# Recyclability of four types of plastics exposed

## to UV irradiation in a marine environment

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#### Abstract

Plastics are the most abundant products in the world and therefore also represent the largest volume of materials found in the sea. Their resistance to degradation makes them dangerous for the marine environment. In this study, the degradation of the four main plastics (Nylon, Polyethylene (PE), Polypropylene (PP), Polyethylene terephthalate (PET)) found in the sea was observed for 6.5 months as they were exposed to UV irradiation in a marine environment. Data on changes in the physical and chemical properties of each of them were collected in order to evaluate the possibilities of material (mechanical) recycling. A thermobalance was used to look for differences in the thermal decomposition of the plastics during this time. In addition, the mechanical properties of each plastic were studied. Results showed that both thermal and mechanical properties were affected, causing a weakening of the material which became less elastic and more rigid. Furthermore, SEM and AFM images were obtained: they

showed cracks, flakes and granular oxidation as well as a loss of homogeneity on the surface of the samples. These changes make mechanical recycling unfeasible, since the quality of the recycled material is insufficient to ensure a high virgin material substitution rate.

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Keywords: Plastics; Degradation; UV irradiation; mechanical properties; marineenvironment; seawater.

The presence of marine debris is a cause for concern for a number of reasons. They are

## 1. Introduction

harmful to organisms and to human health (Coe and Rogers, 1997; Derraik, 2002; 30 Gregory, 2009; Rochman et al., 2013b), they potentially increase the transport of 31 organic and inorganic contaminants (Gaylor et al., 2012; Holmes et al., 2012; Mato et 32 33 al., 2001; Rochman et al., 2013a; Teuten et al., 2009) and provide new habitats and long range delivery of attached organisms to new habitats. In addition, these debris present a 34 hazard to shipping and are aesthetically detrimental, leading to negative socio-economic 35 36 consequences (Mouat et al., 2010). Since the development of the plastics industry, plastic products are the most abundant in 37 the world. Global annual production of plastics is approximately 280 million tons 38 (Koelmans et al., 2014; Rillig, 2012); however, in 2016, 335 million tons of plastic 39 items were produced (PlasticsEurope, 2017). According to published literature, plastic 40 items are the most abundant type of marine litter (Barnes et al., 2009; Landon-Lane, 41 2018; OSPAR, 2007; UNEP-CAR/RCU, 2008; UNEP, 2005, 2009; Vince and Stoett, 42 2018), representing between 60 % to 80% of total marine debris (Gregory and Ryan, 43

- 1997; Niaounakis, 2017a; Sheavly and Register, 2007). Jambeck et al. estimate that
  between 4.8 and 12.7 million tons of this waste ends up in the world's oceans every
  year (Jambeck et al., 2015), of which between 1.15 to 2.41 million tons come from
  rivers(Lebreton et al., 2017). The plastics most frequently found in the marine
  environment are polyethylene (PE), polypropylene (PP), polyethylene terephthalate
  (PET) and Nylon (Heo et al., 2013; Hidalgo-Ruz et al., 2012; Lebreton et al., 2017;
  Martins and Sobral, 2011).
- Plastics are synthetic organic polymers that are malleable and can be moulded into solid objects of different shapes. They are lightweight, inexpensive, strong and durable (Laist, 1987). These properties make them suitable for the manufacturing of a wide range of products (food packaging, household items, shopping bags, facial cleansers...) (Iñiguez et al., 2016), including single use products.

- The main reason plastics are dangerous for the marine environment is their resistance to degradation. The natural decomposition of plastic items in the sea can take hundreds and even thousands of years (Barnes et al., 2009). During this time, chemical contaminants such as polychlorinated biphenyls (PCBs) and dioxins, contained in the plastics are released into the sea (Hahladakis et al., 2018). In addition, the continuous degradation of larger plastics generate microplastics (plastic particles less than 5 mm in diameter), which results in an annual increase in the amount of microplastics in the sea (Andrady, 2011; Wang et al., 2016). These micro-particles also come from primary sources (i.e. microscopic plastics exist in clothes) (Mohamed Nor and Obbard, 2014).
- Degradation is defined as the partial or complete breakdown of a polymer under the influence of several environmental factors such as heat, light, water, mechanical action and microbes (Niaounakis, 2017b). In this way, the environmental conditions to which

- 68 marine plastic debris (MPD) is exposed in various marine habitats (beaches, sea surface,
- 69 water column and seafloor) will accelerate or decelerate degradation. Therefore, the
- decomposition of MPD is less intensive in the sea than on land, because of solar UV
- radiation (seawater is a good heat sink) and mechanical damage (mowing, vehicles, etc).
- 72 In the water column and on the seafloor, MPD degrades very slowly, particularly on the
- 73 seafloor (Andrady, 2000).
- 74 The degradation of most conventional polymers found in the marine environment is
- 75 attributed to the combined action of atmospheric oxygen, sunlight and seawater
- 76 (Andrady, 2005). In this way, plastics undergo five types of degradation in the marine
- 77 environment: hidrolytic degradation, thermooxidative degradation, photodegradation,
- biodegradation and mechanical degradation (Niaounakis, 2017b). The most important
- 79 process in the degradation of plastic debris is considered to be photooxidation, followed
- by mechanical action and thermal oxidation (Niaounakis, 2017b).
- Polyolefins including PE and PP are hydrophobic and are unlikely to hydrolyze in the
- seawater. In general, polymers with pure carbon backbones are resistant to most types
- of degradation, including hydrolysis; polymers with heteroatoms in the backbone
- 84 (polyesters, polyamides and polyurethanes) are highly hydrolysable. Nevertheless, this
- 85 is not true in all cases. PET is an example of polyester, but the aromatic groups it
- 86 contains make this polymer non-degradable under normal conditions (Webb et al.,
- 87 2013). Hydrolysis may not be a significant degradation mechanism for most commonly
- used plastics in the marine environment (Andrady, 2011).
- 89 Oxygen levels and temperatures are the major factors in the initiation of
- 90 thermooxidative degradation of MPD. In the case of seawater, low oxygen content and
- 91 relatively low temperatures inhibit the heat buildup and delay the thermooxidative

degradation of the debris (Andrady, 2011; Pegram and Andrady, 1989). The rate of chemical reaction increases when the temperature is higher, generating greater degradation (Niaounakis, 2017b).

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Photodegradation is the dominant environmental mode of degradation of most of MPD (Niaounakis, 2017b). The UV radiation portion (400-10 nm) of sunlight (Niaounakis, 2017b) plays an important role in plastic degradation through photooxidation. The photooxidative degradation of polymers such as PE, PP and nylon that are exposed to the marine environment begins with UV-B radiation (280-315 nm) in sunlight. During the photodegradation process several polymer changes can be observed as a result of chemical weathering: oxygen-rich functional groups are generated and their molecular weight decreases. The fragmentation rate increases with higher temperatures and oxygen levels (Kershaw, 2015). Normally, photooxidative degradation starts at the outer surface of these plastics (Andrady, 2011) owing to the diffusion-controlled nature of the oxidation reaction (Cunliffe and Davis, 1982), the high UV-B radiation extinction coefficient in plastics, and the presence of fillers that impede oxygen diffusion in the polymer (Qayyum and White, 1993a, b). On plastic surfaces, this deterioration takes the form of pitting, crazing or cracking, discoloration, erosion, or embrittlement. MPD could turn into small pieces (Andrady, 2011; Andrady et al., 1996) because the fragile surface of these plastics is susceptible to fracture by stress, induced by temperature changes or humidity (White and Turnbull, 1994).

The plastics most used commercially such as PP, PET, PE and nylon have very slow biodegradation rates and thus remain semi-permanent when they are disposed of at sea (Andrady, 2000). Microbial species that are rare in nature are necessary for these polymers to be metabolized. Some features that make them resistant to biodegradation are: high molecular weight, high stable C-C and C-H covalent bonds, a highly

hydrophobic nature and the lack of easily oxidisable and/or hydrolysable groups (Gautam et al., 2007; Yang et al., 2014)...

Wave and tide action and abrasion can scratch and fragment the surface of MPD, causing mechanical degradation. Surface alterations in plastic fragments increase polarity as well as the overall surface area and can facilitate the sorption of persistent organic pollutants (POPs) (Fotopoulou and Karapanagioti, 2012, 2015).

Marine debris is collected mostly by boats. In addition, every year, several programs for coastal cleanup such as the International Coastal Cleanup (ICC) are carried out, during which a large amount of marine debris is collected from various coastal areas by numerous volunteers (Iñiguez et al., 2016). However, since 2013, "the Ocean Cleanup" foundation has developed technology to extract plastic waste and keep it from entering ocean waters. The main purpose of this organization is to facilitate the collection of marine debris and to collect larger amounts of debris faster time. Once collected from the sea, the plastic must go through a recycling process.

Plastic recycling has been defined as the process of recovering waste plastics and reprocessing the material to make new useful products (Merrington, 2017). Different forms of recycling exist such as mechanical, chemical and energy recovery recycling. According to some authors, mechanical recycling is the best option for plastic waste treatment when the waste is good enough to make other good quality products from it (Horodytska et al., 2018). For this reason, this study focuses on a recycling process that involves the reuse of plastic rather than its conversion into chemicals or fuels to meet energy needs. This type of recycling has many advantages for the environment and therefore contributes to quality of life. Some of the most important advantages of this process are as follow: the amount of waste drops; raw as well as natural material is

saved, energy and economic resources are saved; greenhouse gas emissions from the manufacturing of plastic are reduced.

Several factors greatly influence the recycling process such as: contaminants, molecular weight, mechanical properties and colour/transparency of the material, among others (Merrington, 2017). If these characteristics are very different from those of the virgin material, they will negatively affect the quality of the final product; this type of recycling would in that case not be advisable.

Following this line of research, this study focuses on the degradation of the four most common polymers found in the sea and examines the similarities and discrepancies in the degradation process of each polymer. The degradation of PP, PE, PET and Nylon in marine environment conditions (submerged in seawater and under UV irradiation) was observed. Data on the changes in some properties were collected over 6.5 months, and comparisons of the four plastics were also performed, in order to assess the recyclability of the different materials.

## 2. Materials and methods

### 2.1. Materials and experimental setting

The degradation of the four most common polymers found in the sea (PE, PP, PET and Nylon), was studied. These plastics came from used items such as cans, water bottles, etc.; they were not virgin materials. The seawater used was extracted from the Mediterranean Sea and two UV lamps TUV PL-L 36W/4P (UVC 250) were selected to simulate natural sunlight.

First, the samples were directly cut (in pieces large enough to later constitute rectangular specimens 60 mm long, 10 mm wide and approximately 1 mm thick) and

placed in glass vessels (1 L) containing seawater. The glass vessels were then transferred into a homemade environmental chamber (Figure 1) (62 cm x 32.5 cm x 42.5 cm in length, width and height respectively) that was equipped with two UV lamps (TUV PL-L 36W/4P) over a total period of 6.5 months. During this time, different samples were taken to measure changes in some of their properties. Specifically, samples were taken at 1.5, 2.5, 4.5 and 6.5 months, and were compared to the plastics before the treatment. In addition, every week, seawater in contact with the plastics was discarded and replaced with new seawater, to maintain the surrounding water's salinity approximately constant throughout the experiment and to compensate for losses due to evaporation.

## 2.2. Tensile test

this, a sample preparation was necessary. The different polymeric materials were made into rectangular specimens 60 mm long, 10 mm wide and approximately 1 mm thick,

The tensile test was suitable for determining each plastic's mechanical properties. For

except for the PE, which was less thick (around 0.7 mm).

Tensile mechanical tests were carried out using an Instron 3344 Universal Test instrument (MA, USA) equipped with a 2000N load cell following ASTM D882-12 (ASTM, 2012) and UNE-EN ISO 527-3 (UNE-EN ISO, 1996) standard recommendations. The rectangular specimens were clamped at a fixed distance of 20 mm between the grips and the slack was removed before the tests. The pressure and speed conditions used were 2.5 bar and 5 mm/s, respectively. To test the reproducibility of the results, six specimens from the sample were tested. The tensile properties studied were tensile strength at break, tenacity and Young's modulus.

#### **2.3. TG runs**

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- In order to better understand the decomposition behaviour of these plastics in the sea,
- thermogravimetric runs were performed.
- 191 Runs for the TG analysis were carried out on a Mettler Toledo
- 192 TGA/SDTA851e/SF/1100 Thermal Gravimetric Analyzer. The decomposition
- temperatures were measured under dynamic conditions in nitrogen atmosphere with a
- total flow rate of 100 mL min<sup>-1</sup>. The experiments were carried out at 10 K min<sup>-1</sup>, at a
- room temperature up to 1173 K. For each run,  $4.0 \pm 0.3$  mg of sample were used.

## 2.4. SEM analyses

- The surface textures of the plastics after the degradation process were clearly illustrated
- through SEM images. Thus, a representative sample of each polymer was studied by
- scanning electron microscopy (SEM) on a Hitachi-S3000N microscope before and after
- 200 6.5 months in marine water and under the UV lamp. Due to the degraded plastic's
- 201 heterogeneous surface texture, the visualization was repeated at different surface sites of
- the materials. In addition, a comparison of the changes in the surface textures between
- both polymer samples (before and after the treatment) was performed.

### 2.5. AFM analyses

- The topography and the roughness of the surface material were analysed using a NT-
- 206 MDT/INTEGRA PRIMA atomic force microscope (AFM) equipped with a steel
- cantilever. To obtain high resolution images, the cantilever has a sharp tip Tap300DLC
- 208 (Budget Sensors) covered with diamond. The analysis was carried out at room
- 209 temperature. The studied area and the scan speed were 10 x 10 μm and 20 μm·s<sup>-1</sup>,
- 210 respectively.

First, a sample preparation was necessary. The samples were cut into small pieces which were fixed with double layer tape on a glass slide in view of fixing them to the support. Thus, these samples were introduced under the microscope. Before starting the analysis, an air flow was used to remove dust from the samples.

Two different scans were performed at different locations for each sample. Phase images and both two-dimensional (2D) and three-dimensional (3D) imaging of the surface topographies were derived from these analyses. The topographic images were obtained using the operation mode 'Tapping' or 'semi-contact', the cantilever oscillation amplitude remaining constant. Phase images are useful when analysing heterogeneous polymer systems with domains that have different mechanical properties. It is possible to determine the phase difference between the sample's disturbing signal (cyclical deformation of the cantilever) when interacting and not interacting with the surface of the sample. Viscoelastic materials undergo deformations as a function of time in case of mechanical disturbance, and the deformation depends on the type of material.

## 3. Results and discussion

### 3.1. Tensile test

As mentioned above, the tensile properties of different materials before and after the degradation process were determined. Table 1 presents the tensile strength at break, tenacity and Young's modulus. The samples taken at 1.5 and 2.5 months did not show significant differences with respect to the untreated material, so they were not included in Table 1 nor are they included in the rest of the results.

As degradation progressed, results showed an increase in Young'modulus in all cases, indicating polymer loss of elasticity. According to these values, the materials' tenacity

decreased, which means the polymers's rigidity increased. These results are consistent with findings since once these plastics are degraded, they become embrittled and break more easily (Niaounakis, 2017b). PET and PP were the most affected materials.

Due to the fact that the original material was less thick, it was not possible to make PE specimens equal to those of the rest of materials. Consequently, the PE specimens were slightly less thick (< 1 mm) and the results obtained in these analyses were a little different from the results obtained for the other polymers.

#### 3.2. Thermogravimetric runs

and untreated material.

The evolution of the thermal behaviour of the plastic materials was followed by thermogravimetry. Samples were subjected to decomposition in the thermobalance at 10 K·min<sup>-1</sup> and were finally compared. As mentioned earlier, nitrogen was used as a carrier gas to test the samples' behaviour in pyrolytic conditions (Iñiguez et al., 2017). Measures were duplicated to test reproducibility, which was found to be very good.

As can be observed, all plastics were affected by contact with marine water and UV radiation (Figure 2). In general, thermal properties were affected, causing a weakening of the plastic over time. This was an expected behaviour, as degradation was facilitated as the polymer was subjected to the degradation process (seawater and UV radiation). An increase in weight at time infinity was also observed, indicating that the inert fraction was continuously increasing during the UV treatment. PE was the most affected sample, showing a very different TG-curve from the beginning of the treatment. The TG

curve of the Nylon was the least affected, revealing small differences between treated

Decomposition began at a lower temperature when the material was partially degraded by the UV, but in some runs the initial decomposition rate was lower. In this way, the Tmax (temperature at which the decomposition rate is maximum) may have increased in some samples, going from 429.6 °C (original Nylon) to 427.9 °C (sample taken at 6.5 months), 451.2 °C (Original PE) to 466.8 °C (sample taken at 6.5 months), 419.1 °C (original PET) to 429.6 °C (sample taken at 6.5 months) and 435.3 °C (original PP) to 447.5 °C (sample taken at 6.5 months).

These results can be compared with those from a previous study performed in our laboratory, in which the pyrolysis and combustion of the same four plastics submerged in marine water (without UV radiation) over 12 months were analysed (Iñiguez et al., 2018). According to Font et al., the presence of inert atmosphere can be found to decelerate decomposition (Font et al., 2005; Iñiguez et al., 2018).

## 3.3. Changes in surface textures

SEM images of the plastics treated by UV irradiation in marine environments before and after 6.5 months were obtained. The most representative images have been included in Figure 3. As shown in this Figure, all four types of original plastics showed relatively homogeneous and compact textures. In contrast, the weathered plastics presented relatively rough surface textures.

In the case of Nylon, PE and PET, granular oxidation and flakes were found on their surfaces after the treatment. Moreover, the treated PP presented clear cracks. All these characteristics (granular oxidation, flakes and cracks) constitute degradation patterns (Cai et al., 2018), some of which have been marked with a circle in Figure 3. However, based on the observation of the degradation patterns of the four types of polymers, it

- was found that crack patterns did not appear on the PET surface, which could be relatedto insufficient UV exposure time.
- These results are compatible with those of previous studies: Song et al. showed that
- crack patterns appeared on PE after 6.5 months of UV exposure (Song et al., 2017)
- while Cai et al. (Cai et al., 2018) showed that PE did not produce any crack patterns
- after 3 months under UV radiation in a marine environment.
- 285 Photo-oxidative degradation was the main reason for the formation of cracks (Cai et al.,
- 286 2018). Our results showed accordingly that cracks and flakes constituted the leading
- degradation patterns after the chemical weathering of these plastic samples. It can thus
- be assumed that larger plastic pieces experience further fragmentation in the marine
- environment and generate microplastics.
- In the same way, the topography and the roughness of the material's surface were also
- analysed by atomic force microscopy (AFM). The most representative images of each
- 292 material have been included in this article. Figure 4 shows phase images and two-
- 293 dimensional (2D) and three-dimensional (3D) imaging of the surface topographies of
- 294 PET, before and after 6.5 months under a UV lamp and submerged in seawater. Figures
- 295 A1, A2 and A3 (Appendix A. Supplementary material) show the images for the other
- three polymers (Nylon, PE and PP respectively).
- 297 The 2D images showed the topography of heights, in which the topography of the
- 298 sample was directly observed. However, these images did not provide much
- 299 information. This may be because the surfaces of all polymers had a certain inclination,
- as can be seen in the 3D images (Bajpai et al., 2016). On the other hand, the phase
- images provided information on surface homogeneity (Jin et al., 2018). As illustrated,
- all plastics showed fairly homogeneous surfaces before the treatment. In contrast, areas

with different mechanical properties appeared in the treated samples (Jin et al., 2018). The darker colour in the images shows the areas of greater hardness in each material, and these areas predominated in the original polymers. Thus, Figures 4, A1, A2 and A3 show that all polymer surfaces were affected by the degradation process, which is consistent with the SEM images.

Horodytska et al. (Horodytska et al., 2018) show that mechanical recycling should be the number one option for plastic waste treatment when the quality of the recycled material is good enough to ensure a high virgin material substitution rate. Nevertheless, the changes observed in the present study make it difficult to use plastics from a marine environment for mechanical recycling, so other treatment processes - chemical recycling and/or energy recovery - (Hahladakis et al., 2018) should be preferred.

## 4. Conclusions

In this work, the four plastics most commonly found in the sea (Nylon, PE, PET and PP) were exposed to UV irradiation in a marine environment for 6.5 months. During that time, all the materials' mechanical properties were affected, indicating a clear loss of elasticity and an increase in the rigidity of each of them.

In general, the thermal properties of these polymers were affected, causing a weakening of the material over time. The degradation of all these samples was easier after the treatment. In addition, cracks, flakes and granular oxidation were common degradation patterns in the chemical weathering of the plastics. In particular, Nylon, PE and PET presented granular oxidation and flakes on their surfaces, and PP showed clear cracks after the treatment.

Moreover, all the plastics before the treatment showed surfaces that were fairly homogeneous. In contrast, areas with different mechanical properties were found in the treated samples. This implies that all polymer surfaces were affected by the degradation process.

In view of obtained results, it is logical to deduce that most plastics extracted from the sea are highly degraded. For this reason, using these materials for mechanical recycling is not feasible. Other treatment processes for this type of plastic waste should thus be used, such as energy recovery. It was difficult to judge which material was the most degraded, but to a greater or lesser degree, all four materials were affected by this degradation process. The level of weathering the samples were subjected to increased with exposure time, and was practically nil during the first two to three months. In this way, salinity, exposure time, UV light and levels of exposure to oxygen were important factors affecting the plastic samples' degree of degradation. However, further research on the degradation processes of plastics in the environment is required. This would increase our knowledge about the source and fate of microplastics and would help us to evaluate the environmental risk for organisms.

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## 6. References

- 349 Andrady, A.L., 2000. Plastics and their impacts in the marine environment. In: Proceedings of
- 350 the International Marine Debris Conference on Derelict Fishing Gear and the Ocean
- 351 Environment, 6–11 August 2000, Honolulu, Hawaii.
- 352 Andrady, A.L., 2005. Plastics in the marine environment: a technical perspective. In:
- 353 Proceedings of the Plastic Debris Rivers to Sea Conference. Long Beach, California: Algalita
- 354 Marine Research Foundation.
- Andrady, A.L., 2011. Microplastics in the marine environment. Marine Pollution Bulletin 62,
- 356 1596-1605.

- 357 Andrady, A.L., Pegram, J.E., Searle, N.D., 1996. Wavelength sensitivity of enhanced
- 358 photodegradable polyethylenes, ECO, and LDPE/MX. Journal of Applied Polymer Science 62,
- 359 1457-1463.
- 360 ASTM, 2012. Standard Test Method for Tensile Properties of Thin Plastic Sheeting, D882-12.
- 361 ASTM International, West Conshohocken, PA.
- Bajpai, A.K., Bhatt, R., Katare, R., 2016. Atomic force microscopy enabled roughness analysis of
- nanostructured poly (diaminonaphthalene) doped poly (vinyl alcohol) conducting polymer thin
- 364 films. Micron 90, 12-17.
- Barnes, D.K.A., Galgani, F., Thompson, R.C., Barlaz, M., 2009. Accumulation and fragmentation
- of plastic debris in global environments. Philosophical Transactions of the Royal Society of
- 367 London B: Biological Sciences 364, 1985-1998.
- Cai, L., Wang, J., Peng, J., Wu, Z., Tan, X., 2018. Observation of the degradation of three types
- of plastic pellets exposed to UV irradiation in three different environments. Science of The
- 370 Total Environment 628-629, 740-747.
- 371 Coe, J.M., Rogers, D.E., 1997. Marine Debris: Sources, Impacts and Solutions. Springer, New
- 372 York.
- 373 Cunliffe, A.V., Davis, A., 1982. Photo-oxidation of thick polymer samples—Part II: The influence
- 374 of oxygen diffusion on the natural and artificial weathering of polyolefins. Polymer
- 375 Degradation and Stability 4, 17-37.
- 376 Derraik, J.G.B., 2002. The pollution of the marine environment by plastic debris: a review.
- 377 Marine Pollution Bulletin 44, 842-852.
- Font, R., Fullana, A., Conesa, J., 2005. Kinetic models for the pyrolysis and combustion of two
- types of sewage sludge. Journal of Analytical and Applied Pyrolysis 74, 429-438.
- Fotopoulou, K.N., Karapanagioti, H.K., 2012. Surface properties of beached plastic pellets.
- 381 Marine Environmental Research 81, 70-77.
- 382 Fotopoulou, K.N., Karapanagioti, H.K., 2015. Surface properties of beached plastics.
- 383 Environmental Science and Pollution Research 22, 11022-11032.
- 384 Gautam, R., Bassi, A.S., Yanful, E.K., 2007. A review of biodegradation of synthetic plastic and
- foams. Applied Biochemistry and Biotechnology 141, 85-108.
- 386 Gaylor, M.O., Harvey, E., Hale, R.C., 2012. House crickets can accumulate polybrominated
- 387 diphenyl ethers (PBDEs) directly from polyurethane foam common in consumer products.
- 388 Chemosphere 86, 500-505.
- 389 Gregory, M.R., 2009. Environmental implications of plastic debris in marine settings—
- 390 entanglement, ingestion, smothering, hangers-on, hitch-hiking and alien invasions.
- 391 Philosophical Transactions of the Royal Society of London B: Biological Sciences 364, 2013-
- 392 2025.
- 393 Gregory, M.R., Ryan, P.G., 1997. Pelagic Plastics and Other Seaborne Persistent Synthetic
- 394 Debris: A Review of Southern Hemisphere Perspectives, in: Coe, J., Rogers, D. (Eds.), Marine
- 395 Debris. Springer New York, pp. 49-66.

- Hahladakis, J.N., Velis, C.A., Weber, R., Iacovidou, E., Purnell, P., 2018. An overview of chemical
- 397 additives present in plastics: Migration, release, fate and environmental impact during their
- use, disposal and recycling. Journal of Hazardous Materials 344, 179-199.
- Heo, N., Hong, S., Han, G., Hong, S., Lee, J., Song, Y., Jang, M., Shim, W., 2013. Distribution of
- 400 small plastic debris in cross-section and high strandline on Heungnam beach, South Korea.
- 401 Ocean Science Journal 48, 225-233.
- 402 Hidalgo-Ruz, V., Gutow, L., Thompson, R.C., Thiel, M., 2012. Microplastics in the Marine
- 403 Environment: A Review of the Methods Used for Identification and Quantification.
- 404 Environmental Science & Technology 46, 3060-3075.
- 405 Holmes, L.A., Turner, A., Thompson, R.C., 2012. Adsorption of trace metals to plastic resin
- 406 pellets in the marine environment. Environmental Pollution 160, 42-48.
- 407 Horodytska, O., Valdés, F.J., Fullana, A., 2018. Plastic flexible films waste management A
- 408 state of art review. Waste Management.
- 409 Iñiguez, M.E., Conesa, J.A., Fullana, A., 2016. Marine debris occurrence and treatment: A
- 410 review. Renewable and Sustainable Energy Reviews 64, 394-402.
- 411 Iñiguez, M.E., Conesa, J.A., Fullana, A., 2017. Pollutant content in marine debris and
- 412 characterization by thermal decomposition. Marine Pollution Bulletin 117, 359-365.
- 413 Iñiguez, M.E., Conesa, J.A., Soler, A., 2018. Effect of marine ambient in the production of
- 414 pollutants from the pyrolysis and combustion of a mixture of plastic materials. Marine
- 415 Pollution Bulletin 130, 249-257.
- Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., Law,
- 417 K.L., 2015. Plastic waste inputs from land into the ocean. Science 347, 768-771.
- 418 Jin, S., Shi, Q., Li, Q., Ou, L., Ouyang, K., 2018. Effect of calcium ionic concentrations on the
- 419 adsorption of carboxymethyl cellulose onto talc surface: Flotation, adsorption and AFM
- 420 imaging study. Powder Technology 331, 155-161.
- 421 Kershaw, P., 2015. Biodegradable plastics and marine litter: misconceptions, concerns and
- 422 impacts on marine environments.
- 423 Koelmans, A.A., Gouin, T., Thompson, R., Wallace, N., Arthur, C., 2014. Plastics in the marine
- 424 environment. Environmental Toxicology and Chemistry 33, 5-10.
- 425 Laist, D.W., 1987. Overview of the biological effects of lost and discarded plastic debris in the
- 426 marine environment. Marine Pollution Bulletin 18, 319-326.
- 427 Landon-Lane, M., 2018. Corporate social responsibility in marine plastic debris governance.
- 428 Marine Pollution Bulletin 127, 310-319.
- Lebreton, L.C.M., van der Zwet, J., Damsteeg, J.-W., Slat, B., Andrady, A., Reisser, J., 2017. River
- plastic emissions to the world's oceans. Nature Communications 8, 15611.
- 431 Martins, J., Sobral, P., 2011. Plastic marine debris on the Portuguese coastline: A matter of
- 432 size? Marine Pollution Bulletin 62, 2649-2653.
- 433 Mato, Y., Isobe, T., Takada, H., Kanehiro, H., Ohtake, C., Kaminuma, T., 2001. Plastic Resin
- Pellets as a Transport Medium for Toxic Chemicals in the Marine Environment. Environmental
- 435 Science & Technology 35, 318-324.
- 436 Merrington, A., 2017. 9 Recycling of Plastics, in: Kutz, M. (Ed.), Applied Plastics Engineering
- 437 Handbook (Second Edition). William Andrew Publishing, pp. 167-189.
- 438 Mohamed Nor, N.H., Obbard, J.P., 2014. Microplastics in Singapore's coastal mangrove
- ecosystems. Marine Pollution Bulletin 79, 278-283.
- 440 Mouat, J., Lopez Lozano, R., Bateson, H., 2010. Economic impacts of marine litter.
- 441 Kommunenes Internasjonale Miljøorganisasjon (KIMO International), UK.
- 442 Niaounakis, M., 2017a. 1 The Problem of Marine Plastic Debris, in: Niaounakis, M. (Ed.),
- 443 Management of Marine Plastic Debris. William Andrew Publishing, pp. 1-55.
- 444 Niaounakis, M., 2017b. 3 Degradation of Plastics in the Marine Environment, Management of
- 445 Marine Plastic Debris. William Andrew Publishing, pp. 127-142.
- OSPAR, 2007. OSPAR Pilot Project on Monitoring Marine Beach Litter: Monitoring of marine
- litter on beaches in the OSPAR region. OSPAR Commission, London.

- Pegram, J.E., Andrady, A.L., 1989. Outdoor weathering of selected polymeric materials under
- marine exposure conditions. Polymer Degradation and Stability 26, 333-345.
- 450 PlasticsEurope, 2017. Plastics- the Facts 2017. An analysis of European plastics production,
- demand and waste data. Available at: www.plasticseurope.org.
- 452 Qayyum, M.M., White, J.R., 1993a. Effect of stabilizers on failure mechanisms in weathered
- 453 polypropylene. Polymer Degradation and Stability 41, 163-172.
- 454 Qayyum, M.M., White, J.R., 1993b. Effect of stabilizers on residual stresses in weathered
- 455 polyethylene. Polymer Degradation and Stability 39, 199-205.
- 456 Rillig, M.C., 2012. Microplastic in Terrestrial Ecosystems and the Soil? Environmental Science &
- 457 Technology 46, 6453-6454.
- 458 Rochman, C.M., Hoh, E., Hentschel, B.T., Kaye, S., 2013a. Long-Term Field Measurement of
- 459 Sorption of Organic Contaminants to Five Types of Plastic Pellets: Implications for Plastic
- 460 Marine Debris. Environmental Science & Technology 47, 1646-1654.
- 461 Rochman, C.M., Manzano, C., Hentschel, B.T., Simonich, S.L.M., Hoh, E., 2013b. Polystyrene
- 462 Plastic: A Source and Sink for Polycyclic Aromatic Hydrocarbons in the Marine Environment.
- 463 Environmental Science & Technology 47, 13976-13984.
- Sheavly, S.B., Register, K.M., 2007. Marine Debris & Plastics: Environmental Concerns, Sources,
- 465 Impacts and Solutions. Journal of Polymers and the Environment 15, 301-305.
- 466 Song, Y.K., Hong, S.H., Jang, M., Han, G.M., Jung, S.W., Shim, W.J., 2017. Combined Effects of
- 467 UV Exposure Duration and Mechanical Abrasion on Microplastic Fragmentation by Polymer
- 468 Type. Environmental Science & Technology 51, 4368-4376.
- Teuten, E.L., Saquing, J.M., Knappe, D.R.U., Barlaz, M.A., Jonsson, S., Björn, A., Rowland, S.J.,
- 470 Thompson, R.C., Galloway, T.S., Yamashita, R., Ochi, D., Watanuki, Y., Moore, C., Viet, P.H.,
- 471 Tana, T.S., Prudente, M., Boonyatumanond, R., Zakaria, M.P., Akkhavong, K., Ogata, Y., Hirai,
- 472 H., Iwasa, S., Mizukawa, K., Hagino, Y., Imamura, A., Saha, M., Takada, H., 2009. Transport and
- 473 release of chemicals from plastics to the environment and to wildlife. Philosophical
- 474 Transactions of the Royal Society of London B: Biological Sciences 364, 2027-2045.
- 475 UNE-EN ISO, 1996. PLASTICS. DETERMINATION OF TENSILE PROPERTIES. PART 3: TEST
- 476 CONDITIONS FOR FILMS AND SHEETS, 527-3:1996. AENOR.
- 477 UNEP-CAR/RCU, 2008. Marine Litter in the Wider Caribbean Region: A Regional Overview.
- 478 United Nations Environment Programme, Nairobi, p. 81.
- 479 UNEP, 2005. Marine Litter an Analytical Overview. United Nations Environment Programme,
- 480 Kenya, p. 47.
- 481 UNEP, 2009. Marine Litter: A Global Challenge. Nairobi: UNEP, 232
- Vince, J., Stoett, P., 2018. From problem to crisis to interdisciplinary solutions: Plastic marine
- 483 debris. Marine Policy.
- Wang, J., Tan, Z., Peng, J., Qiu, Q., Li, M., 2016. The behaviors of microplastics in the marine
- environment. Marine Environmental Research 113, 7-17.
- Webb, H., Arnott, J., Crawford, R., Ivanova, E., 2013. Plastic Degradation and Its Environmental
- 487 Implications with Special Reference to Poly(ethylene terephthalate). Polymers 5, 1.
- 488 White, J.R., Turnbull, A., 1994. Weathering of polymers: mechanisms of degradation and
- 489 stabilization, testing strategies and modelling. Journal of Materials Science 29, 584-613.
- 490 Yang, J., Yang, Y., Wu, W.-M., Zhao, J., Jiang, L., 2014. Evidence of Polyethylene Biodegradation
- 491 by Bacterial Strains from the Guts of Plastic-Eating Waxworms. Environmental Science &
- 492 Technology 48, 13776-13784.

# TABLE LEGENDS Table 1. Mechanical properties of Nylon, PE, PET and PP before and after 4.5 and 6.5 months submerged in marine water and under UV lamp. (Speed = 5 mm/s).

# FIGURE CAPTIONS Figure 1. Experimental setup. Dimensions of homemade environmental chamber equipped with two UV lamps (TUV PL-L 36W/4P). Figure 2. Thermal decomposition of the plastic materials at different time after being submerged in marine water and under UV lamp. Figure 3. SEM images of the four types of plastics. a) SEM images of the four original plastics; b) SEM images of the four weathered plastics (treated under UV radiation and submerged in seawater during 6.5 months). Figure 4. AFM images of PET before and after 6.5 months in seawater and under UV lamp. a) 2D surface topography; b) 3D surface topography; c) Phase images.

Table 1. Mechanical properties of Nylon, PE, PET and PP before and after 4.5 and 6.5 months submerged in marine water and under UV lamp.(Speed = 5 mm/s).

Material	Strain at break	Tensile strength at break (MPa)	Young's modulus (MPa)	Tenacity (MPa)
Nylon Nylon UV_4,5	0.178	136	1312	14
months Nylon UV_6,5	0.133	197	1616	15
months	0.129	208	1677	15
PE PE UV_4,5	2	25	286	46
months PE UV_6,5	0.522	16	443	12
months	0.501	6	560	9
PET UV_4,5	0.328	53	1772	11
months PET UV_6,5	0.171	95	3193	13
months	0.174	109	4269	13
PP PP UV_4,5	0.130	33	955	146
months PP UV_6,5	0.008	12	1680	0.098
months	0.016	23	1688	0.218

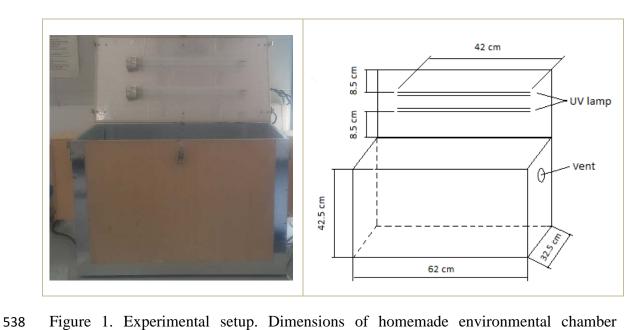


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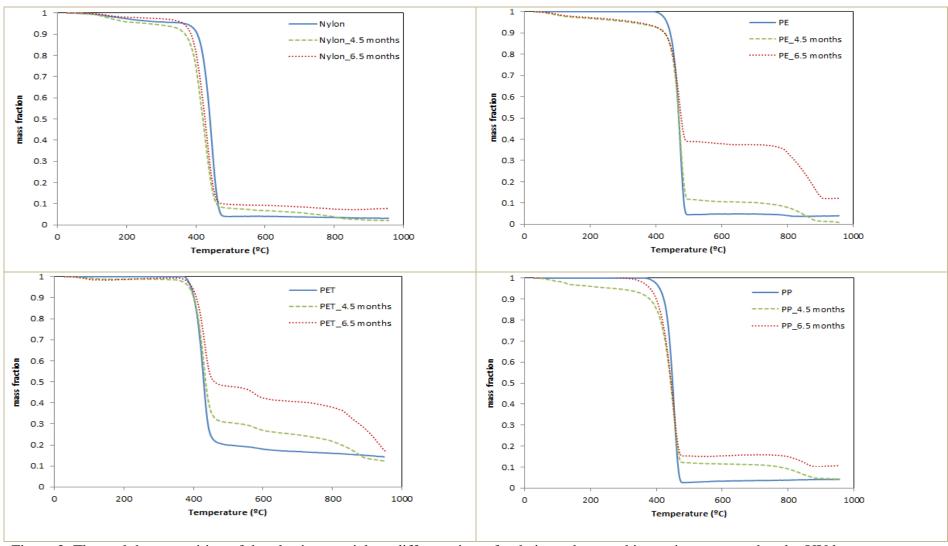


Figure 2. Thermal decomposition of the plastic materials at different time after being submerged in marine water and under UV lamp.

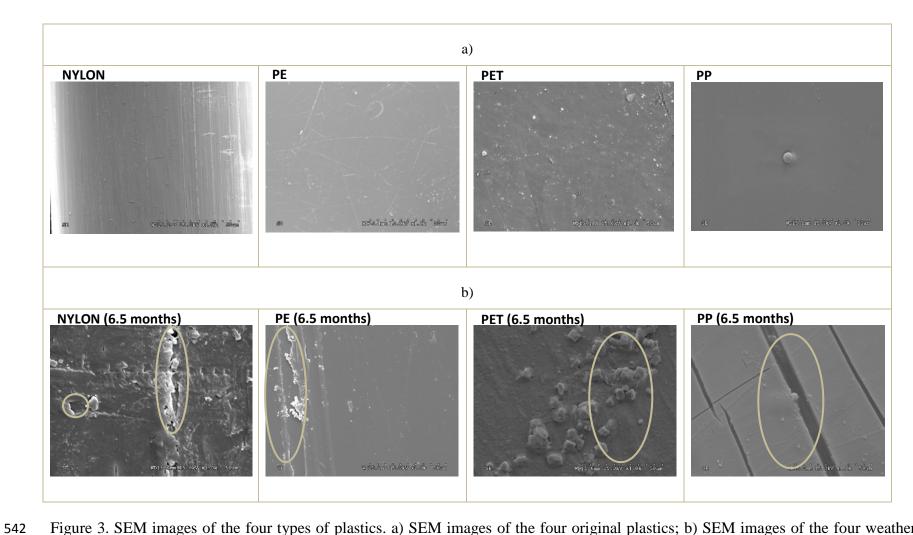


Figure 3. SEM images of the four types of plastics. a) SEM images of the four original plastics; b) SEM images of the four weathered plastics (treated under UV radiation and submerged in seawater during 6.5 months).

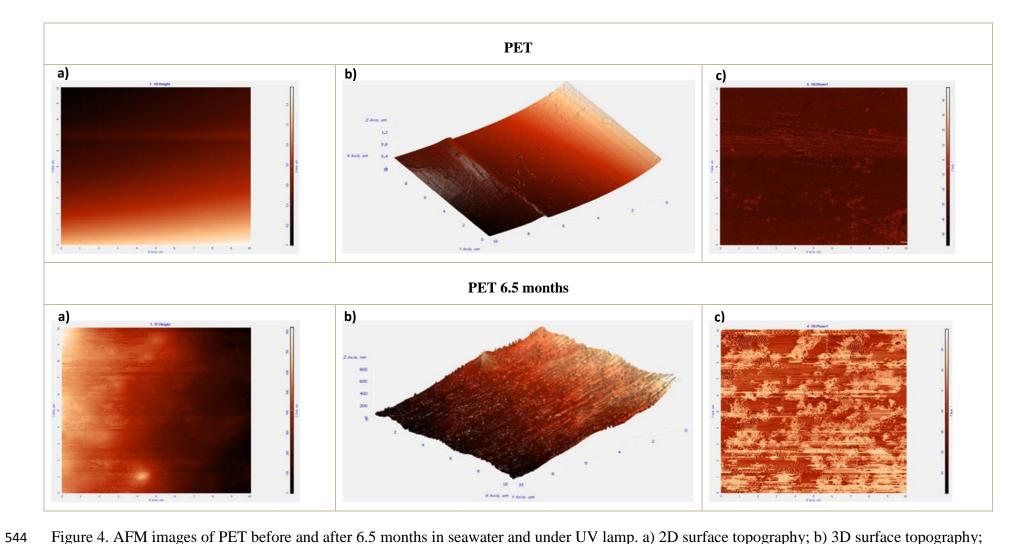


Figure 4. AFM images of PET before and after 6.5 months in seawater and under UV lamp. a) 2D surface topography; b) 3D surface topography; c) Phase images.