Carbohydrate Polymers 165 (2017) 51–60

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

# Processing and characterization of nanocomposite based on poly(butylene/triethylene succinate) copolymers and cellulose nanocrystals

Elena Fortunati[a], Matteo Gigli[b,*,1], Francesca Luzi[a], Franco Dominici[a], Nadia Lotti[b], Massimo Gazzano[c], Amalia Cano[d], Amparo Chiralt[d], Andrea Munari[b], Josè Maria Kenny[a], Ilaria Armentano[e,*], Luigi Torre[a]

[a] *Civil and Environmental Engineering Department, UdR INSTM, University of Perugia, Strada di Pentima 4, 05100 Terni, Italy*
[b] *Civil, Chemical, Environmental and Materials Engineering Dept. (DICAM), University of Bologna, Via Terracini 28, 40131 Bologna, Italy*
[c] *Organic Synthesis and Photoreactivity Institute, CNR, Via Selmi 2, 40126, Bologna, Italy*
[d] *Institute of Food Engineering for Development, Universitat Politècnica de València, Camino de Vera, s/n. 46022 Valencia, Spain*
[e] *Department of Ecological and Biological Sciences (DEB), Tuscia University, Viale dell'Università, snc, 01100 Viterbo, Italy*

ARTICLE INFO

*Article history:*
Received 1 September 2016
Received in revised form 6 February 2017
Accepted 6 February 2017
Available online 9 February 2017

*Keywords:*
Random copolyesters
Cellulose nanocrystals
Bionanocomposite
Extrusion process

ABSTRACT

A new class of biodegradable materials developed by a combination of random eco-friendly copolyesters containing butylene succinate (BS) and triethylene succinate (TES) sequences with cellulose nanocrystals (CNC), is proposed and studied. Polymers and nanocomposite films were prepared by an optimized extrusion process to improve the processability and mechanical response for flexible film manufacturing. Poly(butylene succinate) (PBS) homopolymer and two random copolyesters containing different amounts of TES co-units, P(BS85TES15) and P(BS70TES30), were synthesized by melt polycondensation. The effect of TES and CNC presence and content on the microstructure, tensile properties, thermal characteristics and disintegration under composting conditions, as well as on the toughening mechanism of the blends was investigated.

Material properties were modulated by varying the chemical composition. CNC were used as reinforcement additive and their effect is modulated by the interaction with the three polymeric matrices. The extruded films displayed tunable degradation rates, mechanical properties and wettability, and showed promising results for different industrial applications.

## 1. Introduction

The development of new bio-based, biodegradable and sustainable polymeric systems, by using innovative processing technologies, is an important strategy to reduce the dependence of fossil fuels and support the transition towards a greener and more sustainable future.

In this respect, poly(butylene succinate) (PBS) is undoubtedly an interesting member of the aliphatic polyester class. In view of its good mechanical properties that are comparable with low-density polyethylene and other polyolefins, good thermal resistance and melt processability (Gigli et al., 2016; Zhang & Zhang, 2016), PBS can be considered a promising candidate for the packaging industry. To widen the PBS application range and to improve some of its properties, such as the slow biodegradation rate, different pathways have been followed. Copolymerization and realization of blends and composites are the most explored strategies in this respect (Fabbri et al., 2014; Gigli et al., 2016; Khalil, Galland, Cottaz, Joly, & Degraeve, 2014; Kim, Kim, Lee, & Choi, 2006; Zakharova, Alla, Martinez de Ilarduya, & Muñoz-Guerra, 2015). In particular, the introduction of ether and thio-ether linkages has proven to be a winning strategy to upgrade the characteristics of PBS and of other aliphatic polyesters. By mainly acting on the degree of crystallinity and on the surface wettability, it has been possible to deeply modify the mechanical properties and the biodegradability of the parent homopolymer. (Gigli et al., 2014, 2013).

Cellulose is the most abundant and inexhaustible carbohydrate polymer in nature. Its physical and chemical properties permit to

---

* Corresponding authors.
*E-mail addresses:* matteo.gigli@uniroma2.it (M. Gigli), ilaria.armentano@unitus.it (I. Armentano).

[1] Current address: Department of Chemical Science and Technologies, University of Rome Tor Vergata, Via della Ricerca Scientifica 1, 00133 Roma, Italy.

http://dx.doi.org/10.1016/j.carbpol.2017.02.024

develop different kind of materials and products (Klemm, Heublein, Fink, & Bohn, 2005). In particular, cellulose nanocrystals (CNC) are widely employed as reinforcing agents in lightweight and bio-based polymeric nanocomposites (Habibi, Lucia, & Rojas, 2010; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011). CNC show nanosized dimensions with rod-like shape, high aspect ratio, low density (1.566 g/cm$^3$), and reactive surface (Bitinis et al., 2013), and mechanical properties comparable to other reinforcement materials.

The dispersion in the thermoplastic polymers is a key issue to be improved and evaluated in order to transfer the CNC properties to the polymeric materials and to obtain multifunctional nanostructured polymers with modulated behavior (Dufresne, 2013). In particular, the dispersion of the CNC in hydrophobic thermoplastic polymers is difficult due to the dominant hydrophilic nature of cellulose (Song, Xiao, & Zhao, 2014), and this can limit their efficiency as reinforcing elements (Dufresne, 2013). Different CNC surface modification methods, by using both chemical and physical approaches, have been developed including esterification, etherification, silylation, polymer grafting, adsorbing surfactants or polymer coating (Braun, Dorgan, & Hollingsworth, 2012; Fortunati et al., 2012; Lizundia et al., 2016).

The goal of this research is to develop high innovative renewable bionanocomposites by combining newly synthesized biodegradable copolymers with cellulose nanocrystals as reinforcement phase. The thermal, mechanical, chemical and disintegration properties of the novel developed films were investigated and correlated to CNC content and polymer chain microstructure. The final results could take to the production of biodegradable nanocomposites with cellulose nanocrystals as reinforcing fillers that display comparable properties to inorganic-based reinforced nanocomposites.

## 2. Experimental section

### 2.1. Materials and methods

#### 2.1.1. Polymer synthesis

Dimethylsuccinate (DMS), 1,4-butanediol (BD), triethylene glycol (TEG), glycerol and titanium tetrabutoxide (TBT) (Sigma-Aldrich) were reagent grade products. All the reagents were used as supplied with the exception of TBT that was distilled before use.

Poly(butylene succinate) (PBS) and poly(butylene/triethylene glycol succinate) random copolymers (P(BSxTESy)) were synthesized in bulk by two step melt polycondensation, by employing DMS and BD (PBS synthesis) or DMS and different ratios of BD and TEG (P(BSxTESy) synthesis). In particular, two copolymers containing respectively 15% and 30% of TES co-units have been prepared. A 20 mol% excess of total glycol with respect to DMS was used. A low amount of glycerol (1 mg/g of polymer) was also added to the reaction mixture. TBT was employed as catalyst (about 150 ppm of Ti/g of polymer).

The first stage was run at 180 °C under pure nitrogen flow. When more than 90% of the theoretical amount of methanol was distilled off, the pressure was reduced to about 0.08 mbar and the temperature was gradually risen to 230 °C to facilitate the removal of the excess of glycol. The reactions were carried out until a constant torque was measured.

#### 2.1.2. Cellulose nanocrystals

Commercial microcrystalline cellulose (MCC, supplied by Sigma–Aldrich®, size 10–15 μm) was used as precursor for cellulose nanocrystal extraction, while an acid phosphate ester of ethoxylated nonylphenol (Beycostat A B09 (CECCA S.A.)) was used for their modification. All the other chemicals used for cellulose nanocrystal synthesis were supplied by Sigma–Aldrich®. Cellulose nanocrystals (CNC), 100–200 nm in length and 5–10 nm in width, were obtained by sulfuric acid hydrolysis, and modified by the Beycostat surfactant (s-CNC) (Fortunati et al., 2014; Heux, Chauve, & Bonini, 2000). The surfactant was added to the water suspension containing nanocrystals in portion of 1/1 (wt/wt) using an estimated weight of CNC directly after the hydrolysis process.

### 2.2. Nanocomposite film processing

P(BSxTESy) random copolymers and modified cellulose nanocrystals were dried before processing to eliminate moisture traces and to avoid hydrolysis reactions. Polymers were put into an oven at 50 °C for 24 h, while s-CNC was dried at 70 °C for 4 h. P(BSxTESy) copolymers and nanocomposite based formulations were processed and mixed by using a twin-screw microextruder (Dsm Explore 5&15 CC Micro Compounder). Screw speed, mixing time and temperature profile were optimized during the extrusion procedure. Two different s-CNC concentrations were selected: 1%wt, and 5%wt as shown in Table 1. Polymer and nanocomposite films with thicknesses between 20 and 60 μm were obtained by extrusion with the adequate filmature tip. Screw speed at 100 rpm was set to optimize the material properties, while the temperature profile was set up according to the different melting temperature of the selected copolymers, as reported in Table 1, in the three different extrusion areas. The total processing time was equal to 3 min: pure polymers were mixed for 3 min, while for the nanocomposites preparation the s-CNC were added after 1 min.

### 2.3. Polymer molecular characterization

Polymer structure and composition were determined by means of proton nuclear magnetic resonance (1H NMR) spectroscopy at 20 °C, employing a Varian Inova 400-MHz instrument (Agilent Technologies, USA). Polymer samples were dissolved in deuterated chloroform at a concentration of about 20 mg/mL.

Molecular weights were evaluated by gel-permeation chromatography (GPC) at 30 °C using a 1100 HPLC system (Agilent Technologies, USA) equipped with PLgel 5-μm MiniMIX-C column (Agilent Technologies, USA). A refractive index was employed as detector. Chloroform was used as eluent with a 0.3 mL/min flow and sample concentrations of about 2 mg/mL. A molecular weight calibration curve was obtained with polystyrene standards in the range of molecular weight 2000–100,000 g/mol.

### 2.4. Nanocomposite characterization

All samples were stored over $P_2O_5$ under vacuum at 20 °C before characterization.

#### 2.4.1. Microstructure

Microstructure of the fracture surfaces of polymers and s-CNC based nanocomposite films were investigated by field emission scanning electron microscope (FESEM Supra 25, Zeiss, Germany). Films were previously freeze-cut in liquid nitrogen, gold coated with an Agar automatic sputter coater and then analysed. Optical images were also performed by an inverted microscope, Nikon Epiphot 300.

#### 2.4.2. Thermal characterization

Differential scanning calorimetry (DSC) (DSC6, Perkin Elmer, Waltham, MA, USA) was used for the calorimetric measurements. Aluminium pans containing about 10 mg of polymeric samples were heated up from −70 °C to 40 °C above fusion temperature ($T_m$) (I scan), held for 3 min and then rapidly quenched (about 100 °C/min) to −70 °C. Finally, the samples were reheated to $T_m + 40$ °C (II scan). Both scans were run at a rate of 20 °C/min. The