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Forensic engineering of advanced polymeric materials. Part III - Biodegradation of thermoformed rigid PLA packaging under industrial composting conditions

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ABSTRACT

This paper presents a forensic engineering study on the biodegradation behaviour of prototype packaging thermoformed from PLA-extruded film and plain PLA film under industrial composting conditions. Hydrolytic degradation in water was conducted for reference. The effects of composting duration on changes in molar mass, glass transition temperature and degree of crystallinity of the polymeric material were monitored using gel permeation chromatography (GPC) and differential scanning calorimetry (DSC). The chemical structure of water soluble degradation products of the polymeric material was determined using nuclear magnetic resonance (NMR) and electrospray ionization mass spectrometry (ESI-MS). The results show that the biodegradation process is less dependent on the thermoforming process of PLA and more dependent on the composting/degradation conditions that are applied. The increase in the dispersity index, leading to the bimodal molar mass distribution profile, suggests an autocatalytic hydrolysis effect at the early stage of the composting process, during which the bulk hydrolysis mechanism dominantly operates. Both the prototype PLA-packaging and PLA rigid film samples were shown to have a gradual increase in opacity due to an increase in the degree of crystallinity.

1. Introduction

Forensic engineering of advanced polymeric materials (FEAPM) deals with evaluating and understanding the relationships between these materials' structure, properties and behaviour before, during and after practical applications have been implemented. The concept of FEAPM, has been presented previously in Parts I and II (Rydz et al., 2015; Sikorska et al., 2014).

The use of non-degradable materials as food packaging causes growing pollution of environment and the difficulties in recycling are stemming from contamination of these materials by food. Generally in the case of polymeric packaging materials the typical end-of-life options (depending on the materials properties) include recycling, monomer recovery, incineration with energy recovery as well as composting or landfill. However, the typical recycling facilities are not equipped to dispose of food contaminated polymeric packaging therefore currently most of this kind of packaging is disposed of in landfills. A challenge is to develop a technology for disposal of polymeric packaging together with contamination from food. In this case the application of the biodegradable polymers (which undergo biodegradation in compost) has become very useful. The use of biodegradable polymers can help to reduce the problem of plastic accumulation in landfills. Moreover, organic recycling (composting) process allows biopolymer waste products to participate in fundamental ecological material cycles. The stable compost that is formed from biodegradable packaging together with other components can be used for different purposes, e.g. in agriculture and horticulture as a fertilizer, as a plant growth substrate and for land re-cultivation (Abe et al., 1995).

Polylactide (PLA) is one of the commercially available biodegradable polymeric materials used for manufacturing packaging (Abe et al., 1995; Li and McCarthy, 1999; Chen et al., 2004; Zhang et al., 2008; Majid et al., 2002; Freier et al., 2002; Andersson et al., 2010a, 2010b; Yoshie et al., 2000; Mukai et al.,

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1993; Kunioka et al., 2006; Żenkiewicz et al., 2013; Arias et al., 2014).

It is generally considered that the bulk hydrolytic mechanism operates dominantly in the degradation of PLA (Rudnik and Briassoulis, 2011; Hakkarainen et al., 1996; Sikorska et al., 2015). Hydrolytic degradation of PLA consists of four stages: water absorption, cleavage of ester bonds, and diffusion of water soluble oligomers and solubilization of fragments. When a thick sample is subjected to degradation, an autocatalytic process usually takes place since the interior becomes more acidic due to the generation of more carboxylic acid groups with the cleavage of ester bonds, and these acidic groups are very slow to diffuse out of the material. (Rudnik and Briassoulis, 2011; Grizzi et al., 1995; Andersson et al., 2010a) In contrast carboxylic acids generated on the surface layer can leave the surface immediately. The semi-crystalline nature of PLA also affects degradation behaviour, as water diffused into the sample first cleaves the ester bonds in the amorphous regions. After most of the ester bonds in the amorphous region are broken down, water starts to attack the crystalline regions. During degradation, water works as a plasticizer to the PLA, thus enhancing the mobility of the polymer chains. This enhanced mobility leads to an increase in the degree of crystallinity, resulting in a loss of transparency of the plastics. At later stages of the degradation of PLA when the molar weight is reduced significantly and fragmentation occurs, the presence of various enzymes can accelerate the degradation such as proteinase K, serine protease from the fungus *Tritirachium album* (Reeve et al., 1994; Cai et al., 1996), lipase, esterase, and alcalase (Lee et al., 2014). Proteinase K preferentially degrades PLLA as opposed to PDLA (Reeve et al., 1994; MacDonald et al., 1996). Different enzymes have been shown to present different degradation behaviour, e.g. alcalase is more efficient than lipase and esterase (Lee et al., 2014).

When PLA is used as a biodegradable packaging material, it is either discarded into the environment to naturally degrade or it is collected for composting. In the natural environment, such as in soil burial and in an aquatic system, degradation is rather slow because the temperature is usually lower than 30 °C (Rudnik and Briassoulis, 2011) and very few PLA-degrading microorganisms are distributed in the environment (Tokiwa and Calabia, 2006), e.g. in an environmental research report presented by the California Department of Resources Recycling and Recovery, the degradation of PLA was tested in a simulated marine environment for a period of six months at 25 °C. Only 3% of the PLA samples were degraded into CO_2. The degradation of PLA is also very slow in many soil tests such as in natural Mediterranean soil (Rudnik and Briassoulis, 2011) and in Costa Rican soil (Ho et al., 1999). After an 11-month' burial test in Mediterranean soil at an average temperature of 21 °C and 40% moisture, the mass loss was very small, although the mechanical properties and degree of crystallinity had changed remarkably.

Composting involves the conversion of a mixture of organic substances into CO_2, H_2O and humus under a biodegradation process by a microbial community composed of various populations in aerobic conditions and in solid phase. Composting conditions are quite different from an environmental landfill because the latter lacks sufficient temperature, moisture, oxygen and microorganisms (Rudnik and Briassoulis, 2011). Under landfill conditions, few bioplastics can fulfil the requirements of various testing standards such as ASTM 6400 used in the United States, DIN 54900 used in Germany, and EN 13432 used in most other European countries in which degradation is evaluated by the amount of CO_2 release during the metabolic processes, where the polymer is used as a carbon source for the microorganisms. An evaluation of biodegradability by determining the amount of CO_2 released from poly(lactic acid)/starch/coir biocomposites was also conducted (Iovino et al., 2008). At compost conditions enzymatic degradation may occur at later stages because of the presence of various microorganisms (Sikorska et al., 2015). Therefore, the degradation of PLA in compost conditions should be much more complex than degradation under physiological conditions or environmental conditions. These polyesters can be degraded enzymatically only after preliminary hydrolytic degradation has taken place (Penczek et al., 2013).

Composting of PLA has been studied under simulated conditions, e.g. in compost piles specially prepared for this purpose or in compost bins (Rudnik and Briassoulis, 2011; Mohee et al., 2008). Bayerl et al. investigated the FLAX/PLA composite under conditions similar to those of household compost, prepared in the form of an erected composting pile (Bayerl et al., 2014). The biodegradation of PLA in a spring water bottle, a tray and a deli container under real composting conditions ($T > 55$ °C, >65% relative humidity and pH 7.5) was performed by Kale et al. These packaging items were subjected to a composting test for 30 days (Kale et al., 2006). Rudnik and Briassoulis investigated the composting of PLA films and fibers under home composting conditions similar to those of a soil burial (Rudnik and Briassoulis, 2011). Ho et al. investigated the composting of PLA films. During the compost study, the temperature and relative humidity of the rows were maintained at 55–60 °C and 50–70%, respectively. Rapid loss of the mechanical properties and molar masses of the samples studied were observed during the first period of degradation process. A slight decrease in glass transition temperature (T_g) and melting temperature (T_m) and an increase in crystallinity were also observed (Ho et al., 1999).

Studies on the organic recycling PLA-based products, performed in natural, non simulated conditions, are very important in order to gain a better understanding of the compostable polymers (bio) degradation processes in environments to which they are disposed of after use.

The review of the literature presented here shows that both the mechanism and rate of biodegradation of polylactide and of polymeric materials developed on its basis are related to many factors. Among them, the process conditions (e.g. temperature, humidity) and the ratio between sample surface to sample weight are the most important. However, according to the best of our knowledge information on the (bio)degradation of prototype packaging items made from biodegradable polymeric materials under industrial composting conditions is rather limited. Diverse implementations of biodegradable polymers require case specific characterization and optimization of the material properties, its preparation, processing and recycling. Pulling these different elements together under the common thread of FEAPM provides a central driving force for the otherwise disconnected works and constitutes the novelty of this research. Such approach is important for the packaging sector as well as the life cycle of the prototype compostable packages (e.g. trays).

The results of comparative studies on the biodegradation of PLA rigid films and on prototype PLA packaging (a tray) thermoformed from them, under industrial composting conditions are presented here. In this study degradation of materials was conducted under real industrial composting condition in the Station of Mechanical-Biological Waste Treatment in Zabrze. In order to verify the influence of composting conditions on the biodegradation process two industrial composting systems were used, i.e. a static composting open-air pile and a KNEER system with containers. Additionally, to identify degradation products which can migrate to the environment from the samples studied, abiotic degradation tests were carried out under laboratory conditions. The thermoforming process may influence the thermal properties, mechanical resistance, thickness distribution and homogeneity of the package. Thus, degradation processes of PLA rigid films and PLA-based