Plastic waste from marine environment: Demonstration of possible routes for recycling by different manufacturing technologies

F. Ronkay [a,b], B. Molnar [a,b], D. Gere [a], T. Czigany [a,c,*]

[a] Department of Polymer Engineering, Faculty of Mechanical Engineering, Budapest University of Technology and Economics, H-1111 Budapest, Muegyetem rkp. 3, Hungary
[b] Imsys Ltd, Material Testing Laboratory, Mozaik Street 14/A, H-1033 Budapest, Hungary
[c] MTA-BME Research Group for Composite Science and Technology, H-1111 Budapest, Muegyetem rkp. 3, Hungary

ABSTRACT

The increasing amount of marine plastic waste poses challenges including, not only the collection, but also the subsequent recyclability of the plastic. An artificial accelerated weathering procedure was developed, which modelled the marine environment and investigated the recyclability of weathered and non-weathered PET. Marine conditions were simulated for poly(ethylene terephthalate) (PET) bottle material and high-density polyethylene (HDPE) cap material. It consisted of 2520 h cyclical weathering, alternating the sample between a salt spray and a Xenon-chamber—this corresponds to roughly 3–4 years on the surface of an ocean.

It was proved that the molecular weight of PET is a function of weathering time and can be described mathematically. Microscopic examination of the surface of the PET bottles and HDPE caps proved that these surfaces were damaged. After weathering, manufacturing tests were performed on the PET material by extrusion, injection moulding, 3D printing and thermoforming. Quantitative comparison between products manufactured by the same technology was performed in order to compare the qualities of products made from original PET, non-weathered PET waste, which was the example of classical recycling, and weathered PET. In the case of products made from weathered PET, certain mechanical and optical properties (e.g. impact strength and transparency) were significantly impaired compared to the original PET and the recycled, non-weathered PET. Certain other properties (e.g. strength and rigidity) did not change significantly. It was proved that the samples from weathered plastic material can be successfully recycled mechanically and used to manufacture plastic products.

1. Introduction

1.1. Background

The population of the world is constantly increasing; at the moment it is 7.7 billion (United Nations, 2019). However, it is predicted that Earth cannot support more than 10 billion people if the current trends continue (Kin et al., 2019; Taagepera, 2014; United Nations, 2019). It has been estimated that 6789 million metric tons of non-fiber plastics were produced between 1950 and 2017, and production is growing every year (Geyer et al., 2017; Nova-Institut, 2015). Much of the plastic is used for packaging, which becomes waste very quickly. Between 1950 and 2015, about 6300 million metric tons of primary and secondary (recycled)

waste was produced, of which only 9% was recycled, 12% was incinerated and 79% was deposited in waste dumps or simply thrown away illegally. Thanks to selective waste collection, less and less recyclable waste goes to landfill (Geyer et al., 2017), but it is very important that as much collected waste as possible is recycled (Czigany, 2020). Unfortunately, due to irresponsible behaviour, much of the waste is still deposited or thrown away in the environment (Tuffi et al., 2018).

1.2. Marine debris – Statistical background

Much data can be found in the literature about the composition of marine debris; plastic waste is 40–80% of the total amount of marine waste (see Supplementary Table S1), but only this is in the limelight because much of the plastic waste floats on the surface of the water, while other waste sinks to the bottom of the sea (Polasek et al., 2017; Schneider et al., 2018; Bergmann and

* Corresponding author at: Department of Polymer Engineering, Faculty of Mechanical Engineering, Budapest University of Technology and Economics, H-1111 Budapest, Muegyetem rkp. 3, Hungary.

E-mail address: czigany@eik.bme.hu (T. Czigany).

Klages, 2012; Pham et al., 2014; Coe and Rogers, 1997; Iñiguez et al., 2016).

The first articles on oceanic plastic waste were published in the early 1970s (Jambeck et al., 2015; Law, 2017). The importance of this topic has increased considerably in the past decades. The number of publications with the keywords "marine plastics debris" has greatly increased since 1975. It is mentioned in these studies that most of this marine debris originates from dry land (Andrady, 2011; Jambeck et al., 2015; PlasticsEurope, 2018). The majority of plastic waste enters the oceans through rivers between May and October; the 20 most polluted rivers are responsible for two-thirds of all marine debris (Lebreton et al., 2017). Roughly 18% of marine plastic debris is attributed to the fishing industry, therefore marine plastic waste is divided into two main categories: waste connected to fishing (buoys, lines, nets and other fishing gear) and consumer plastic waste (buckets, bottles, foamed polystyrene, bags/films and miscellaneous plastics) (Andrady, 2011; Eriksen et al., 2014; Galimany et al., 2019). The literature lists different data about the amount and location of oceanic plastic waste (see Supplementary Table S2).

Several research projects have found that about 70% of plastic waste is at the bottom of the sea, 15% floats on the surface of the water and 15% is on seashores (Iñiguez et al., 2016; PlasticsEurope, 2018; Whitacre, 2012).

Waste with a density higher than that of seawater (e.g. glass, metals, rubber, PVC, PS) sinks to the bottom of the sea, while waste lighter than seawater floats on the surface (e.g. PE, PP, or PET bottles with air in them) (PlasticsEurope, 2018; Simeonova and Chuturkova, 2019). However, materials with a lower density than that of seawater can sink in the water, ending up in deep water or in the sediment, as deposits on floating plastic (e.g. seashells, algae and sea plants) can, after a time, increase apparent density to above that of seawater (Andrady, 2017; Cózar et al., 2014; Fazey and Ryan, 2016; Woodall et al., 2014; Ye and Andrady, 1991).

The type and proportion of plastics (PE, PP, PVC, PS, PET, PA) in marine plastic waste and its form (e.g. bottles, film, textile) is only estimated in most research (Andrady, 2017; Hidalgo-Ruz et al., 2012; Iñiguez et al., 2018; Li et al., 2016); a review article summarised 104 articles in which 259,822 metric tons of marine debris was collected with 16 different methods of collection (Schneider et al., 2018) but the composition of the waste was not examined. The estimates may be based on the fact that a very large proportion of plastics (42%) is used by the packaging industry, therefore its lifetime is only a few months so it become waste very quickly (Gere and Czigány, 2018; Geyer et al., 2017). Also, PE, PP and PA (nylon) are used most in the fishing industry (Andrady, 2011). Cellulose acetate (the material of cigarette filters) can be found in considerable amounts on seashores (Iñiguez et al., 2016).

The literature also often classifies marine debris by size. The most common classification is microplastics, mesoplastics and macroplastics, but the size ranges of these are not uniform. For example, microplastic is defined differently; some researchers call plastic particles smaller than 5 mm microplastics, while others define microplastics as plastic particles smaller than 0.5 mm (Andrady, 2011, 2017; Hartmann et al., 2019). Nowadays most research is focused on the origin, properties and effects of microplastics. According to the literature, (Andrady, 2011; Dauvergne, 2018) there are two kinds: primary and secondary microplastics. Primary microplastics are microbeads mostly used in cosmetics and in industrial abrasives as synthetic 'sandblasting' media (beads of acrylic plastics and polyester). Secondary microplastics are formed by larger plastic pieces breaking into smaller parts, either during use of the product or due to weather conditions (Andrady, 2017).

1.3. Collecting and recycling marine plastic waste

Marine plastic debris can be a source of plastic material for recycling. However, collecting marine plastic waste is more complicated than collecting municipal waste due to the fact that microplastics on the surface and the bottom of the sea are difficult to detect and collect (Andrady, 2017). The mechanical recycling of marine plastic waste also poses a greater challenge than recycling land-based waste because marine waste can contain a considerable amount of sand, salt, shells, algae and marine plants, some even stuck to the surface of the waste. The density of sand and sediments is typically 2.65 g/cm^3, so they can probably be separated by traditional methods based on density difference (Fazey and Ryan, 2016; Hidalgo-Ruz et al., 2012; Iñiguez et al., 2016). In addition to contaminants, degradation induced by weather and the environment is also a problem. Plastic waste can heat up to 40 °C on seashores, which further accelerates weathering and degradation by sunlight. If the same plastic floats in seawater at the same location, degradation is slower due to the lower temperature (Andrady, 1990, 2011, 2017; Pegram and Andrady, 1989), and also because foulants on floating waste filter out some of the solar UVR (ultraviolet radiation) that is responsible for starting oxidative processes (Weinstein et al., 2016). In the case of plastic waste that has sunk in oceans, degradation is far slower due to the lack of UVB radiation, lower temperatures and lower oxygen concentration, therefore the waste is unlikely to break up into smaller pieces (Andrady, 2011; Muthukumar et al., 2011). According to the literature, in the case of marine plastic waste, other degradation processes (biodegradation, thermo-oxidative degradation, thermal degradation, hydrolysis) are several orders of magnitude slower than photo-oxidative degradation (Andrady, 2011). The mechanical degradation caused by waves and the tide can also be mentioned. The degradation usually causes chain scission, which means that the molecular weight decreases and, as a result, the viscosity decreases. These decreases, not only cause problems during processing, but also affect the properties of products made from recycled plastic (Duarte et al., 2016; Gere and Czigany, 2020).

In the past decades, the number of publications and projects on the collection of marine plastic waste has increased. Most publications focus on ways of reducing marine waste and the biological effects of marine plastic debris (Schneider et al., 2018). Schneider et al. (2018) reviewed 132 studies, articles and projects in their review article, most of these did not deal with the recycling of collected waste at all. Those that include recycling mention mechanical recycling, pyrolysis and incinerating as possible methods, but none report practical results or uses (Iñiguez et al., 2016; Schneider et al., 2018).

Natural weathering of oceanic litter takes a long time and follow-up is difficult, therefore artificial modelling of environmental effects is necessary to investigate the change of material properties. There are several methods and standards for the artificial weathering of plastics (e.g. accelerated weathering by UV (ISO 4892–3, ASTM D1435) or by Xenon arc (ISO 4892–2, ASTM D2565) (González-López et al., 2020; Vedrtnam et al., 2019; Wypych, 2013). However, there is no universally accepted method or standard for the artificial (accelerated) weathering of commodity thermoplastics in marine conditions. For this reason, some researchers have experimented with simple methods, such as an aquarium, UV lamp and seawater (Iñiguez et al., 2018).

In summary, increasing effort is being made to collect marine plastic waste, therefore it is important to prepare for its targeted recycling. Based on the available literature, little is known about the morphological changes and the recyclability of PET bottles collected from the oceans and seashores. The goal in this article is to analyse the morphological changes and the possibility of secondary processing of PET bottles that have spent years in a marine

environment by using standard tests modelling an oceanic environment. Examining the possible mechanical recycling of weathered waste with the help of manufacturing experiments is the further goal.

2. Experimental

2.1. Materials

NeoPET 80 (Neo Group, Lithuania) granules with an intrinsic viscosity (IV) of 0.80 ± 0.01 dl/g were used in the experiments as original raw material ("original PET"), while PET bottle flakes (Jász-Plasztik Kft, Hungary) from collected, washed and sorted post-consumer PET bottles with an IV value of 0.77 ± 0.02 dl/g were used as secondary material ("non-weathered PET"). Grinding the bottles had no effect on the surface quality of the plastic and does not change its chemical and physical properties (e. g. molecular weight, density, crystallinity), only the size.

PET bottles may or may not float depending on several factors, the most important of which is whether the cap closes properly. For this reason, the environmental resistance of HDPE (high density polyethylene) bottle caps is an important question. Post-consumer bottle caps were used to investigate this.

2.2. Methods

2.2.1. Weathering method

In order to facilitate the accurate tracking of the weathering of the PET flake and HDPE cap samples investigated, and to make the weathering process faster, an artificial weathering method was developed that included artificial UV weathering with dry and wet cycles and salt spray cycles.

The environmental effects to be modelled are determined by the environment at the location of the waste. One of the most critical areas from the point of view of plastic waste is the Great Pacific Garbage Patch (Lebreton et al., 2018). The weather conditions in this area can be determined from meteorological databases. Based on the data, the average sea surface temperature (SST) in the past ten years has been 21.7 °C (NOOA, 2019), while the average intensity of the sun in the short wave range has been 108.1 W/m^2 (Copernicus Climate Change Service, 2019). These were considered the boundary conditions of the model.

The goal was to create a model that can be universally used, even on a larger number of samples, and which takes into account major environmental effects (sunlight, temperature, seawater).

The artificial weathering process consisted of cycles. One cycle lasted 7 days (168 h) and included one day in the salt spray chamber and six days of weathering in the Xenon chamber.

15 cycles of artificial weathering were performed with a total time of 2520 h, of which 2150 h was irradiation in the Xenon chamber. In this time, the total irradiation energy in the 300–400 nm (UV) range was 465 MJ/m^2, which corresponds to roughly 3–4 years on the surface of an ocean.

It is known that the PET is a hydrophilic polymer, even if some publications define PET as hydrophobic because, due to the polarity of the ester segments, it can generally absorb less than 1% of water from the surrounding environment, (Benvenuta-Tapia et al., 2018; Dubelley et al., 2017; Negoro et al., 2016; Zhang et al., 2019). Therefore, it was proved with experiments that the hydrophilic PET bottle (wall thickness 0.15–0.35 mm) saturates in the salt spray chamber in 24 h, after previous drying until the equilibrium state at 65 °C was reached, and the moisture content of the samples reaches a state of equilibrium in 144 h (6 days) in the Xenon chamber. The time to reach saturation and equilibrium determined the length of the cycles.

The salt spray cycle was performed in a SF/450 type chamber (C + W, United Kingdom) in accordance with ASTM B117, with the use of artificial seawater in accordance with ASTM D1141-98 (Re-approved 2013).

The samples were weathered in a Xenon chamber with a Q-SUN XE-3-HS device (Q-LAB, USA) in accordance with ISO 4892-2, method 'A', a daylight filter and continuous irradiation. The intensity of irradiation was 600 W/m^2 in the 300–800 nm range. The PET bottle flakes were evenly distributed on a tray in the Xenon chamber. The Xenon chamber cycle consisted of two sub-cycles in accordance with the standard: a 102-minute dry sub-cycle (65 °C black-standard temperature, 38 °C chamber temperature, 50% RH) plus an 18-minute wet, rain sub-cycle.

Although there is no exact method to determine the weathering acceleration factor, a factor of 10 to15 can be estimated based on the fact that the average intensity of irradiation is 6 times that of natural sunlight and chamber temperature is ca. 16 °C higher than in nature. This estimation corresponds to the findings of Philip and Al-Azzawi (2018), who compared the natural and artificial weathering of PET samples and achieved one year of natural weathering with about 25 days of artificial weathering.

2.2.2. Characterization methods

In the experiments, some of the PET flakes and HDPE caps were weathered. The degradation of PET bottle flakes was tracked through molecular degradation, which was characterized by Intrinsic Viscosity (IV). IV was measured in accordance with ASTM D4603, and calculated with the Billmeyer equation. The IV value of the PET material was determined with a computer-controlled RPV 1 automatic solution viscometer (PSL Rheotek, USA) equipped with an optical sensor. A phenol-tetrachloroethane mixture (Sigma-Aldrich, USA) in the ratio of 60/40 w/w% was applied as a solvent; concentration was 0.50 g/dl, and examination temperature was 30 °C.

Morphology (crystalline fraction) and melting temperature are important characteristics from the point of view of processability; their change in PET bottle flakes was examined as a function of weathering time with a DSC131 EVO type (Setaram, France) differential scanning calorimeter (DSC). Heating and cooling rates were 10 °C/min, and the tests were done in a nitrogen atmosphere. The endothermic peak during the first heating indicates the proportion of the ordered, crystalline part of the material and its melting temperature, while the exothermic peak in the cooling phase shows the tendency to crystallize after the thermal history was deleted. The percentage crystallinity (χ_c) of the endothermic or exothermic peaks was calculated according to (Eq. (1)).

$$\chi_c \ [\%] = \left(\Delta H_m / \Delta H_m^0 \right) \cdot 100, \tag{1}$$

where ΔH_m [J/g] is the endothermic or exothermic peak area (enthalpy) and ΔH_m^0 is the melting enthalpy of a perfect PET crystal equal to 140 J/g (Wu et al., 2019).

During weathering, the total time was split into 9-day periods, and IV and DSC tests were performed once in each period on two samples. From the results, the mean and standard deviation were determined.

The surface changes of bottle flakes and caps were examined with a microscope at the end of the weathering process. An EVO MA10 (Carl Zeiss AG, Germany) scanning electron microscope (SEM) and a Stemi 508 (Carl Zeiss AG, Germany) stereo microscope were used. In the case of the PET bottle flakes, there was no evidence that any microplastics were produced. However, signs of microplastics were noticed during the weathering of HDPE caps. When the surface of the caps is damaged, microparticles can break off, which can be determined by measuring mass. An AS60/220.R2

(Radwag USA LLC, USA) analytical balance was used for this and for moisture absorption/release measurement.

2.2.3. Processing methods

In order to prove that PET bottle material exposed to marine conditions can be recycled with widely used plastic processing technologies, five different manufacturing methods were tested. The tests were filament and sheet extrusion, injection moulding, 3D printing and thermoforming. The tests were performed, not only on weathered PET, but also on non-weathered PET and original PET. In this way, it was possible to compare differently weathered products exposed to various degrees of degradation.

Using different materials made it possible to examine whether the additional degradation during recycling is different in the case of materials of different origin. The parameters and equipment used for the various processing technologies, were as follows.

Filaments were produced on an LTE 26-48 (Labtech Scientific, Thailand) twin-screw extruder (L/D = 48, screw diameter: 26 mm). Before extrusion, the materials were dried at 160 °C for 4 h. Zone temperatures between the hopper and the die were between 245 °C and 270 °C for the original PET and between 230 °C and 260 °C for the different PET bottle flakes. Screw rotational speed was 18 rpm in each case. The diameter of the filaments produced was 1.32 ± 0.12 mm.

Some of the filaments were used for prototype production with a Craftbot 3 (CraftUnique Kft., Hungary) (dual head) printer. The temperature of the printing head was 300 °C, while the temperature of the tray was 80 °C. A nozzle with a diameter of 0.8 mm and layer thickness of 200 μm was used.

Some of the filaments were granulated and dried at 160 °C for 4 h before injection moulding. This was done in a 50 MEtII (Mitsubishi, Japan) electric injection moulding machine. Zone temperatures varied from 260 °C to 275 °C, and mould temperature was 60 °C. Injection speed was 100 mm/s, holding pressure was 40 MPa and back pressure was 3 MPa. Flat specimens of size 60 mm × 60 mm × 2 mm were manufactured.

Further tests were performed on the injection moulded samples made from non-weathered original PET material, non-weathered PET flakes and weathered PET flakes. The functionality of the injection moulded samples is mostly determined by their mechanical and optical properties. Mechanical properties were characterized with tensile and Charpy impact tests, based on the ISO 527-2 and the ISO 179-1 standards, respectively. The tensile tester was a 3369 (Instron, USA), and crosshead speed was 10 mm/min. For the Charpy impact tests, a 5113.10/01 impact tester (Zwick Roell Group, Germany) was used with a 5.4 J pendulum. The tests were performed at room temperature. In the tensile tests, 3 samples of each material were tested, while 10 samples of each material were tested in the case of notched Charpy impact tests.

Optical properties were measured with a spectro-guide 45/0 spectrophotometer (BYK Gardner, Germany) and a haze-gard dual transparency meter (BYK Gardner, Germany).

Films were produced from the different PET materials with an LTE 25-30/C (Labtech Scientific, Thailand) single-screw extruder and an LCR 300 (Labtech Scientific, Thailand) flat film line. The temperature profile on the extruder (from the feed section to the die) was 260–265–270–275–280 °C, and the temperature of the die was 280 °C. The rotational speed of the screw was 100 1/min and pulling speed was 10 m/min. The width of the films was 270 mm and their nominal thickness was 300 μm.

Thermoforming of the manufactured sheets was carried out on a VFP-0705-2SL (OVM, Hungary) semi-industrial scale machine. An aluminium mould was used. During preheating, the 100 °C ceramic heaters spent 20 s over the sheets, which were cooled with fans for 20 s after a delay of 5 s.

The structure of the experiments is shown schematically in Fig. 1.

3. Results and discussion

3.1. Change of PET bottles during weathering

Pictures of the weathering process can be found in the Supplementary Material I.

The Intrinsic Viscosity (IV) of PET characterizes its molecular weight. Fig. 2 shows the measured points and the fitted function of how IV changes as a function of time spent in the Xenon chamber. The function can be modelled with an exponential proportional rate decrease function (Eq. (2)). (In Fig. 2 the function is shown with the dashed grey trend line):

$$IV(t) = IV_0 - IV_{\Delta,\infty}(1 - \exp(-kt)), \tag{2}$$

where $IV(t)$ [dl/g] is the IV value as a function of time; IV_0 [dl/g] is the initial IV; t [h] is the time spent in the Xenon chamber; k [1/h] is a proportionality factor; $IV_{\Delta,\infty}$ [dl/g] is theoretical IV reduction at infinite time. The corresponding values from regression analysis are: IV_0 = 0.7698, $IV_{\Delta,\infty}$ = 0.2049, k = 0.0018. The detailed statistical analyses can be found in Supplementary Material."

According to the fitted model, the IV reduction expected at infinite time is 0.21 dl/g, therefore, in the case of an initial IV of 0.77 dl/g, the IV of the weathered material will probably not fall below 0.56 g/dl. This value indicates that the material can still be reused industrially (Frounchi, 1999). Since the decreasing IV tends to a constant, it can be assumed that, in addition to chain scission, a small degree of branching also occurs and these two processes produce an equilibrium of molecular weight (Venkatachalam et al., 2012). Cross-linking is not likely as, during the measurement of solution viscosity, there were no insoluble parts indicating cross-linking (Bikiaris and Karayannidis, 2003).

The surface of PET bottles changed considerably during weathering. Fig. 2 shows the smooth surface of the bottles before weathering and the surface after the full period of weathering. No small parts broke off, therefore no PET microplastics were created during the experiment.

Changes in morphological properties were analysed by ANOVA analysis (statistical details can be found in Supplementary Material). The crystalline fraction of the PET flakes did not change significantly during weathering; it was between 29.9% and 32.5%, with an average value of 31.4% (Fig. 3/a). The melting temperatures shown by Fig. 3/b decreased significantly during the weathering. The cause of this decrease is that UV radiation can damage molecular chains, both amorphous and crystalline parts, on the fold surface of the crystallite, which increases the free energy of the crystallite. This, in turn, influences melting temperature (Fechine et al., 2002).

The differences between the crystalline properties of materials cooled under the same conditions after heating primarily indicate differences in the molecular structure of the materials. Crystallinity on cooling (Fig. 3/c) and crystallization temperature (Fig. 3/d) at the end of the weathering are significantly higher than before the test.

3.2. Change of HDPE caps during weathering

The full weathering process was also performed on the HDPE caps of PET bottles. After 2150 h of weathering, the surface of the caps displayed slight cracking (Fig. 4). The damaged surface was examined by scanning electron microscope (SEM) and it was found that the surface was cracked and small plastic particles
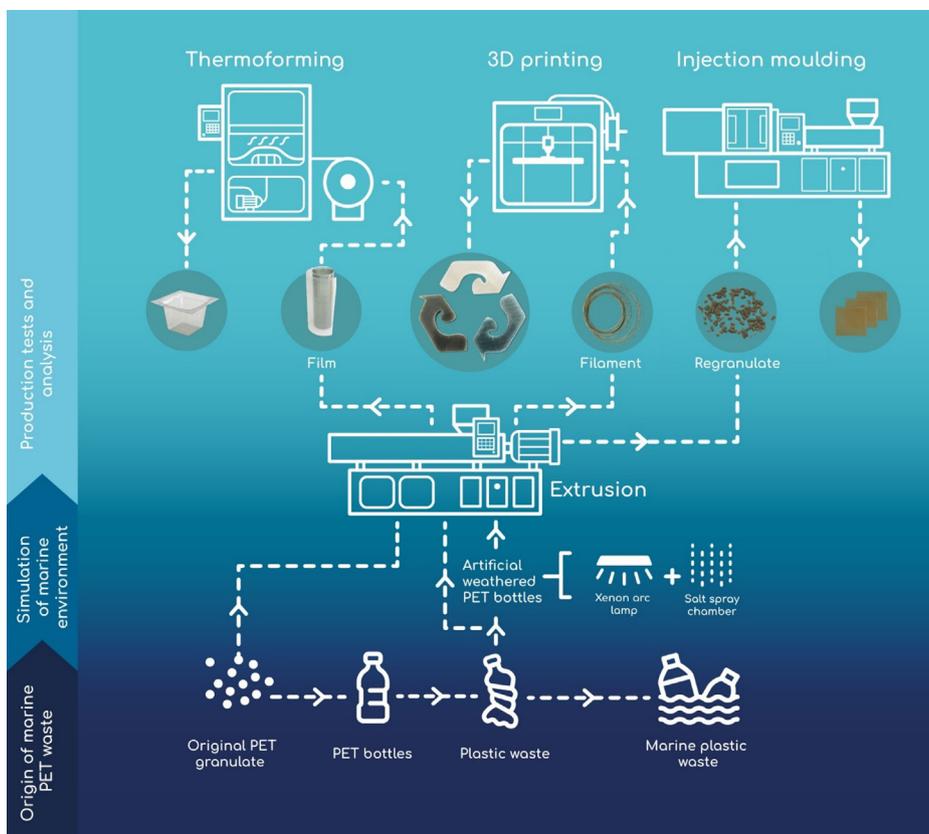
Fig. 1. Possible recycling routes of plastic waste. The raw materials of the experiments were original PET granulate and plastic waste. Marine plastic waste was simulated by artificial weathering with the use of Xenon- and salt spray chambers. In the recycling tests, products were manufactured with different technologies. In the case of extrusion, thermoforming and injection moulding only photos of the products made from weathered PET are shown, while in the case of 3D printing, photos of all the three types of product (made from original PET, non-weathered PET and weathered PET) are provided.
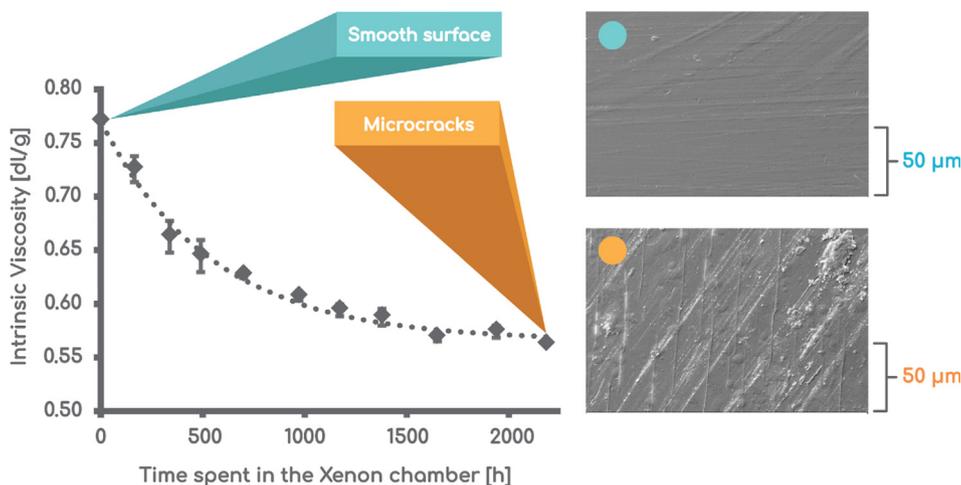
Fig. 2. Change of PET bottle properties during weathering. (Left) The change of Intrinsic Viscosity as a function of time spent in the Xenon chamber. (Upper right) The scanning electron microscope image of the surface of the PET bottle before weathering and (Lower right) after 2150 h in the Xenon chamber.

broke off. Damage was slight, the mass reduction of the cap was only 1.5 mg (0.096% of the total mass), but the parts that broke off were in the range 10–100 μm, therefore they are considered microplastics.

In the accelerated weathering process (simulating 3–4 years in marine environment), the damage the caps suffered did not prevent them from closing properly so the bottles they were on would not have sunk to the bottom of the sea.

3.3. PET products manufactured with different technologies

The test results showed that all five manufacturing technologies can be successfully used, even with weathered PET (Fig. 5).

The IV values of the materials investigated and the products made from them with various technologies can be found in Table 1. The reduction in IV indicates that, at the processing temperature of recycling (250–280 °C), hydrolytic and thermal degradation occurs. This
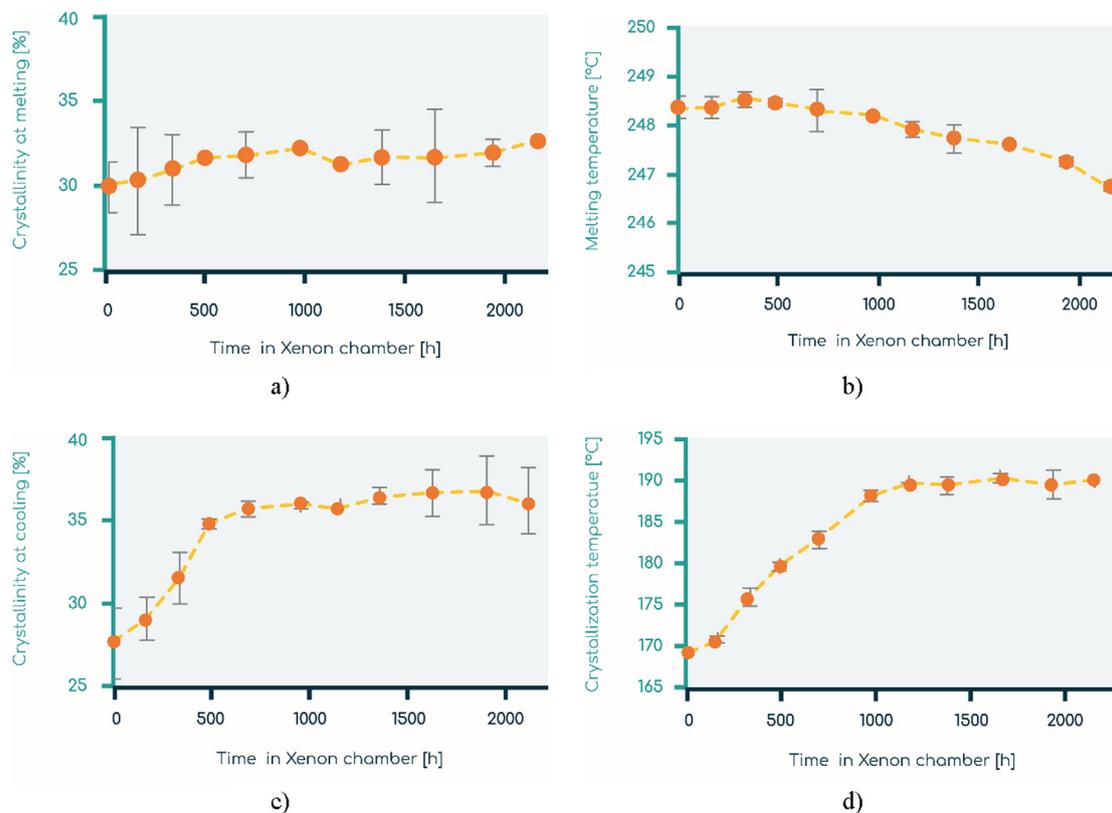
Fig. 3. The change in characteristics determined by DSC as a function of time spent in the Xenon chamber (A: the crystalline fraction determined from the melting peak during heating; B: melting peak temperature during heating; C: the crystalline fraction determined from the crystallization peak during cooling; D: crystallization peak temperature during cooling).
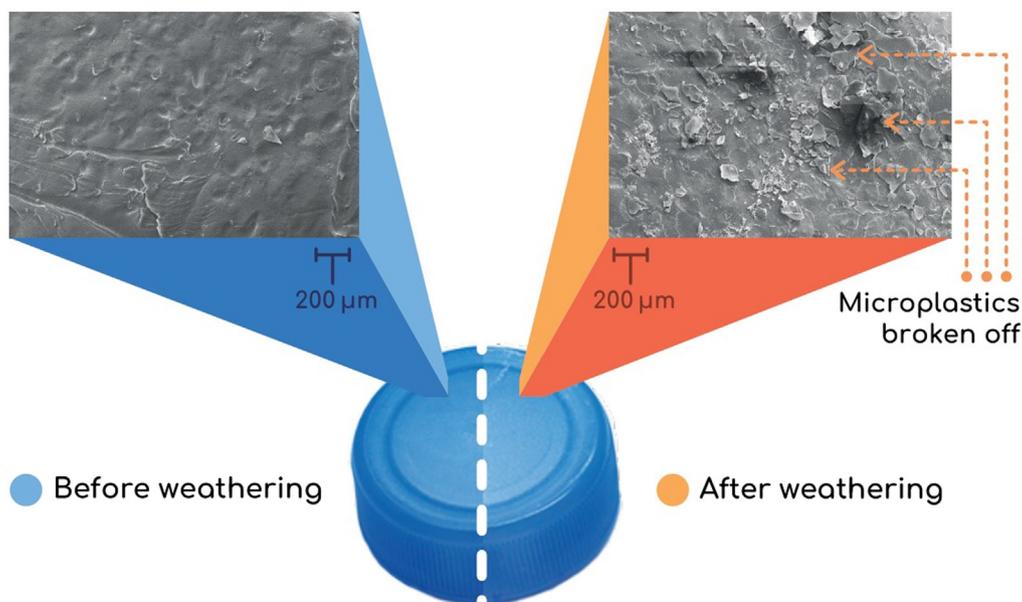

Fig. 4. Change of HDPE caps properties during weathering. Photo and scanning electron microscope images (Left: 0 h; Right: 2150 h in the Xenon chamber).

degradation is most pronounced during injection moulding, which can be attributed to the highest processing temperature and the highest shear rates experienced by the melt. In the case of this technology, IV decreases by 0.13 ± 0.01 dl/g for the original PET, by 0.26 ± 0.01 dl/g for the non-weathered PET and by 0.10 ± 0.01 dl/g for the of weathered PET. Filament and sheet extrusion cause less degradation. Therefore, during filament production, the

IV reduction is only 0.08 ± 0.01 dl/g for the original PET, 0.05 ± 0.01 dl/g for the non-weathered PET and 0.02 ± 0.01 dl/g for the weathered PET, while during sheet extrusion the IV reduction is only 0.02 ± 0.02 dl/g for the original PET, 0.06 ± 0.01 dl/g for the non-weathered PET and, finally, 0.03 ± 0.01 dl/g for the weathered PET.

Since the functionality of plastic products is mostly determined by aesthetics and mechanical performance, the mechanical and

Fig. 5. Products manufactured by different technologies, made from original, non-weathered PET and weathered PET.

Table 1
The IV values of the different materials and the various products manufactured from them.

IV [dl/g]	Product from original PET	Product from non-weathered PET bottles	Product from weathered PET bottles
Raw material	0.80	0.77	0.56
Extruded filament	0.72	0.72	0.54
3D printed product	0.70	0.69	0.52
Injection moulded product	0.66	0.52	0.45
Extruded film	0.76	0.72	0.53
Thermoformed product	0.75	0.72	0.53

optical properties of injection moulded products were examined. The transparency of the sample injection moulded from original PET was 89 ± 3%, the transparency of the sample made from non-weathered PET bottle was 62 ± 3%, while that of the product made from weathered PET bottle was 43 ± 2%. There are significant differences between the results of the three samples. Products manufactured from weathered PET bottles will, therefore, definitely not be suitable for transparent products. To characterize colour change, the sample made from non-weathered PET bottle was used as reference and deviation from this in the CIElab colour space was examined. Difference along the L* (lightness) axis was −20.0 ± 0.6 (measured sample is lighter than the reference); difference along the a* (green–red) axis was 12.2 ± 1.0 (measured sample is more red than the reference), while along the b* (blue–yellow) axis it was 22.7 ± 0.9 (measured sample is yellower than the reference). The results of the three samples differed significantly. The detailed statistical analyses can be found in Supplementary Material.

These results indicate that the weathered sample became considerably darker and its colour shifted towards red and yellow, in other words, significant browning occurred. This can be attributed to UV radiation and the molecular degradation due to the processing technology.

Mechanical properties on specimens cut out from the injection moulded samples were measured using tensile and Charpy impact tests. The tensile strength (52.2 ± 0.8 MPa for non-weathered, and 51.9 ± 1.6 MPa for weathered) and Young's moduli (1263 ± 15 MPa for non-weathered, and 1257 ± 49 MPa for weathered are the same as those of the original material (tensile strength: 52.6 ± 1.8 MPa and modulus: 1262 ± 56 MPa). The detailed statistical analyses can be found in Supplementary Material. The toughness of the samples was characterized by their strain at break (determined in the tensile test) and their Charpy impact strength. Fig. 6 contains the results as a function of the IV of the samples. The strain at break of the specimens made from weathered PET is roughly half that of
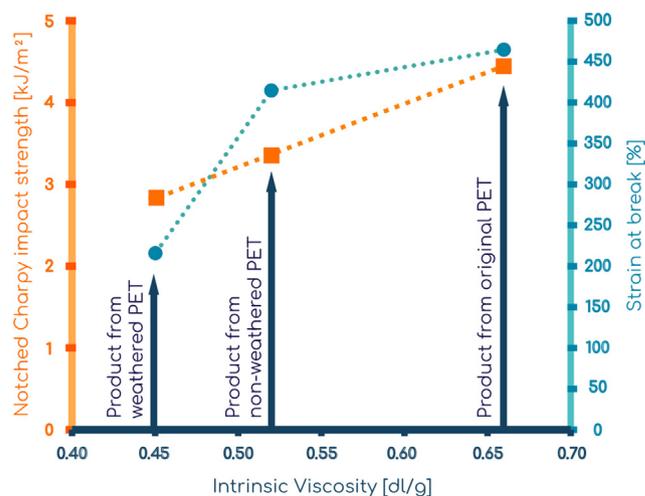

Fig. 6. The impact strength and strain at break of the injection moulded samples as a function of Intrinsic Viscosity.

samples made from non-weathered PET or original PET, but their strain is still over 200%, which is enough for being applied in injection moulded products.

The impact strength of the specimen made from non-weathered PET is 22% lower ($3.4 ± 0.7$ kJ/m^2), while the impact strength of the specimen manufactured from weathered PET is 37% less ($2.8 ± 0.5$ kJ/m^2) than the corresponding value of the part made from original PET ($4.4 ± 0.5$ kJ/m^2). This is a considerable decrease in toughness. The detailed statistical analyses can be found in Supplementary Material. In summary, degradation decreased molecular weight, as a result of which the toughness of the parts was reduced, and this can limit applicability.

3.4. The prospects for PET recycling

Impaired aesthetics and fragility may limit the usability of products from recycled weathered plastic but, if necessary, the negative effects of degradation can be compensated for with different methods (e.g. colourants, solid-state polymerization reaction, chain extender additives (Awaja and Pavel, 2005; Bocz et al., 2019)).

In summary, it was proved that, even although the PET bottles may float on the surface of oceans for years, recycling is still possible after cleaning and sorting. An important task is to find areas of application, i.e. product ideas from recycled plastic. An example is presented of a sun cream jar made from an injection moulded preform (Fig. 7). The concept was to make such products from recycled oceanic plastic waste that are connected to the sea; in this way they indicate that their user supports the protection of the environment. The blue colour of the product indicates that it was made from recycled marine plastic debris, and the traditional international logo of recycling was also redesigned to be wavy so that it also refers to the recycling of marine plastic waste.

It was shown that the marine plastic debris needs to be collected, not only to protect marine life and the environment, but also because these plastics can be recycled successfully and so they can be excellent materials for new products. At the same time, it is also important that littering and depositing plastic waste should be stopped as plastics enter the waters due to human negligence. Sustainable development and the future of Earth and humankind depends on the change of approach to waste, as climate change as a result of urbanizatio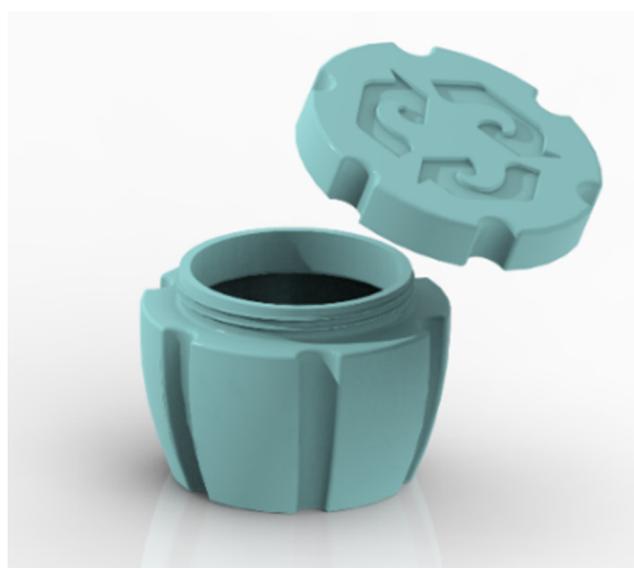n, the increasing volume of transport and the increasing use of fossil fuels already endangers life on Earth. Therefore, a lot more attention should be paid to renewable energy sources and continuous recycling. Teaching people to value products, whether they are metal, ceramic, wood or plastic is of paramount importance. It is recommended that the term "disposable" is replaced with "recyclable," and "single-use" with "multiple-use" (Czigany, 2020). This can also help today's discarded plastic waste to become recyclable and valued products.

4. Conclusions

An artificial, accelerated weathering procedure was developed, with which 3–4 years of exposure in a marine environment was modelled. It was found that, in this period, the HDPE caps of bottles are damaged but not enough to let water into the bottle, which would cause the bottle to sink. It was shown that the material of the PET bottles is damaged as a result of UV radiation, the molecular chains get shorter but degradation slows with time.

Five processing technologies were tested using the weathered material. Filaments were successfully manufactured and used for 3D printing, the filaments were granulated and used for injection moulding and extruding sheets, and thermoformed samples were produced from the sheets. Injection moulding can be an excellent choice for recycling as the technology is productive and widely used, and so it requires a lot of material. For this reason, functional tests were performed on injection moulded samples. It was shown that, due to weathering and degradation during recycling, transparency is significantly impaired, and considerable colouring also occurs (colours shifted towards brown). The strength and rigidity of the parts does not change noticeably. However, the rigidity of the recycled parts is an issue which manifested itself in the reduction of strain at break and fracture energy.

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.

Author contributions

R.F. and C.T. designed the experiments; M.B., G.D., and R.F. performed the experiments; all authors contributed to data analysis; R.F. and C.T. wrote the manuscript.

Data and materials availability

All data is available in the main text and in the Supplementary Material.

Fig. 7. Product design for recycled, weathered PET bottles.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2020.09.029.

References

Andrady, A.L., 1990. Weathering of polyethylene (LDPE) and enhanced photodegradable polyethylene in the marine environment. J. Appl. Polym. Sci. 39, 363–370. https://doi.org/10.1002/app.1990.070390213.

Andrady, A.L., 2011. Microplastics in the marine environment. Mar. Pollut. Bull. 62, 1596–1605. https://doi.org/10.1016/j.marpolbul.2011.05.030.

Andrady, A.L., 2017. The plastic in microplastics: A review. Mar. Pollut. Bull. 119, 12–22. https://doi.org/10.1016/j.marpolbul.2017.01.082.

Awaja, F., Pavel, D., 2005. Recycling of PET. Eur. Polym. J. 41, 1453–1477. https://doi.org/10.1016/j.eurpolymj.2005.02.005.

Benvenuta-Tapia, J.J., González-Coronel, V.J., Soriano-Moro, G., Martínez-De la Luz, I., Vivaldo-Lima, E., 2018. Recycling of poly(ethylene terephthalate) by chain extension during reactive extrusion using functionalized block copolymers synthesized by RAFT polymerization. J. Appl. Polym. Sci. 135, 46771. https://doi.org/10.1002/app.46771.

Bergmann, M., Klages, M., 2012. Increase of litter at the Arctic deep-sea observatory HAUSGARTEN. Mar. Pollut. Bull. 64, 2734–2741. https://doi.org/10.1016/j.marpolbul.2012.09.018.

Bikiaris, D.N., Karayannidis, G.P., 2003. Synthesis and characterisation of branched and partially crosslinked poly(ethylene terephthalate). Polym. Int. 52, 1230–1239. https://doi.org/10.1002/pi.1264.

Bocz, K., Molnár, B., Marosi, G., Ronkay, F., 2019. Preparation of low-density microcellular foams from recycled PET modified by solid state polymerization and chain extension. J. Polym. Environ. 27, 343–351. https://doi.org/10.1007/s10924-018-1351-z.

Coe, J.M., Rogers, D.B., 1997. Marine Debris. Springer, New York. 10.1007/978-1-4613-8486-1.

Copernicus Climate Change Service, 2019. Data based on ERA5 reanalysis which are available via the Copernicus Climate Change Service (C3S) Climate Data Store (CDS) (https://climate.copernicus.eu/climate-data-store).

Cózar, A., Echevarría, F., González-Gordillo, J.I., Irigoien, X., Úbeda, B., Hernández-León, S., Palma, A.T., Navarro, S., García-de-Lomas, J., Ruiz, A., Fernández-de-Puelles, M.L., Duarte, C.M., 2014. Plastic debris in the open ocean. P. Natl. Acad. Sci. USA 111, 10239–10244. https://doi.org/10.1073/pnas.1314705111.

Czigany, T., 2020. Disposable or single-use plastics? Neither!!! Recyclable or reusable plastics!. Express Polym. Lett. 14. https://doi.org/10.3144/expresspolymlett.2020.1. 1–1.

Dauvergne, P., 2018. Why is the global governance of plastic failing the oceans?. Global Environ Chang. 51, 22–31. https://doi.org/10.1016/j.gloenvcha.2018.05.002.

Duarte, I.S., Tavares, A.A., Lima, P.S., Andrade, D.L.A.C.S., Carvalho, L.H., Canedo, E.L., Silva, S.M.L., 2016. Chain extension of virgin and recycled poly(ethylene terephthalate): Effect of processing conditions and reprocessing. Polym. Degrad. Stabil. 124, 26–34. https://doi.org/10.1016/j.polymdegradstab.2015.11.021.

Dubelley, F., Planes, E., Bas, C., Pons, E., Yrieix, B., Flandin, L., 2017. Water vapor sorption properties of polyethylene terephthalate over a wide range of humidity and temperature. J. Phys. Chem. B 121, 1953–1962. https://doi.org/10.1021/acs.jpcb.6b11700.

Eriksen, M., Lebreton, L.C.M., Carson, H.S., Thiel, M., Moore, C.J., Borerro, J.C., Galgani, F., Ryan, P.G., Reisser, J., 2014. Plastic pollution in the world's oceans: More than 5 trillion plastic pieces weighing over 250,000 tons afloat at sea. PLoS One 9, e111913. https://doi.org/10.1371/journal.pone.0111913.

Fazey, F.M.C., Ryan, P.G., 2016. Biofouling on buoyant marine plastics: An experimental study into the effect of size on surface longevity. Environ. Pollut. 210, 354–360. https://doi.org/10.1016/j.envpol.2016.01.026.

Fechine, G.J.M., Souto-Maior, R.M., Rabello, M.S., 2002. Structural changes during photodegradation of poly(ethylene terephthalate). J. Mater. Sci. 37, 4979–4984. https://doi.org/10.1023/A:1021067027612.

Frounchi, M., 1999. Studies on degradation of PET in mechanical recycling. Macromol. Symp. 144, 465–469. https://doi.org/10.1002/masy.19991440142.

Galimany, E., Marco-Herrero, E., Soto, S., Recasens, L., Lombarte, A., Lleonart, J., Abelló, P., Ramón, M., 2019. Benthic marine litter in shallow fishing grounds in the NW Mediterranean Sea. Waste Manage. 95, 620–627. https://doi.org/10.1016/j.wasman.2019.07.004.

Gere, D., Czigány, T., 2018. Rheological and mechanical properties of recycled polyethylene films contaminated by biopolymer. Waste Manage. 76, 190–198. https://doi.org/10.1016/j.wasman.2018.02.045.

Gere, D., Czigany, T., 2020. Future trends of plastic bottle recycling: Compatibilization of PET and PLA. Polym. Test. 81, 106160. https://doi.org/10.1016/j.polymertesting.2019.106160.

Geyer, R., Jambeck, J.R., Law, K.L., 2017. Production, use, and fate of all plastics ever made. Sci. Adv. 3, e1700782. https://doi.org/10.1126/sciadv.1700782.

González-López, M.E., Martín del Campo, A.S., Robledo-Ortíz, J.R., Arellano, M., Pérez-Fonseca, A.A., 2020. Accelerated weathering of poly(lactic acid) and its biocomposites: A review. Polym. Degrad. Stabil. 179, 109290. https://doi.org/10.1016/j.polymdegradstab.2020.109290.

Hartmann, N.B., Hüffer, T., Thompson, R.C., Hassellöv, M., Verschoor, A., Daugaard, A. E., Rist, S., Karlsson, T., Brennholt, N., Cole, M., Herrling, M.P., Hess, M.C., Ivleva, N.P., Lusher, A.L., Wagner, M., 2019. Are we speaking the same language? Recommendations for a definition and categorization framework for plastic debris. Environ. Sci. Technol. 53, 1039–1047. https://doi.org/10.1021/acs.est.8b05297.

Hidalgo-Ruz, V., Gutow, L., Thompson, R.C., Thiel, M., 2012. Microplastics in the marine environment: A review of the methods used for identification and quantification. Environ. Sci. Technol. 46, 3060–3075. https://doi.org/10.1021/es2031505.

Iñiguez, M.E., Conesa, J.A., Fullana, A., 2016. Marine debris occurrence and treatment: A review. Renew. Sust. Energ. Rev. 64, 394–402. https://doi.org/10.1016/j.rser.2016.06.031.

Iñiguez, M.E., Conesa, J.A., Fullana, A., 2018. Recyclability of four types of plastics exposed to UV irradiation in a marine environment. Waste Manage. 79, 339–345. https://doi.org/10.1016/j.wasman.2018.08.006.

Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., Law, K.L., 2015. Plastic waste inputs from land into the ocean. Science 347, 768–771. https://doi.org/10.1126/science.1260352.

Kin, C.S., Ut, I.M., Hang, L., Hou, U.I., Weng, N.K., Ha, U.S., Hin, L.K., Heng, C.K., Tim, T. S., Kuai, C.I., Shan, L.W., 2019. Predicting Earth's carrying capability of human population as the predator and the natural resources as the prey in the modified Lokta-Volterra equations with time-dependent parameters. arXiv 1904.05002.

Law, K.L., 2017. Plastics in the marine environment. Annu. Rev. Mar. Sci. 9, 205–229. https://doi.org/10.1146/annurev-marine-010816-060409.

Lebreton, L., Slat, B., Ferrari, F., Sainte-Rose, B., Aitken, J., Marthouse, R., Hajbane, S., Cunsolo, S., Schwarz, A., Levivier, A., Noble, K., Debeljak, P., Maral, H., Schoeneich-Argent, R., Brambini, R., Reisser, J., 2018. Evidence that the Great Pacific Garbage Patch is rapidly accumulating plastic. Sci. Rep. 8, 4666. https://doi.org/10.1038/s41598-018-22939-w.

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. Nat. Commun. 8, 15611. https://doi.org/10.1038/ncomms15611.

Li, W.C., Tse, H.F., Fok, L., 2016. Plastic waste in the marine environment: A review of sources, occurrence and effects. Sci. Total Environ. 566–567, 333–349. https://doi.org/10.1016/j.scitotenv.2016.05.084.

Muthukumar, T., Aravinthan, A., Lakshmi, K., Venkatesan, R., Vedaprakash, L., Doble, M., 2011. Fouling and stability of polymers and composites in marine environment. Int. Biodeter. Biodegr. 65, 276–284. https://doi.org/10.1016/j.ibiod.2010.11.012.

Negoro, T., Thodsaratpreeyakul, W., Takada, Y., Thumsorn, S., Inoya, H., Hamada, H., 2016. Role of crystallinity on moisture absorption and mechanical performance of recycled PET compounds. Enrgy. Proced. 89, 323–327. https://doi.org/10.1016/j.egypro.2016.05.042.

NOOA, 2019. NOOA – Earth System Research Laboratory – Physical Sciences Division.

Nova-Institut, 2015. Bio-based building blocks and polymers in the world – capacities, production and applications: Status quo and trends toward 2020. Nova-Institut GmbH, Hürth.

Pegram, J.E., Andrady, A.L., 1989. Outdoor weathering of selected polymeric materials under marine exposure conditions. Polym. Degrad. Stabil. 26, 333–345. https://doi.org/10.1016/0141-3910(89)90112-2.

Pham, C.K., Ramirez-Llodra, E., Alt, C.H.S., Amaro, T., Bergmann, M., Canals, M., Company, J.B., Davies, J., Duineveld, G., Galgani, F., Howell, K.L., Huvenne, V.A.I., Isidro, E., Jones, D.O.B., Lastras, G., Morato, T., Gomes-Pereira, J.N., Purser, A., Stewart, H., Tojeira, I., Tubau, X., Van Rooij, D., Tyler, P.A., 2014. Marine litter distribution and density in European seas, from the shelves to deep basins. PLoS One 9, e95839. https://doi.org/10.1371/journal.pone.0095839.

Philip, M., Al-Azzawi, F., 2018. Effects of natural and artificial weathering on the physical properties of recycled poly(ethylene terephthalate). J. Polym. Environ. 26, 3139–3148. https://doi.org/10.1007/s10924-018-1191-x.

PlasticsEurope, 2018. PlasticsEurope Annual Review 2017-2018. PlasticsEurope AISBL, Brussels.

Polasek, L., Bering, J., Kim, H., Neitlich, P., Pister, B., Terwilliger, M., Nicolato, K., Turner, C., Jones, T., 2017. Marine debris in five national parks in Alaska. Mar. Pollut. Bull. 117, 371–379. https://doi.org/10.1016/j.marpolbul.2017.01.085.

Schneider, F., Parsons, S., Clift, S., Stolte, A., McManus, M.C., 2018. Collected marine litter – A growing waste challenge. Mar. Pollut. Bull. 128, 162–174. https://doi.org/10.1016/j.marpolbul.2018.01.011.

Simeonova, A., Chuturkova, R., 2019. Marine litter accumulation along the Bulgarian Black Sea coast: Categories and predominance. Waste Manage. 84, 182–193. https://doi.org/10.1016/j.wasman.2018.11.001.

Taagepera, R., 2014. A world population growth model: Interaction with Earth's carrying capacity and technology in limited space. Technol. Forecast. Soc. 82, 34–41. https://doi.org/10.1016/j.techfore.2013.07.009.

Tuffi, R., D'Abramo, S., Cafiero, L.M., Trinca, E., Vecchio Ciprioti, S., 2018. Thermal behavior and pyrolytic degradation kinetics of polymeric mixtures from waste packaging plastics. Express Polym. Lett. 12, 82–99. https://doi.org/10.3144/expresspolymlett.2018.7.

United Nations, 2019. World population prospects 2019: Highlights. United Nations, Department of Economic and Social Affairs, Population Division, New York.

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. (Ed.), Polyester. IntechOpen, London, pp. 75–98. https://doi.org/10.5772/48612.

Vedrtnam, A., Kumar, S., Chaturvedi, S., 2019. Experimental study on mechanical behavior, biodegradability, and resistance to natural weathering and ultraviolet radiation of wood-plastic composites. Compos. Part B: Eng. 176, 107282. https://doi.org/10.1016/j.compositesb.2019.107282.

Weinstein, J.E., Crocker, B.K., Gray, A.D., 2016. From macroplastic to microplastic: Degradation of high-density polyethylene, polypropylene, and polystyrene in a salt marsh habitat. Environ. Toxicol. Chem. 35, 1632–1640. https://doi.org/10.1002/etc.3432.

Whitacre, D.M., 2012. Reviews of Environmental Contamination and Toxicology. Springer, New York. 10.1007/978-1-4614-3414-6.

Woodall, L.C., Sanchez-Vidal, A., Canals, M., Paterson, G.L.J., Coppock, R., Sleight, V., Calafat, A., Rogers, A.D., Narayanaswamy, B.E., Thompson, R.C., 2014. The deep sea is a major sink for microplastic debris. R. Soc. Open Sci. 1, 140317. https://doi.org/10.1098/rsos.140317.

Wu, H., Lv, S., He, Y., Qu, J.-P., 2019. The study of the thermomechanical degradation and mechanical properties of PET recycled by industrial-scale elongational processing. Polym. Test. 77, 105882. https://doi.org/10.1016/j.polymertesting.2019.04.029.

Wypych, G., 2013. Handbook of Material Weathering. ChemTec Publishing, Toronto.

Ye, S., Andrady, A.L., 1991. Fouling of floating plastic debris under Biscayne Bay exposure conditions. Mar. Pollut. Bull. 22, 608–613. https://doi.org/10.1016/0025-326X(91)90249-R.

Zhang, Y., Chen, S., Wang, H., Luo, M., 2019. Separation of polyvinylchloride and acrylonitrile-butadiene-styrene combining advanced oxidation by $S_2O_8^{2-}/Fe^{2+}$ system and flotation. Waste Manage. 91, 80–88. https://doi.org/10.1016/j.wasman.2019.04.048.