

Fragmentation of Disposed Plastic Waste Materials in Different Aquatic Environments

Olivija Plohl^a, Noemi Sep^b, Lidija Fras Zemljič^a, Annamaria Vujanović^b, Maja Čolnik^b, Yee Van Fan^c, Mojca Škerget^b, Jiří Jaromír Klemeš^c, Lidija Čuček^b, Julija Volmajer Valh^{a,*}

^aUniversity of Maribor, Faculty of Mechanical Engineering, Institute of Engineering Materials and Design, Smetanova 17, SI-2000 Maribor, Slovenia

^bUniversity of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, SI-2000 Maribor, Slovenia

^cBrno University of Technology - VUT Brno, Faculty of Mechanical Engineering, Sustainable Process Integration Laboratory SPIL, NETME Centre, Technická 2896/2, 616 69 Brno, Czech Republic
julija.volmajer@um.si

Among the most pressing environmental issues is the rapidly increasing accumulation and fragmentation of plastic waste materials, particularly in freshwater and marine environments. In this study, polyethylene terephthalate (PET) plastic waste, as one of the major environmental concerns, was exposed to various aquatic environments in the form of plastic bottles and non-woven fibres to investigate the end-of-life behaviour and the formation of micro-, and nanoplastics during the degradation process. The research focuses on tracking plastic waste in model waters (with pH values of 4, 7 and 10) and real waters (seawater and tap water). Both the solid and liquid phases were analysed for fragmentation and leaching of plastics after one month of observation. In the solid phase, gravimetric analysis, presence of functional groups by Fourier Transform Infrared Spectroscopy (ATR-FTIR), morphology and size by optical microscope were measured. In the liquid phase, ecological parameters (pH, conductivity, turbidity, chemical oxygen demand (COD) and total organic carbon (TOC)) and micro/nanoplastic formation (particle size and FTIR analysis under the microscope) were characterised. The results show that PET debris litter to the aquatic environment, in the form of non-woven fibres, has greater negative environmental impacts on turbidity, COD and micro/nano fragment formation. The outcomes of this study indicate a potentially hazardous risk of improperly treated plastic material in various aquatic environments, especially with the type of material structure, such as fibre structure, due to the increased release of micro/nanoplastic into the aquatic environment, which may have serious eco-toxicological effects on wildlife. This study underlies that due to the rapid fragmentation of fibrous PET plastic material, the latter should be properly collected and processed.

1. Introduction

Plastic production is continuously increasing globally. In 2020, nearly 370 Mt of plastics were produced worldwide, of which 55 Mt was produced in Europe (Plastics Europe, 2021). More than 90 % of plastics are petroleum-based and non-biodegradable. One of the best-known and most widely used petroleum-based polymers is polyethylene terephthalate (PET), with a global market volume of 24.23 Mt in 2021, and it is expected to further grow at an annual growth rate of more than 4.2 % (Tiseo, 2021). PET is a linear, high-molecular-weight thermoplastic and semicrystalline polymer consisting of two monomeric units, terephthalic acid and ethylene glycol, linked by ester bonds. PET has excellent tensile strength, chemical resistance and high thermal stability and is widely used in various industries, such as food, pharmaceutical and textile industries. Nearly 60 % of PET's production is used for fibre applications, and the remaining 40 % is used for plastic bottles. PET is considered a highly recyclable material. However, according to a recent report (Dhaka et al., 2022), only 42 % of bottles from PET are recycled, 20 % are incinerated, and the remaining 38 % end up in landfills or in natural environments.

Globally, only 10 % of all plastic waste produced is recycled (Geyer et al., 2017), resulting in a huge footprint of plastic waste (Klemeš et al., 2020). In the EU, 32.5 % of all plastic waste is recycled, so the situation is somewhat better (European Parliament, 2021), but the level of circularity is far from sustainable. A large proportion of PET plastics end up in landfills at the end of their life cycle or are released into the environment in an uncontrolled manner, leaving a large environmental footprint (Klemeš et al., 2020). At current growth rates, the accumulation of plastic waste in landfills and/or natural environments is expected to be nearly 12,000 Mt worldwide by 2050 (European Parliament, 2021).

Under normal conditions in nature, plastics have slow degradation rates. The degradation mechanisms of plastics in the environment can be either physical or chemical. Physical degradation appears in terms of structural changes such as cracking, embrittlement and flaking, while chemical degradation is related to changes at the molecular level such as bond cleavage or oxidation of long polymer chains to form new molecules, usually with much shorter chain lengths (Chamas et al., 2020). The results of both physical and chemical degradation, or their combination, lead to the formation of microplastics and later nanoplastics. Both microplastics and nanoplastics are among the most harmful environmental pollutants, posing a growing threat not only to marine and freshwater ecosystems but also to agricultural production, groundwater, plant growth, and even human and animal health. The need for better experimental studies under well-defined conditions and methods to simulate polymer degradation has been highlighted (Chamas et al., 2020).

In this study, the degradation of PET plastic waste in the form of plastic bottles and non-woven fibres in various water bodies was investigated regarding their negative impact on the environment. Such end-of-life behaviour assessment is essential in quantifying the environmental footprint of plastic litter (Klemeš et al., 2020) and for the subsequent mitigation strategies.

2. Materials and methods

Two PET materials in the form of plastic bottles and PET fibres were studied regarding their degradation process. Both PET materials were obtained from Slovenian companies. PET and PET fibre samples were cut into small round-shaped pieces (1 x 1 cm). Twenty pieces of the samples were weighed and placed into Erlenmeyer flasks, where 150 mL of aquatic medium was added. The samples were exposed to five different aquatic mediums: model waters (with pH values of 4, 7 and 10) and real waters (tap water and seawater). Flasks containing the samples were sealed and left for one month at room temperature. The flasks were hand-shaken once every week.

After one month, the samples were first filtered through a colander with a mesh of 5 mm in diameter to remove the larger pieces. The pieces were dried at 70 °C and 10 kPa in a vacuum dryer to a constant weight. The samples were further analysed using an optical microscope Spotlight 200i FT-IR Microscopy System with an Attenuated Total Reflection (ATR) accessory containing a diamond crystal. For each sample, 16 scans with a resolution of 4 cm⁻¹ were taken. The spectra were measured at ambient temperature over a wavenumber interval between 4,000 and 400 cm⁻¹.

The obtained filtrates were filtered again through polyether sulfone (PESU) filters with an effective pore size of 0.2 µm, which have been weighed before use. The PESU filters were also dried to constant mass at 70 °C and 100 mbar and weighted again to determine the mass of fragmented microplastic left on the filters. Microplastics retained on the filters were examined under an optical microscope and analysed using ATR FTIR Spotlight 200i FT-IR Microscopy System. Water samples before and after the second filtration were also tested for qualitative properties such as pH (ISO 10523:2008), conductivity (SIST EN 27888:1998), turbidity (SIST EN ISO 7027:2020), chemical oxygen demand (COD) (GSO ISO 6060:2015), particle size distribution (PSD) (Zetasizer Nano ZS®, Malvern Instruments Ltd., UK) and total organic carbon (TOC) (Shimadzu TOC-L analyser, Shimadzu Co., Japan; calibration curves were made with potassium hydrogen phthalate from 0 to 50 ppm). Table 1 shows abbreviations for the samples in different water bodies.

Table 1: Sample abbreviations in different water bodies, exposed to different waters for one month period

Material	Water body (Model water)			Water body (Real system)	
	pH 4	pH 7	pH 10	Sea water	Tap water
PET	PET-pH4	PET-pH7	PET-pH10	PET-SW	PET-TW
PET fibres	PET-fib-pH4	PET-fib-pH7	PET-fib-pH10	PET-fib-SW	PET-fib-TW

3. Results and discussion

The two PET plastics that differ in morphology were aged in the form of squares, while the PET-fib plastics were aged in the form of fibres, and their diameter was about 20–30 µm. The mass loss of PET after a month

in the different aquatic environments can be seen in Figure 1. In general, PET plastic did not lose its mass significantly, except in the sample, PET-pH7 mass loss was more notable. In contrast, PET-fib plastic loses its mass more significantly, and the largest mass loss in the model water was observed in water with pH 10 (0.573 %), while in the real water bodies, this loss was more pronounced for seawater (sample PET-fib-SW) and accounted for about 1.35 % of the mass loss. With higher pH, PET-fib may undergo hydrolysis and thus hydrolytic degradation. Infrared spectroscopy was performed on all untreated and aged PET and PET fibre samples (Figure 2) to reveal the presence of typical functional groups in both PET plastics. The samples show similar infrared spectra, which is due to the presence of functional groups in the structure. The most pronounced band at $1,730\text{ cm}^{-1}$ corresponds to the C=O ester, at $1,408\text{ cm}^{-1}$ to the C-C phenyl ring, and in the wavenumber range $1000\text{--}1250\text{ cm}^{-1}$ two peaks are seen which are assigned to the C-O ester. At wavenumber 727 cm^{-1} band is seen for the C-H functional group, while at larger wavenumbers, i.e. $2,976\text{ cm}^{-1}$, this corresponds to the -CH ethyl group (Mecozzi and Nisini, 2019). No specific change was observed regarding IR spectra for all aged samples in different aqueous environments. However, a smaller shift of the C = O ester functional group to larger wavenumbers was observed, possibly due to the oxidation process. The observation suggests PET is generally stable compared to PET material in fibre form, which is consistent with the results reported in the literature (Shams et al., 2020), highlighting the destabilising effect of seawater on nanoscale PET.

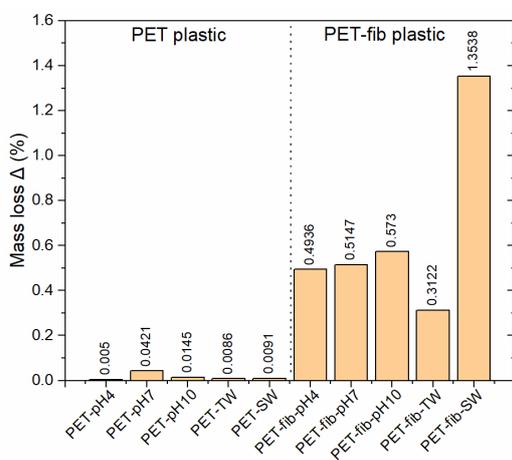


Figure 1: Mass loss of PET and PET fibre plastic after one month aging in different aquatic environments.

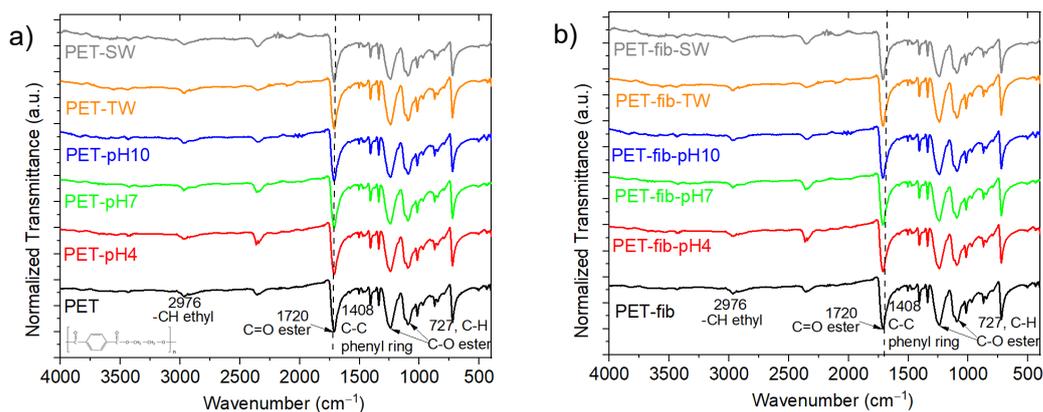


Figure 2: IR spectra for aged a) PET and b) PET fibre plastic materials in different water bodies.

An optical microscope was used to show the changes caused by the leaching process after ageing of both types of PET plastics in model and real water systems. In Figure 3, microscopy images of PET and PET fibres samples are shown for the initial samples and samples after one month of leaching in model water at pH 7. Other microscopy images were similar to those shown in Figure 3. In the case of PET samples, during the leaching, only minor damage to the surface of PET samples was observed with no particular changes in the

morphology, as shown as dark spots (Figure 3b). For PET fibres, it is even more difficult to see the effects of leaching due to overlapping fibres, which are typical when processed in the non-woven electrospinning process (Ellison et al., 2007). After filtration of the aqueous leached phase after the two plastic fragments through the PESU filter, the sample was dried, and the residues remaining on the filter were also examined with the optical microscope. Figure 4 shows optical microscopy images of reference filter PESU and all the PET and PET fibre samples after one month of leaching. Compared to the reference, no visible changes were observed, except for the PET-SW sample, which is either due to the residual plastic material on the filter and/or the presence of salt from the seawater. In addition to PET plastics, large PET fibre fragments also remained on the filter after filtration (Figure 4b). These leached fragments disintegrated from the PET fibres materials into individual micro and nanofibers. This suggests that plastic morphology is directly related to plastic fragmentation and the leached PET fibres may have negative environmental effects (Silva et al., 2021).

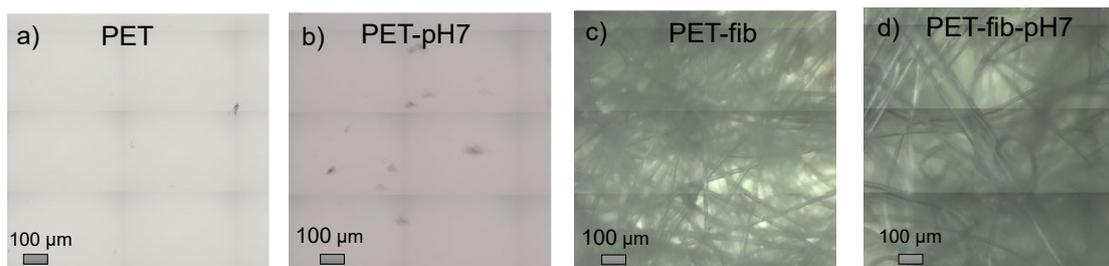


Figure 3: Optical microscopy images of samples a) virgin PET and c) PET fibres and b) PET and d) PET fibres samples after one month leaching in model water at pH 7 (PET-pH7 and PET-fib-pH7)

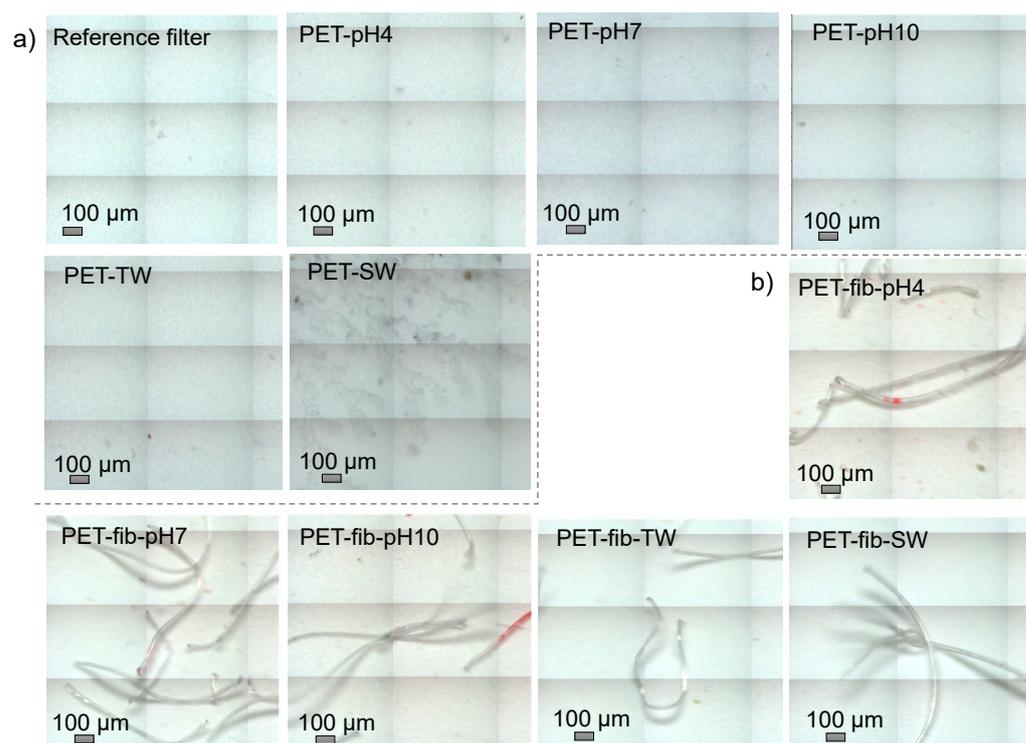


Figure 4: Optical microscopy images of a) PET and b) PET-fib plastic materials after one month of leaching, fragments left on the PESU filter after the second filtration process.

The liquid phase was further analysed for some water quality parameters, such as pH, conductivity, and turbidity before and after leaching of PET and PET fibres, as shown in Table 2. For model waters, pH values decreased after leaching, especially for water at pH \approx 10. For the real systems (tap and seawater), an increase in pH values was observed after leaching. Similar to pH, the conductivity of all the samples decreased after leaching in model waters, while for real waters, conductivity slightly decreases for PET samples and slightly

increases for PET fibres samples. Turbidity, an indicator of leached plastic particles, increased for all PET fibre samples after leaching, indicating the presence of fragments. On the contrary, in PET samples, turbidity remained the same after leaching. It is known that most microplastic pollution is caused by surface fragmentation of PET textiles due to the constant shedding of fibres (Jönsson et al., 2018).

Table 2: Water quality parameters after PET and PET fibre fragmentation in different water systems

		PET					
Parameters		pH	pH	Conductivity	Conductivity	Turbidity	Turbidity
		before	after	($\mu\text{S}/\text{cm}$) before	($\mu\text{S}/\text{cm}$) after	(NTU) before	(NTU) after
Model systems	pH 4	4.05	3.98	55.2	44.4	0	0
	pH 7	6.96	6.38	3.42	2.15	0	0
	pH 10	9.95	6.94	6.88	4.54	0	0
Real systems	Tap water	7.66	8.65	453	437	0	0
	Sea water	8.14	8.25	49,400	48,700	0.32	0.33
		PET fibres					
Parameters		pH	pH	Conductivity	Conductivity	Turbidity	Turbidity
		before	after	($\mu\text{S}/\text{cm}$) before	($\mu\text{S}/\text{cm}$) after	(NTU) before	(NTU) after
Model systems	pH 4	4.04	3.89	65.7	60.6	0	0.08
	pH 7	7.03	5.58	3.68	3.30	0	0.23
	pH 10	9.94	6.85	5.66	4.90	0	0.22
Real systems	Tap water	7.66	8.56	453	454	0	0.18
	Sea water	8.14	8.20	49,400	49,600	0.32	0.49

For the liquid phase containing the leached fragments of both plastic materials (PET and PET fibres), COD (Figure 5a), TOC (Figure 5b) and the size of the plastic particles (Figure 5c) were measured. The COD content, as a parameter for the presence of organic material, was greater for PET fibres in all the cases, except for the case of seawater, where the COD was determined to be below 3 mg/L O₂. This result indicates the increased amount of fragmented PET fibres in the filtered liquid phase. On the contrary, for PET samples, similar COD values were measured as in the water bodies, except for the water at pH 10, the value of COD was increased. TOC value, as a measure of the total amount of carbon in organic compounds in water systems, was surprisingly greater in some initial waters (model water with pH 10 and tap water) than after fragmentation. When comparing TOC values for PET and PET fibres, some minor differences were observed in the water bodies, with PET fibres usually having slightly higher values than those of PET. Finally, the dynamic light scattering technique was used to measure the average particle size for both PET plastic fragments in all water bodies. Particle sizes were detected to be in the micron range. Except for samples in model water at pH 4, PET fibre fragments have a higher size distribution in water bodies, with the largest particle sizes found in tap water. The size distribution for PET leached plastics was similar in all water bodies.

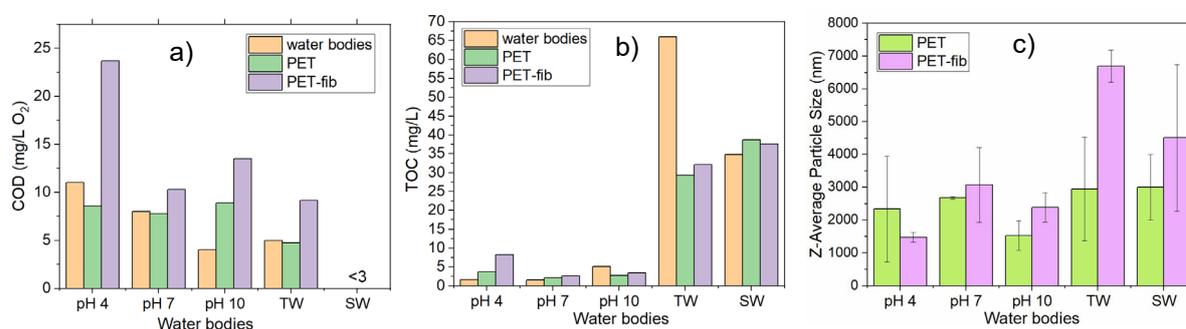


Figure 5: a) COD, b) TOC, and c) particle size of measured samples after fragmentation in water bodies

4. Conclusions

Two different commonly used plastic waste, PET and PET fibres, were exposed to different models and real water systems over one month period to determine their potential fragmentation. Both plastics differed in their

morphology, PET being a solid material and PET fibres being in the form of fibres. Gravimetric analysis of the solid plastics in different water bodies showed a small mass loss of PET after one month, whereas PET fibres lost more mass, especially in seawater. The presence of functional groups revealed no significant changes in the case of PET samples; only PET fibres showed minor changes in the band and the position of the ester group, which can be attributed to a possible oxidation process. With an optical microscope, fragmented micro and nanofibers were detected in all water bodies for samples containing PET fibres, while for PET plastics, no fragmented particles were observed. For the filtered liquid phase, pH values decreased after leaching in model waters, while in real waters, pH values increased. Conductivity mostly decreased for both PET plastics after leaching, except for PET fibres, conductivity slightly increased in real waters. Turbidity is an indicator of released particles after leaching increased only for PET fibres in all water bodies. In addition, COD values increased for almost all PET fibres samples, while for PET samples, they were similar to the values of original water bodies. The largest fragment sizes were determined for samples leached in tap water, especially in the case of PET fibres. The results of this study indicate the importance of plastic waste morphology, as plastic microfibers lead to greater fragmentation in all model and real waters and also have major negative ecological impacts. In the future, the study could focus on fragmentation originating from a promising replacement of petroleum-based plastics with bio-based ones or the use of recycled materials whose mechanical properties can be improved by adding fillers. Another promising option would be to recycle the plastics to minimise contamination. Finally, more attention should be paid to the risks and the ecological footprint, as well as to eco-toxicological measures.

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