



Erosion as a possible mechanism for the decrease of size of plastic pieces floating in oceans



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ABSTRACT

A sea water wave tank fitted in an artificial UV light weathering chamber was built to study the behaviour of polypropylene (PP) injected pieces in close ocean-like conditions. In air, the same pieces sees a degradation in the bulk with a decrease of mechanical properties, a little change of crystal properties and nearly no change of surface chemistry. Weathering in the sea water wave tank shows only a surface changes, with no effect on crystals or mechanical properties with loss of small pieces of matter in the sub-micron range and a change of surface chemistry. This suggests an erosion dispersion mechanism. Such mechanism could explain why no particle smaller than about one millimeter is found when collecting plastic debris at sea: there are much smaller, eroded from plastic surfaces by a mechano-chemical process similar to the erosion mechanism found in the dispersion of agglomerate under flow.

1. Introduction

Polymer pieces are present at sea in very large quantities, threatening marine eco-system. The initial recognition that plastics present in seas cause a problem dates from 1972 (Carpenter and Smith, 1972). The first international conference related to these issues was held in 1984 and media coverage started when a sailor Charles Moore reported in 1997 that he has been navigating among a sea of plastics in a specific area in the Pacific Ocean. The reasons why wastes are ended in the sea are well documented, with a larger fraction of debris being from land-based sources, the remaining being from ocean-based sources with four major sources, tourism-related litter at the coast, sewage-related debris, fishing-related debris and wastes from ships and boats (Jambeck et al., 2015), with a strong accumulation in specific areas (Cózar et al., 2014). Not surprisingly considering the production of polymers, over 300 millions tons (Plastics Europe, 2017), most of debris in oceans is plastics, with a proportion between 60 and 80% (Gregory and Ryan, 1997; Barnes, 2002; Derraik, 2002; Ryan, 2014).

The presence of plastics litter has been observed worldwide. They are present in special concentration points on sea surface, called oceanic gyres (Moore et al., 2001), on shorelines, in sediments and even deep in sea (Galgani et al., 2000). Plastics can be seen in all ocean

locations including Antarctic (Barnes et al., 2009). Entanglement in marine debris or ingestion of debris is affecting marine life in a very significant way, with most of species being touched (Willcox et al., 2015). For example, in the Mediterranean, sea turtles are seriously endangered by entanglement and ingestion of marine debris (Lazar and Gracan, 2010). Ingestion of plastics bits by birds is decreasing stomach availability for food intake, reducing bird fitness and affecting long-distance migration (Spear et al., 1995). The ingestion of plastic debris by small fish and seabirds may also cause internal injury and death following blockage of intestinal tract (Carpenter and Smith, 1972; Ryan, 1988; Rothstein, 1973; Zitko and Hanlon, 1991). The presence of plastic debris on the sea floor is affecting the living organisms and is altering the structure of benthic communities. Fishing nets lost by boats destroy the coral reefs and “ghost fishing” (*i.e.* the fact that a lost net lost is still active in deep sea) is killing fish for years (Brown and Macfadyen, 2007). Plastic parts are slowly broken in the environment (Colton et al., 1974; Thompson et al., 2004) down to pieces with sizes lower than 5 mm called microplastics in the literature (Hidalgo-Ruz et al., 2012). Polymer pellets and these “microplastics” are accumulating and transporting hydrophobic pollutants, releasing potentially toxic chemicals and transporting invasive alien species (Ryan et al., 2009; Thompson et al., 2009). Large quantities of plastic microparticles

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in excess of 100,000 items/km² can be measured (Thompson et al., 2009; Gregory, 1978), although only a few percent of the estimated dumping is counted (Ter Halle et al., 2016). Plastics in the sea are causing several risks (do Sul and Costa, 2014).

A critical question is the way(s) that a polymer piece takes to disperse, i.e. to decrease its size. A recent study (Ter Halle et al., 2016, 2017) showed that the ways debris are floating and moving is changing their degradation paths. The analysis of size distribution of debris showed a lack of debris lighter than 1 mg. The authors explain this finding by suggesting that there is a discontinuity in the rate of fragmentation with a faster fragmentation of the small cubic debris than the parallelepipedic ones. Size attrition can have several reasons such as mechanical stresses due to waves, action of salted water, photo-degradation or biological degradation by microorganisms.

Dispersion is the process by which the size of a particle suspended in a fluid is reduced (Bolen and Colwell, 1958; Astruc, 2001; Bagster and Tomi, 1974; Seyvet and Navard, 2001). A particle will be split into several particles. Dispersion must not be confused with distribution, which is the process that will scatter all the filler particles and dispersed fragments into the suspending fluid (Manas-Zloczower and Feke, 1989). We are taking one of the many issues linked to the dispersion (i.e. the size decrease) of plastic debris at the sea. A commodity polymer like polypropylene, floating in seawater was subjected to three potential dispersion reasons, (1) mechanical stresses due to waves, (2) action of salted water and (3) UV irradiation. In real oceanic conditions, other factors are acting as the action of biological degradation by microorganisms, which is not taken into account in the present study. To perform this study, water tank mimicking the action of waves was built placed in a weathering chamber and filled with floating polypropylene pieces. These pieces were moved by the waves and at the same time irradiated by UV light in well-controlled conditions. The changes in chemical, physical and mechanical properties between sea weathered and air-weathered conditions experiments were compared.

The main concept which is brought in this paper is to consider that tiny pieces of polymer at the surface can be damaged by cracks and behave as pseudo-agglomerates, thus able to disperse by an erosion mechanism.

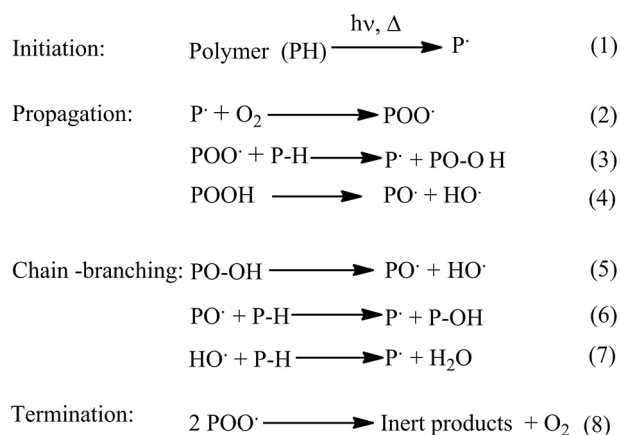
1.1. Chemical degradation, dispersion and distribution

Polymers degrade through three main mechanisms a sea, photo-degradation, biodegradation, mechano-chemical degradation and hydrolysis. In our study, no biofilm was formed on the sample surface and hydrolysis was shown not to bring chain scission (Massey et al., 2007). Photo-oxidation and mechano-chemical degradation are the two main mechanisms leading to a reduction of size. The chemical degradation is the change of chemical species in the material.

1.1.1. Chemical degradation caused by photo-oxidation

Most researchers agree with the chemical degradation mechanism for polypropylene (the polymer studied in this paper) presented in Scheme 1 (Singh and Sharma, 2008; Gijzman et al., 1993, 1999; Subowo et al., 1986; Baum, 1974).

The initiation step proceeds with the formation of alkyl radicals (Eq. (1)) as result photo-oxidation. The propagation step continues with the reaction of macroradicals with oxygen, and the formation of hydroperoxides groups (Eqs. (2), (3)). Hydroperoxides are a source of free-radicals which further initiates chain scission (Eq. (4)) and chain-branching (Eqs. (5), (6), (7)). The radicals capture hydrogen from the tertiary carbons of polymeric backbone leading to carbonyl groups formation on the surface of polypropylene samples (Eq. (8)). As a result of the degradation process, changes in physical, chemical and mechanical properties have been observed (Singh and Sharma, 2008; Severini et al., 1988; Gijzman et al., 1993, 1999; Qin et al., 2005). The photo-oxidized material becomes more brittle (Shyichuk et al., 2001) during outdoor exposure (White and Turnbull, 1994) and it is suggested



Scheme 1. Degradation mechanism of polypropylene.

that the mechanical failure is the result of micro-cracks formation on the surface (Raab et al., 1982; Qureshi et al., 1989; Galli et al., 1984). In the case of polymers, like polyolefins, objects floating in the seawater, several factors must be taken into consideration when comparing to air aged samples. The air weathered samples are directly exposed to the sun light, resulting in an accelerated degradation process due to photo-oxidation and to the increase of the temperature on the samples surface. Thus, the mechanical stress created between the heated and non-heated surfaces can be the cause of cracking.

This heating process may or not exist in ocean, the objects being either continuously turned and washed by water or blocked with one face expose to sun, as shown by Ter Halle et al. (2016).

1.1.2. Dispersion by mechanical forces

Four physical mechanisms can be taken into consideration when dispersing plastics in the ocean: rupture, erosion, cavitation and collision (Bolen and Colwell, 1958; Astruc, 2001; Bagster and Tomi, 1974; Seyvet and Navard, 2001). Cavitation is not acting in water. Collision can be a possible mechanism (Seyvet and Navard, 2000), difficult to assess in the ocean context. Rupture is the macroscopic separation of objects, which is responsible for the decrease of size of the floating objects (bottles, nets) into small pieces, which are classically collected. It is often called fragmentation. As we will be seen below, forces exerted by sea waves cannot break large undamaged plastic pieces because rupture is occurring when shear stresses are larger than a cohesion stress, an unlikely event even in case of strong tempests. In normal sea conditions, the rupture mechanism is thus not effective, the waves are also not able to extract small pieces from the surface of large undamaged plastic debris because the surface is not having weak points. But when the surface has been first weakened by the chemical mechanisms described above, then erosion could occur: a small piece can detach by erosion, a phenomenon well described in the area of dispersion of agglomerated objects such as carbon black or silica submitted to shearing in elastomers (Seyvet and Navard, 2001). A schematic illustration of such erosion mechanism is given in Fig. 1.

In the case of erosion of carbon black immersed in a viscoelastic matrix (Collin and Peuvrel-Disdier, 2005), the evolution of the eroded volume as a function of time as follows (Eq. (9)):

$$\frac{R_0^3 - R(t)^3}{R_0^3} = C \times \gamma' t \quad (9)$$

where, C is a constant, R₀ is the initial radius of the agglomerate, R(t) the radius at time t and γ' the applied shear rate. Thus, the eroded volume depends on the amount of shear deformation.

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