



Bionanocomposite films based on plasticized PLA–PHB/cellulose nanocrystal blends



M.P. Arrieta^a, E. Fortunati^{b,*}, F. Dominici^b, J. López^a, J.M. Kenny^{b,c}

^a Instituto de Tecnología de Materiales, Universitat Politècnica de Valencia, 03801 Alcoy-Alicante, Spain

^b Materials Engineering Centre, UDR INSTM, NIPLAB, University of Perugia, 05100 Terni, Italy

^c Institute of Polymer Science and Technology, CSIC, Juan de la Cierva 3, Madrid 28006, Spain

ARTICLE INFO

Article history:

Received 1 September 2014

Received in revised form 5 December 2014

Accepted 19 December 2014

Available online 2 January 2015

Keywords:

Poly(lactic acid)

Poly(hydroxybutyrate)

Cellulose nanocrystals

Plasticizer

Blends

Nanocomposites

ABSTRACT

Optically transparent plasticized poly(lactic acid) (PLA) based bionanocomposite films intended for food packaging were prepared by melt blending. Materials were plasticized with 15 wt% of acetyl(tributyl citrate) (ATBC) to improve the material processability and to obtain flexible films. Poly(hydroxybutyrate) (PHB) was used to increase PLA crystallinity. The thermal stability of the PLA–PHB blends was improved by the addition of 5 wt% of cellulose nanocrystals (CNC) or modified cellulose nanocrystals (CNCs) synthesized from microcrystalline cellulose. The combination of ATBC and cellulose nanocrystals, mainly the better dispersed CNCs, improved the interaction between PLA and PHB. Thus, an improvement on the oxygen barrier and stretchability was achieved in PLA–PHB–CNCs–ATBC which also displayed somewhat UV light blocking effect. All bionanocomposite films presented appropriate disintegration in compost suggesting their possible applications as biodegradable packaging materials.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The use of bio-based and biodegradable polymers for food packaging applications is currently increasing in order to reduce the consumption of non-renewable resources and prevent the accumulation of plastics waste, respectively. Simultaneously, the food packaging industry demands the development of simple packaging formulations produced by easy, readily available and cost effective processing technologies such as melt blending approaches (Arrieta, Fortunati, et al., 2014b). At the same time, consumers demand high quality food with long shelf-life and also they desire see through the packaging to perceive the foodstuff aspect. Thus, food packaging are required to contain food products and protect them from the surroundings avoiding contamination, humidity and oxidations process as well as being enough transparent to allow seeing the food thought the packaging.

Poly(lactic acid) (PLA) is the most used biopolymer as short term film for food packaging, due to its many advantages such as high transparency, availability in the market, ease of processing, economically competitive and environmentally benign characteristics (Armentano et al., 2013; Auras, Harte, & Selke, 2004). In view of the fact that PLA also shows some poor barrier properties, increasing

PLA crystallinity become necessary for the intended use. Thus, melt blending PLA with another more crystalline biopolymer with similar melting temperature, such as poly(hydroxyalkanoates) (PHAs), has gain considerable attention for the food packaging sector. Among PHAs, poly(hydroxybutyrate) (PHB), produced by controlled bacterial fermentation, is the most common representative of PHA (Zhang & Thomas, 2011) and also widely studied for food packaging applications (Bucci, Tavares, & Sell, 2007).

The miscibility between PLA and PHB is dependent on the processing temperature, the proportion and the molecular weight of the second component. PLA shows partial miscibility with low molar mass PHB (Hu, Sato, Zhang, Noda, & Ozaki, 2008) while presents optimal miscibility in the melt state (Blümm & Owen, 1995). It has been reported that some transesterification reactions among PLA and PHB chains take place when they are melt blended in 75:25 proportion (Zhang & Thomas, 2011; Zhang, Xiong, & Deng, 1996). As a result, melt blending PLA with 25 wt% of fully bio-based and biodegradable poly(hydroxybutyrate) have gained special interest in the development of films for food packaging sector. The addition of highly ordered stereochemical structure of PHB at this proportion, produces a reinforcing effect since it crystallizes as small spherulites that act as nucleating agents for PLA (Zhang & Thomas, 2011), increasing its crystallinity (Abdelwahab et al., 2012; Arrieta, Fortunati, et al., 2014a; Arrieta, Fortunati, et al., 2014b; Arrieta, López, Hernández, & Rayón, 2014; Arrieta, Samper, López, & Jiménez, 2014) and, thus, improving the film

* Corresponding author. Tel.: +39 0744492921; fax: +39 0744492950.
E-mail address: elena.fortunati@unipg.it (E. Fortunati).

final barrier properties (Arrieta, Fortunati, et al., 2014b; Arrieta, López, Hernández, et al., 2014; Arrieta, Samper, et al., 2014). Moreover, PLA–PHB (75:25) blends showed increased Young's modulus (Arrieta, Fortunati, et al., 2014b; Arrieta, López, Hernández, et al., 2014; Arrieta, Samper, et al., 2014) and somewhat higher UV blocking than neat PLA (Arrieta, Fortunati, et al., 2014b). Conversely, PHB has small processing window, showing the melting temperature, at about 170–180 °C, close to the degradation temperature, typically centered at 270 °C (Koller, Salerno, Dias, Reiterer, & Braunegg, 2010). As a consequence, PLA–PHB blends show lower thermal stability with respect to neat PLA (Arrieta, López, Hernández, et al., 2014; Arrieta, Samper, et al., 2014).

On the other hand, a new approach is growing up in the packaging sector focused on the development of bio-based nanocomposites (bionanocomposites) since the addition of nanofillers lead to an enhancement in the thermomechanical performance, of bio-based polymers (Armentano et al., 2013; Rhim, Park, & Ha, 2013). To guarantee the packaging green nature, the ideal nanoparticles should be bio-based and biodegradable. Cellulose derivatives are optimal reinforcing materials for bioplastic industry since they are bio-based, biodegradable, stiff, lightweight, non-abrasiveness to the processing equipment and highly abundant in the nature at low cost (Brinchi, Cotana, Fortunati, & Kenny, 2013; Frone, Berlioz, Chailan, & Panaiteanu, 2013; Rayón, Ferrandiz, Rico, López, & Arrieta, 2014). Hence, cellulose nanocrystals (CNC), extracted from several plant fiber crops, have proven to be promising filler for the production of PLA based bionanocomposite films intended for food packaging (Fortunati, Armentano, Zhou, Iannoni, et al., 2012; Fortunati, Armentano, Zhou, Puglia, et al., 2012; Fortunati et al., 2014; Fortunati, Peltzer, Armentano, Jiménez, & Kenny, 2013; Fortunati, Peltzer, et al., 2012). The homogeneous dispersion of high polarity CNC into the hydrophobic polymers matrices, such as the case of PLA and PHB, could be favored modifying the nanocrystal surfaces by their hydroxyl group interaction with a surfactant, leading to CNC surface functionalization (CNCs) (Fortunati, Armentano, Zhou, Iannoni, et al., 2012). In previous works, the processing performance, compatibility and thermal stability of PLA–PHB (75:25) blend were improved by the addition of 5 wt% of nanocellulose (CNC) and eventually modified by means a surfactant (CNCs) synthesized from microcrystalline cellulose (MCC) by acid hydrolysis (Arrieta, Fortunati, et al., 2014a). The strategy of modified CNCs allows to obtain ternary bionanocomposite films with improved properties for the food packaging field: fully biodegradable, increased tensile properties, optimal transparency with somewhat UV blocking effect, improved oxygen barrier and water resistance (Arrieta, Fortunati, et al., 2014b).

Another PLA–PHB blends drawback for film manufacturing is the inherent brittleness of PLA and PHB (Arrieta, Samper, et al., 2014). Plasticization is often used to improve biopolymers processability and other properties required for food packaging applications. In this sense, the use of plasticizers has demonstrated to be an effective way to improve the processability of PLA–PHB blends, at the same time that increased the stretchability of the obtained films (Abdelwahab et al., 2012; Arrieta, Castro-López et al., 2014; Arrieta, López, Hernández, et al., 2014; Arrieta, Samper, et al., 2014) and sped up the polymer disintegration in compost conditions, in relation to their post-use (Arrieta, López, Hernández, et al., 2014; Arrieta, López, Rayón, & Jiménez, 2014). Acetyl tributyl citrate (ATBC), obtained from naturally occurring citric acid and accepted to be in contact with food products (European Food Safety Authority, 2012), at 15 wt% has shown effectiveness to increase PLA–PHB blend elongation at break better than other plasticizers such as poly(ethylene glycol) (PEG) (Arrieta, Samper, et al., 2014) and D-limonene (Arrieta, López, Hernández, et al., 2014). Although, the addition of plasticizers make easy PLA and PHB chain mobility increasing the material oxygen permeability, plasticized

PLA–PHB blends with ATBC showed lower oxygen permeation than those PLA–PHB blends plasticized with other plasticizers such as PEG (Arrieta, Samper, et al., 2014) and D-limonene (Arrieta, López, Hernández, et al., 2014).

The main objective of the present research is to develop high performance and multifunctional flexible bionanocomposite films based on PLA–PHB blends through melt blending technology with improved properties for biodegradable food packaging proposes. Since the use of preformed masterbatches is a useful and cost-effective technique for industrial applications, PLA–PHB masterbatches were prepared by melt extrusion. Subsequently, PLA and PLA–PHB masterbatch were reinforced with synthesized cellulose nanocrystals (CNC) or modified cellulose nanocrystals (CNCs) and further plasticized with ATBC through melt blending technology directly followed by a film forming process. The influence of the plasticizer addition on the processing of the innovative quaternary systems was reported. The structural, thermal and mechanical properties of the obtained films were evaluated. Moreover, since these materials are intended for the biodegradable food packaging sector, surface wettability, oxygen barrier, UV-blocking effect and the transparency were studied as well as their disintegration under composting conditions at a laboratory-scale level.

2. Experimental

2.1. Materials

Poly(lactic acid) (PLA 2002D, $M_n = 98,000 \text{ g mol}^{-1}$, 4 wt% D-isomer) was supplied by NatureWorks (USA) and poly(hydroxybutyrate) (PHB) was acquired by NaturePlast (France). Microcrystalline cellulose (MCC, dimensions of 10–15 μm) and acetyl tributyl citrate (ATBC, $M = 402 \text{ g mol}^{-1}$, 98% purity) were purchased from Sigma–Aldrich.

2.2. Cellulose nanocrystal synthesis and modification

Cellulose nanocrystals (CNC) were synthesized from microcrystalline cellulose by a sulphuric acid hydrolysis (64 wt/wt%) at 45 °C for 30 min with continuous stirring following the recipe used by Fortunati and colleagues (Fortunati, Armentano, Zhou, Iannoni, et al., 2012).

An acid phosphate ester of ethoxylated nonylphenol (STEFAC TM 8170, Stepan Company, Northfield) was used in 1/1 (wt/wt) to modify the surface of CNC (CNCs).

A freeze-drying procedure was conducted to obtain CNC and CNCs powders. The yield reaction resulted in ca. $21 \pm 5\%$ and the obtained nanocrystals displayed dimensions ranging from 100 to 300 nm in length and between 5 and 10 nm in width (Arrieta, Fortunati, et al., 2014a).

2.3. Bionanocomposite preparation

Bionanocomposites were manufactured by using a twin-screw microextruder (DSM explorer 5&15 CC Micro Compounder) at screw speed of 150 rpm and mixing time of 3 min. While PLA pellets and ATBC were previously dried overnight at 80 °C, PHB pellets and cellulose nanocrystals (CNC and CNCs) were dried at 40 °C for 4 h.

PLA and PLA–PHB (75:25) blends were plasticized with 15 wt% of ATBC according with previous work (Arrieta, Samper, et al., 2014). Plasticized PLA and PLA–PHB were reinforced with 5 wt% of CNC or CNCs (Arrieta, Fortunati, et al., 2014a; Fortunati, Armentano, Zhou, Iannoni, et al., 2012).

PLA pellets, were put in the microextruder manually to reach a head force of 1200 N using a mixing temperature profile with a

Download English Version:

<https://daneshyari.com/en/article/1383263>

Download Persian Version:

<https://daneshyari.com/article/1383263>

[Daneshyari.com](https://daneshyari.com)