



Environmental scenarii for the degradation of oxo-polymers

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HIGHLIGHTS

- Production of oligomers under conditions mimicking various environmental scenarii.
- Extensive characterization of oxidized oligomers by NMR and LC-MS.
- Longer exposure to abiotic conditions modify the composition of oligomers.
- An important fraction of oligomers is trapped in the polymer matrix.

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ABSTRACT

The fate of oxo-polymers in nature is strongly dependent on environmental conditions, mainly on the intensity and duration of sunshine, which vary with the season and the climate. In this work, we report the effect of different scenarii on the production and the molecular composition of oligomers released from oxo-biodegradable HDPE films. Under our experimental conditions, the duration of accelerated weathering corresponded to a period of 3 months to 3 years of exposure to outside conditions under temperate climate. In addition, the oligomers were extracted in three different solvents: i) water to mimics the natural environment; ii) acetone and chloroform to identify oligomers trapped in the polymer matrix. The combination of high-resolution mass spectrometry and ¹H NMR spectroscopy gives an extensive picture of the relative concentrations and the structural compositions of the extracted oligomers in the different tested conditions. In particular, the masses, the number of oxygen and carbon atoms could be determined for up to 2283 molecules. Globally the concentration and the size of oligomers increased with the duration of extraction, the level of aging of the polymer and the use of non-polar solvents. Surprisingly, the presence of highly oxidized molecules in acetone and chloroform extract, suggested an important swelling of HPDE films in these solvents and a better diffusion of these oligomers in the matrix. In nature, the biodegradability of oligomers could result from processes occurring both at the molecular (oxidation) and the macromolecular (diffusion and release) levels.

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1. Introduction

Biodegradable polymers were developed to limit plastic pollution induced by anthropogenic activities. Oxo-biodegradable materials were produced for single-use applications and non-collectable items such as mulching films, carrier bags and packaging. Once released into the environment, these polymers undergo photo and thermo-oxidation which lead to the fragmentation of the matrix into small oxidized oligomers. The degradation of

these compounds by microorganisms is well documented and numerous scientific publications confirmed that after oxidation, the material is readily consumed by microorganisms (Chiellini et al., 2007; Eyheraguibel et al., 2017; Fontanella et al., 2010; Jakubowicz, 2003; Koutny et al., 2006a; Ojeda et al., 2009). However, an extended literature search also points out that the level of biodegradation can vary a lot under different experimental conditions (Kumar Sen and Raut, 2015; Kyrikou and Briassoulis, 2007) reflecting thus different environmental conditions.

Various rates of biodegradation are reported in the literature within a range of 5–60% (Abrusci et al., 2013; Chiellini et al., 2003; Vazquez-Morillas et al., 2016). Such variability can be explained by

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the different experimental designs, the methods used to assess the degradation and the use of abiotic and biotic conditions poorly controlled (Ammala et al., 2011). In order to compare the rate of degradation, numerous parameters should be considered such as the polymer composition and formulation, the weathering conditions, the composition of microbial consortiums and the incubation period. While the choice and the set-up of the two last parameters can modulate the level of biodegradation, the composition of tested material and the abiotic conditions of oxidation are critical to observe any biodegradation. Indeed, long term exposure to microorganisms will leave more time for polymer consumption ensuring the degradation of the material. However, the differences in composition and formulation of polymers can limit their capacity to biodegrade. Linear polyolefins, exposed to natural weathering, undergo different oxidative degradation according to their composition. PP and oxo-HDPE-LLDPE degrade more rapidly, whereas HDPE and LLDPE, degrade more slowly (Ojeda et al., 2011). When the matrix contains pro-oxidant additives, HDPE is less efficiently oxidized than LDPE and LLDPE, which leads to a lower biodegradation (Fontanella et al., 2010). Under the same conditions, PP films were shown to be less biodegraded than PE films containing the same additives (Fontanella et al., 2013). Comparative studies on the effect of pro-oxidant additives have confirmed that pro-degrading activity increases the rate of oxidation and fragmentation of the polymer but have also underlined the different efficiency of additives (Abrusci et al., 2013; Fontanella et al., 2010; Pablos et al., 2010). Fe, Mn stearates were reported to be more efficient than Ca stearate (Pablos et al., 2010). Fontanella et al. (2010) mentioned that the relative amount of metal in the complex is determinant and can be a limiting factor for biodegradation. In their study, the use of high concentration of cobalt did inhibit the growth of *R. rhodochrous* strains.

Finally, the main factors controlling the biodegradability are the abiotic conditions leading to the oxidation and fragmentation of the polymer. The polymer oxidation was demonstrated under natural weathering conditions (Corti et al., 2012; Ojeda et al., 2011) or under accelerated aging conditions consisting of thermo-oxidation (Chiellini et al., 2007), photo-oxidation (Cornell et al., 1984) or both (Bonhomme et al., 2003; Fontanella et al., 2013, 2010). Once the oxidation reaches a plateau, physico-chemical changes lead to the fragmentation of the polymer. A substantial drop in the molecular weight is accompanied by the production of broad spectrum of low molecular weight and oxidized fractions. These oligomers are hydrosoluble and can diffuse to the environment to be readily assimilated and mineralized by microorganisms (Albertsson et al., 1987; Hakkarainen and Albertsson, 2004; Koutny et al., 2006a). As bacteria can biodegrade compounds with molecular weight up to 1500 Da (Chiellini et al., 2003; Haines, 1975; Potts et al., 1973), oxidized oligomers can be considered as a substrate and their assimilation constitutes the first step of biodegradation. Oligomers characterization is a good indicator to estimate the biodegradability potential of oxo-polymers and few study focused on their analysis to predict the fate of oxo polymer in the environment (Chiellini et al., 2007; Roy et al., 2013). Recently, we proposed a new methodology to characterize the complex mixture of oligomers generated from oxidized polymers using NMR and high resolution mass spectrometry (Eyheraguibel et al., 2017). Quantitative and qualitative data analysis provided extensive information on the structure and the chemical composition of the oligomers by sorting them into classes of molecules. Changes in type and distribution of these oligomers were used to describe biodegradation processes.

This new and global approach was used in the present work to characterize in detail oligomers extracted from HDPE films and to propose scenarii on the fate of oxo-biodegradable polymers in the environment. Short term, medium term and long term of

accelerated weathering, corresponding to 3 months to 3 years of natural weathering, were considered to assess the impact of abiotic conditions on the production and the chemical properties of oligomers released from oxo-biodegradable HDPE films. The characterization of complex oligomer mixtures was carried out using high accuracy mass measurement and ^1H NMR spectroscopy. Qualitative and quantitative data were combined to describe changes in the molecular composition of the oligomers resulting from different photo- and thermo-oxidation of the polymers. Organic solvent extractions were performed to study the presence of hydrophobic compounds that would be available but not readily released under natural conditions characterized by the presence of water.

2. Materials and methods

2.1. Tested material

The material samples were transparent HDPE blown films, 20 μm thick. The films composition was a commercial formulation containing iron photo-inducer (322 ppm) supplying radicals through a photo-redox process and an organometallic type manganese thermo-inducer (232 ppm), catalyzing the primary hydroperoxide decomposition. The oxidation state of the catalysts was Mn^{2+} and Fe^{3+} and the ligand was stearate. To balance the pro-degradant activity of the photo- and thermo-inductor during the first year of storage and use under indoor conditions phenolic antioxidants were utilized in the blends.

2.2. Abiotic treatment

HDPE films were aged under accelerated laboratory conditions in order to mimic the abiotic oxidation occurring in natural conditions. Irradiation procedures were carried out in a SEPAP 12.24 unit with film samples mounted on metallic plates and placed on a rotating carousel. The conditions were set with a wavelength longer than 300 nm, and the temperature of the exposed surface at 60 ± 1 °C. The photo-aging was limited to 40 h to avoid the fragmentation of the film and the loss of material. This time of exposure corresponded to the photochemical induction period required to obtain the total photo-transformation of phenolic antioxidants into inactive compounds.

Exposure in SEPAP unit was followed by either 25, 100 or 300 h of thermal oxidation of the films in an aerated oven at 60 °C to generate samples with various level of oxidation. The samples were labelled respectively as short-term (ST), medium-term (MT) and long-term (LT) exposure (Table S1). These different ageing times corresponded to an exposition of 6 months to 3 years in outdoor conditions (Koutny et al., 2006b).

2.3. Extraction of oligomers and samples preparation

Soluble oligomers were extracted from the oxidized films using a rotary shaker at room temperature. 150 mg of sample were incubated for 7 days into water. To determine the impact of the solvent on the extraction efficiency and determine if non polar solvent could extract a larger amount of compounds, the same extraction was performed in acetone and chloroform. The solvent supernatant containing extracted oligomers and the solid film residue were separated by centrifugation. The solid residue was then dried and the weight loss of the sample was used to estimate the extraction rate. To determine the impact of extraction time on the amount of extracted oligomers, a kinetic study was performed by incubating 150 mg of oxidized films in water for 1 day, 7 days and 21 days.

In all cases, the liquid extracts were aliquoted to a specific

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