

Chapter 3

Persistence of Plastic Litter in the Oceans

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Abstract The increasing global production and use of plastics has led to an accumulation of enormous amounts of plastic litter in the world's oceans. Characteristics such as low density, good mechanical properties and low cost allow for successful use of plastics in industries and everyday life but the high durability leads to persistence of the synthetic polymers in the marine environment where they cause harm to a great variety of organisms. In the diverse marine habitats, including beaches, the sea surface, the water column, and the seafloor, plastics are exposed to different environmental conditions that either accelerate or decelerate the physical, chemical and biological degradation of plastics. Degradation of plastics occurs primarily through solar UV-radiation induced photo oxidation reactions and is, thus, most intensive in photic environments such as the sea surface and on beaches. The rate of degradation is temperature-dependent resulting in considerable deceleration of the processes in seawater, which is a good heat sink. Below the photic zone in the water column, plastics degrade very slowly resulting in high persistence of plastic litter especially at the seafloor. Biological decomposition of plastics by microorganisms is negligible in the marine environment because the kinetics of biodegradation at sea is particularly slow and oxygen supply for these processes limited. Degradation of larger plastic items leads to the formation of abundant small microplastics. The transport of small particles to the seafloor and their deposition in the benthic environment is facilitated by the colonization of the material by fouling organisms, which increase the density of the particles and force them to sink.

Keywords Synthetic polymer • Mechanical properties • Weathering • Embrittlement • Photo oxidation • Microplastics

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3.1 Introduction

Studies on the occurrence of marine litter on beaches and as flotsam generally find plastics to be the major component of the mix of debris (Galgani et al. 2015). Plastics have diverse uses and are gaining popularity in building and packaging applications because of their ease of processing, durability and relatively low cost (Andrady and Neal 2009). However, this predominance of plastics in litter is not the result of relatively more plastics being littered compared to paper, paperboard or wood products reaching the oceans, but because of the exceptional durability or persistence of plastics in the environment. Data on plastic debris on sediments are more limited (Spengler and Costa 2008) but suggest that plastics represent a significant fraction of the benthic debris as well (Watters et al. 2010). Quantitative information on the density of litter on beaches or in the ocean classified according to the class of plastic, are not available. Usual classification is by geometry (e.g. fiber) or by product type (e.g. cigarette butts). Also the surveys of water-borne plastic debris collected via neuston net sampling of surface waters (Hidalgo-Ruz et al. 2012) and even beach studies (Ng and Obbard 2006; Browne et al. 2011) close to the water line, seriously underestimate the magnitude of plastic litter. Not only do these exclude the negatively buoyant plastics but also fragments smaller than the mesh-size of the nets used.

3.2 Buoyancy and Sampling Errors

Of the five classes of the commonly used plastics (or commodity thermoplastics), polyethylenes (PE) and polypropylenes (PP) as well as the expanded form of polystyrene or polystyrene foam (EPS) are less dense than sea water while others such as poly (vinyl chloride) (PVC) and poly(ethylene terephthalate) (PET) are negatively buoyant and sink into the mid water column or to the sediment (Andrady 2011). Significantly, one of the key fishing-gear related plastics, nylon or polyamide (PA), also belongs to this category and hence the negative buoyancy of these items likely explains their virtual absence in beach litter or flotsam surveys, despite their high volume use at sea. However, there are exceptions to this general expectation that is based on the properties of the pure resins such as with virgin resin pellets or prills found commonly in sampled debris. Some plastic products are compounded with fillers and other additives that alter the density of the virgin plastic material. These additives are needed to ensure ease of processing the plastic as well as to obtain the mechanical properties demanded of the final product. Where the density is increased because additives, such as fillers, are incorporated, the material may not float in surface water and, therefore, not be counted in net sampling. Accordingly, plastics such as PS, PET and PVC, which are denser than sea water, should be missing from floating samples as well. In fact, however, they might be included in flotsam samples because products such as bottles, bags and

Table 3.1 Marine debris items removed from the global coastline and waterways during the 2009 international coastal cleanup

| Rank | Debris item | Count (millions) | Plastic used |
|------|--------------------------|------------------|--------------|
| 1 | Cigarette filter | 2.19 | CA |
| 2 | Plastic bags | 1.13 | PE |
| 3 | Food wrapper/container | 0.94 | PE, PP |
| 4 | Caps and lids | 0.91 | PP and HDPE |
| 5 | Beverage bottles | 0.88 | PET |
| 6 | Cups, plates and cutlery | 0.51 | PS |
| 7 | Glass bottles | 0.46 | – |
| 8 | Beverage cans | 0.46 | – |
| 9 | Straws stirrers | 0.41 | PE |
| 10 | Paper bags | 0.332 | – |

Data from Ocean Conservancy. CA Cellulose acetate, HDPE High-density polyethylene

foams made from these plastics trap air. This is clearly the case with EPS foam used in floats, bait boxes and insulation that generally constitutes a highly visible and major fraction of persistent litter in the ocean environment.

The main items of debris are different plastic products (or their fragments) as illustrated in the global beach clean data compiled by Ocean Conservancy for 2009. The data in Table 3.1 summarize the beach cleanup efforts regularly sponsored by the organization: beach cleanup is carried out by volunteers who also count and tabulate the litter over an area assigned to each person. The data are aggregated and summarized by the Ocean Conservancy.

A second inefficiency in sampling of plastic debris at all marine sites is the minimum particle size isolated. The procedure of using plankton nets to sample water and separating particles visually after sieving or by floatation from sediment samples invariably fails to catch the micro-sized fragments of plastics. Commonly used nets have a mesh size of about 330 μm . While the meso-sized plastics are reasonably represented in these samples the micro-sized and nano-scale particles are grossly underestimated. Since a great majority of the floating litter is generated on land and transported to the ocean, one would expect the resin types in the litter to be consistent with the production volume shown in Table 3.2. As the mass fraction of the unsampled microplastics is likely miniscule by comparison to the macroplastic debris, the statistics of plastics by resin type in water samples show PE and PP to be the most abundant, consistent with the production data in Table 3.2.

3.3 Fate of Plastics Entering the Oceans

Common plastics used in packaging and encountered in the marine environment are persistent recalcitrant materials. In common with other organic materials they do ultimately degrade but the rate at which environmental degradation proceeds is painstakingly slow for plastics. Several agencies can potentially bring about the

Table 3.2 The common classes of plastics found in ocean debris and those used in fishing gear along with their densities and the fraction of their global volume production. Items of lower specific gravity than seawater ($\sim 1.02 \text{ g cm}^{-3}$) float

| Plastic | Specific gravity (g cm^{-3}) | Percentage of production ^a | Main uses |
|------------------------------------|---|---------------------------------------|-------------------------|
| Polyethylene (PE) | 0.91–0.94 | 29.1 | Packaging, fishing gear |
| Polypropylene (PP) | 0.83–0.85 | 18.0 | Packaging, fishing gear |
| Polystyrene (PS) and foam (EPS) | 1.05 (variable) | 7.8 | Packaging, food service |
| Poly(vinyl chloride) (PVC) | 1.38 | 15.3 | Packaging |
| Poly(ethylene terephthalate) [PET] | 1.37 | 20.0 | Packaging |
| Nylon (PA) | 1.13 | ~ 1 | Fishing gear |
| Cellulose acetate (CA) | 1.29 | < 1 | Cigarette filter |

^aPercentage production is based on data taken from plastics news (accessed: December 2014): <http://www.plasticsnews.com/article/20100305/FYI/303059995/global-thermoplastic-resin-capacity-2008>

degradation (or chemical breakdown of the polymer molecules with consequent change in material properties) in the environment. These are primarily as follows:

- (a) solar UV-induced photodegradation reactions
- (b) thermal reactions including thermo-oxidation
- (c) hydrolysis of the polymer
- (d) microbial biodegradation

Of these, only the first or the light-induced oxidative degradation is particularly effective in the ocean environment and that only with plastics floating at the sea surface or littered on beaches (Cooper and Corcoran 2010). Slow thermal oxidation of plastics also proceeds in concert with photo-oxidation, especially on beaches. However, no hydrolysis or significant biodegradation of plastics is anticipated in the ocean.

Different measurable properties of a plastic might be altered as a result of weathering. Some of these are properties that are directly relevant to the performance of common products made from them (Singh and Sharma 2008). Others are changes at the molecular level that might be used to detect early stages of degradation. The popularly used characteristics of common plastics are as follows:

- (a) decrease in average molecular weight of the plastic. This is conveniently measured using gel permeation chromatography (GPC) and also using solution (or melt) viscosity
- (b) loss in bulk mechanical properties of the plastic, such as the tensile properties, compression properties or the impact properties
- (c) loss in surface properties of the material including discoloration, micro-cracking or 'chalking' (release of white filler from filled plastic surfaces on weathering)
- (d) changes in spectral characteristics that are markers for oxidative degradation or photodegradation. For polyolefins, the relative intensity of the carbonyl absorption band (in the Fourier transformed infra-red or the FTIR spectrum), which increases in percent crystallinity or level of unsaturation, might be monitored.

3.3.1 Photo-Oxidative Degradation

Photo-oxidation of polyolefin plastics is a free-radical reaction that is initiated by solar UV radiation. The sequence of oxidative chemical reactions involved, results in (a) incorporation of oxygen-containing functionalities into the polymer molecules, and (b) scission of long chain-like polymer molecules reducing the number-average molecular weight of the plastic material. Of these, it is the latter that drastically affects the useful properties of the polymer. Even at low levels of oxidation (often a percent or less) very substantial loss in mechanical strength can occur. High-energy UV-B (290–315 nm) and medium energy UV-A (315–400 nm) solar wavelengths are particularly efficient in facilitating photo-degradation of polymers (Andrady 1996). However, the fraction of longer wavelength radiation in sunlight is very much larger compared to that of the UV radiation and most of the light-induced damage occurs in the UV-A and/or the visible region of the spectrum.

The approximate region of the solar spectrum that accounts for the most degradation is represented by an activation spectrum. Activation spectra are generated in experiments where samples of a plastic are exposed to solar or solar-simulated radiation behind a series of cut-on filters that allow only wavelengths higher than a cut-on wavelength to be transmitted through them. The degradation rates for samples behind different filters can be used to construct the activation spectrum (for a discussion of the experimental procedures involved in generating such spectra see Singh and Sharma 2008). Figure 3.1 shows an activation spectrum for yellowing of polycarbonate exposed to solar radiation. It is clear from the figure that the UV-A region of sunlight (320–340 nm) causes the greatest damage, despite the shorter more energetic wavelengths <320 nm being present in the spectrum. The shorter wavelengths account for less than ~5 % of the solar radiation spectrum.

Rates of degradation are markedly increased at higher ambient temperatures as the activation energies for oxidative degradation of common plastics are low

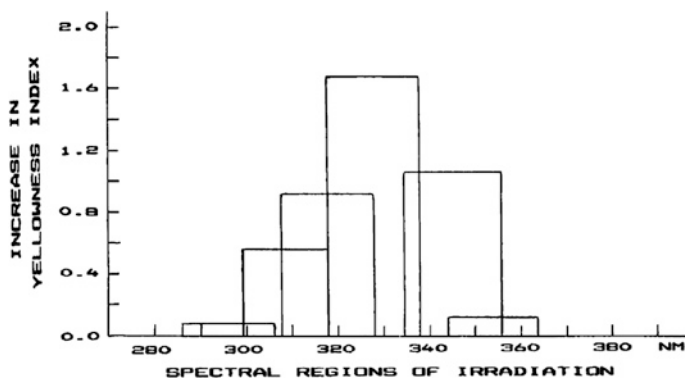
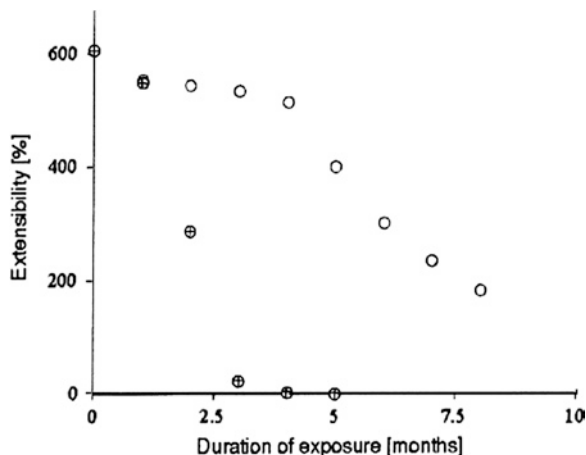


Fig. 3.1 Activation spectrum for yellowness index of un-stabilized lexan polycarbonate film (0.70 mm) exposed to natural sunlight facing 26°South in Miami, FL. Reproduced with permission from Andrady et al. (1992)

Fig. 3.2 Change in extensibility of polyethylene sheet samples after exposure to solar UV radiation in Dhahran, Saudi Arabia. The *open symbols* are for samples maintained at 25 °C. The *filled symbols* are for samples exposed at ambient temperatures of 26–36 °C. Reprinted with permission from Andrady et al. (1998)



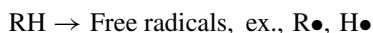
(Hamid and Pritchard 1991; Tocháček and Vrátníčková 2014). Plastics lying on hot sand on beaches undergo faster photo-oxidation relative to those floating on water and being, therefore, maintained at a lower temperature. The same phenomenon is also responsible for differences in the rates of weathering of differently colored plastics. Darker shades of plastics exposed to sunlight tend to absorb more of the infrared energy in the solar spectrum, reaching higher sample temperatures. Consequently, they weather faster relative to lighter colored plastics. A particularly good measure of degradation in plastics is tensile extensibility. Figure 3.2 shows the effect of sample temperature on the loss in tensile extensibility of polyethylene film samples exposed in Dhahran, Saudi Arabia. One set of samples was exposed at ambient temperature of 26–36 °C. Another set of samples was maintained at a constant temperature of 25 °C. At different durations of exposure the samples (typically dumbbell-shaped pieces) were removed periodically for testing. In this test the dumbbell shaped sample (5–6 in. long) is held at its ends in a pair of grips and pulled along its long axis at a constant speed of 500 mm/min. The sample first extends and then snaps. The ratio of the grip separation at the point the sample snaps to that at the start of the extension, expressed as a percentage, is the extensibility or ultimate strain of the sample.

3.3.2 Mechanisms of Photo-Oxidation

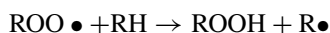
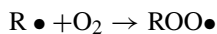
The basic mechanism of light-induced degradation for the two plastics used in highest volume and therefore most numerous in marine debris, PE and PP, is well known. It is a free-radical reaction initiated by UV radiation or heat and propagated via hydrogen abstraction from the polymer. The polymer alkyl radicals formed react with oxygen to yield peroxy radicals, $ROO\bullet$, that are converted to a peroxide moiety by hydrogen abstraction. As peroxide products can themselves

dissociate readily into radicals, the reaction sequence is autocatalytic. The main reactions involved in the sequence are as follows (François-Heude et al. 2015):

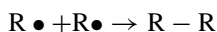
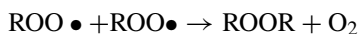
1. Initiation:



2. Propagation:

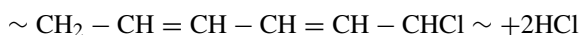
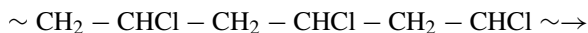


3. Termination:



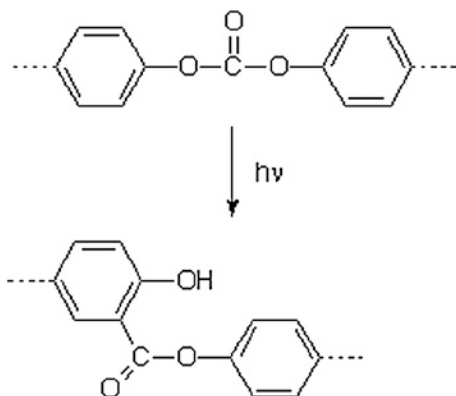
From a practical standpoint, it is the chain scission that accompanies this cyclic reaction sequence, which is of greater interest. The chain scission event is believed to be associated with one of the propagation reactions and is responsible for the loss in mechanical properties of the plastic material after exposure. Different mechanical properties (such as ultimate extensibility, the tensile modulus, or impact strength) having different functional dependence on the average molecular weight will change at different rates with the duration of exposure. There is, thus, no 'general' weathering curve for a given polymer but only for specific modes of damage of the polymer material under exposure to a specified light source such as sunlight or radiation from a xenon lamp. Chain scission is often directly estimated from gel permeation chromatography. Being associated with the number of propagation cycles it can also be correlated with the products of the chemical reactions, especially the accumulation of carbonyl compounds $\{>\text{C}=\text{O}\}$. This is often monitored using the relative intensity of the relevant bands in the FTIR spectrum of the polymer and has been demonstrated to correlate well with the ultimate extensibility of the sample (Andrady et al. 1993).

Other reactions that contribute to changes in the useful properties of plastics following exposure to solar radiation are also evident with common plastics. Yellowing discoloration of poly(vinyl chloride) (PVC) is an example of such a reaction. This is a light-induced de-hydrochlorination reaction that generates short sequences of conjugated unsaturation in the polymer (Andrady et al. 1989):



These absorb on the blue region and make the plastic appear yellow. However, polyolefins (both PE and PP) as well as PS also yellow on exposure to sunlight but the mechanism of such yellowing and the identity of the species involved are

not well known. Polycarbonate (PC) plastic used in glazing applications is another example of a material that undergoes yellowing under exposure to sunlight. The main photodegradation reaction of PC, however, is a rearrangement reaction (Fries reaction) with no change in spectral qualities (Factor et al. 1987):



A second reaction that yields yellow oxidation products also occurs along with it, however, the mechanistic details of the second reaction are unknown.

3.3.3 Weathering Under Marine Conditions

While the main agencies involved and the mechanisms of weathering in the marine environment are the same as those on land environments, the rates at which weathering proceeds can be significantly slower in the former (Pegram and Andradý 1989). To better understand the differences, the marine environment must be regarded in separate zones: the beach environment, the surface water environment, and the deep water/benthic environment. The availability of weathering agencies in these are different as summarized in Table 3.3.

Availability of sunlight to initiate the degradation reactions is restricted in the case of floating plastics because of bio-fouling of their surface in seawater. Initial

Table 3.3 Comparison of the availability of weathering agents in the different zones within the marine environment

| Weathering agent | Land ^a | Beach | Surface water | Deep water or sediment |
|-----------------------------------|-------------------|-------|---------------|------------------------|
| Sunlight | Yes | Yes | Yes | No |
| Sample temperature | High | High | Moderate | Low |
| Oxygen levels | High | High | High/moderate | Low |
| Fouling (screens solar radiation) | No | No | Yes | Yes |

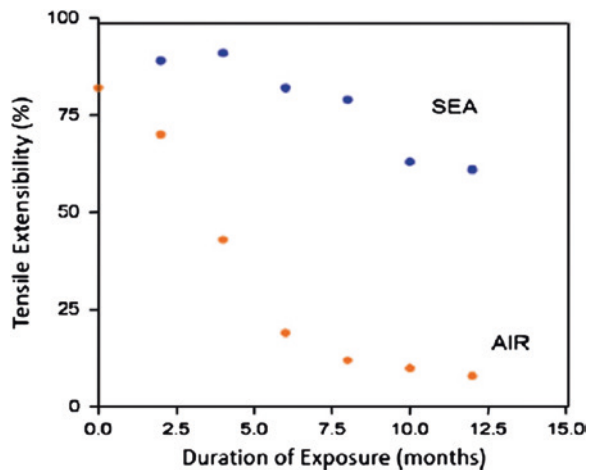
^aLand environment included for comparison

exposure of the plastic results in the formation of a surface biofilm (Lobelle and Cunliffe 2011) that is rapidly colonized by algae and other marine biota including encrusting organisms that increase the density of the plastic causing it to sink in seawater (Thangavelu et al. 2011). The plastic particles that sink due to this process may re-emerge at a later time once the foulants are foraged by marine consumers and the plastic decreases in density (Ye and Andrady 1991). Fouling shields the surface of plastic from exposure to sunlight interfering with the initiation of the oxidation process. This is a significant reason for the retardation of weathering degradation in plastics floating in seawater (Pegram and Andrady 1989). Also, attenuation of solar UV radiation in seawater is very rapid and light-induced initiation reactions cannot occur at depths beyond the photic zone.

The primary reason for the retardation of weathering degradation in floating samples is the relatively lower sample temperatures. In contact with a good heat sink (i.e. seawater), the samples do not undergo heat build up and reach high temperatures as in the case of samples exposed on land. The combined effect of these factors in retarding degradation is illustrated in Fig. 3.3 that compares the loss in extensibility of polypropylene exposed in Biscayne Bay, FL, floating in water and on land during the same period. This observation of retardation of the weathering at sea is generally true for all common plastic materials. With expanded polystyrene foam (EPS) plasticization by water and wave action result in the foam breaking up readily into individual beads of the polymer. However, the weathering degradation of these beads is a slow process.

Initial stages of oxidative breakdown of the plastic materials result in a marked decrease in their mechanical properties. However, the high-polymer nature persists even at extensive degradation where the mechanical integrity of the plastic material is fully compromised. Andrady (2011) as well as Klemchuk and Horng (1984) have demonstrated that for polyethylenes weathered even to the point of embrittlement with no extensibility of the material, the average molecular weights persisted in the 10s of thousands g/mole. These will likely not be further photodegraded so

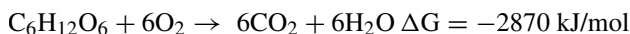
Fig. 3.3 Change in percent original tensile extensibility of polypropylene film exposed in air and floating in seawater at a beach location in Biscayne Bay, FL. Reproduced with permission from Andrady (2011)



that, being fouled or submerged in water, slow biodegradation is the only feasible mechanism for their removal from the environment.

Plastic debris in the ocean generally accumulates a biofilm that contains numerous diverse microorganisms (Ho et al. 1999). Such marine biota can secrete enzymes that can biodegrade common plastics such as polyethylenes as evidenced by surface depressions and pits caused by these on the plastic debris (Zettler et al. 2013). But, the relevant species are rare and the kinetics of biodegradation at sea is particularly slow. While strictly speaking, plastics do biodegrade at sea due to the action of marine organisms, however, the rate of the process is far too slow to either remove plastic debris from the environment or even to obtain obvious decreases in mechanical integrity attributable solely to this process. The exceptions are those plastics, such as aliphatic polyesters, that have structural features that allow facile biodegradation (Kita et al. 1997; Sudhakar et al. 2007) by a host of microorganisms present in the ocean. Biodegradation converts the carbon sequestered in the plastic to carbon dioxide (Narayan 2006). With a simple substrate such as glucose, the products depend on whether the process is aerobic or anaerobic (Tokiwa et al. 2009):

Aerobic biodegradation:



Anaerobic biodegradation:



Most of the common plastics are hydrocarbons and the stoichiometry will be different from above (Shimao 2001).

3.4 Microplastics in the Oceans

An emerging pollutant of concern in the marine environment is microplastic material or plastic fragments of a size-range that allows their interaction with marine plankton (Cole et al. 2011). Their presence in surface water (Barnes et al. 2009; Song et al. 2014), beaches and sediment (Katsanevakis et al. 2007) has been reported from many parts of the world, including even the Arctic (Obbard et al. 2014). Additionally, microplastics have been reported in estuaries and freshwater bodies (Lima et al. 2014).

Many different definitions of the size scale that constitute ‘microplastics’ are reported in the research literature (Gregory and Andrady 2003; Betts 2008; Fendall and Sewell 2009). But there is growing consensus for categorizing microplastics as being <1 mm and >1 μm with the larger fragments that include virgin resin pellets being called ‘mesoplastics’. Most of the studies that document the existence of plastic debris in the world’s oceans focus almost exclusively on

mesoplastics and larger pieces. Studies on true microplastics (<1 mm fraction) are rare because identification and quantification of the microscopic particles is challenging (Löder and Gerds 2015). Plankton nets used to sample surface waters have a mesh size of ~330 microns and collect the mesoplastics. A majority of the literature, however, uses the term ‘microplastics’ loosely to mean both meso- and micro-scale particles. A clear definition of the particle sizes is important because it is the particle-size distribution that determines the set of marine organisms that are able to interact, particularly ingest, the microdebris. For instance, microplastics (as well as nanoplastics) are ingestible by zooplankton (Frias et al. 2014) at the bottom of the food pyramid while the mesoplastics including virgin plastic pellets are found in species such as dolphins (Di Benedetto and Ramos 2014).

While virgin plastics such as the prills used in manufacturing plastic products are generally non-toxic and not digestible by any marine organism, large fragments may cause distress due to physical obstruction of the gut or filter appendages (Kühn et al. 2015). The main concern, however, is that microplastics concentrate persistent organic pollutants (POPs) in seawater via partition. The distribution coefficients for organic compounds including POPs range in the 10^4 – 10^6 . Their ingestion by marine organisms provides a credible pathway to transfer the environmental pollutants dissolved in water into the marine food web. Therefore, relatively low mass fractions of the microplastics can transport a disproportionately high dose of POPs into an ingesting organism. Where the organism is small as with zooplanktons (Frias et al. 2014; Lima et al. 2014), assuming high bioavailability, the body burden of the POPs that might be released into the organism can be significant. This is a particular concern as it involves the lower echelons of the marine food web, where any adverse impact may affect the entire food chain and potentially the global fish supply (Betts 2008). Others have suggested that this transfer pathway is likely of limited importance under equilibrium conditions (Gouin et al. 2011; Koelmans et al. 2013, 2014). At least in the lugworm *Arenicola marina*, conservative modeling suggests that the transfer of POPs (Bisphenol A and nonylphenol) from microplastics into the organism yields concentrations below the global environmental concentration of these chemicals (Koelmans et al. 2014).

The origins of meso-, micro- and nano-plastics in the oceans are attributed to either products that incorporate such particles (such as cosmetics, sandblasting media, virgin pellets) or to the weathering degradation of larger plastic debris in the marine environment (Thompson 2015). In the former instance they are referred to as primary micro-particles being introduced into the ocean already as micro-debris while in the latter case they are generated in the ocean environment from macro-debris. As already pointed out (Table 3.3), where microplastics are derived from larger plastic litter, the process occurs particularly efficiently on beaches and least efficiently in deep water or sediment.

While weathering related oxidative mechanisms for polyolefins (PE and PP) are well known (Ojeda 2011), the concurrent embrittlement of the material has not been adequately studied. This is to be expected as material scientists have little interest in the weathering process beyond the point at which the material has lost its useful properties; embrittlement, however, occurs after this stage. It is the embrittlement phenomenon that is particularly interesting as it has the potential to generate microplastics. Associated with the oxidation reactions described in the previous section

is an autocatalytic chain scission reaction. This is easily demonstrated by monitoring the change in average molecular weight of the plastic during weathering [for instance by gel permeation chromatography (GPC)] (Ojeda 2011). For instance, with PP exposed to UV radiation in an accelerated laboratory weathering experiment the molecular weight of the polymer at the surface of a test piece decreased by 51 % in six weeks of exposure (O'Donnell et al. 1994). At greater depths of a sample, the effect is less pronounced for two reasons: the attenuation of UV radiation with depth that restricts the initiation reaction and the limitation of the reaction due to slow diffusion of oxygen at greater depths.

Chain scission occurs exclusively in the amorphous fraction of semi-crystalline polymers and that, too, preferentially in the surface layer that is several hundred microns in thickness. This can, in theory, lead to two types of fracture: (a) the bulk fracture and (b) surface layer removal due to stresses on highly weathered samples. The former results in a sample such as virgin prills being fragmented gradually into several daughter particles. The latter results in a large number of particles

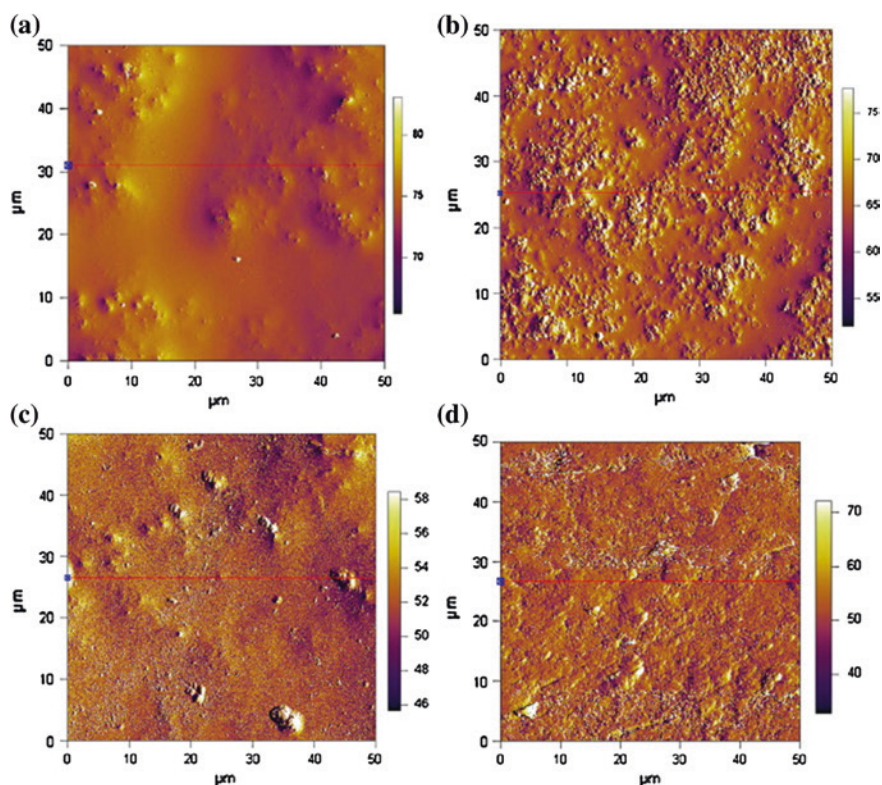
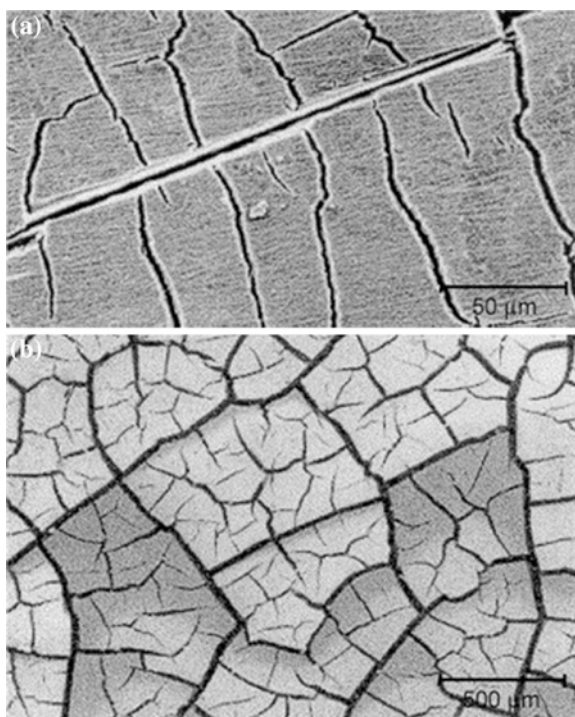


Fig. 3.4 AFM surface images of primer only-coated samples obtained at various UV exposure and salt fog tests: **a** 0 days, **b** 16 days of UV exposure, **c** 0 days of UV light after 80 days of salt fog, and **d** 16 days of UV exposure followed by 80 days of salt fog. Reproduced with permission from Asmatulu et al. (2011)

derived from the surface layer with particle size, at least in one dimension, equal to the thickness of that layer. Possibly both modes of fragmentation occur in natural weathering of plastics on beaches or in seawater.

Plastic samples collected from beach or surface water environments show surface patterns consistent with surface erosion and cracking due to weathering. The cracks and pits on the surface of PE and PP samples from the ocean environment are similar to those seen on samples exposed to weathering (or UV radiation) in the laboratory. It is reasonable to expect that it is this fragmentation process that yields derived microplastics in the ocean environment. The early evolution of surface damage from exposure to UV radiation can be easily discerned from atomic force microscopy (AFM) of the surface. Figure 3.4 shows the changes on an epoxy primer coating, exposed to UV radiation and/or salt fog. These micro-cracks propagate in time to form surface features that are easily visible under a low-power microscope. The cracks appear first on the edges and propagate towards the center of sample surface. The evolution of surface cracks under exposure to UV light has been reported for HDPE (Shimao 2001), LDPE (Cole et al. 2011) and PP (Yakimets et al. 2004). Some of the plastic samples collected from beaches as well as from surface waters in the ocean have extensive yellowing and cracking (Ogata et al. 2009; Cooper and Corcoran 2010). Figure 3.5 shows micrographs that illustrate this phenomenon.

Fig. 3.5 Development of visible cracks on exposure of LDPE samples to laboratory accelerated weathering. **a** Exposed to a xenon source (Atlas WeatherOmeter) for 1600 h at 63.5 °C and **b** exposed to a UV fluorescent lamp (QUV WeatherOmeter) for 800 h at 60.5 °C. Reproduced with permission from Küpper et al. (2004)



3.5 Conclusions

The degradation mechanisms, pathways and kinetic expressions are well-established in the literature. Detailed information is available particularly on the plastics used in high volume such as PE and PP. However, these studies either do not progress beyond the weakening of the plastic material to a point it cannot be used or the fragmentation process has not been investigated. Hitherto, there has been little interest in studying the fragmentation process or the changes in the ensuing particle size distribution of the plastics. With growing interest in microplastics in the ocean this aspect of polymer degradation will receive more attention.

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