



To what extent are microplastics from the open ocean weathered?☆



Alexandra ter Halle^{a,*}, Lucie Ladirat^a, Marion Martignac^a, Anne Françoise Mingotaud^a, Olivier Boyron^b, Emile Perez^a

^a Laboratoire des IMRCP, Université de Toulouse, CNRS UMR 5623, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse Cedex 9, France

^b C2P2 - LCPP Group, UMR CNRS 5265, Université de Lyon, ESCPE Lyon, Bat 308F, 43 Bd du 11 Novembre 1918, 69616 Villeurbanne, France

ARTICLE INFO

Article history:

Received 8 February 2017

Received in revised form

19 April 2017

Accepted 19 April 2017

Keywords:

Microplastic

Marine debris

Polymer

Polyethylene

Photodegradation

Photo-oxidation

Environmental degradation

Biodegradation

ABSTRACT

It is necessary to better characterize plastic marine debris in order to understand its fate in the environment and interaction with organisms, the most common type of debris being made of polyethylene (PE) and polypropylene (PP). In this work, plastic debris was collected in the North Atlantic sub-tropical gyre during the Expedition 7th Continent sea campaign and consisted mainly in PE. While the mechanisms of PE photodegradation and biodegradation in controlled laboratory conditions are well known, plastic weathering in the environment is not well understood. This is a difficult task to examine because debris comes from a variety of manufactured objects, the original compositions and properties of which vary considerably. A statistical approach was therefore used to compare four sample sets: reference PE, manufactured objects, mesoplastics (5–20 mm) and microplastics (0.3–5 mm). Infrared spectroscopy showed that the surface of all debris presented a higher oxidation state than the reference samples. Differential scanning calorimetry analysis revealed that the microplastics were more crystalline contrarily to the mesoplastics which were similar to references samples. Size exclusion chromatography showed that the molar mass decreased from the references to meso- and microplastics, revealing a clear degradation of the polymer chains. It was thus concluded that the morphology of marine microplastic was much altered and that an unambiguous shortening of the polymer chains took place even for this supposedly robust and inert polymer.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Plastic debris is known to be present in all compartments of the environment worldwide (Moore, 2008; Schlining et al., 2013; Zhao et al., 2014; Bakir et al., 2014; Donohue et al., 2001; Fisner et al., 2013; Karapanagioti et al., 2011; Ogata et al., 2009; Zbyszewski and Corcoran, 2011; Eriksen et al., 2013; Faure et al., 2015; Zylstra, 2013). Studies of plastic pollution in oceans over almost four decades (Wong et al., 1974) have found that it is distributed across all the oceans due to its buoyancy and durability (Law et al., 2014) and accumulates in subtropical convergence zones in the five basins (Eriksen et al., 2014). Despite the growing number of research studies on the matter, the extent of the impact of this pollution on ecosystems remains to be estimated. The chemical dangers are sufficiently worrying to have led some researchers to

claim that plastic waste should be regarded as hazardous (Rochman et al., 2013). A significant finding is that plastic debris fragments, termed microplastics (300 µm – 5 mm), have been accumulating in the oceans. It has recently been estimated that there is a minimum of 5.25 trillion plastic particles in the oceans (Eriksen et al., 2014). Another serious concern is the occurrence of micrometric and nanometric plastic debris not visible to the naked eye (Andrady, 2011). These very small particles present particular properties (mobility, surface properties and bioavailability), which make them a matter of concern in terms of danger to marine ecosystems (Cole et al., 2013, 2015). Currently, it would be highly desirable to better understand the mechanical integrity of plastic at advanced stages of weathering in order to estimate the processes of formation of the smallest plastic particles. In parallel, there is a need to develop reliable alternatives to the existing methods for the identification and counting of the smallest particles in natural samples, as mentioned recently by Filella (2015).

In order to provide clues for understanding the sources and fate of plastic debris in the ocean, Moret-Ferguson et al. (2010), discussed spatial and temporal trends in the characteristics of

☆ This paper has been recommended for acceptance by Maria Cristina Fossi.

* Corresponding author.

E-mail address: ter-halle@chimie.ups-tlse.fr (A. ter Halle).

microplastics (size, mass, density). They concluded that plastic debris mostly consisted of fragments less than 10 mm in size, nearly all of which were lighter than 0.05 g. Elemental analysis suggested that the debris was mostly polyethylene (PE) and polypropylene (PP). This is in agreement with data in the literature (Anderson et al., 2015; Hidalgo-Ruz et al., 2012). Rios et al. (2007) determined that, in coastal areas, the ratio of PE to PP was generally around 10%–90%, whereas (ter Halle et al. 2016) found that, in the North Atlantic subtropical gyre, these proportions were inverted (90% PE and 10% PP). Together, PE and PP account for most of the global plastic production (38% and 24% of the global production, respectively) and they are typically used in the manufacturing of single-use disposable packaging (PlasticEurope). Because PE is the most produced plastic and the dominant plastic debris found in the concerned 7th Continent expedition, we have focused the present study on this polymer.

The weathering of polymers has been studied in various environments but their formulations (referred to as plastics) have been less considered. Furthermore, most studies have focused on the early stages of degradation because they correspond to the useful lifetime of the product (Anderson et al., 2015). Information about highly weathered plastics in the environment is very limited (Andrady, 2011; Anderson et al., 2015; Moore, 2007; Jambeck et al., 2015; Andrady et al., 2015). The dominant cause of degradation of PE outdoors is solar UV radiation (Gewert et al., 2015). The mechanism of PE photo-oxidation is well understood and involves free-radical-mediated reactions (Arnaud et al., 1984; Gardette et al., 2013; Lacoste and Carlsson, 1992; Yang et al., 2006; Catalina et al., 2002; Cornell et al., 1984). PE is a non-absorbing polymer, which means it does not contain chromophoric species absorbing in the range of solar light frequencies. Light absorption is, however, necessary to induce photochemical reactions. In the case of PE photodegradation, the absorption of light is attributed to unidentified chromophores (Arnaud et al., 1984; Gardette et al., 2013; Lacoste and Carlsson, 1992). There is a great variety of candidates. The chromophores could be formed during polymer processing, e.g. by formation of double bonds upon heating, or enter into the composition of additives to the plastic. Light absorption by these chromophores results in the formation of radicals, which can react following different pathways: abstraction of a hydrogen atom from the macromolecular chain, addition to an unsaturated group (crosslinking reaction), or addition to oxygen (Arnaud et al., 1984; Cornell et al., 1984). Once free radicals are generated along the polymer chains, they may react with atmospheric oxygen to generate peroxy radicals, which undergo further reactions, leading to alcohols, acids, aldehydes, ketones or unsaturated groups (Arnaud et al., 1984; Gardette et al., 2013; Lacoste and Carlsson, 1992; Yang et al., 2006; Catalina et al., 2002). Subsequently, random chain scission and crosslinking lead to a decrease or increase of the molar mass respectively (Arnaud et al., 1984; Gardette et al., 2013; Lacoste and Carlsson, 1992). The changes in the chemical structure and morphology of the material modify the macroscopic properties of the material. After changes in color and crazing of the surface, weathering can lead to embrittlement and disintegration of the plastic (Gewert et al., 2015). After advanced stages of degradation, the plastic debris develops surface features and becomes weak and brittle; any mechanical force (e.g. wind, waves, biting by animals or human activity) can break the highly degraded, weakened plastics into fragments (Gewert et al., 2015). There are no methods to determine the age of microplastics collected in the field. In other words, we cannot estimate the duration of outdoor exposure of the plastic debris collected (Gewert et al., 2015). However, it is possible to quantify the extent of weathering of a sample by Fourier transform infrared spectroscopy (FTIR) or Raman spectroscopy by considering the carbonyl

formation (carbonyl indices) (Hakkarainen and Albertsson, 2004).

The present study focuses on the physicochemical characterization of microplastics collected in the North Atlantic subtropical gyre. The samples were characterized by FTIR and electron microscopy which are techniques classically used for the characterization of plastic debris. However, we also describe the use of differential scanning calorimetry (DSC) and size exclusion chromatography (SEC); which are fundamental techniques for polymer characterization but surprisingly have not been used so far for the characterization of microplastics. We therefore demonstrate here that this constitutes a new approach providing new insight of the complex processes of plastic weathering. The aim of the study was to assess possible degradation patterns regarding the polymer structure, at both molecular and microscopic levels.

2. Materials and methods

2.1. Polyethylene reference materials

Six samples of PE (CAS 9002-88-4) were obtained as reference materials (also referred to as virgin pellets). Three PE pellets were purchased from Sigma Aldrich (Saint Louis, MO, USA). They included: high density PE (HDPE) pellets presenting a melt flow index (MFI) of 2.2 g/10 min (this material is referenced as HDPE-2.2); HDPE pellets with an MFI of 12 g/10 min, a melting point between 125 and 140 °C and a density of 0.952 g mL⁻¹ at 25 °C (referenced as HDPE-12); and linear low density PE (LLDPE) pellets presenting an MFI of 1.0 g/10 min and a melting point between 100 and 125 °C with a density of 0.918 g mL⁻¹ at 25 °C (referenced as LLDPE-1). Three other PE samples were purchased from Goodfellow (Huntingdon, UK): HDPE pellets (3 mm) presenting an MFI of 0.3 g/10 min (referenced as HDPE-3mm); medium density PE (MDPE), which was a powder of 350 µm particles (referenced as MDPE-350µm), and LDPE consisting of 1 mm pellets (referenced as LDPE-1mm).

2.2. Polyethylene objects and packaging items

Thirty eight PE items (high density and low density) randomly selected in the environment of our everyday life were analyzed (see details in Table SI 2). They were household products, newly purchased for the purpose of the study. They were not exposed to UV prior testing.

2.3. Sample collection

Mesoplastics were collected by the boat in the North Atlantic subtropical gyre in May 2014 and June 2015 during the French Expedition 7th Continent sea campaign. The plastic debris was collected by the sailing vessel Guyavoile in the accumulation area determined by studying a surface net tow data set (Law et al., 2010). The mesoplastics were visible from the Guyavoile and floated on the sea surface. Three mesoplastics were collected in May 2014 and eight in June 2015 (eleven in total, see details in Table SI 1). Microplastics were collected in the same area using a manta net, details of how they were collected, sorted out and stored are described elsewhere (ter Halle et al., 2016).

2.4. Fourier transform infrared (FTIR) spectroscopy

Infrared spectra were recorded using a Thermo Nicolet Nexus spectrometer equipped with a diamond crystal ATR accessory and a deuterated triglycine sulfate (DTGS) detector. Background and sample spectra were acquired using 16 scans at a spectral resolution of 4 cm⁻¹. The recorded data were corrected in order to obtain

Download English Version:

<https://daneshyari.com/en/article/5749136>

Download Persian Version:

<https://daneshyari.com/article/5749136>

[Daneshyari.com](https://daneshyari.com)