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Effect of silver nanoparticles and cellulose nanocrystals on electrospun poly(lactic) acid mats: Morphology, thermal properties and mechanical behavior

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ABSTRACT

The fabrication of ternary fibrous mats based on poly(lactic) acid (PLA), cellulose nanocrystals (CNCs, both pristine (p-CNCs) and modified with a commercial surfactant (s-CNCs)) and silver (Ag) nanoparticles by electrospinning is reported. Amounts of 1 and 5 wt.% were selected for Ag and CNCs, respectively. Neat PLA and binary PLA/Ag, PLA/p-CNCs and PLA/s-CNCs were produced as references.

The CNCs and Ag influence on the microstructural, thermal and mechanical properties was investigated. The Ag and/or p-CNCs addition did not remarkably affect fiber morphology and average size dimension (between (468 ± 111) and (551 ± 122) nm), whereas the s-CNCs presence led to the deposition of a honeycomb-like network on a underneath layer of randomly oriented fibers. The efficiency of the surfactant use in promoting the CNC dispersion was demonstrated. A slight enhancement (e.g. around 25%, in terms of strength) of the mechanical properties of p-CNCs loaded fibers, particularly for PLA/Ag/p-CNCs, was revealed, whereas mats with s-CNCs showed a decrement (e.g. around 35–45%, in terms of strength), mainly imputable to the delamination between the upper honeycomb-like layer and the lower conventional fibrous mat.

1. Introduction

Electrospinning consists in a cheap and user friendly technique to fabricate polymeric, ceramic and composite fibrous membranes, with diameters ranging from hundreds to tens of nanometers (Frenot & Chronakis, 2003) and could be integrated with conventional techniques to create innovative multifunctional patterned micro/nano-structures, starting from different materials. Electrospun membranes are considered promising and excellent candidates for applications in filtration, food texture alterations, encapsulation of food additives, active and bioactive packaging elements, separation membranes, reinforcement in composite materials (Bianco, Di Federico, & Cacciotti, 2011; Lamastra et al., 2012), intelligent, functional and active packaging sectors for food and pharmaceuticals (Kriegel, Arrechi, Kit, McClements, & Weiss, 2008; Lagaron & Lopez-Rubio, 2011; Sanchez-Garcia, Lopez-Rubio, & Lagaron, 2010; Weiss, Takhistov, & McClements, 2006). In particular, food industry could employ electrospun fibers in several ways: as a building/reinforcement element of composite green food packaging material, as building elements of the food matrix for imitation/artificial foods, as nanostructured and microstructured scaffolding for bacterial cultures, as edible carriers for encapsulation of food additives or to modify food properties and in the design of novel active and bioactive packaging technologies (Lagaron & Lopez-Rubio, 2011).

Electrospun fibers provide additional advantages compared to film and sheet carriers due to their nano- or submicron-scale diameter and consequent very large surface area, and, thus, are ideal as sensors (Arecchi, Scampicchio, Drusch, & Mannino, 2010), for biomolecules and enzymes immobilization, controlled release (Jiang et al., 2005) and filtration (Ramakrishna et al., 2010).

Several polymers have been employed to prepare electrospun fibers and among them PLA is receiving a lot of attention, since it is a renewable resources derived thermoplastic polyester, commercially available and widely used in packaging industry, due to its high transparency, stiffness and thermoformability (Siracusa, Rocculi, Romani, & Dalla Rosa, 2008). Moreover it is not only biodegradable, but also compostable and thus its employment is strongly desirable, in order to minimize the environmental impact

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of petroleum based plastics (Petersen, Nielsen, & Olsen, 2001) as well as the environmental concerns raising from waste management (Lagaron & Lopez-Rubio, 2011). Plastic recycling, in fact, is not often economically viable, especially in the case of food packaging due to the contamination of food (Kijchavengkul, Auras, Rubino, Ngouajio, & Fernandez, 2006). However compostable polymers still present a lot of drawbacks with respect to the conventional petroleum-based polymers used in packaging applications, such as inherent brittleness, low impact resistance, fair thermal properties, toughness, water vapour and gas barrier properties. Thus, in order to improve some of these properties, several kinds of fillers have been recently proposed, including natural and synthetic cellulose fibers (Fortunati, Puglia, Santulli, Sarasini, & Kenny, 2012), regenerated cellulose fibers (Lim, Son, Lee, Park, & Cho, 2001), wood fibers (Huda, Drzal, Misra, & Mohanty, 2006), recycled newspaper fibers (Huda, Drzal, Mohanty, & Misra, 2007), plant fibers from kenaf (Ochi, 2008), and microfibrillated cellulose (MFC) (Galina Rodionova, Lenes, Eriksen, & Gregersen, 2011).

Cellulose nanocrystals (CNCs) have been widely used as reinforcement fillers, since they present good mechanical properties, are biodegradable and biocompatible and present low density. However, they are difficult to process, since they tend to agglomerate and show low thermal stability; thus it is very challenging to obtain good CNCs dispersion and to preserve their properties in polymeric matrices by means of common processing techniques, such as extrusion and melt spinning processes (Oksman, Mathew, Bondeson, & Kvien, 2006). To overcome these drawbacks, electrospinning was used in this work, since it takes place at ambient conditions and it has been already proven to be particularly suitable for encapsulating thermally labile molecules and/or low temperature degradable fillers (i.e. cellulose nanocrystals) (Qi, Hu, Xu, & Wang, 2006).

In order to promote stability in the dispersion of the CNCs, their surface was modified using a surfactant that, on the basis of previous papers (Bondeson & Oksman, 2007; Bondeson, Mathew, & Oksman, 2006; Fortunati, Armentano, Zhou, Puglia, et al., 2012; Fortunati, Armentano, Zhou, Iannoni, et al., 2012; Heux, Chauve, & Bonini, 2000; Oksman et al., 2006), was an acid phosphate ester of ethoxylated nonylphenol.

In the present paper the production and characterization of multifunctional ternary poly(lactic acid) (PLA) fibers, loaded with cellulose nanocrystals (CNCs, both pristine and modified with a surfactant) and silver nanoparticles, by electrospinning technique is reported for the first time. Silver nanoparticles were added since they showed good conductivity, chemical stability, catalytic activity and, mainly, inherent antimicrobial properties that make them appealing for applications in biomedical and food packaging sectors.

In previous reports (Shi et al., 2012; Xiang, Joo, & Frey, 2009), only binary fibrous systems composed of PLA and pristine CNCs have been investigated and the use of the modified CNCs as fillers in electrospun PLA fibers has not been considered yet.

The main purpose of this work was to investigate the influence of the co-presence of the cellulose nanocrystal and silver nanoparticle fillers on the morphological, thermal and mechanical properties of the produced fibrous mats, reporting the neat PLA and binary systems as references.

2. Materials and methods

2.1. Materials

Poly(lactic) acid (PLA 3051D, specific gravity of 1.25 g/cm^3, molecular weight (M_n) of *ca.* 1.42×10^4 g/mol) was supplied by *Nature Works*®, USA. Commercial silver nanopowder (Ag, P203, size distribution range 20–80 nm) was purchased by *Cima NanoTech*®, USA.

Microcrystalline cellulose (MCC, dimensions of 10–15 mm) was supplied by *Sigma–Aldrich*, Italy.

2.2. Synthesis of pristine and modified cellulose nanocrystals

Cellulose nanocrystal (p-CNCs) suspension was prepared from microcrystalline cellulose by sulphuric acid hydrolysis following the recipe used by Cranston and Gray (2006). Hydrolysis was carried out with 64% (w/w) sulphuric acid at 45 °C for 30 min with vigorous stirring. After removing the acid, dialysis, and ultrasonic treatment were performed. The resultant cellulose nanocrystal aqueous suspension was approximately 0.5% (w/w) by weight and the yield was *ca.* 20%. The obtained pristine cellulose crystals showed the typical acicular structure with the dimensions ranging from 100 to 200 nm in length and 5–10 nm in width as previously reported (Fortunati, Armentano, Zhou, Puglia, et al., 2012; Fortunati, Armentano, Zhou, Iannoni, et al., 2012).

Cellulose nanocrystals were modified with a surfactant, an acid phosphate ester of ethoxylated nonylphenol, in order to increase the dispersion in the polymer matrix and to enhance the final properties of nanocomposite porous systems. The CNCs modified with surfactant (designed as s-CNCs) were prepared by adding the Beycostat A B09 (CECCA S.A.) (Heux et al., 2000) to the suspension containing nanocrystals, in portion of 4/1 (w/w), using the weight of p-CNCs estimated at the end of the hydrolysis process. This high content of surfactant is necessary to re-disperse the cellulose nanostructures in organic solvent after the freeze-drying process. The pH of the suspension was then adjusted to 8.5 using the same 0.25 wt.% NaOH solution as above.

2.3. Preparation of PLA based suspensions

2.3.1. PLA/Ag binary suspensions

The Ag nanoparticles disagglomeration was performed in chloroform ($CHCl_3$, 99%, *Carlo Erba Reagents*) by sonication for 1 h in an ice bath. Successively, proper amounts of PLA pellets and of N,N-dimethylformamide (DMF, $(CH_3)_2NOCH$, 99.8%, *Carlo Erba Reagents*) were added to the Ag nanoparticle suspensions in order to obtain the desiderated amounts (i.e. PLA concentration of 15% (w/v) with respect to the solvents, solvent mixture $CHCl_3$:DMF in a volume ratio 67:33, Ag nanoparticles amount of 1 wt.% with respect to the polymer, Table 1).

Finally, the obtained hybrid suspension was magnetically stirred at around 40–50 °C for 2–3 h and then at room temperature for 12–24 h, in order to promote the complete dissolution of the polymer.

The Ag content (i.e. 1 wt.%) was properly selected on the basis of previous reports (Fortunati, Armentano, Zhou, Puglia, et al., 2012; Fortunati, Armentano, Zhou, Iannoni, et al., 2012).

2.3.2. PLA/CNCs binary suspensions

In order to obtain an effective dispersion of the pristine and modified CNCs, a proper amount of the freeze-dried CNCs was suspended in N,N-dimethylformamide (DMF, $(CH_3)_2NOCH$, 99.8%, *Carlo Erba reagents*) and ultrasonicated (*Sonics Vibracell CV33*) for 2 min at 40% amplitude in an ice bath. Afterwards proper amounts of PLA pellets and of chloroform were added to the CNCs suspension in order to obtain the desiderated composition (i.e. PLA concentration of 15% (w/v) with respect to the solvents, solvent mixture $CHCl_3$:DMF in a volume ratio 67:33, CNCs amount of 5 wt.% with respect to the polymer, Table 1).