



## Surface properties of beached plastic pellets

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### ARTICLE INFO

#### Article history:

Received 4 May 2012

Received in revised form

25 August 2012

Accepted 31 August 2012

#### Keywords:

Eroded plastic pellets

Point of zero charge

Polyethylene

Polypropylene

Surface groups

Marine debris

### ABSTRACT

The presence of pollutants on plastic debris is an emerging environmental hot topic. Understanding the surface alteration of plastics while in the marine environment increases our understanding of the pollutant–plastic debris interaction. Plastic pellets are widely distributed throughout the world oceans. Eroded and virgin polyethylene (PE) and polypropylene (PP) pellets were studied for their surface properties to better understand the interaction between plastic and compounds in marine environment. Surface properties such as point of zero charge, surface area and pore volume, surface topography, functional groups and acid–base behavior are important factors which affect sorption. Virgin plastic pellets had homogeneous smooth surfaces that do not have any acid–base behavior. Eroded PE demonstrates an altered surface that at seawater pH acquires a negative charge due to ketone groups. The uneven surface and possible functional groups could have been formed from the erosion processes while floating at the sea surface and might explain the interaction of eroded plastics with microbes and metals.

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### 1. Introduction

The global production of plastic has increased from 1.5 million tonnes in 1950 to 230 million tonnes in 2009, with an average annual growth of around 9% (PlasticsEurope, 2010). Part of this plastic pollutes the marine environment due to improper waste management and coastal and maritime activities. At the same time, there is an increase in the global effort allocated by the scientific community to better understand the effect of plastic marine pollution (NOAA-UNEP, 2012; Derraik, 2002; Galgani et al., 1996). Within the last decade, it was clearly demonstrated that marine plastics break into smaller pieces and also that marine plastics interact with chemicals while floating at the sea surface (Hidalgo-Ruz et al., 2012; Van et al., 2012; cited references in Andrady, 2011 and in Cole et al., 2011; Karapanagioti et al., 2011; GESAMP, 2010; Ogata et al., 2009; Rios et al., 2007; Endo et al., 2005; Mato et al., 2001).

As international plastic production continues to increase, it is crucial not only to understand the geographic distributions and quantities of plastics in the marine environment (e.g. Hidalgo-Ruz et al., 2012), but also to consider the specific properties of plastic particles themselves (Morét-Ferguson et al., 2010). Plastics can be altered by thermal, oxidative, radiative, and mechanical means as well as biological agents (Albertsson et al., 1987). The alteration of the plastic surface in the marine environment can explain the affinity of the eroded plastics for chemicals that the virgin plastic

would not sorb. Such chemicals include metals and organic pollutants with polar functional groups (Holmes et al., 2012; Ashton et al., 2010). Previous studies have shown that sorption of phenanthrene onto plastic pellets had a different distribution coefficient for virgin than for beached plastic pellets (Karapanagioti and Klontza, 2008). Furthermore, the sorption of trace metals onto virgin plastic pellets was observed to be much lower than onto beached plastic pellets (Holmes et al., 2012).

Plastic pellets are the raw materials for plastic production and since they do not contain dyes are easier to study than fragments of different plastics. Although the interaction of plastic pellets with chemicals in the marine environment has been extensively studied (Holmes et al., 2012; Ashton et al., 2010; Karapanagioti and Klontza, 2008) few studies have examined their surface properties (e.g. Endo et al., 2005 have calculated the carbonyl index – the ratio of the absorbance at  $1717\text{ cm}^{-1}$  to a reference one at  $720\text{ cm}^{-1}$  – which is a common indicator for polymer weathering). In the present study, the alteration of the surface of beached plastic pellets is studied as a first attempt to understand the surface alteration of marine plastics actually sampled from beaches. There are several studies presenting the alteration of plastic surfaces using laboratory or controlled conditions in field studies (Kyriakou et al., 2011; Cheng et al., 2005; Yang et al., 2005; Gulmine et al., 2003) but none to our knowledge that actually presents detailed characterization of beached plastic pellet surfaces. In the present study a combination of different techniques is employed in order to demonstrate (a) the major surface alteration due to exposure of plastic pellets in the marine environmental conditions and (b) the

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**Table 1**

BET surface area (SA), open surface area (OSA) determined through nitrogen sorption and *t*-plot, pore volume (PV), micropore volume ( $\mu$ PV) determined through nitrogen sorption and *t*-plot, and pore size (PS) for all plastic pellet types studied.

	Average mass used (g)	Average pellets used	BET SA <sup>b</sup> (m <sup>2</sup> /g)	OSA <sup>a</sup> (m <sup>2</sup> /g)	PV <sup>b</sup> (cm <sup>3</sup> /g)	$\mu$ PV <sup>a</sup> (cm <sup>3</sup> /g)	PS <sup>b</sup> (Å)
Virgin PE	0.48	17	0.13 ± 0.005	0.039	0.0006 ± 0.00008	0.000033	220 ± 12
Eroded PE	0.52	17	0.17 ± 0.02	0.056	0.0005 ± 0.00004	0.000039	170 ± 46
Virgin PP	0.62	28	0.11 ± 0.009	0.0087	0.0003 ± 0.00004	0.000038	180 ± 17
Eroded PP	0.51	23	0.15 ± 0.006	0.020	0.0006 ± 0.0001	0.000051	250 ± 46

PE: Polyethylene; PP: Polypropylene.

<sup>a</sup> *t*-plot analysis was performed for selected samples.

<sup>b</sup> Values reported as mean ± standard deviation based on 3 replicates for virgin and 4 replicates for eroded pellets.

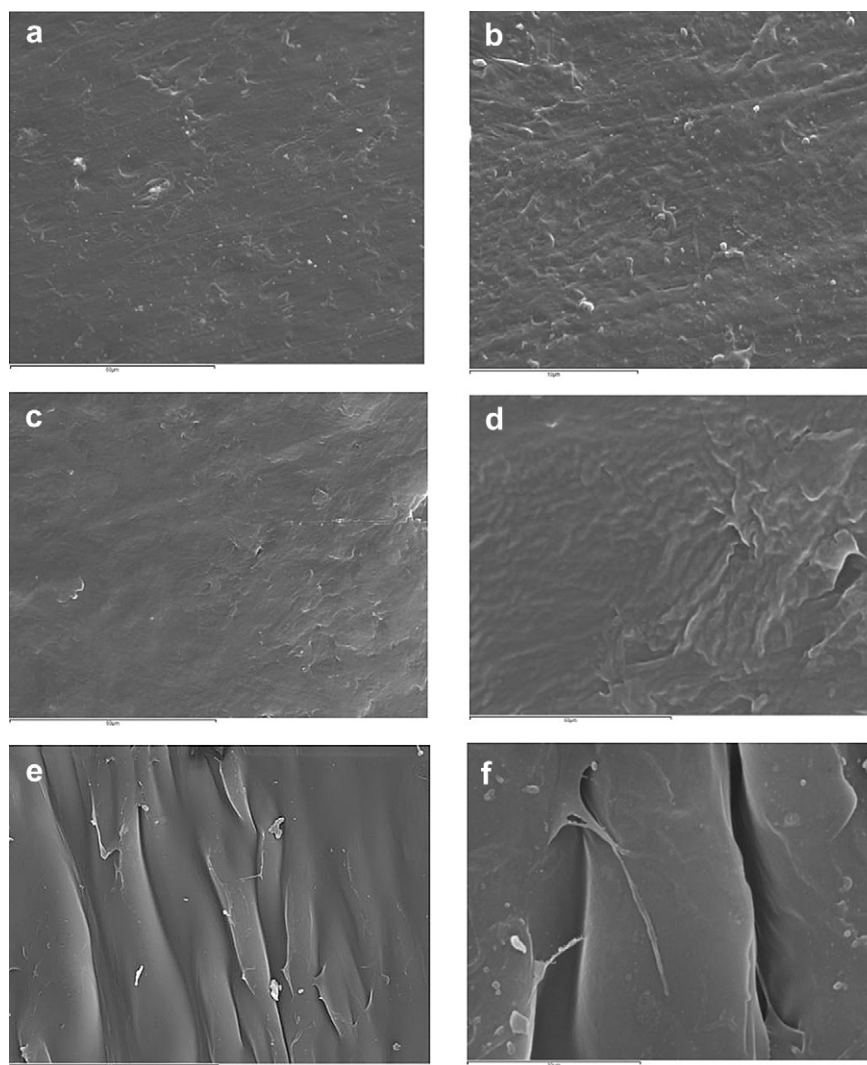
differences between the alteration of polyethylene (PE) and polypropylene (PP) plastic pellets.

## 2. Materials and methods

### 2.1. Materials

In the present study, polyethylene (PE) and polypropylene (PP) plastic pellets were tested. Approximately 3200 pellets were

used in total; almost 850 pellets from each of four types (virgin PE, eroded PE, virgin PP, and eroded PP). Virgin PE and PP plastic pellets were obtained from a local manufacturer and their polymer classification was verified by Dr. H. Takada's group from the Laboratory of Organic Geochemistry (LOG), Tokyo University of Agriculture and Technology, Japan. Eroded PE and PP plastic pellets were also provided by LOG. These pellets were collected from 47 beaches all over the world. The pellets were classified as PE, PP, or "other" by near-infrared spectroscopy in Japan



**Fig. 1.** The surface topography of virgin plastic pellets from SEM for (a) high density PE pellets enlarged 1000 times (Note the gray scale bar at the bottom of the image; scale bar 60  $\mu$ m), (b) high density PE pellets enlarged 5000 times (scale bar 10  $\mu$ m), (c) low density PE pellets enlarged 1000 times (scale bar 60  $\mu$ m), (d) low density PE pellets enlarged 5000 times (scale bar 10  $\mu$ m), (e) PP pellets enlarged 1000 times (scale bar 60  $\mu$ m), (f) PP pellets enlarged 5000 times (scale bar 10  $\mu$ m).

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