ARTICLE IN PRESS

Waste Management xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

(Bio)degradable polymeric materials for a sustainable future – part 1. Organic recycling of PLA/PBAT blends in the form of prototype packages with long shelf-life

Marta Musioł [a,*], Wanda Sikorska [a], Henryk Janeczek [a], Wojciech Wałach [a], Anna Hercog [a], Brian Johnston [b], Joanna Rydz [a]

[a] Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 34. M. Curie-Skłodowska St., 41-819 Zabrze, Poland

[b] University of Wolverhampton, Faculty of Science and Engineering, Department of Biology, Chemistry and Forensic Science, Wulfruna Street, Wolverhampton WV1 1SB, UK

ARTICLE INFO

Article history:
Received 30 November 2017
Revised 12 April 2018
Accepted 19 April 2018
Available online xxxx

Keywords:
Organic recycling
Biodegradation
Hydrolytic degradation
Packages
Poly(butylene adipate-*co*-terephthalate)
Polylactide
Talc

ABSTRACT

Prediction studies of advanced (bio)degradable polymeric materials are crucial when their potential applications as compostable products with long shelf-life is considered for today's market. The aim of this study was to determine the effect of the polylactide (PLA) content in the blends of PLA and poly(butylene adipate-*co*-terephthalate) (PBAT); specifically how the material's thickness corresponded to changes that occurred in products during the degradation process. Additionally, the influence of talc on the degradation profile of all samples in all environments was investigated. It was found that, differences in the degradation rate of materials tested with a similar content of the PLA component could be caused by differences in their thickness, the presence of commercial additives used during processing or a combination of both. The obtained results indicated that the presence of talc may interfere with materials behavior towards water and consequently alter their degradation profile.

1. Introduction

The key to achieving success and increased presence in the bioeconomy industry is to understand both the advantages and limitations of biodegradable and biobased products. Biodegradable polymers are now the material of choice due to the plastics industry needing to change their strategy as a result of years of pollution. This influence has become the steady driving force behind the manufacturing sector in Europe over the last few years (Rydz et al., 2018). Conventional polymers available today are thought to have many advantages, such as good processability, hydrophobicity and having excellent barrier properties. However, these materials are characterised by high resistance to biological agents and the widespread use of them for packaging has made them the cause of an array of environmental problems. Plastic waste deposited in landfills occupies more new areas of ground each year and even threatens our oceans. One of the ways to solve this growing problem is to introduce and promote the consistent usage of packaging made from natural or biodegradable polymers into the market (Ghanbarzadeh and Almasi, 2013; Sam et al., 2016; Narodoslawsky et al., 2015). Biodegradable packages with special marks or indicators could be separated from the municipal waste stream and directed into organic recycling. This could be achieved by collecting them together with the organic waste arising from households (Höglund et al., 2012; Kale et al., 2006, 2007a; Musioł et al., 2015; Sikorska et al., 2008, 2012; Swift, 2015). According to PlasticsEurope and European Bioplastics (nova-Institute) the amount of global plastic production in 2017 was estimated at 340 million tonnes; of this amount 2.05 million tonnes are biobased plastics and 880,000 tonnes are biobased biodegradable polymers (Report European Bioplastics, 2017). Therefore, it is extremely important to increase consumer awareness about biodegradable polymeric materials and introduce them to the market, so biodegradable packaging will become an integral part of their lives. The global introduction of biodegradable polymeric materials for packaging must be preceded by a number of changes, such as the development of new technology, the improvement of the infrastructure of composting, as well as the financial capacity and the appropriate policies that are required (DSTI/STP/BIO (2013)6/FINAL, 2013; Shahzad et al., 2017; Narodoslawsky, 2010; Koller et al., 2017). Thus, research, especially proof of concept

* Corresponding author.
E-mail address: mmusiol@cmpw-pan.edu.pl (M. Musioł).

https://doi.org/10.1016/j.wasman.2018.04.030
0956-053X/

studies, in this area are still required. The value chain of biodegradable polymeric materials comes from the production of polymers through to the consumer and then through waste management (PLASTICE project) and research should be carried out at every link of this chain.

The term biodegradable is used to describe those materials, which are degraded by the enzymatic action of microorganisms (bacteria and fungi). Biodegradation can occur under aerobic and anaerobic conditions. The final degradation products of the process under aerobic conditions are CO_2, H_2O and biomass (Adamus et al., 2006; Sikorska et al., 2015). The literature reviewed indicates that aliphatic polyesters are now considered potential biomaterials for applications in agriculture, medicine, pharmacy and packaging (Rydz et al., 2015a; Sikorska et al., 2014; Musioł et al., 2016a, 2016ba). PLA exhibits a high tensile modulus, resistance to UV radiation and fats, and the ability to be processed by conventional methods (Ahmed and Varshney, 2011; Ingrao et al., 2015; Jabeen et al., 2015; Kale et al., 2007b, Jost and Kopitzky, 2015). However, there are several examples where PLA-based materials did not meet the requirements as a packaging material, especially for long shelf-life products (Rydz et al., 2013a, 2013b, 2015b). Aliphatic-aromatic copolyesters can be applied in package production due to the good functionality of their aromatic polyesters and the biodegradability of aliphatic polyesters (Witt et al., 2001; Rychter et al., 2006, 2010, 2011; Żenkiewicz et al., 2013). PBAT is a linear statistical aliphatic-aromatic copolyester consisting of 1,4-butanediol and terephthalic acid monomers as rigid units and 1,4-butanediol and adipic acid monomers as flexible units. PBAT with the content of terephthalic acid higher than 35 mol% has better mechanical and thermal properties (Siyamak et al., 2012; Bohlmann, 2005). However, the increase of its content is followed by a significant decrease in the biodegradation rate as the growing amount of aromatic units elevates resistance against microorganisms (Vroman and Tighzert, 2009; Kijchavengkul et al., 2010). On the market, BASF (Ecoflex®) and Novamont (Origo-Bi™, former Eastar-Bio™/Eastman with 30–70% renewable content) PBAT producers are widely known (Jiang and Loos, 2016; News/Press releases, 2013a, 2013b). Additionally, PBAT is processable on conventional blow film plants applied for low-density polyethylene what can contribute to the reduction of the cost of producing the material (Plasticsportal.net). The PBAT copolyester is used commercially in food packaging, as an agricultural plastic and it is also used in sporting goods. Recent studies have shown that the aliphatic-aromatic copolyester and polylactide commercial blend demonstrates good stability during aging in cosmetic simulants, which is important for prospective applications of this polymeric material as compostable packing for products with a long shelf-life (Sikorska et al., 2017).

2. Materials and methods

This paper presents a (bio)degradation study of PLA and PBAT blends in the form of prototype packages with long shelf-life. The biodegradation tests were performed under industrial composting conditions in a pile and in a container system. Additionally, an abiotic degradation test was carried out under laboratory conditions. The selected materials allowed the determination of the effect of PLA content (17 and 40 mol%) in the films on their degradation process and a comparison of the degradation of materials with different thickness and the same molar content (40 mol%) of PLA. The changes of molar mass, molar-mass dispersity, composition and thermal properties of the samples were observed during an incubation period in degradation media and the resultant material was characterised by GPC, ^{1}H NMR, TGA and DSC techniques, respectively.

2.1. Materials

The case study on organic recycling was performed with prototype materials prepared by blowing (blends of PBAT with PLA) containing 17 and 40 mol% of PLA into films (marked respectively as F/17 and F/40) and 40 mol% of PLA in form of disposable bags (marked as T/40). The samples were prepared by the Bioerg Company in Poland, by extrusion to produce on test stands of conventional flat proportions using a single-screw extruder. The technical details concerning the materials, additives and processing methods are commercially protected. Table 1 presents the description of plain samples before degradation tests.

2.2. Environments

The comparative (bio)degradation studies of blends in the form of films and disposable bags were conducted under industrial composting conditions in two systems: a static composting open-air pile and a KNEER container system. The abiotic degradation in distilled water at 70 °C was performed to indicate that the control of both moisture and temperature is an important factor that affects the degradation of the investigated materials.

2.2.1. (Bio)degradation test under industrial composting conditions

The composting process was carried out at the Mechanical-Biological Waste Treatment Station in Zabrze (Upper Silesia, Poland) in a static composting open-air pile (located at: latitude 50° 18′ 30,71″ N and longitude 18° 48′ 18,52″ E) in a KNEER container system, as described by Musioł et al. (2011). In the composting pile, samples were incubated for 21 days at an average temperature of 61 °C (±5 °C) with an average pH of 6.9. The samples were run in triplicate and the experiments were conducted between September and October 2015. In the container system, the samples were incubated for 21 days in three cages at an average temperature of 60 °C (±5 °C) with an average pH of 7.5. The cages with the materials studied were placed into composting systems at a depth of 1 m below the compost surface.

2.2.2. Abiotic degradation test under the laboratory conditions

The samples were incubated in distilled water at 70 °C over a period of 70 days, according to norm ISO (International Standard: ISO 15814). The samples were inserted into 30-mL screw-capped vials, containing 25 mL of medium, and then placed in a laboratory oven at 70 °C. The samples were each run in triplicate. After a specified time of incubation the samples were removed from the vials and cleaned by washing in distilled water, they were then drained on blotting paper and then dried to a constant mass under a vacuum at 25 °C.

2.3. Measurements

2.3.1. Gel Permeation Chromatography (GPC) analysis

The GPC experiments for the PLA/PBAT samples were conducted as described previously by Sikorska et al. (2015).

Table 1
Plain materials studied – prototype products of Bioerg Company, Poland.

Product type	Sample name	PLA content [mol%]	Thickness [mm]
Film	F/17	17 ± 0.5	0.02 ± 0.01
	F/40	40 ± 1.0	0.03 ± 0.01
Disposable bag market	T/40	40 ± 0.5	0.10 ± 0.01

Please cite this article in press as: Musioł, M., et al. (Bio)degradable polymeric materials for a sustainable future – part 1. Organic recycling of PLA/PBAT blends in the form of prototype packages with long shelf-life. Waste Management (2018), https://doi.org/10.1016/j.wasman.2018.04.030