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Fabrication of multifunctional cellulose nanocrystals/poly(lactic acid) nanocomposites with silver nanoparticles by spraying method

Hou-Yong Yu[a,b,*], Xing-Yuan Yang[a], Fang-Fang Lu[a], Guo-Yin Chen[a], Ju-Ming Yao[a,c,**]

[a] The Key Laboratory of Advanced Textile Materials and Manufacturing Technology of Ministry of Education, College of Materials and Textiles, Zhejiang Sci-Tech University, Hangzhou 310018, China

[b] State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

[c] National Engineering Lab for Textile Fiber Materials & Processing Technology, Zhejiang Sci-Tech University, Hangzhou 310018, China

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ABSTRACT

The poly (lactic acid) (PLA)/functionalized cellulose nanocrystals formates (CNFs) were prepared by solution casting and then the binary films were sprayed with silver ammonia aqueous solution to fabricate PLA/CNF/Ag ternary nanocomposites. It was found that both deposited silver (Ag) nanoparticles and CNFs showed efficient reinforcing effect on the thermal, mechanical, barrier properties and antibacterial activity of PLA matrix. Especially, the maximum decomposition temperature (T_{max}) and Young's modulus of PLA/CNF/Ag(6) nanocomposite film increased by 15.5 °C and 48.7%, respectively. Meanwhile an obvious reduction in the water vapor permeability was detected. Furthermore, the migration levels of the ternary nanocomposite films were well below the permitted limits in both non-polar and polar food simulants (60 mg kg^{-1}), and they showed a significant antibacterial activity influenced by the Ag contents. This study reveals that the novel nanocomposite films will offer a good perspective for food packaging applications.

1. Introduction

Traditional packaging materials, including flexible films and rigid containers, have the largest markets for plastic material consumption, but they are considered as one of the main sources of environment problems for post-consumption disposal of wastes (Díez-Pascual & Díez-Vicente, 2014; Wang, Yu, Zhang, He, & Zhang, 2013; Yu, Qin, Sun, Yang, & Yao, 2014a). Therefore, the development and use of biodegradable polymer based nanocomposites from renewable resources in packaging fields have been stimulated by public concerns and interests for environmental protection. Poly(lactic acid) (PLA) is one of the renewable and ideal biopolymer matrix, and shows great potential for the commercial large-scale production of biodegradable packaging materials due to its excellent processability, high transparency and stiffness equivalent to some commercial petroleum-based polymers (Fortunati, Armentano, Iannoni, & Kenny, 2010; Fortunati et al., 2012a). However, neat PLA has many drawbacks for packaging application, such as brittleness, poor thermal stability and water vapor barrier property, and high migration level (Bordes, Pollet, & Avérous, 2009; Bledzki, Franciszczak, & Meljon, 2015; Fortunati et al., 2012b; Martino, Jimenez, Ruseckaite, & Averous, 2011). As food packaging materials, the nanocomposites need strong antimicrobial activity against many human pathogen bacteria. Therefore, the addition of inorganic, organic nanofillers and nanohybrids will be considered as an adequate alternative to overcome such problems and consequently to improve the possibilities for PLA based packaging materials (Fortunati, Latterini, Rinaldi, Kenny, & Armentano, 2011; Hossain et al., 2012; Ramos et al., 2014).

Recently, cellulose nanocrystals (CNCs) are widely used as biobased nanofillers to enhance the mechanical, thermal and barrier properties of biopolymer matrix, due to their high aspect ratio, outstanding mechanical properties, wide availability of sources, fully degradable and renewable characters (Gong, Pyo, Mathew, & Oksman, 2011; Jonoobi, Aitomäki, Mathew, & Oksman, 2014; Li, Wu, Song, Qing, & Wu, 2015), compared to other inorganic reinforcing fillers. Nevertheless, the unmodified CNCs usually show poor compatibility with water insoluble polymers like PLA (Cacciotti, Fortunati, Puglia, Kenny, & Nanni, 2014; Shi et al., 2012),

* Corresponding author at: The Key Laboratory of Advanced Textile Materials and Manufacturing Technology of Ministry of Education, College of Materials and Textiles, Zhejiang Sci-Tech University, Hangzhou 310018, China. Tel.: +86 571 86843618; fax: +86 571 86843619.

** Corresponding author at: National Engineering Lab for Textile Fiber Materials & Processing Technology, Zhejiang Sci-Tech University, Hangzhou 310018, China. Tel.: +86 571 86843251; fax: +86 571 86843619.

E-mail addresses: phdyu@zstu.edu.cn (H.-Y. Yu), yaoj@zstu.edu.cn (J.-M. Yao).

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due to hydrophilic character. Meanwhile nonfunctional CNCs cannot endow PLA with antibacterial property for food packaging applications.

Nowadays, the effects of combining CNCs and silver (Ag) nanoparticles as reinforcements have been used to improve the performance of nanocomposites (Fortunati, Peltzer, Armentano, Jiménez, & Kenny, 2013; Fortunati et al., 2014). The Ag nanoparticles are well known for improving the antibacterial properties of polymeric materials, and widely used as antibacterial additives in food applications (Fortunati et al., 2013; Yu et al., 2014b). The silver nitrate and silver zeolites are approved by Food and Drug Administration/Centre for Food Safety and Applied Nutrition (FDA/CFSAN-USA) and European Food Safety Authority (EFSA, 2005). Fortunati et al. (2012a) prepared the ternary PLA/CNC/Ag nanocomposites by directly mixing three components via the melting extrusion and solution casting methods (Fortunati et al., 2012b, 2014). They have reported that the CNCs as reinforcing agents can improve the mechanical and barrier properties of PLA, while Ag nanoparticles as antibacterial agents can endow antibacterial activity to PLA matrix. The introduction of both CNC and Ag nanoparticles cannot enhance greatly the properties of PLA (Fortunati et al., 2013, 2014). With the addition of 5 wt% surfactant modified CNC and 1 wt% Ag, the Young's modulus increased by 25% from 2400 MPa for neat PLA to 3000 MPa for the ternary nanocomposite, but the Young's modulus of the ternary nanocomposite was lower than that of the binary nanocomposites reinforced with CNCs only (Fortunati et al., 2014). Moreover, the Ag nanoparticles inside the PLA would weaken the nucleation effect of CNC, resulting in a slight increase of cold crystallization temperature compared with the binary nanocomposites. Further, the maximum decomposition temperature (T_{max}) of the ternary nanocomposite was reduced by 25 °C with respect to PLA matrix, and lower than that of the binary nanocomposites. It indicates that incorporation of both CNC and Ag nanoparticles induced poor thermal stability of the nanocomposites (Fortunati et al., 2010), in which the Ag nanoparticles hindered the formation of hydrogen bonding interaction between PLA and CNC, resulting in the reduction of T_{max} of nanocomposites (Fortunati et al., 2010). Moreover, with the incorporation of 1 wt% Ag, the ternary nanocomposites showed the unconspicuous antibacterial ratios (60–75%) for both *Escherichia coli* (*E. coli*) and *Staphylococcusaureus* (*S. aureus*) after incubation for 3 h or 24 h, which was ascribed to the limited contact area between cell membrane of bacteria due to Ag nanoparticles embedded inside the nanocomposite films. In this nanocomposite, a large number of Ag nanoparticles cannot contribute to antibacterial ratio, leading to Ag waste and high cost for nanocomposites (Fortunati et al., 2014). From above, the embedded Ag nanoparticles would weaken the interaction between PLA and CNC, crystallization ability and antibacterial activity of the resultant nanocomposites.

In this work, Ag nanoparticles were deposited on PLA/CNF binary films via novel spraying method, in which the deposited Ag nanoparticles do not affect the formation of hydrogen bonding interaction between PLA and CNFs, and contact adequately the cell membrane of bacteria to induce strong antibacterial activity (without Ag embedded inside PLA). The unexpected effects of Ag nanoparticles with different contents on the morphology, microstructure, crystallization behavior, mechanical, thermal and water vapor barrier and overall migration properties of the resulting PLA/CNF nanocomposite films were investigated.

2. Experimental

2.1. Materials

Poly(lactic acid) (PLA) was supplied by Bright China Industrial Co. Ltd. Commercial microcrystalline celluloses (MCCs) (rubby-shaped fragments with particle size of 10–30 μm) were supplied from Shanghai Chemical Reagents (Shanghai, China). Silver nitrate ($AgNO_3$), formic acid (HCOOH), hydrochloric acid (HCl), ammonia solution ($NH_3 \cdot H_2O$), chloroform, isooctane and ethanol were purchased from Guoyao Group Chemical Reagent Co., Ltd. Silver ammonia aqueous solution ($Ag(NH_3)_2(OH)$) was prepared by adding 4 mL of 25% ammonia to 100 mL of a 4% (w/w) silver nitrate solution. The final stage of ammonia addition was performed dropwise to give a clear solution.

2.2. Preparation of CNFs

The CNFs were prepared through a simple mixed acid hydrolysis approach (Yu et al., 2014b). Briefly, MCCs were added into 90% HCOOH/10% HCl mixed acid solution at 90 °C for 4 h, which was subsequently cooled to room temperature and neutralized with 3 M $NH_3 \cdot H_2O$ aqueous solution. The suspension was centrifugated with deionized water to collect the precipitates. The obtained products were freeze-dried for 48 h and denoted as CNFs (cellulose nanocrystal formates). The formate contents on the CNFs (about 0.84 mmol/g) were determined by pH titration of forming HCl obtained from oxime reaction between formate groups and hydroxylamine hydrochloride.

2.3. Preparation of PLA/CNF/Ag nanocomposites

Each PLA/CNF nanocomposite film was fabricated by adding 5 mL well-dispersed 10 wt% CNF suspension into PLA solution in chloroform via solution casting with a total 20 mL mixture, and the final ratio of PLA and CNF was 9:1 (w/w). The PLA/CNF/Ag nanocomposite films were fabricated by a novel solvent evaporation and spraying method (Scheme 1(a)). Briefly, the prepared silver ammonia aqueous solution ($Ag(NH_3)_2(OH)$, 1 M) with various volumes of 2, 4, 6 and 8 mL were sprayed on the surface of PLA/CNF nanocomposite films by using a sprayer at a rate of 0.4 mL/min under UV-irradiation condition. It should be noted that the nozzle size of the sprayer was 50–150 μm, the atomization gas pressure for spraying was 0.8 MPa, the droplet sizes (size distribution) were 100–250 μm, and the distance of spraying was 90 mm. In addition, the way to control the spray volume was pouring ideal volume (2 mL, 4 mL, 6 mL and 8 mL) of $Ag(NH_3)_2(OH)$ aqueous solution into spray bottle. Under the ideal spray conditions, the higher yield and lower porosity of substrate films (PLA/CNF/Ag) could be achieved. After spraying $Ag(NH_3)_2(OH)$ aqueous solution, the ternary nanocomposite film was dried at 50 °C for 24 h until the weight did not change. It has been reported that silver nanoparticles formed from the $Ag(NH_3)_2(OH)$ solution after spraying via UV-irradiation condition (Hidaka, Honjo, Horikoshi, & Serpone, 2007; Xu, Qiao, Qiu, & Chen, 2008). Finally, a series of PLA/CNF/Ag nanocomposite films were obtained in thin rectangular strips shape with an area of 30 cm^2, and the thickness were about 200–300 μm. According to the spraying volume of $Ag(NH_3)_2(OH)$, the samples were denoted as PLA/CNF/Ag(2), PLA/CNF/Ag(4), PLA/CNF/Ag(6) and PLA/CNF/Ag(8), respectively. In order to ensure reproducibility of spraying, three replicates were performed for each sample. The stability of Ag nanoparticles on the film surface was determined by observing the FE-SEM images of the washed nanocomposite (washed by water twice) and migrated nanocomposite films (after migration test).

2.4. Characterization of nanocomposites

2.4.1. Morphology and optical property

The film surfaces (size distribution of Ag nanoparticles) and fractured morphologies were observed on a field emission scanning electron microscopy (FE-SEM, VL-TRA 55, Carl Zeiss, Germany,