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Forensic engineering of advanced polymeric materials Part IV: Case study of oxo-biodegradable polyethylene commercial bag – Aging in biotic and abiotic environment

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ABSTRACT

The public awareness of the quality of environment stimulates the endeavor to safe polymeric materials and their degradation products. The aim of the forensic engineering case study presented in this paper is to evaluate the aging process of commercial oxo-degradable polyethylene bag under real industrial composting conditions and in distilled water at 70 °C, for comparison. Partial degradation of the investigated material was monitored by changes in molecular weight, thermal properties and Keto Carbonyl Bond Index and Vinyl Bond Index, which were calculated from the FTIR spectra. The results indicate that such an oxo-degradable product offered in markets degrades slowly under industrial composting conditions. Even fragmentation is slow, and it is dubious that biological mineralization of this material would occur within a year under industrial composting conditions. The slow degradation and fragmentation is most likely due to partially crosslinking after long time of degradation, which results in the limitation of low molecular weight residues for assimilation. The work suggests that these materials should not be labeled as biodegradable, and should be further analyzed in order to avoid the spread of persistent artificial materials in nature.

1. Introduction

The use of plastic products, especially polyolefins, has increased considerably in recent years due to their good processability, mechanical properties, durability and low cost (Ammala et al., 2011; Restreopo-Folrez et al., 2014). The fact that conventional plastics do not degrade easily in nature is somewhat problematic since parallel to the growth in use the amount that inadvertently finds its way into nature is increasing as well (Bekyarova et al., 2007; Roy et al., 2005). Difficulties in ensuring efficient management of plastic waste in the municipal solid waste stream require new solutions, particularly for the packaging industry (Musioł et al., 2010; 2011). The "back to nature" via biodegradation seems to be a very attractive approach (Chapman, 2012). Narayan (2016) pointed out that "biodegradation is the processes during which plastics products are completely removed from the environment compartment in a timely, safe and efficacious manner by use of microorganisms existing in the disposal environment".

Oxo-biodegradation is described as complex series of chemical reactions with the action of oxygen, ultraviolet light and/or heat in which the long chains of polyethylene molecules are broken down. The term "oxo-biodegradation" is used when the both degrading phenomenon are demonstrated (Thomas et al., 2010).

Polyethylene is generally considered as a non-biodegradable plastic widely used as a packaging material. For several decades producers of conventional polyethylene are searching for methods which would accelerate the degradation of the material in the environment. Solutions include the introduction of "weak" structural elements such as carbonyl groups in the hydrocarbon backbone or side chains, olefinic bonds, the addition of a biodegradable polymer, or the use of pro-oxidants or photoinitiators (Albertsson et al., 1998; Magagula et al., 2009; Martelli et al., 2009; Roy et al., 2008; Rydz et al., 2017). The goal of all these approaches is to develop lifetime programmable polyethylene (Albertsson et al., 1998). Most degradable polyolefin systems are designed to undergo oxidation in air (oxo-degradation). The changes in chemical structure resulting from oxidation should lead to the breakdown of the polymer chain into smaller fragments which can then be bioassimilated and mineralized (Ammala et al., 2011). This is in line with polymer degradation meaning changes in polymer properties by bond scissions and subsequent chemical transformation (Singh and Sharma, 2008).

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Currently, a number of polyolefin products are marketed as "oxo-biodegradable" where the degradation is described to consist of a two-stage process. The first is an abiotic process in which oxygen from the air reacts with the polymer which then undergoes chain scission resulting in low molecular fragments with functional groups such as carboxy, formyl hydroxy and ester linkage (Albertsson et al., 1998; Ammala et al., 2011; Chiellini et al., 2006). Products of the oxidation initiated by heat are very similar to those resulting from photo degradation (Wiles and Scott, 2006). The second stage is a biotic process involving the consumption of polymer oxidation products by microorganisms (Ammala et al., 2011).

For a polymer to undergo biodegradation, a reduction of molecular weight has to take place at the first stage. Only after that bioassimilation, can the second step occur. It is not very clear how much degradation is needed before the microorganisms are able to attack it for bioassimilation. Haines and Alexander (1974) reported that only alkanes with low molecular weights (<620 Da) can be biodegraded. Restreopo-Folrez et al. (2014) reported the molecular weight should be less than 50 carbons. Yoon et al. (2012) investigated the biodegradation of low molecular weight polyethylene (LMWPE). They stated that the PE with molecular weight up to 1700 in presence of *Pseudomonas* sp. E4 underwent biodegradation reaching at almost 30% after 80 days. Generally speaking, the molecular weight should be much smaller than the virgin plastics. This means that a drastic reduction of the polyolefin molecular weight must occur as a condition for later biotic mineralization. Also, a significant disintegration of the material was observed before the molecular mass reduced to 5000 (Albertsson et al., 1998). The fate of the fragmented material is a great concern because they may undergo other changes like crosslinking, resulting in persistence in the environment (Thomas et al., 2012).

The European Commission is still waiting for assessment and legislative conclusion concerning the influence of usage "oxo-bio degradable" plastic bags on the environment. Taking this environmentally responsible decision takes time and detailed research. The packages labeled as "biodegradable" cause a confusion of the consumers. Also, the phrase "oxo-biodegradable" is not clear for the public. Those two words may suggest that people can throw these packages wherever they want, because the microorganisms and oxygen will do the rest. According to the above statements, these materials may be placed in the environment without any control. Thus, determination of the extent of degradation of those kinds of materials in the environment and placing of detailed information on the packages is an urgent task.

The forensic engineering studies on advanced polymeric materials (FEAPM) deal with the evaluation of the relationships between their structure, properties and behaviour before, during and after practical applications (FEAPM I-III) (Musioł et al., 2016; Rydz et al., 2015; Sikorska et al., 2014). Hauling together specific characterization and optimization of the material properties, its preparation, processing and recycling under the common thread of FEAPM provides a central driving force for the otherwise disconnected works and should allow to avoid failures of the commercial products manufactured from them. In this contribution we describe the FEAPM case study on aging of commercial oxo-biodegradable polyethylene bag (ECObag) under industrial composting conditions and in distilled water at 70 °C.

2. Experimental

2.1. Materials

The test material was a commercial polyethylene shopping bag ECObag (Fig. 1), which was purchased from a Polish supermarket. The bag contained commercial Totally Degradable Plastics Additives (TDPA®) and was labeled as an "ECObag – bag that undergoes 100% biodegradation in 12 months". The thickness of the HDPE film was 22 μm.

The TDPA® additive are produced by EPI Environmental Technologies Inc., Canada. Normally "oxo-biodegradable" bags contain 2% of TDPA. According to the website of EPI Environmental Products Inc., the level of TDPA® amount is recommended to be in the range of 2–10% depending on the specific application and the performance required (EPI, 2016).

2.2. Degradation under industrial composting conditions/in compost environment

The investigated material consisting of PE and the TDPA® additive was subjected to degradation testing in the composting pile (sample designated as PE-CP), at the Sorting and Composting Station in Zabrze (Upper Silesia, Poland). The compost contained 40% leaves, 30% branches and 30% grass. The static composting open-air pile is located at: latitude 50° 18′ 30.71″ N and longitude 18° 48′ 18.52″ E. Experiments were conducted between late summer and beginning of autumn with daily rainfall below 2.0 mm. The average open-air temperature during this time remained about 12 °C. The compost was not turned during this period. The composting pile was built over a concrete slab with holes to create a chimney effect of airflow. At the time of starting the PE degradation test the composting was already going on for 3 weeks.

A series of 8 specimens (size 4 × 5 cm) was cut from the original bag. The specimens were weighted and inserted into a special stainless steel cage and cover with compost from composting pile (Musioł et al., 2011).

The cage were placed into the composting pile, at the depth of one meter under the surface (total height of composting pile was 4 m). The average temperature at the environment (pile) was 64 °C. The average pH in the composting pile was pH = 6.9. During the 10 week test period the variation in pH was below 20% (6.3–7.5).

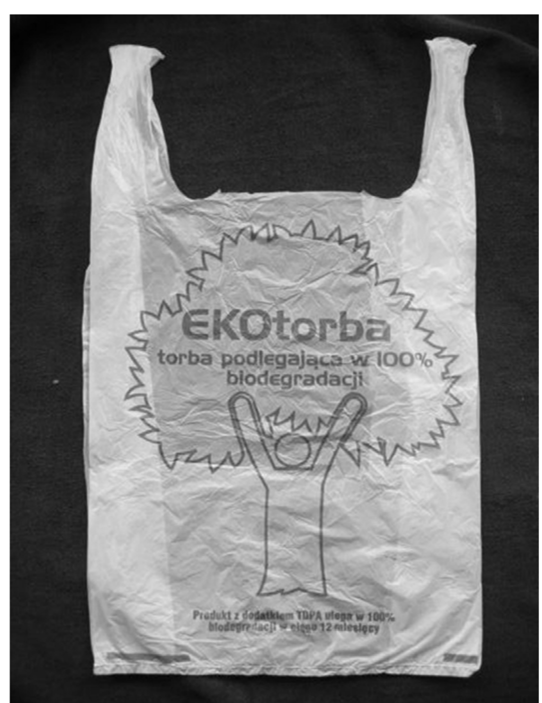

Fig. 1. A photograph of the commercial bag ECObag from a Polish supermarket.

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