



# Influence of thermooxidative degradation on the in situ fate of polyethylene in temperate coastal waters

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## ABSTRACT

Polyethylene is a commonly used polymer in plastic products and is often found as marine litter. Nevertheless there is limited knowledge about what happens to the material when it ends up in the sea. Polyethylene films were therefore thermally oxidised to four different levels of degradation. The films were then placed in stainless-steel cages in the sea off the Swedish west coast for 12 summer weeks. Subsamples were analysed with respect to biofouling, degradation and buoyancy. All levels showed a continued oxidation in the field. The pre-degraded films started fragmenting and the non-degraded films showed a decrease in tensile strain. All levels showed increased biofouling with higher presence of filamentous algae and bryozoans on pre-degraded materials. The density ( $\text{kg}\cdot\text{m}^{-3}$ ) of the films was seen to increase slightly, and the apparent density for the pre-degraded films (density of the films with biofilm) showed a strong increase, which resulted in sinking.

## 1. Introduction

More than 90 million tonnes of polyethylene (PE) are produced annually. It is a versatile polymer that is used in many different products such as packaging, toys, household items, construction materials and electronics (PlasticsEurope, 2015). Over the last decade there has however, been a growing concern about the increasing amounts of plastic debris found in the environment; PE is often specifically reported in plastic pollution studies (Andrady, 2017) on beaches (Frias et al., 2010), in surface waters (Karlsson et al., 2016), sediment (Clunies-Ross et al., 2016) and in fish (Wagner et al., 2017). Marine plastic debris is however not a new phenomenon. In fact, it has been more than 40 years since marine explorers and scientists started reporting that plastic debris was being transported with currents to the middle of the ocean (Heyerdahl, 1971; Venrick et al., 1973). A few years after these first reports, it was already observed that positively buoyant plastics with a low density, such as PE, would eventually end up at the seafloor (Holmström, 1975). This discovery indicated that the properties of the materials changed once in the environment, due to degradation and interactions with other processes in the ocean. Still, the understanding of macro- and microplastic distribution, abundance and fate is still in its infancy. Recently several scientists have therefore called attention to the need for a better understanding of the effects of degradation and biofilm formation, on plastics in the marine

environment (Jahnke et al., 2017; Rummel et al., 2017; Da Costa et al., 2018).

Degradation is an important process that affects the distribution and fate of PE in the marine environment. The properties and longevity of the material varies depending on the service conditions in different application demands and the usage of different additives (Gewert et al., 2015); some commercial PE products have a long service life due to the presence of antioxidants and stabilizers. Furthermore, compared to plastics on land, plastics in the marine environment are often subjected to lower temperatures, limited access to oxygen and lower ultraviolet (UV)-light exposure which can result in a lower rate of degradation (Pegram and Andrady, 1989; Andrady et al., 1993; Muthukumar et al., 2011). However, although the mineralization of plastic is expected to be a slow process, the first signs of abiotic degradation, such as a reduction of tensile strain and fragmentation, can be seen after only 4–8 weeks (O'Brine and Thompson, 2010; Weinstein et al., 2016).

The degradation of PE typically begins with the formation of alkyl macro radicals when subjected to temperature, shear stress and catalyst residues (Selonke et al., 2012). The presence of oxygen is crucial for the degradation process; it reacts with the polymer, changing its chemical structure and reducing the molecular weight (Gewert et al., 2015). In the environment, UV-radiation will also initiate the macro radical formation (Selonke et al., 2012). The following reactions lead to the chain scission and formation of degradation products such as ketones,

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aldehydes, alcohols and carboxylic acids (Krehula et al., 2014); thus, PE degradation is typically dominated by the formation of carbonyl groups and vinyl species (Krehula et al., 2014). Nonetheless, degradation pathways differ depending on the environment and in compost environments carbonyl groups and vinyl species have been shown to be transformed into carboxylates (Weiland et al., 1995). Furthermore, if there are very low levels of oxygen when polymer degradation has been initiated, the formed macro radicals may instead react with each other resulting in crosslinking, branching and formation of unsaturated groups such as vinyl and transvinylene groups (Selonke et al., 2012). Studies have also shown that the degradation products can then be utilized by microorganisms as nutrients to produce CO<sub>2</sub>, water and biomass (Chiellini et al., 2003; Albertsson, 1993; Sen and Raut, 2015; Abraham et al., 2017). This mineralization or biodegradation process predominantly happens once the polymer has reached a low molecular weight distribution (Prasun et al., 2014).

Another process to consider for the transport and fate of plastics in the marine environment is biofouling; the adhesion of biofilm and other fouling organisms to the plastic surface. The adhesions of organisms to plastics have been shown to affect the apparent density (buoyancy) of the material, which could thus affect transportation patterns (Holmström, 1975; Weinstein et al., 2016). In the ocean, biofilm formation consisting of macromolecular adhesion, bacteria, microalgae and other microorganisms will rapidly cover any exposed surfaces (Cooksey and Wigglesworth-Cooksey, 1995). These surface associated communities often have a high level of extracellular polymers that work as binding agents (Cooksey and Wigglesworth-Cooksey, 1995). Biofilm formation and other types of biofouling are, however, complex processes; the organisms that foul a substrate can vary dependent on the type of fouling organisms that are present (Cooksey and Wigglesworth-Cooksey, 1995), the water flow or shear (Lehtola et al., 2006), the substrate (Muthukumar et al., 2011), and is also dependent on season and location (Ye and Andradý, 1991; Oberbeckmann et al., 2014). Additionally, the resulting vertical transportation is not necessarily a one-way ticket as other processes such as defouling, can cause the plastic to resurface (Ye and Andradý, 1991).

Although biofouling is thought to be a complex process, it remains important to investigate its effects on plastic particles in the ocean. Biofouling can not only affect transportation and degradation patterns but also sorption and leaching of chemicals from the plastic material (Jahnke et al., 2017), as well as the affinity with which animals ingest it, as plastic with biofilm appears more similar to food particles for some organisms (Savoca et al., 2017; Vroom et al., 2017; Bråte et al., 2018).

Before plastic enters the marine environment it often carries a degradation history; the material starts degrading during manufacturing,

and continues to degrade during its usage. It may also be exposed to degradation processes during a period as terrestrial litter. The effects of these processes on plastics in the marine environment are, however, poorly understood. Although plastic found in environmental samples are often degraded and have macro- and micro- fouling most models for risk assessments or fate prediction use pristine particles, which are likely to behave differently. These processes and their effects are, therefore, important to study in order to understand the transportation patterns and effects of marine plastic debris. This information is especially relevant for coastal regions where biological productivity and marine plastic pollution is high, as it is likely that the effects of degradation with biological processes affect the transportation, fate and properties of the plastics (Jahnke et al., 2017; Rummel et al., 2017). This study, therefore, set out to investigate PE degradation in coastal waters and to look more specifically at early signs of degradation for non-degraded and pre-degraded PE in coastal waters; differences in biofouling for different levels of degradation, and; effects of degradation and biofouling on material density and apparent density as a measure of buoyancy. Material PE in regular consumer products, such as food packaging, contain usually only small amount of stabilizers for the melt processing. Most of the stabilizers are consumed during processing and the rest after disposal. We therefore chose to use polyethylene without additives for this study.

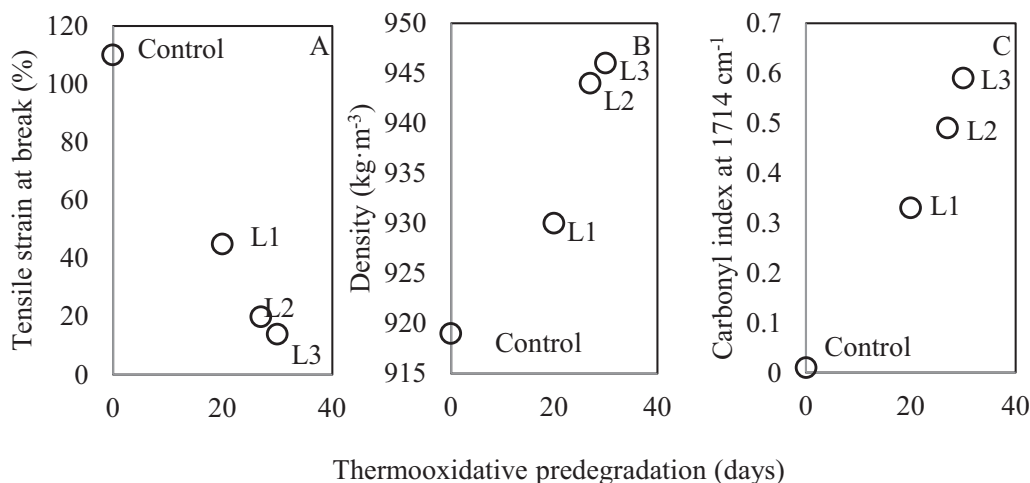
We hypothesize that pre-degraded PE will continue to oxidise, thus showing an increase in carbonyl and carboxylate groups and a reduction in molecular weight. Oxidation is expected to lead to higher crystallinity and an increase in material density. We also hypothesize that the PE will have increasing levels of biofouling throughout the experiment and that the amounts will differ between the levels of preoxidation; being more biofouling on peroxidised films, which may further affect the buoyancy of the PE.

## 2. Materials and methods

Low density polyethylene (LDPE), without additives, was provided by Borealis (CA8200, CAS-No 9002-88-4). The test material was made into a 40–50 µm thick film stripes in March 2016 by SP (Technical Research Institute of Sweden) using a micro-compounder.

### 2.1. Thermo-oxidative degradation

The PE film was exposed to accelerated ageing through thermo-oxidative degradation in a heat oven at 90 °C for 20, 27 and 30 days (according to ISO 2578); the pre-degradation resulted in three different levels of degradation designated L1, L2 and L3 respectively. The unaged material is designated "control". The degraded material showed a



**Fig. 1.** Characteristics of the thermo-oxidatively pre-degraded starting materials and the control. Graphs show changes in; A) tensile strain at break (%), B) density (kg·m<sup>-3</sup>) and C) carbonyl index at 1714 cm<sup>-1</sup> in comparison to the reference peak at 1462 cm<sup>-1</sup>. In the text samples are referred to as Lx<sub>nweeks</sub>, where Lx corresponds to their level of pre-oxidation and n is the number of weeks the samples were in the field.

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