffusion of oxygen radicals, generated by the decomposition of H₂O₂, into its interior and therefore facilitates the thermo-oxidative degradation (Gonçalves et al. 2007). The pronounced changes on the PA66 surface in this study were likely caused by internal stresses from water absorption and/or thermal effect (Ksouri et al., 2017). It is safe to assume that the increase in temperature that resulted from the oxidation of the sewage sludge was responsible to the worsening of the cracking of the surface. Therefore, unlike what has been suggested by Li et al. (2020), the effects of the purification process on the PA66 surface observed in this study showed that oxidative pretreatments can cause significant changes on the surface morphology of PA66 microplastics, which should be taken into account when analyzing the results.

After the control test, it was observed that the final true mass of

PA66 was higher than the initial true mass. Based on the SEM, in which surface peeling was detected but not significant loss of material, it can be considered that this increase in the true mass is due to the absorption and bonding of water molecules to the structure that was not removed during drying and could be detected in the TGA curve, a phenomenon also reported by (Baena et al., 2018). While for the virgin polymer the bonded water content was almost negligible, after the purification process TGA indicated a water content of around 4%. On the other hand, in the first H₂O₂ step in the purification process, it was noticed that, for PA66, there was no mass uptake, but a tendency for mass loss. In this case, what changed from the control test is the heat generation from sewage sludge oxidation. Therefore, the decrease in mass may be attributed to higher polymer degradation due to an increase in temperature and this being more pronounced than the sorption mechanism on the structure even though it is known that the diffusion rate of water, and thus the mass uptake, also increases with the increase of temperature (Ksouri et al., 2017).

The exposure to H₂O₂ induced the embrittlement of PA66 and reduction of tensile strength. Furthermore, water absorption during immersion is also a cause of decrease in tensile strength. Because of the ingress of water on the PA66 structure during the control test and purification process, the motion of the molecules on the amorphous portion is facilitated (Gonçalves et al. 2007). Additionally, water molecules are small and polar, being able to interfere with the hydrogen bonds between PA66 chains (Ksouri et al., 2017). In this sense, water can be considered to have a plasticizer effect, which explains the increase in the elongation at break and the reduction on the glass transition temperature observed on DSC.

It is assumed that the degradation effects on a semi-crystalline polymer occur preferentially in its amorphous regions (Gonçalves et al., 2007; Al-Azzawi 2015) as the diffusion of molecules does not occur on the core of the crystalline domains. However, the surface and boundary regions of those crystalline domains can suffer from oxidation, leading to scission of tie molecules that connects the crystallites (Eriksson et al., 1997). Therefore, the decrease detected in the melting temperature is suggested to occur. Again, the variations observed in DSC were more pronounced after the purification process due to the increase in temperature of the system.

After the purification process, CI showed inconsistency considering the literature. According to Eriksson et al. (1997), the CI is an indicative of the thickness of material layer that suffered oxidation. Also, the same authors noted that the increase in temperature would raise the CI in the surface (Eriksson et al., 1997). Therefore, due to the extent of the surface cracking and the increase in temperature, the CI after the purification process was expected to be higher than the CI after the control test, which did not occur. On the other hand, it could also be considered that CI after the purification process was lower because, due to surface cracking and consequent material loss, the surface at the end of the process is almost virgin.

4.5. Effects of purification process on SBR

According to Ehrenstein and Pontgratz (2013), SBR is very resistant to water, because of its hydrocarbon backbone, but very susceptible to attack by oxidants. This is due to the double bonds in the structure, which are considered to be easily subjected by radical attack (Guo et al., 2014). Therefore, in this study, it can be considered that thermo-oxidation is the degradation mechanism SBR undergoes.

In this study, SBR experienced embrittlement due to the crosslinking reactions between the double bonds and free radicals that were established as a consequence of the exposure to a thermo-oxidative environment (Ehrenstein and Pontgratz 2013). This

crosslink formation was confirmed with DSC results, since with increasing crosslinking degree, the glass transition temperature shifts to higher temperature (Schawe 2002). Because of the embrittlement, the surface cracked, and it resulted in the reduction of tensile strength. The increase in crosslinks on the surface also led to hardening of SBR, which reflected on the drastic reduction on the elongation of break.

Regarding FTIR, the results were not agreeing with literature in some aspects. It was considered that the absorption peaks at 660, 870 and 960 cm⁻¹ were related to the vinyl group in the butadiene portion. Their intensities increased after SBR degradation. However, according to Guo et al. (2014), their intensities were meant to decrease, since this would indicate the attack of double bonds during degradation and the establishment of crosslinks on the SBR matrix. The bands related to the benzene units at 720 cm⁻¹ and in the region between 1200 and 1500 cm⁻¹ behaved in a doubtful way considering that, according to Guo et al. (2014), they were meant to remain almost invariable, since degradative processes are likely to happen in the vinyl portion rather than in the benzene portion of the structure. In the spectra, a peak at 1400 cm⁻¹ disappeared after both the control test and the purification process and one appeared at 1320 cm⁻¹ after the purification process. Because of bands related to benzene units did not behave in the expected manner, CI might not be calculated correctly.

Despite the aforementioned results, it was possible to detect changes that indicated oxidation. The emerging bands between 1600 and 1800 cm⁻¹ reflect the formation of carbonyl species (Guo et al., 2014), the peak intensity related to hydrocarbon vibrations at 2800 to 3000 cm⁻¹ declined and the increase in peak at 1000 cm⁻¹ could be related to the formation of C–O bonds (Guo et al., 2014). Moreover, the disappearance of the peak at 1538 cm⁻¹, related to the C–S bond resulted from the sulphur vulcanization of the rubber (Karabork et al., 2014), after the control test and the purification process might be associated to the devulcanization of SBR's surface, since sulphur groups are oxidized by strong oxidizing agents (Rios et al., 2006).

Based on surface images and on the FTIR spectrum (indicated by the Si–O vibration band at 1070 cm⁻¹) of the virgin SBR, the presence of silica as a filler can be observed. Besides the effects of oxidative degradation described, it appears that the filler also influences the changes that arise from the exposure to the control test and the purification process. The microscopy images revealed that the embrittlement discussed previously was also responsible for the loss of material from the surface and subsequent chalking, or exposure of the fillers. The detachment of some of these exposed filler particles (Fig. 2 (g)–(i)) indicates that the mass loss of SBR is associated to this as well. However, no decrease in mass was detected during immersion, which might be a result of higher absorption of solution over the mass loss caused by the experiments. SBR itself is considered hydrophobic due to its non-polar structure, but silica contains hydroxyl groups, thus its polarity enables the absorption of water on the rubber and its swelling (Choi and Ha 2007).

SBR surface clearly suffered from the control test and the purification process, based on the microscope images, it is not possible to draw conclusions of which one impacted the surface the most. However, even though some results were inconclusive, based on the mass gain, elongation at break, thermal properties and CI, it can be suggested that the control test was more severe to SBR. It could be hypothesized that it is due to oxygen availability. Thermal oxidation rises when temperature increases. However, according to Guo et al. (2014), in a short time and under air, almost no thermal oxidation of SBR occurs at 130–140 °C and very slow thermal oxidation occurs at 160–170 °C. In water, the same trend can be considered. Therefore, considering the temperature range the

Table 1
The overall effect of the purification process on the selected polymers.

Polymer	Mass variation	Surface characteristics	Mechanical properties	Thermal properties	Functional groups	Cl
LLDPE	○	●	●	○	○	●
HDPE	○	●	○	○	○	●
PP	○	●	●	○	○	●
PS	○	○	○	○	○	○
PET	○	●	●	○	●	●●
PA66	●●	●●	●●	●●	●●	●●
SBR	●●	●●	●●	○	●●	●

○ negligible or no effect.

● some effect observed.

●● pronounced effect.

samples were exposed to in this study, it is not expected that temperature will be decisive on the SBR degradation, even when the system's temperature rises due to the oxidation of the sewage sludge. In fact, according to Crabtree and Kemp (1946), heat and water alone do not cause permanent changes or substantial rubber degradation, but their combination with oxygen. During the purification process, part of the oxygen reactive species was being consumed on the sewage sludge oxidation, thus less oxygen would be available to react with the rubber, limiting its degradation and the creation of oxygenated species (Petri et al., 2018). Furthermore, the consumption of oxygen on the oxidation of the sewage sludge could explain the inexistence of deeper pitting on the surface, as it was observed on the surface after the control test.

4.6. Relevance of the study on the analysis of microplastics from sewage sludge

The results are relevant to evaluate the suitability of the purification process regarding to its effects on the degradation of the MPs. Table 1 summarizes the findings regarding to the degradation of the polymers. It is known that a method which is extensively aggressive to the MPs is not desired, since it impairs their further detection, identification and characterization.

The tensile test is relevant as an indicative of the susceptibility of the microplastic to fragment into smaller pieces after the purification process. In the case of this study, PA66 and SBR MPs, would have great chance to fragmentate, invalidating the analysis of particle size and shape during MPs characterization.

Microscope images evaluated the surface's state after the pre-treatment. This is a straightforward observation to qualitatively predict how aggressive the digestion would be on the MPs. Based on microscope images, it can be considered that the proposed purification method is not suitable for PA66 and SBR MPs, having potential for their complete destruction. Especially, if it is considered that MPs have higher surface area than the polymer samples used in this study, which raises the rate of chemical reactions. From this point of view, the purification process could even be too aggressive for PET MPs.

This present assessment is also relevant in case of MPs analysis with micro-FTIR and pyrolysis-gas-chromatography-mass spectroscopy, techniques based on the macromolecular structure and bonds of the MPs. This is due to the fact that after the purification process the material's structure could be considerably altered to a point that the identification by these methods is more challenging or impaired.

5. Conclusions

Seven common polymers (LLDPE, HDPE, PP, PS, PET, PA66 and SBR) were submitted to a purification process of sewage sludge involving SDS and H₂O₂. Moreover, the effect of the chemicals used

on the purification process without the sewage sludge portion was similarly studied (control test).

The purification process did not affect significantly the LLDPE, HDPE, PP and PS. In case of PET, at the temperature range of our study, it was more prone to hydrolysis than oxidation due to the attack of water. Virgin PA66 and SBR were affected the most. It was assumed that the changes in properties of PA66 was due to the plasticizer effect of water and to oxidation. In case of SBR, it was assumed to be due to the loss of some filler from the structure and oxidation.

The study highlights that, although in different intensities and manners, the purification process affected all the selected polymers. The presence of the sewage sludge and its oxidation led to increased polymer degradation in most of the cases. The rubber was the exception and the digestion chemicals were more harming than the chemicals plus the sewage sludge.

This study shows that, in terms of MPs preservation, the purification process used is suitable for studying many MP types in the sewage sludge. PA66 and SBR, though, could have a significant chance to fragmentate and therefore distort the MP analysis results. It should be considered that any modification on the purification process, such as temperature, digestion chemicals, time, and amount of sewage sludge, has the potential to increase or decrease the degradation of MPs. Therefore, the performed analysis of the polymer's degradation only applies to the proposed purification process. However, solid insights into the effects of SDS and H₂O₂ on MPs can be gathered when designing a purification process.

Author contributions

Conceptualization: MCLB, ES. Data curation: MCLB. Formal analysis: MCLB, ES. Funding acquisition: MK, ES. Investigation: MCLB, MK, ES. Methodology: MCLB, ES. Project administration: MK, ES. Supervision: MK, ES. Validation: MCLB, MK, ES. Writing - original draft: MCLB, MK, ES. Writing - review & editing: MCLB, MK, ES.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2020.116235>.

References

- Al-Azzawi, F., 2015. Degradation Studies on Recycled Polyethylene Terephthalate. Doctoral thesis. London Metropolitan University, p. 221.
- Arhant, M., Le Gall, M., Le Gac, P., Davies, P., 2019. Impact of hydrolytic degradation on mechanical properties of PET - towards an understanding of microplastics formation. *Polym. Degrad. Stabil.* 161, 175–182.
- Baena, L.M., Zuleta, E.C., Calderón, J.A., 2018. Evaluation of the stability of polymeric materials exposed to palm biodiesel and Biodiesel-Organic acid blends. *Polymers* 10 (5), 511.
- Birch, Q.T., Potter, P.M., Pinto, P.X., Dionysiou, D.D., Al-Abed, S.R., 2020. Sources, transport, measurement and impact of nano and microplastics in urban watersheds. *Rev. Environ. Sci. Biotechnol.* 19 (2), 275–336.
- Carr, S.A., Liu, J., Tesoro, A.G., 2016. Transport and fate of microplastic particles in wastewater treatment plants. *Water Res.* 91, 174–182.
- Choi, S., Ha, S., 2007. Influence of reinforcing systems and microstructures of SBR on water swelling behaviors of SBR composites. *엘라스토머* 42 (2), 102–106.
- Crabtree, J., Kemp, A.R., 1946. Weathering of soft vulcanized rubber. *Ind. Eng. Chem.* 38 (3), 278–296.
- Duan, J., Han, J., Zhou, H., Lau, Y.L., An, W., Wei, P., Tam, N.F., 2020. Development of a digestion method for determining microplastic pollution in vegetal-rich clayey mangrove sediments. *Sci. Total Environ.* 707, 136030.
- Ehrenstein, G.W., Pongratz, S., 2013. Resistance and Stability of Polymers. Hanser Publishers, Munich.
- Eriksson, P., Boydell, P., Eriksson, K., Månson, J.E., Albertsson, A., 1997. Effect of thermal-oxidative aging on mechanical, chemical, and thermal properties of recycled polyamide 66. *J. Appl. Polym. Sci.* 65 (8), 1619–1630.
- Gewert, B., Plassmann, M.M., MacLeod, M., 2015. Pathways for degradation of plastic polymers floating in the marine environment. *Environmental Science. Processes & Impacts* 17 (9), 1513–1521.
- Gonçalves, E.S., Poulsen, L., Ogilby, P.R., 2007. Mechanism of the temperature-dependent degradation of polyamide 66 films exposed to water. *Polym. Degrad. Stabil.* 92 (11), 1977–1985.
- Guo, L., Huang, G., Zheng, J., Li, G., 2014. Thermal oxidative degradation of styrene-butadiene rubber (SBR) studied by 2D correlation analysis and kinetic analysis. *J. Therm. Anal. Calorim.* 115 (1), 647–657.
- Guo, X., Wang, J., 2019. The chemical behaviors of microplastics in marine environment: a review. *Mar. Pollut. Bull.* 142, 1–14.
- Hou, L., Kumar, D., Yoo, C.G., Gitsov, I., Majumder, E.L.-W., 2021. Conversion and removal strategies for microplastics in wastewater treatment plants and landfills. *Chem. Eng. J.* 406, 126715.
- Hurley, R.R., Lusher, A.L., Olsen, M., Nizzetto, L., 2018. Validation of a method for extracting microplastics from complex, organic-rich, environmental matrices. *Environ. Sci. Technol.* 52 (13), 7409–7417.
- Karabork, F., Pehlivan, E., Akdemir, A., 2014. Characterization of styrene butadiene rubber and microwave devulcanized ground tire rubber composites. *J. Polym. Eng.* 34 (6), 543–554.
- Karami, A., Golieskardi, A., Choo, C.K., Romano, N., Ho, Y.B., Salamatinia, B., 2017. A high-performance protocol for extraction of microplastics in fish. *Sci. Total Environ.* 578, 485–494.
- Ksouri, I., De Almeida, O., Haddar, N., 2017. Long term ageing of polyamide 6 and polyamide 6 reinforced with 30% of glass fibers: physicochemical, mechanical and morphological characterization. *J. Polym. Res.* 24 (8), 1–12.
- Lares, M., Ncibi, M.C., Sillanpää, M., Sillanpää, M., 2018. Occurrence, identification and removal of microplastic particles and fibers in conventional activated sludge process and advanced MBR technology. *Water Res.* 133, 236–246.
- Li, X., Chen, L., Ji, Y., Li, M., Dong, B., Qian, G., Dai, X., 2020. Effects of chemical pretreatments on microplastic extraction in sewage sludge and their physicochemical characteristics. *Water Res.* 171, 115379.
- Li, Q., Wu, J., Zhao, X., Gu, X., Ji, R., 2019. Separation and identification of microplastics from soil and sewage sludge. *Environ. Pollut.* 113076.
- Löder, M.G.J., Imhof, H.K., Ladehoff, M., Löschel, L.A., Lorenz, C., Mintenig, S., Gerdt, G., 2017. Enzymatic purification of microplastics in environmental samples. *Environ. Sci. Technol.* 51 (24), 14283–14292.
- Magnusson, K., Norén, F., 2014. Screening of Microplastic Particles in and Down-Stream a Wastewater Treatment Plant. IVL Swedish Environmental Research Institute, 22 pp.
- Mendoza, L.M.R., Balcer, M., 2019. Microplastics in freshwater environments: a review of quantification assessment. *Trac. Trends Anal. Chem.* 113, 402–408.
- Nuelle, M., Dekiff, J.H., Remy, D., Fries, E., 2014. A new analytical approach for monitoring microplastics in marine sediments. *Environ. Pollut.* 184, 161–169.
- Pędziwiatr, P., Mikołajczyk, F., Zawadzki, D., Mikołajczyk, K., Bedka, A., 2018. Decomposition of hydrogen peroxide- kinetics and review of chosen catalysts. *Acta Innovations* 26, 45–52.
- Petri, B.G., Watts, R.J., Tsitonaki, A., Crimi, M., Thomson, N.R., Teel, A.L., 2011. Fundamentals of ISCO using persulfate. In: Siegrist, R., Crimi, M., Simpkin, T. (Eds.), *In Situ Chemical Oxidation for Groundwater Remediation*. SERDP/ESTCP Environmental Remediation Technology, vol. 3. Springer, New York, pp. 33–88.
- Prata, J.C., da Costa, J.P., Girão, A.V., Lopes, I., Duarte, A.C., Rocha-Santos, T., 2019. Identifying a quick and efficient method of removing organic matter without damaging microplastic samples. *Sci. Total Environ.* 686, 131–139.
- Rios, Rachel R.V. A., Gontijo, Manuela, Ferraz, Vany P., Lago, Rochel M., Araujo, Maria Helena, 2006. Devulcanization of styrenebutadiene (SBR) waste tire by controlled oxidation. *J. Braz. Chem. Soc.* 17 (3), 603–608.
- Sammon, C., Yarwood, J., Everall, N., 2000. An FT-IR study of the effect of hydrolytic degradation of the structure of thin PE films. *Polym. Degrad. Stabil.* 67, 149–158.
- Schawe, J.E.K., 2002. Application Handbook Elastomers, vol. 2. Schwerzenbach: Mettler Toledo.
- Sun, J., Dai, X., Wang, Q., van Loosdrecht, Mark C. M., Ni, B., 2019. Microplastics in wastewater treatment plants: detection, occurrence and removal. *Water Res.* 152, 21–37.
- Talvitie, J., 2018. Wastewater Treatment Plants as Pathways of Microplastic to the Aquatic Environment. Doctoral dissertation. Aalto University, 68 pp.
- Venkatachalam, S., Nayak, S.G., Labde, J.V., Gharal, P.R., Rao, K., Kelkar, A.K., 2012. Degradation and recyclability of poly(ethylene terephthalate). In: Saleh, H.E. (Ed.), *Polyester*. InTechOpen.
- Woodard, Curran, 2006. Methods for testing wastewaters from industry. In: Woodard, Curran (Eds.), *Industrial and Waste Treatment Handbook*, second ed. Butterworth Heinemann, US, US, pp. 149–334.
- Yan, Z., Zhao, Y., Zhao, H., Zhu, Q., Qiao, R., Ren, H., Zhang, Y., 2020. An efficient method for extracting microplastics from feces of different species. *J. Hazard Mater.* 121489.
- Zarfl, C., 2019. Promising techniques and open challenges for microplastics identification and quantification in environmental matrices. *Anal. Bioanal. Chem.* 411, 3743–3756.
- Zhang, Z., Chen, Y., 2019. Effects of microplastics on wastewater and sewage sludge treatment and their removal: a review. *Chem. Eng. J.* 122955.