



Review

The plastic in microplastics: A review



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ABSTRACT

Microplastics [MPs], now a ubiquitous pollutant in the oceans, pose a serious potential threat to marine ecology and has justifiably encouraged focused biological and ecological research attention. But, their generation, fate, fragmentation and their propensity to sorb/release persistent organic pollutants (POPs) are determined by the characteristics of the polymers that constitutes them. Yet, physico-chemical characteristics of the polymers making up the MPs have not received detailed attention in published work. This review assesses the relevance of selected characteristics of plastics that composes the microplastics, to their role as a pollutant with potentially serious ecological impacts. Fragmentation leading to secondary microplastics is also discussed underlining the likelihood of a surface-ablation mechanism that can lead to preferential formation of smaller sized MPs.

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1. Introduction

The presence of small fragments of plastics, generally referred to as ‘microplastics’, in the oceans (Anderson et al., 2016; Browne et al., 2011) estuaries (Browne et al., 2010; Lima et al., 2015; Zhao et al., 2014), bodies of freshwater (Free et al., 2014; Sanchez et al., 2014; Biginagwa et al., 2016) and even in the remote arctic ice (Zarfland

Matthies, 2010; Hubard et al., 2014) is now well established. These have been sampled from beaches (Retama et al., 2016; Liebezeit and Dubaish, 2012; Browne et al., 2011), surface water (Cózar et al., 2014; Law and Thompson, 2014), marine sediment (Kedzierski et al., 2016; Galgani et al., 2000; Van Cauwenberghe et al., 2015) as well as in the marine biota (Wesch et al., 2016; Desforges et al., 2015). They are a unique, potentially bio-accumulating pollutant in the marine ecosystem that compromises the ability of the already-stressed oceans to deliver critical ecosystem services that support life on land. Unlike with large plastic debris, MPs in the oceans cannot be cost-effectively detected,

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collected for recycling or other managed disposal. In coastal regions floating MP counts as high as 10^3 – 10^4 per m^3 are not uncommon and this lack of an effective removal mechanism is a particularly serious concern. Floating MPs invariably accumulate in the sediment and their impact on the benthic ecosystem is unknown.

Primary microplastics [MPs] are industrially manufactured as microbeads of different sizes and are used in personal care products (Fendall and Sewell, 2009) generally as exfoliants (Darling et al., 2015; Leslie, 2015), in sand-blasting media (Sundt et al., 2014) or as the larger virgin plastics pellets intended as raw materials for fabrication of products (Browne et al., 2011). These pellets enter the environment via 'leakage' during manufacture, transportation or use. For instance, in the EU (along with Sweden and Switzerland), ~4360 MT of microbeads were used in year 2012 {UNEP 2015} while in the US, the consumption is estimated at US ~2.5 mg of microbeads per user per day (Gouin et al., 2011). With the primary MPs, production volumes Barnes et al. (2009) are tractable and their use is beginning to be regulated (Rochman et al., 2015b). But, far more abundant in the oceans are the secondary MPs (Barnes et al., 2009) typically derived from fragmentation of larger plastic debris items either during use of products or due to weathering degradation of their litter. Input of these is far more difficult to estimate. Secondary MPs include textile fiber fragments invariably released during laundering of synthetic fabrics (Fendall and Sewell, 2009; Browne et al., 2011) and fragments of post-use agricultural mulch films left in the field (Kyrikou and Briassoulis, 2007). Weathering breakdown of plastic litter in the beach environment (Andrady, 2011), however, is the likely predominant source of secondary MPs (Hidalgo-Ruz et al., 2012). Though their volumes in the oceans are intractable, secondary MPs have very high spatial and temporal variability.

2. Plastics production

The global production of plastic resins in recent years is about 300 MMT annually. Given the remarkable societal benefits plastics provide (Andrady and Neal, 2009) this figure will almost certainly continue to increase in the future. Nearly a half of the current production is in Asia while NAFTA and EU countries each account for about a 20% share. Plastic litter is more likely at locations of product fabrication and in urban centers of high population density. They are the more likely locations for high incidence of litter and where they are coastal or near rivers, more probable sources of marine litter.

Based on available data, (Fig. 1) the increase in global plastics production with population growth in recent years is non-linear suggesting that per-capita consumption of plastics is also on the increase. Most of the common plastics resin production is used in packaging with a relatively short lifetime and ends up routinely in litter as well as in municipal solid waste [MSW]. Plastics account for 10–15% by weight of MSW depending on the location. A small fraction of this waste, an estimated

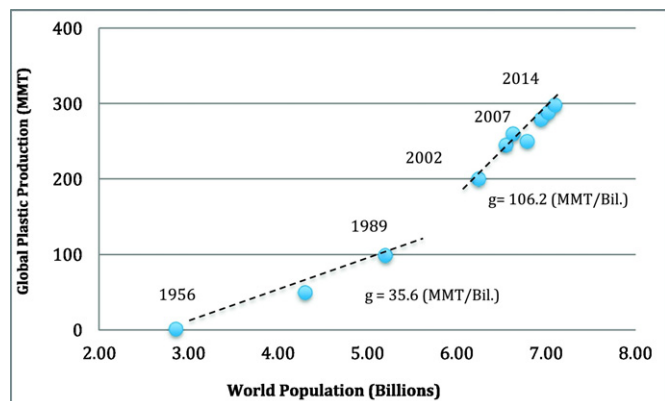


Fig. 1. The change in global production of plastics with the population, showing non-linear increase in production.

4.8–12.7 MMT/year invariably ends up in the oceans, assuming only about a 2% of waste plastics ends up as litter (Jambeck et al., 2015). The global production of PE and PP (the most common in marine MPs) grew at the rate of 8.7% per year (1950–2012) (Gourmelon, 2015), increasing the likely fraction that ends up as marine litter as well.

Incidence of MPs at different locations has been quantified using a variety of techniques and expressed in different units making the data difficult to compare (Hidalgo-Ruz, et al., 2012). In general there is a trend towards finding more MPs in coastal environments near population centers (Sul and Costa, 2014; Jambeck et al., 2015). Eriksen et al. (2014) estimates the load of floating plastics in the oceans to be 270,000 MT. The estimates exclude MPs that filter through the plankton nets used to gather the data the study was based on. Microplastics in oceans and their potential adverse impacts have been reviewed (Andrady, 2011; Browne et al., 2011; Cole et al., 2011; Barnes et al., 2009; Moore et al., 2008). While the weight fraction of MPs in plastic litter will be relatively small, they are able to interact with a very wide variety of marine organisms, ranging from zooplanktons (Ferreira et al., 2016) to fin whales (Fossi et al., 2016).

3. Consequences of MPs in the oceans

Over the recent years, concerns on plastic debris in oceans have expanded to include ingestion-related distress to organisms (Setälä et al., 2014; Neves et al., 2015; Jacobsen et al., 2010) in addition to the traditional issues of ghost fishing, entanglement and the ecological impact of rafting species (Gregory, 2009) discussed in 1980s and 1990s. These new concerns also center around the presence of low-molecular weight chemical species in the plastic that might be bioavailable to ingesting organisms and may present a toxic hazard to them; three categories of such compounds are known in plastics.

- Persistent organic pollutants (POPs) present in seawater and sorbed very efficiently by MPs (Teuten et al., 2009; Endo et al., 2005; Engler, 2012). The equilibrium distribution coefficient K for common POPs in water-plastic systems ranges from 10^3 to 10^5 in favor of the plastic. This makes their ingestion a credible potential route by which sorbed POPs can enter the marine food web (Bakir et al., 2012). The potential toxic outcome from ingestion invariably depends on bioavailability of POPs, the body mass of ingesting organism, the concentration of the POPs 'cocktail' in the MP and their propensity to bioaccumulate in the organism. Even at non-lethal concentrations, MPs can alter key aspects of behavior (Ferreira, et al. 2016) such as reduction in predation in species such as *Goby* (Lobelle and Cunliffe, 2011) and result in adverse health outcomes (Rochman et al., 2016).
- Additives are chemicals intentionally added to plastics during their manufacture or processing (Andrady, 2016). These include stabilizers, plasticizers or flame retardants. Plasticizers, for instance are used at relatively high concentrations (10–50%), added to ensure the functionality of the product, can be bioavailable to ingesting organisms (Oehlmann et al., 2009). MPs derived from compounded plastics may contain such additives.
- Residual monomers in plastics. Common plastics found in marine MPs, polyethylenes [PE] and polypropylenes [PP] do not have any residual monomer. But, polystyrene [PS] also found in significant quantities in debris, can contain 0.1–0.6 wt% of styrene monomer and oligomers (Garrigós et al., 2004; Andrady, 2016).

The chemical-laden MPs, once ingested by small organisms, can move across trophic boundaries (Setälä et al., 2014; Farrell and Nelson, 2013) potentially affecting their predators at higher levels of the food pyramid. Finding MPs in commercial seafood species (Rochman et al., 2015a, 2015b; Van Cauwenberghe and Janssen, 2014; Li et al., 2015) provides the impetus needed to clarify both the exposure routes and bioavailability of POPs transferred via MPs.

Table 1

Some material characteristics of the plastics that influence the behavior of their microparticles.

Characteristic	Influence on behavior of MPs	Comments
1. Density	Buoyancy in seawater determines where in the water column the MP is likely to initially reside in.	Density ranges of classes of plastics are generally known but can be modified by fillers as well as by surface foulants.
2. Partial crystallinity	The degree of crystallinity determines the ease of oxidative degradation and fragmentation during weathering.	General ranges of values are available for different plastics but these can change based on sample history
3. Oxidation resistance or weatherability	Chemical structures determine how easily oxidizable the plastic will be in the environment. Fragmentation is a consequence of extensive oxidative degradation.	Ease of oxidation suggested by the chemical structure may be very different in compounded plastics that incorporate stabilizers and additives.
4. Biodegradability	Determines the rate of mineralization and potential partial removal of plastics from the water column or sediment	Common plastics are generally bio-inert. Exceptions do exist in synthetic plastics as well as biopolymers.
5. Residual monomer	Toxicity of leaching residual monomers in MPs to marine organisms that ingest plastics.	Both residual monomer levels in common plastics as well as their toxicities are reliably known.
6. Transport props.	Bioavailability of residual monomers, additives and POPs sorbed by the MPs depends on their leaching rates in the gut environment.	These properties are known for virgin resins but can change because degree of crystallinity can be varied by sample history or additives.
7. Additives	Concentration and toxicity of additives in MPs may contribute to the adverse impacts on ingesting species.	Chemistry, levels of use in plastics and toxicities, are generally known. But these levels for endocrine disruptors is not reliably known.
8. Surface properties	Rate of fouling of floating debris determines rates of weathering and sinking of MPs.	Surface properties and fouling rates for common plastics are known.

Toxicity concerns on POPs and additives in MPs are based on laboratory exposure that for the most part tend to use concentrations unlikely to be encountered in the field or on selected single-species and employing short durations of observations. These findings, while indicative of potential adverse biological impacts, still require robust assessment in terms of realistic exposures anticipated in the field. Reports of ingestion of MPs in natural environments are available (Van Cauwenbergh, et al. 2015) but the diversity of methodologies used to isolate them and the different metrics used to quantify them do not allow an unambiguous assessment of MP loads in organisms.

Despite being a plastics-related problem the research literature on MPs are typically sparse on characteristics of the polymers that constitute the MPs. Clearly, the nature of the polymer making up the MPs (along with any additives), play a key role not only in determining ease of their generation but also of their environmental fate, and potential impacts to the ecosystem. This review is on the polymers that constitute MPs and seek to discuss how the characteristics of commodity thermoplastics commonly encountered as MPs determine their environmental impacts.

Table 1 lists the characteristics of polymers that constitute MPs reported in the literature.

4. Range of microplastics particle sizes

The term 'microplastics' is loosely used in the literature to include a surprisingly broad range of particles sizes (Gregory and Andrady, 2003) varying from ~5 mm (e.g. virgin resin pellets) to those a few microns in diameter. In field studies it is the mesh size of nets used to sample surface water (Law et al., 2010) or the sieves used in sampling beach sand (Hidalgo-Ruz et al., 2012) that primarily determine the lower-size limit of sampled MPs. With sampling methodologies not standardized, what is reported as floating MPs in most cases excludes those with sizes smaller than the net mesh size of about 330 µm. However, the average particle size of MPs in surface waters increases exponentially with decreasing particle size (Song et al., 2014). Smaller MPs also presented lower rise velocities and were therefore more susceptible to vertical transport (Reisser, et al., 2015). Also, the particle size invariably determines the population of marine organisms likely to ingest them (Davison and Asch, 2011). It is therefore useful to have a sub-classification of size classes included within the broad category of microplastics.

A practical scheme recently proposed by GESAMP (WG-40) (GESAMP, 2015) serves this purpose and is summarized in Table 2. However, in contrast to general usage of the term, it uses the term 'microplastics' to exclusively mean particles of size between 1 and 1000 µm. Virgin plastic pellets, a salient constituent of plastic debris

especially in 1980s (Karapanagioti and Klontza, 2007; Moreira et al., 2016) are classified differently as 'mesoplastics.' A European classification in 2013 proposed an alternative sub-classification and is included in Table 1 for comparison. The GESAMP scheme relates to a logical sub-division of particles, but in the present discussion we will use the original broader definition of 'microplastics.'

5. Polymers as pollutants

Polymers have the unique molecular structure of long chain-like molecules made up of repeating chemical structural units (or 'mers'). The structure of the single repeat unit alone is therefore adequate to chemically specify a homopolymer.¹ For instance, the structure $(-\text{CH}_2-\text{CH}_2-)_n$ represents polyethylene. When n or the number of repeat units is in the hundreds, the polyethylene is a viscous liquid or a soft wax whereas when n is in 100s of thousands, the polyethylene is a useful solid plastic. Average molecular weights, M_n (g/mol), for common plastics can therefore be very high often reaching up to millions g/mol. The longer molecular chains allow for stronger Van der Waal attractive forces between them and copious entanglement of the chains, obtaining exceptional mechanical properties such as modulus, strength and fracture toughness.

The subset of polymers² that can be melt processed into useful products is identified as 'thermoplastics.' Post-use thermoplastics can be readily recycled by re-melting them to form other products. Other polymers both natural (e.g. cellulose or natural rubber) and synthetic (e.g. poly(vinyl alcohol) [PVA]) cannot be melt-processed and are not considered to be plastics. Five major commodity plastics commonly encountered in MPs are thermoplastics: (polyethylene [PE], polypropylene [PP], poly(vinyl chloride) [PVC], polystyrene [PS] and poly(ethylene terephthalate) [PET]. Typical ranges of selected properties for these classes of plastics are given in Table 3.

Also frequently found in MPs are fibers that are melt-spun plastics uniaxially drawn to obtain a very high levels of crystallinity.

A second category of man-made polymer cannot be melt processed because they have a network structure (or are cross-linked) are the 'thermoset polymers'. Polyurethane foams used in floats, epoxy adhesives or paints, reinforced unsaturated polyester composites (GRP) used in vessel fabrication, and rubber tires are examples of thermosets used in the marine environment. Though not often discussed in the

¹ There are also copolymers where two or more types of repeat units occur in a single chain of the polymer.

² While strictly incorrect, the terms polymer and plastics are used interchangeably in this paper.

Table 2

Classification of plastics debris in the environment, based on GESAMP (2015).

Class	Size ranges GESAMP	Visualization	Technique	Size ranges (MSFD GES)*
Macroplastics	100–2.5 cm	Naked eye	Visual counting	>2.5 cm
Mesoplastics	2.5 cm–0.1 cm (1000 µm)	Naked eye or optical microscope	Neuston nets or sieving	0.5 cm–2.5 cm
Microplastics	0.1 cm (1000 µm) to 1 µm	Optical microscope	Microfilters <1 µm separation	0.5 cm (5000 µm) to 1 µm
Nanoplastics	<1 µm	Electron microscope	Nanofilters	<1 µm

* MSFD GES Technical Subgroup on Marine Litter (2013) Monitoring Guidance for Marine Litter in European Seas. Draft Report of European Commission. Brussels. (Van Cauwenberghe, L., et al., Microplastics in sediments: A review of techniques, occurrence and effects, Marine Environmental Research (2015), <http://dx.doi.org/10.1016/j.marenvres.2015.06.007>).

literature, thermoset polymers also contribute to ocean MPs. Common polymers associated with MPs are summarized in Fig. 2.

A majority of floating MPs in the oceans as well as those collected from beaches are reported to be either PE or PP and can be easily identified as such either using infrared spectroscopy [FTIR] in the ATR mode (Brown et al., 2010; Mintenig et al., 2016; Song et al., 2014; Nor and Obbard, 2014) or Raman spectroscopy (Browne et al., 2011; Van Cauwenberghe et al., 2013; Vianello et al., 2013; Frère et al., 2016). The latter is a relatively easier and faster semi-automated technique. Most Raman instruments are able to match the sample spectra to a spectral library to identify the specific plastic in MPs. Raman spectroscopy does not work well with the smaller or dark-colored microplastics and FTIR microscopy (Harrison et al., 2012) may have to be used. An emerging, faster technique for identification of MPs is hyperspectral imaging (Driedger et al., 2015) that yields false-color near infrared images of the particles (Karlsson, et al., 2016). Advantage of this technique is that multiple samples can be imaged and identified automatically, simultaneously. Visual identification of MPs despite its simplicity is prone to serious error (Song et al., 2015; Hidalgo-Ruz et al., 2012).

It is critical to appreciate that the generic term for a class of plastic such as 'polyethylene' [PE] includes a large number of different grades. While they are all PEs they differ in molecular weight, strength, crystallinity, weatherability and at times even the detailed chemical structure (in terms of crosslinking and functional groups that may be present.). This is illustrated in Table 4 that lists different ranges of properties for several grades of polyethylenes. This is not even comprehensive as it do not include very-low density (VLDPE), ultra-low density (ULDPE) or cross-linked grades of PE. Different applications require different grades of polyethylene. For instance, most linear low density (LLDPE) and low density (LDPE) polyethylene resin is extruded into films for plastic bags whereas the tougher less permeable high-density resin (HDPE) is blow molded into milk and chemical jugs. Different grades of PEs differ in their susceptibility to weathering and fragmentation as well as densities. Accordingly, the fate, behavior and ecological impact of their MPs in the ocean environment will also likely differ.

6. Density of plastics and sinking

Density of MPs invariably determines (via their buoyancy in sea water) the range of marine organisms they will encounter. Surface water sampling (Zhang, et al., 2015) as well as beach sampling generally finds PE and PP to be the dominant MPs often with some expanded PS

(Law, et al., 2010). PE and PP represent 30, and 27% of the global manufacture of resin (in 2015) and a majority of their compounded products even with additives and fillers, still float in seawater. Floating MPs typically accumulate encrusting foulants that have a ballasting effect over a period of time, increasing their apparent density (Cózar et al., 2014) causing them to sink in the water column (Ye and Andrady, 1991; Francesca and Fazey, 2016) ending up in deep water or in the sediment (Claessens, et al., 2011; Woodall et al., 2014). Even with positively buoyant plastics, floating in surface waters will therefore only be a transient phase of their fate before they are invariably fouled, entangled with other debris or grazed, to end up in the benthic sediment. Reductions in surface fouling on sinking plastics due to grazing may re-float them temporarily resulting in bobbing float-sink cycles (Ye and Andrady, 1991) before they are finally settle down in deep water or sediment.

But, floating plastics such as PP, PE and EPS share the photic zone with phytoplankton exponentially decreasing in concentration from surface to about 5 m (Kooi et al., 2016). Marine organisms including marine mammals (Lusher et al., 2015), seabirds that pick food particles off the surface of the water (Tanaka et al., 2013), fish species (Neves et al., 2015; Nadal et al., 2014), invertebrates (Goldstein and Goodwin, 2013; Von Moos et al., 2012) and zooplanktons (Ferreira et al., 2016) feeding in the euphotic zone, are well documented to ingest floating MPs. Rafting sessile species (Keswani et al. 2016; Kirstein et al., 2016) and pathogenic microorganisms (Zettler et al., 2013) adhere to floating plastics and can be transported over long distances to end up as foreign species on distant ecosystems. In some cases, depending on the species, these can be invasive and disrupt the compositional equilibrium of the ecosystem.

A potential mechanism of vertical transport of MPs is where the smaller meso- and nanoplastics form homo-aggregates or co-aggregates with phytoplankton (Long et al., 2015) and sink along with the biomass with entrapped denser debris. Transparent exopolymer particles (TEP) abundant in the marine euphotic zone (Underwood et al., 2004), secreted by phytoplankton (Long et al., 2015), (especially diatom species (Passow, 2002)) are good natural flocculants (Engel, 2004) and a very likely candidate to facilitate such aggregation. TEPs are charged acidic polysaccharides known to readily entrain dust and debris (Passow et al., 2001) and to form aggregates with phytoplankton (Thornton, 2004; Wang et al., 2016). The size range of MPs that might sink, entrained in TEP or phytoplankton aggregates is not clear but data on the sinking rates of MPs are beginning to emerge in the literature (Ballent et al., 2013; Long et al., 2015; Kowalski et al., 2016).

Table 3

Nominal values of selected properties of plastics in MP.

	LDPE	HDPE	PP	PS	PET	PA-6	PA-66
Glass transition (°C)	–100	–80	–25	+100	+69		+50
Density (g/cm ³)	0.91 to 0.925	0.959 to 0.965	0.90	1.04	1.29 to 1.40	1.13 to 1.15	1.13 to 1.15
Crystallinity (%)	30–50	80–90	30–50	0	10–30	30–50	30–50
UV/oxidation resistance	Low	Low	Low	Mod.	Good	Good	Good
Strength (psi)	600–2300	5000–6000	4500–5500	5000–7200	7000–10,500	6000–24,000	14,000
Surface energy (MJ/m ²)*	32.4	32.4	33	40.6	45.1	38	41.4

* "Adhesion & Adhesives - Science & Technology", A J Kinloch, Chapman & Hall, London, 1987.

LDPE – Low-density polyethylene; HDPE – High-density polyethylene; PP – Polypropylene; PS- Polystyrene; PET – Poly(ethylene terephthalate); PA-6 – Polyamide 6 (Nylon 6); PA-66 – Nylon 66.

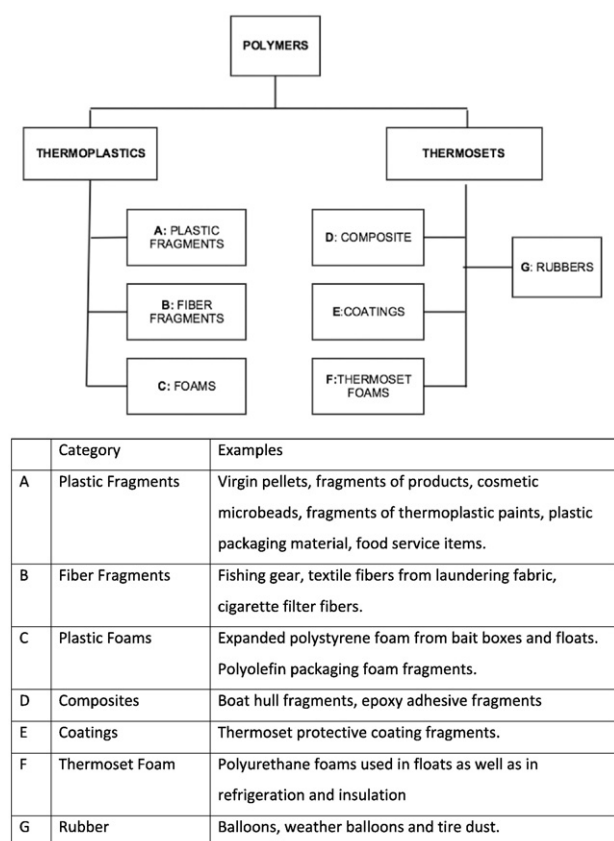


Fig. 2. A classification of synthetic polymers encountered in marine debris and in MPs, with examples of debris in each category.

Laboratory studies show TEP-entrained 2 μm PS beads to have a sinking rate of several hundred meters per day in seawater as opposed to only 4 mm/day for the individual beads (Long et al., 2015). Though the MP concentrations used in the study were higher than might be expected in the environment, TEP aggregates in the field would also entrain denser inorganic dust and debris making this a particularly credible but as yet unproven mechanism for vertical transport of MPs. Sinking of particles in the oceans via fecal pellets (Cole et al., 2013; Long et al., 2015) (the ‘biological pump’) accounts for translocation of ~10% of primary production into the sediment (Wakeham and Lee, 1993).

The lack of an increasing temporal trend in the abundance of MPs in surface waters in global datasets, despite the increasing rate of global plastic production, has been pointed out (Law and Thompson, 2014; C  zar et al., 2014; Woodall et al., 2014; Eriksen et al., 2014; Halle, et al., 2016) and sometimes attributed to a ‘missing’ fraction of MPs. Net sampling used in quantifying floating MPs is not particular efficient and may account for at least some of the discrepancy. This sinking phenomenon that transports MPs vertically to deep water or sediment may also contribute to this ‘missing fraction’. Reports show marine sediment to be rich in MPs (Van Cauwenberghe et al., 2015; Lucy et al., 2014; Woodall et al., 2014) but what fractions of these are PE or PP is not known.

Table 4

An illustration of the diversity of plastic resins that fall under the generic term ‘polyethylene.’

	Density (g/cm ³)	Crystallinity (%)	Avg. molecular weight (g/mol) $\times 10^3$	Tensile strength (psi) $\times 10^3$
Linear low density	0.92–0.93	~20%		–
Low density	0.91–0.925	30–50	10–30	0.6–2.3
Medium density	0.926–0.94	50–70	30–50	1.2–3.0
High density	0.941–0.95	70–80	50–250	3–5.5
Linear high density	0.959–0.965	80–90	250–1500	5–6
Ultra-high MW	0.93–0.94	~95	3000–6000	~7

7. Crystallinity of plastics

Plastics such as PE, PP and PET have a partly crystalline morphology with some short segments of the long polymer chains in the bulk, aggregated into oriented parallel bundles to obtain crystal-like domains of short-range order that can be several hundred angstrom units in dimension. These ‘crystallites’ melt, re-form and grow similar to conventional crystals of organic compounds. But bulk of polymer will also have (usually a larger fraction of) randomly oriented or amorphous chains, generally as the dominant fraction. Essentially, semi-crystalline plastics are therefore made up of micro-scale hard crystallites embedded in a soft amorphous matrix. This morphology was modeled by a ‘fringed-micelle’ structure in early studies (Bryant, 1947) as depicted in Fig. 3. But the crystallites can also be spherulites with radial crystalline lamellar with trapped inter-lamellar amorphous polymer chains. With PP for instance, the spherulite measure typically, $40 \pm 3 \mu\text{m}$ (Van der Wal et al., 1998). Partial crystallinity generally makes the plastic tougher but at very high degrees of crystallinity it can render the material brittle. This morphological model of plastics is important because of its bearing on ease of crack formation and fragmentation of semi-crystalline plastics such as PE, PP and PET in weathering.

Crystallinity in plastics is conveniently estimated using X-ray diffraction, Raman spectroscopy or thermal analysis, especially Differential Scanning Calorimetry (DSC). DSC measures the melting enthalpy H_m (J/g) of the plastic material and its ratio with that of the 100% crystalline plastic, $H_{m,0}$ (J/g) yields an estimate of percent crystallinity.

$$\text{Percent crystallinity} = (H_m/H_{m,0}) \times 100$$

But, fractional crystallinity in plastics is not an inherent characteristic property of the polymer and depends not only on its chemistry (and tacticity of polymer) but also on Mn (g/mol), chain branching, thermal history and processing. Crystalline content can be easily changed by physical or thermal treatment of the polymer affecting its inherent weatherability, strength or density. In spinning textile fibers, for example, the plastic is drawn uniaxially to high extensions to encourage very high degrees of crystallization to yield uni-axially strong plastic fiber.

Given their molecular structure, amorphous or ‘glassy’ polymers such as PS and PVC are inherently not crystallizable. Naturally, they show no crystalline melting point, but when gradually heated, these develop a degree of softness or flexibility at a characteristic temperature (called the glass transition temperature, T_g). At T_g , the heat energy imparted to the plastic is just sufficient to allow limited thermal motion in short sections of the polymer chains. Below this temperature the plastic is a brittle glassy material but it becomes a rubber at $T > T_g$. Higher the temperature of use relative to the T_g of a polymer, more flexible will the polymer be during use. As seen in Table 3, PE and PP have very low T_g values and are therefore characterized by flexible molecular chains at ambient temperatures.

Percent crystallinity is particularly important characteristic for MPs for several reasons:

- Higher degrees of crystallinity result in correspondingly higher density of MPs rendering them negatively buoyant. This determines its location in the water column and can therefore select the range of marine organisms the MPs can interact with.



Fig. 3. Schematic representation of a semi-crystalline plastic showing ordered segments (thick lines) of polymer chains that have crystal-like properties embedded in an amorphous (thin lines) polymer matrix.

- b) The loading of POPs compounds in highly crystalline plastics will be relatively lower compared to that in amorphous plastics as only the amorphous fraction of semi-crystalline polymer is able to dissolve the POPs compounds.
- c) Oxidative degradation in weathering also occurs primarily in the amorphous fraction of the plastic, as oxygen permeability in the crystalline fraction is relatively lower than in amorphous regions.
- d) The fragmentation of embrittled plastics tend to occur by crack propagation in the degraded amorphous regions. Initial ductile deformation of embrittled plastic debris subjected to stress is in the amorphous fraction.

The stress imposed on semi-crystalline polymers such as PE or PP is initially accommodated not by deforming the crystallites but by extension (or compression) of the amorphous fraction and tie molecules that bind crystallites together (Peterlin, 1977; Kennedy et al., 1994). At very high strains, for instance beyond the yield point, some deformation (re-melting) of crystalline lamella will occur changing the fraction and distribution of crystalline fraction (Fig. 4).

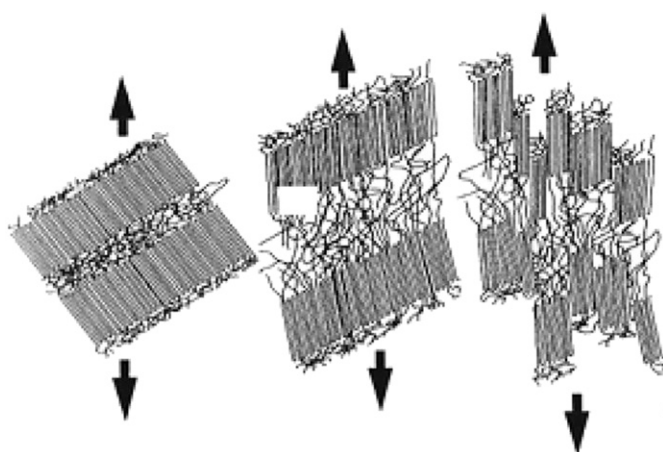


Fig. 4. Deformation of a semi-crystalline plastic at different strains. (Reproduced with permission from Arencón and Velasco (2009).)

8. Consequences of weathering

Weathering of plastics eventually leads to fragmentation and the creation of secondary or daughter MPs. Depending on the chemistry of the polymer, bulk morphology and where it is exposed at, the MPs degrade at different rates in the marine environment (Gregory and Andrady, 2003; Andrady, 2011). The term 'degradation' (and terms such as biodegradation) can have different meanings. It may refer to a partial chemical change of the plastic where the properties of the material change or its average molecular weights changes. As used here, however, the term means complete degradation or mineralization where the plastic is digested into small molecules, typically CO_2 and H_2O . Only mineralization completely removes the polymer from the ocean environment and is therefore of value from an ecological standpoint.

The relative importance of different environmental factors in bringing about weathering in the marine environment is qualitatively illustrated in Table 5. Exposure to solar UVR is the only significant mechanism that results in rapid environmental degradation of polymers. Solar radiation initiates autocatalytic thermal oxidation that is primary responsible for the degradation process. While biodegradation (and even hydrolysis) does occur at sea (Zettler et al., 2013), the reactions proceed too slowly to result in significant levels of environmental degradation of common plastics under outdoor conditions (Andrady, 1998; Andrady, 2011).

Clearly, most conducive to rapid weathering degradation is exposure in the beach zone; compared to exposures on beach the weathering of floating plastics is considerably slower (Andrady, 2011; Andrady and Pegram, 1990, 1989). This is primarily because of the relatively lower sample temperatures of the debris floating in water compared to those exposed on sand. Also, surface foulants on floating samples screen out the solar UVR responsible for initiation of oxidation reactions almost totally (Weinstein et al., 2016) and retards weathering degradation. MPs collected from surface waters show less surface cracking indicative of degradation, on the bottom fouled surface compared to top surface exposed to sunlight (Halle et al., 2016). Degradation rates in deep water and sediment are also minimal for the same reason (Muthukumar et al., 2011). No known mechanism exists for degradation and therefore the removal of plastics that lie beyond the photic zone suggesting a slow accumulation of plastics in the benthos over the years. The global standing stock of floating plastics was estimated by Sherman and van Sebille (2016) to be 93–236 TMT/year.

Given the favorable weathering environment on beaches it is reasonable to speculate that majority of the secondary MPs are in fact generated on beaches or on land and then washed off into the ocean. Cleaning beaches of accumulating plastic debris is therefore a critical component in controlling microplastics pollution.

Typically, several changes are observed in common plastics undergoing weathering. These changes for polyolefins are summarized in the Fig. 5 below.

8.1. Yellowing discoloration

PE, PP, PS, PET, polycarbonate [PC] and poly(vinyl chloride) [PVC] all turn yellow to yellow-orange as a result of oxidation. This is generally

Table 5

Qualitative summary of the factors that facilitate degradation of MPs in different zones in the marine environment.

Zone	Solar UVR	Sample temperature	Oxygen availability	Fouling
Beach	High	Very high	Very high	No
Surface water	High ^a	Low	High	Yes
Midwater-deepwater	No	Low	Low	No
Marine sediment	No	Very low	Very low	Yes

^a Depends on the kinetics of fouling that shields solar UVR from the surface.

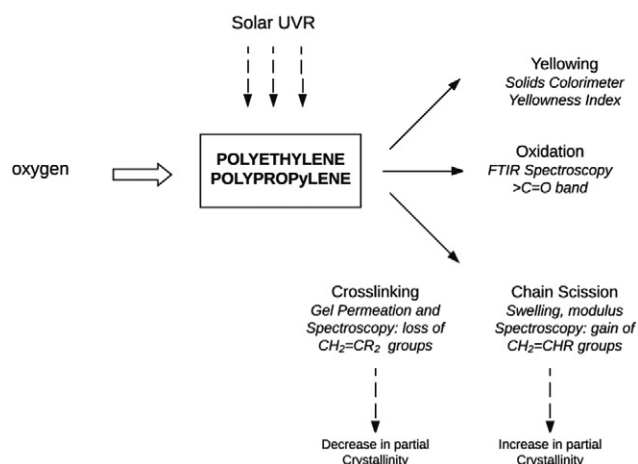


Fig. 5. Schematic diagram of changes in polyolefin polymer subjected to solar UV-facilitated oxidation.

due to the accumulation of degradation products of the polymer itself (as with PVC, PC and PS) or that from the thermal stabilizers used in the resin. Stabilizers such as phenolic antioxidants compounded into the plastic during pellet manufacture or subsequent compounding can oxidize into yellow (usually quinone) compounds. With PVC, photodegradation involves loss of HCl gas from polymer with the formation of conjugated unsaturation that are yellow in color. Yellow coloration can be quantified with a solids colorimeter, and expressed as Yellowness Index (preferably according to ASTM D 1925-70 or E 313-15e1). The hue obtained is typically indicated on the L^*, a^*, b^* color space. Color is readily quantified using coordinates in a 3-dimensional color space originally proposed by CIE where the vertical axis L^* refers to lightness of the color while a^* and b^* define position of the color in a 2-dimensional surface where $a^* = 0$ and $b^* = 0$ corresponding to grey. All perceivable colors can be quantitatively described using of coordinates a^* and b^* ; the color typically shifts from white to yellow to yellow-red on extended exposure to solar UVR.

8.2. Accumulation of oxidized moieties

Fourier Transform Infra-red Spectroscopy (FTIR) of weathered plastics typically show an increase in oxygenated moieties such as aldehydes, ketones, carboxylic acids, hydroperoxides and alcohol groups in the plastic with the duration exposure. Some of these, especially carbonyl $\{>C=O\}$ functionalities, can be used to quantify the degradation process during early stages of degradation. De-convoluted high-resolution spectra (Philippart et al., 1999) resolve the peaks associated with different moieties. The ratio of the area under $>C=O$ absorption band to one that is invariant by oxidation (e.g. 1456 cm^{-1} or 720 cm^{-1} and 730 cm^{-1} for PE) (Zerbi et al., 1989) yields an index that might be used to quantify the degree of oxidation (Harrison et al., 2012; Andradý et al., 1993; Carrasco et al., 2001). This method of quantification of $>C=O$ strictly applies only in early stages of weathering because initial products themselves degrade subsequently, often with the loss of CO_2 (Fernando et al., 2007). Where the quantification attempted using

broad spectral regions as opposed to individual peaks (Brandon et al., 2016) the quantification obtained is far less reliable (Table 6).

FTIR spectroscopy may also be used to follow chain scission and crosslinking that accompany oxidation. Crosslinking generally results in a decrease in the vinylidene unsaturation generally present in polyolefins ($-\text{CH}=\text{CR}_2$) and usually also changes its crystallinity. The modulus increases because of the crosslinks resisting imposed strain and the material does not dissolve completely in solvents yielding a gel fraction. Chain scission results instead in an increase of vinyl functionalities ($-\text{CH}_2=\text{CHR}$) and a decrease in the average $\text{Mn}(\text{g/mol})$ of the polymer as determined by a method such as Gel Permeation Chromatography [GPC].

8.3. Changes in crystallinity

Early stages of weathering increases the degree of crystallinity of the oxidized plastic (Rouillon et al., 2016). Two factors contribute to this increase. The amorphous polymer is preferentially degraded in weathering, increasing fractional crystallinity. Also, the short segments of polymer generated by chain scission in degradation migrate together and crystallize by 'chemi-crystallization' (Rabello and White, 1997; Yadong et al., 2015). This increase in crystallinity (as evidenced by X-ray diffraction), differential scanning calorimetry (DSC) or indirectly using FTIR spectroscopy (Carrasco et al., 2001; Zerbi et al. 1989) is relatively more likely in the surface layer where oxidation primarily occurs. However, as relatively more crosslinking occurs in later weathering some of the crystallinity might be reduced.

8.4. Changes in mechanical properties

Chain-scission, crosslinking and crystallinity directly impact bulk mechanical properties of plastics, particularly tensile elongation at break and tensile modulus. While routinely used to monitor weathering in macroplastic debris, these measurements are not always practical with MPs. The measured bulk properties even with thick dog-bone samples are typically averages between those of a highly degraded surface layer and a virtually intact interior of the plastic material. Only at higher extents of weathering, will the radical species involved in oxidation can be available for reaction within the interior of a thick sample. As the rate of weathering depends on the thickness of samples it is important to use standardized test pieces (such as ASTM Type IV or V) in weathering studies. For PE film samples FTIR measurements were shown to correlate with the decrease in average tensile extensibility for weathered PE films (Andradý et al., 1993; Carrasco et al., 2001), but this may not hold for different plastics or other mechanical properties.

9. Signatures of weathering on microplastics collected from the field

Three important limitations apply to measurements of physical or mechanical properties of MPs sampled from the marine environment.

First, the duration of outdoor exposure (or age) of sampled MPs cannot be reliably estimated by any such measurements used to quantify the extent of weathering. This has been attempted by comparing carbonyl indices of lab-weathered samples with those found in the field (Brandon et al., 2016; Veerasingam et al., 2016). But, even the gross differentiation of field samples into 'younger' and 'older' MP debris is unlikely to be reliable. Changes in the properties measured depend on both the total dose of solar UVR received by the MP as well as the sample temperatures during the period of exposure. As exposure could occur on both beaches as well as while floating in water (as well as during use), the temperature history of the MPs is not known and duration of field exposure cannot be reliably estimated from spectroscopic data on field-collected MPs.

Second, none of the metrics discussed directly assess the key parameter that determines the formation of secondary MPs in the field, the extent of chain scission or crosslinking reactions that occur during

Table 6

Assignment of absorption bands in FTIR to oxidation products of polyethylene. Adapted from Gardette et al. (2013).

Functionality	Structure	Absorption band [cm^{-1}]
Ketones	$>C=O$	1718
Carboxylic acids	$-\text{COOH}$	1713
Esters	$-\text{COOR}$	1735
Lactones	$-\text{O}-C=O$	1780
Unsaturation	$-C=C-$	1640

weathering. Fragmentation kinetics of weathered plastics invariably depends on these critical changes in the material. While techniques such as sol/gel analysis, viscometry and gel-permeation chromatography (GPC) (Giroris et al., 1996) do measure these, not only are they tedious but converting the data into values of percent scission or crosslinking, is not straight forward as it relies on several simplifying assumption. This coupled with the heterogenous morphology of semi-crystalline plastics makes it difficult to model the fragmentation process based on scission and crosslinking data.

Third, some of the MPs in field samples are fragments of products (as opposed to virgin pellets.) Additives used in compounding, especially UV stabilizers, used in products can drastically retard the weathering process. As environmental MPs are of unknown composition (with respect to initial stabilizer content and potential leaching losses) their weathering data is variable and cannot even be compared to each other.

It is possible to anticipate approximate relative rates of weathering for virgin resin pellets (without UV stabilizer) under controlled laboratory exposure conditions.

Unstabilized PP, for instance, is expected to weather faster than unstabilized PE under comparable exposure because the former can form more stable tertiary radicals (Gewert et al., 2015). But the opposite has been also reported for field -sampled MPs possibly because of the effects of unknown additives in them (Cooper and Corcoran, 2010). For polyolefins, the UV stability decreases as HDPE > LLDPE > LDPE > PP in outdoor exposure (Gulmine et al., 2003) but different grades of plastic resin within even a single class such as LLDPE can show variations in stability.

10. Fragmentation by surface ablation

Very little is known about the fragmentation of plastics debris consequent to weathering. Understandably, industrial research was almost exclusively focused on ensuring maximum service life of plastic products strived to understand and control early stages of weathering degradation of plastics. There has been little interest, hitherto, in studying further weathering or fragmentation of essentially post-use plastics waste. With burgeoning interest in marine MPs, however, the fragmentation of litter or unmanaged waste in rivers, estuaries and beach environments need to be studied. To appreciate the complexity of the process several key dimensions of weathering responsible for fragmentation need to be appreciated.

Fragmentation likely occurs due to mechanical forces (wave action, abrasion with sand and contact with animals) acting on highly weathered plastic debris (Corcoran et al., 2009). Weathering in semi-crystalline plastics such as PP and PE generally yields a surface that is laterally heterogeneous as crystalline and amorphous phases that degrade at very different rates. Once initiated, oxidation reactions cluster around the points of initiation leading to blocks of oxidation (Celina and George, 1993) as radicals do not diffuse well in the solid phase (Billingham, 1989). Cracks develop in inter-crystalline regions due to facile degradation of amorphous phase and grow to invariably propagate into deeper layers (in z-direction) providing a site for macro-fragmentation of the material. The result of these cracks propagating even deeper will be fragmentation that essentially split a fragment or an MP granule into one or more large daughters.

However, a second possible mode of fragmentation via surface-ablation that is often neglected can also occur. The initiation of oxidative degradation in plastics is well known to be localized to a thin surface layer (Wise et al., 1997; Gillen and Clough, 1992; Pospisil, et al., 2006). This is partly because solar UVR is rapidly attenuated within plastics and also because oxidation in polymers can be diffusion-limited. Oxygen cannot diffuse in beyond a surface layer rapidly enough to match the rate the gas is consumed within the bulk (as oxygen permeability in common plastics is low). This favors a gradual decrease in the rate of oxidation from the exposed surface to interior bulk of a fragment of plastic at any given time (Shyichuk and White, 2000; Celina, 2013).

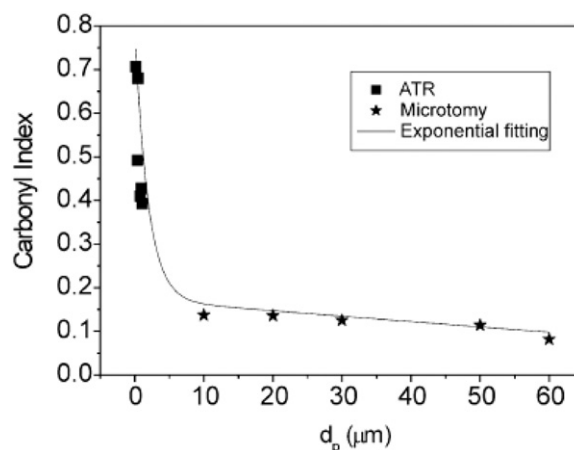


Fig. 6. Change in carbonyl index with depth from surface of polyolefin (LDPE) samples exposed in weatherometer for 400 hrs. as measured by FTIR on microtomed sections. Reprinted with permission from Gulmine et al. (2003).

The result is the localization of oxidation primarily in a surface layer of thickness d , where d is of the order of magnitude of D_0/k where D_0 is the diffusion coefficient for oxygen in the amorphous phase of plastic and k is the pseudo-first order rate constant of oxygen consumption (Audouin et al., 1994).

This layer-effect in weathering is well known and has been experimentally verified for several common plastics. Oxidation-induced changes in morphology (Sarwade and Singh, 1999) and scission reactions (leading to changes in M_n (g/mol)) were shown to be localized in the surface layers of plastics (Giroris et al., 1996; La Mantia and Gardette, 2002; Ricon-Rubio et al., 2001). In polymer samples (PE, PP and PET) exposed to laboratory accelerated weathering the thickness d (microns) of this layer was estimated spectroscopically to be of the order of 100–200 μm (Shyichuk and White, 2000; Giroris et al., 1996). With PP exposed to Xenon radiation that simulate sunlight, an exposure duration of 264 h at 70 °C yielded $d \sim 200 \mu\text{m}$ (Giroris et al., 1996). As might be expected the value of d is temperature dependent and varies with the duration of exposure (Giroris et al., 1996). This layer effect was also reported for thermoset polyester-urethane coatings (Li et al., 2003). Figs. 6 and 7 illustrates the surface-layer degradation reported for PP and LDPE exposed to weatherometers under accelerated exposure.

The weathered surface layer will not only be highly cross-linked and have a different fractional crystallinity but also will be rich in hydrophilic oxidation products (Kaczmarek et al., 2002). Exposed to moisture, this

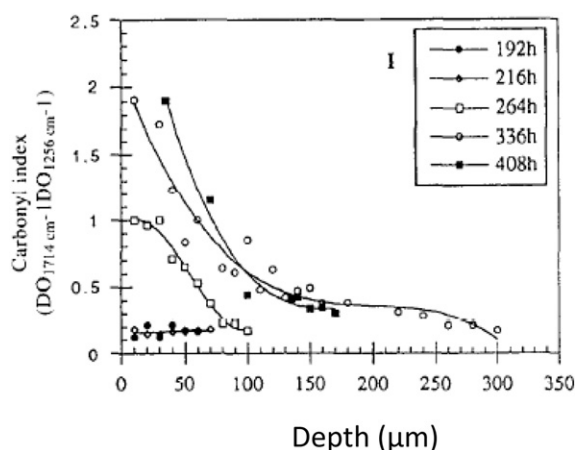


Fig. 7. Change in Carbonyl index with depth in PP exposed in a Xenotest 150 weatherometer at 70 °C. Reprinted with permission from Giroris et al., (1996).

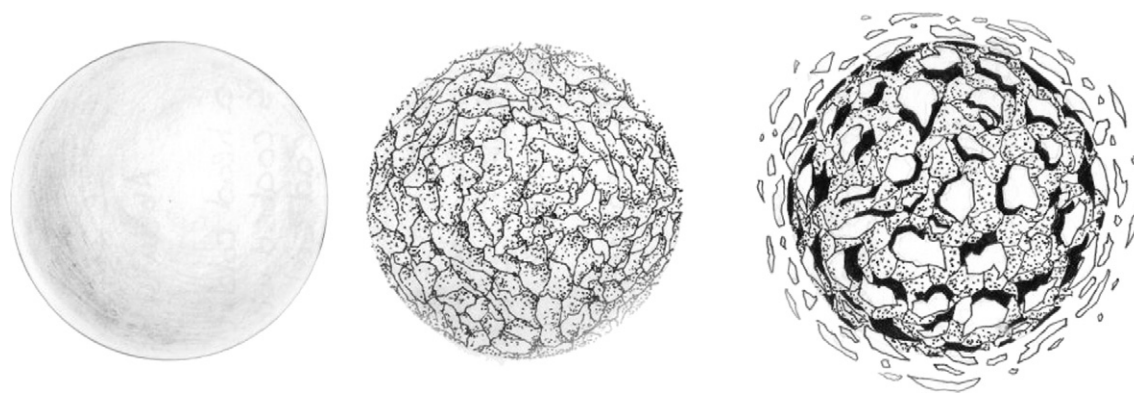


Fig. 8. Artists rendition of surface ablation fragmentation process in a spherical MP. Left: As-produced spherical bead. Middle: Weathered bead with extensive surface cracking. Bead with extensive surface. Right: Bead with partially fragmented surface layer.

layer will therefore have different swelling behavior compared to underlying bulk plastic. Repeated swell/dry cycles in outdoor weathering (especially in beach environments) would therefore likely compromise the integrity of the interface between the surface layer and underlying virgin polymer leading to fragmentation by delamination. Wave action or interaction with biota can subsequently disintegrate and detach the brittle layer into micro-scale particles (MPs) or secondary MPs. Fig. 8 shows an artist's rendition of surface-ablation fragmentation debris of a spherical mesoplastic.

In the surface-ablation mode of degradation described above, a large numbers of daughter fragments with a narrow particle-size distribution are expected as a result on weathering. Their average size depends on layer thickness d (microns) and the size scale of surface heterogeneity. It should be feasible to distinguish experimentally between the progressive reduction in particle size by macro-fragmentation and the numerous smaller daughters formed in ablation fragmentation. Assuming a spherical parent particle of diameter D , the number N of homogeneous spherical daughters, each having a diameter equal to d , resulting from fragmentation can be estimated by geometric considerations.

$$N = 8 + \left(\frac{6D^2}{d^2} \right) - (12D/d)$$

However, the process more likely obtains a normally distributed set of daughters with an average thickness dimension of the surface layer. The bulk fragmentation of the MP yielding large daughters also will progress along with the surface-ablation mode of fragmentation.

Some preliminary data on the creation of large amounts of small particles on weathering followed by mechanical stress have been reported (Andrady et al., 2016; Shim, 2016). But, robust data to verify the surface-ablation model of fragmentation during weathering is yet to be reported. However, the mechanism of surface-ablative fragmentation underlines the importance of beach cleaning as a means of reducing the incidence of secondary microplastics in the oceans.

11. Conclusions

The physical and structural characteristics of polymers that compose the MPs play an important role in determining how much of an ecological threat they pose in the marine environments. Fate of MPs in the oceans depend on their density relative to that of sea water and the ease of weatherability that is dictated by their chemical structure as well as additives incorporated into the plastic formulation. Percent crystallinity of the plastic is similarly important as both their fracture behavior during fragmentation and release rates of any POPs sorbed in the MPs depend on it. With ingestible secondary MPs generated by fragmentation, both the loading of POPs and the rate of their release in the gut of the ingesting organisms, determine toxicity. Fragmentation in

weathering may result in gross fracture of plastic debris into several large daughters. But the light-induced degradation being primarily a surface phenomenon, a surface ablation mechanism leading to large numbers of very small daughter MPs a few microns in size, is also likely. Given the wide-ranging influence of polymer properties on the fate of MPs it is critical that research include better characterization of the plastic that compose the microplastic.

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