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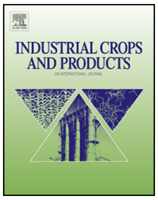

Biodegradable electrospun bionanocomposite fibers based on plasticized PLA–PHB blends reinforced with cellulose nanocrystals

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ABSTRACT

Electrospun biobased and biodegradable nanocomposites for sustainable flexible films were developed. Poly(lactic acid) (PLA) was blended with 25 wt% of poly(hydroxybutyrate) (PHB) to produce bead-less fibers and plasticized with 15 wt% of acetyl(tributyl citrate) (ATBC) to obtain flexible materials. The system was further loaded with cellulose nanocrystals (CNC) in 1 wt% and 5 wt% to obtain bionanocomposites with improved thermal and mechanical resistance. The morphological, structural, thermal and mechanical performance of electrospun bionanocomposites was investigated. The effect of ATBC was characterized by a decrease of the glass transition temperature and an increase in the elongation at break. Meanwhile, CNC improved the thermal and mechanical resistance of mats. Thus, good performance for the intended use was achieved for the bionanocomposite loaded with 1 wt% of CNC (PLA–PHB–ATBC–CNC1), which also showed appropriate surface water resistance. All electrospun bionanocomposites were fully disintegrated under composting conditions showing their possible applications as compostable flexible film materials.

1. Introduction

There is a growing attitude to substitute the use of non-renewable polymers for sustainable polymers, particularly in short term applications. In particular, two are the main advantages when biobased and biodegradable polymers are used in short-term applications. In fact, they allow to reduce the global dependence on fossil petrol sources for their production and at the same time they provide composting as a simple and sustainable disposal option (Arrieta et al., 2014d; Auras et al., 2004; Bucci et al., 2007; Kale et al., 2007b). Thus, biodegradable polymers represent an alternative to reduce the great amount of plastic waste due to they can be degraded to water and carbon dioxide under environmental conditions by micro-organisms (Erceg et al., 2005). Poly(lactic acid) (PLA) is a linear thermoplastic polyester derived from the fermentation of renewable agricultural crops, such as starch, cellulose and other polysaccharides. Moreover, it is compostable disappearing completely in less than one month (Arrieta et al., 2014e; Dolores et al., 2014; Kale et al., 2007a) and it is currently the most used biobased and biodegradable polymer for short-term applications. However, the main drawbacks of PLA are that it shows lower thermal and mechanical performance with respect of their petrochemical counterparts (Arrieta et al., 2013; Burgos et al., 2014). Thus, many researchers are focusing their attention on the improvement of PLA properties by blending (Arrieta et al., 2014a,f; Boufarguine et al., 2013), copolymerizing with other biopolymers (Navarro-Baena et al., 2014,2015; Peponi et al., 2012a,b; Yang et al., 2015) or by means of the development of bionanocomposites (Armentano et al., 2013; Arrieta et al., 2014b; Jamshidian et al., 2010; Peponi et al., 2014b; Rhim et al., 2013).

Poly(hydroxybutyrate) (PHB) is also a biobased and biodegradable biopolyester produced by biosynthesis through bacterial fermentation, mainly those that belong to the genres *Alcaligenes*, *Azobacter*, *Bacillus*, and *Pseudomonas* (Bucci et al., 2007). PHB is also a brittle polymer, as its enzymatic polymerization leads to the formation of macromolecules with highly ordered stereochemical structure and, as a result, with large crystallinity (Arrieta et al., 2014d; Imre and Pukánszky, 2013). There are not many commercial application of PHB since it presents some drawbacks for the industrial production of film applications such as narrow processing window, high brittleness and, as compared with conventional plastics, it is still more expensive than conventional plastics (Arrieta et al., 2014e; Bucci et al., 2007; Wei et al., 2015). Nonetheless, PHB results very interesting for the improvement of some PLA

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properties, since the highly ordered stereochemical structure of PHB increases the PLA crystallinity. Thus, PLA–PHB blends are considered as promising candidates for flexible films (Abdelwahab et al., 2012; Arrieta et al., 2014d).

To overcome the inherent brittleness of both biopolymers, plasticizers are frequently added to PLA-PHB systems (Abdelwahab et al., 2012; Armentano et al., 2015; Arrieta et al., 2014a,e,f,2015). Plasticizers for biodegradable plastics present more stringent requirements for health and safety issues since they will be released into the environment after the product service (Arrieta et al., 2014a; Quintana et al., 2013). Acetyl(tributyl citrate) (ATBC) obtained from naturally occurring citric acid has been suggested as one of the most efficient plasticizers for PLA (Arrieta et al., 2014f; Courgneau et al., 2011), for PHB (Erceg et al., 2005) and also for their blends (Arrieta et al., 2014a,f,2015 which does not raise a safety concern for the environment and for food contact materials (i.e.,: food packaging, agricultural mulch films, etc.) (European Food Safety Authority, 2012).

Moreover, the development of bionanocomposites is another interesting way to improve PLA properties since the addition of nanofillers is able to considerably improve the final properties of the reinforced material (i.e.,: thermal, mechanical, etc.) (Armentano et al., 2013; Arrieta et al., 2015a; Peponi et al., 2014b; Sanchez-Garcia and Lagaron, 2010). Nanofillers display a high surface to volume ratio, which is ideal for applications that involve composite materials for multifunctional technologies (Lagarón et al., 2005). Polymer nanocomposites are multiphase materials where at least one of the constituent phases, commonly the nanofiller, has at least one dimension in the nanoscale range (<100 nm) (Peponi et al., 2014b; Raquez et al., 2013). Cellulose is the most abundant polymer on earth, it is renewable and has an annual production of 1.5×10^{12} tons (Qing et al., 2015). Cellulose derivatives at the nanometer scale, such as cellulose nanocrystals (CNC), have received increasing interest as biobased and biodegradable reinforcing materials for bioplastic industry due to the emerging potential associated with nanomaterials and nanotechnology (Bucci et al., 2007; Kale et al., 2007b; Peponi et al., 2014b; Rayón et al., 2015). The extraction of CNC, from several plant fiber crops, is often performed through acid hydrolysis using sulfuric acid to remove the amorphous cellulose and form highly crystalline cellulose (Luzi et al., 2014). CNC have proven to be optimal nanofillers for PLA (Fortunati et al., 2012; Peltzer et al., 2014; Sanchez-Garcia and Lagaron, 2010), PHB (Chen et al., 2015; Patrício et al., 2013) and PLA–PHB blends (Arrieta et al., 2014b,c,2015a) for biobased and biodegradable film applications because of cellulose derivatives present several advantages such as they are biobased, biodegradable, stiff, lightweight and highly abundant in the nature at low cost (Peponi et al., 2008a,b; Rayón et al., 2013; Sanchez-Garcia and Lagaron, 2010; Sonseca et al., 2014). Thus, CNC have been proposed as the next-generation of biobased nanofillers to develop fully green nanocomposites for biobased and biodegradable polymers not only due to the CNC green nature, but also because it has inherently high specific strength and modulus, with good thermal stability (Chen et al., 2015). Particularly, in the case of PLA–PHB blends CNC improve the interaction between PLA and PHB matrices leading to an improvement on the mechanical, thermal and barrier properties of the final bionanocomposites (Arrieta et al., 2014b,c,2015a).

Electrospinning technology has gained considerable attention for the production of thin films composed by ultrathin polymeric fiber networks with diameters ranging from the submicrometer level down to the nanometer range (bellow 100 nm) that offer large surface areas, small inter-fibrous pore size and high porosity with interest in several industrial fields for the production of short-term applications, such as food packaging, agricultural mulch films, filtration membranes, etc. (Nicosia et al., 2015; Toncheva et al., 2014; Torres-Giner et al., 2008). Electrospinning is one of the most efficient, simple and versatile processing techniques that can be used for the fabrication of nanofibers due to its ability to control nanofibers compositional, structural and functional properties through a relatively simple and cost-effective approach (Kriegel et al., 2008; Mujica-Garcia et al., 2014; Peponi et al., 2014a; Sonseca et al., 2012). The strategy to blend PLA with PHB and then process them by electrospinning technology allows obtaining a fully biobased and biodegradable thin film composed by a network of non woven fibers with the desired characteristics owing to PHB improves PLA electrospun final material by reducing the beads formation (Arrieta et al., 2015b). In a previous work, electrospun films based on different proportion of PLA-PHB were studied and further plasticized with acetyl tri-*n*-butyl citrate (ATBC) to get a flexible material and it has been shown that some transesterification reactions between PLA and PHB chains take place when they are blended in 75:25 proportion, respectively. PLA–PHB (75:25) showed the thinner fibers, less beads and improved mechanical properties, while ATBC reduced the glass transition temperature and increased the stretchability of the final PLA–PHB–ATBC mat (Arrieta et al., 2015b).

In this work, electrospun nanocomposites based on PLA–PHB (75:25) plasticized with 15 wt% of ATBC and further loaded with CNC at 1 wt% and 5 wt% were prepared. The influence of CNC on the plasticized PLA–PHB electrospun fibers morphology and size was studied. The obtained electrospun bionanocomposites were fully characterized in terms of structural, thermal, mechanical and surface wettability properties. Moreover, since these materials are intended for biodegradable short-term applications their disintegration under composting conditions at a laboratory-scale level was also evaluated.

2. Materials and methods

2.1. Materials

Poly(lactic acid) (PLA 3051, Mn = 110,000 Da, 3 wt% D-isomer) was supplied by NatureWorks (USA), Poly(hydroxybutyrate) (PHB, under the trade name P226, Mw = 426,000 Da) was supplied by Biomer (Krailling, Germany) and acetyl-tri-*n*-butyl citrate (ATBC, $M = 402\ \text{g mol}^{-1}$, 98% purity) and microcrystalline cellulose (MCC, dimensions of 10–15 μm) were purchased from Sigma–Aldrich (Madrid, Spain).

2.2. Chemicals

Sulfuric acid (99.9% purity), Chloroform (99.6% purity) and dimethylformamide (DMF) (99.5% purity) were supplied by Sigma–Aldrich.

2.3. Cellulose nanocrystals synthesis

Cellulose nanocrystals were obtained following the recipe of (Fortunati et al., 2012). Briefly, a sulfuric acid hydrolysis of 64% (wt/wt) of microcrystalline cellulose (MCC) was carried out at 45 °C for 30 min with continuous stirring. The obtained CNC solution was diluted in ultrapure water (1:200) while the acid was further eliminated by centrifugation; the sediment was then dialyzed until neutral pH. An ion exchange resin was added to the cellulose suspension for 24 h and it was then removed by filtration followed by ultrasonic treatment (2 min in an ice bath). Nanocrystal solutions were neutralized (1.0% (w/w) of $0.25\ \text{mol l}^{-1}$ NaOH) and finally freeze-dried to obtain a powder.