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Rosin modified cellulose nanofiber as a reinforcing and co-antimicrobial agents in polylactic acid /chitosan composite film for food packaging

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ABSTRACT

Cellulose nanofiber (CNF) was modified by rosin and used as a reinforcement filler within a polylactic acid (PLA) matrix. The resulting film was then coated with chitosan (CHT) to prepare a two-layer composite film for antimicrobial food packaging. The FT-IR spectra of rosin modified CNF (R-CNF) displayed a clear peak at 1730 cm^{-1}, which confirmed the successful esterification of CNF by rosin. The R-CNF showed a better dispersion in PLA matrix than CNF and the loading of R-CNF had a significant effect on the mechanical properties of the resulting film. A percolation network was formed when the R-CNF loading was 8%, where the composite film displayed optimum mechanical properties. The antimicrobial test showed that the R-CNF/PLA/CHT composite film exhibited excellent antimicrobial performance against *E. coli* and *B. subtilis*, which could be attributed to the synergistic antimicrobial effect of CHT and rosin.

1. Introduction

Petroleum-based plastics such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), polyvinyl alcohol (PVA) are currently the most prevalent raw materials mainly due to their low cost, good mechanical performance and good barrier properties (Bouwmeester, Hollman, & Peters, 2015; Koelmans, Bakir, Burton, & Janssen, 2016; Carole, Pellegrino, & Paster, 2004). On the other hand, the large consumption of petroleum-based plastics has posed serious environmental impacts due to the non-biodegradability of these plastics. Exploring bio-based and biodegradable plastics for packaging applications is considered a promising method to solve the current environmental problem causing by the disposal of non-biodegradable plastics.

Polylactic acid (PLA) is one of the most attractive bio-based and biodegradable polymers used as a short term film for food packaging (Ingrao et al., 2015) due to its high transparency, good processability, and comparable mechanical properties to its counterpart of fossil-based polymers such as polyethylene and polypropylene (Raquez, Habibi, Murariu, & Dubois, 2013; Gu et al., 2017). However, PLA also shows high brittleness, low thermal stability, and poor barrier properties, which have limited its applications for food packaging. Various strategies have been adopted to remedy these limitations. Incorporation of nanosized reinforcements is one of the most feasible routes to enhance the mechanical, barrier, and physical properties of PLA. Cellulose nanofibers (CNF) possess high stiffness and low density. In addition, they are renewable and biodegradable. These features make CNF a promising candidate as reinforcement filler for polymers. Studies have shown that the incorporation of CNF into the PLA matrix has improved the oxygen barrier and mechanical properties of PLA films (Zhu et al., 2016; Lin, Gèze, Wouessidjewe, Huang, & Dufresne, 2016; Rhim, Park, & Ha, 2013; Reddy, Vivekanandhan, Misra, Bhatia, & Mohanty, 2013). However, the inherent hydrophilicity of CNF is one of the main obstacles that hinder its compatibility with hydrophobic PLA. Nevertheless, the large amount of hydroxyl groups on CNF also facilitates the surface modification of CNF. Therefore, several chemical strategies, such as esterification (Espino-Perez, Domenek, Belgacem, Sillard, & Bras, 2014; Sato et al., 2016), salinization (Robles, Urruzola, Labidi, & Serrano, 2015), and polymer grafting (Hatton et al., 2016; Navarro et al., 2015) have been developed to tune the interfacial compatibility between PLA and CNF.

Antimicrobial food packaging can inhibit the growth of spoilage microorganisms and therefore enhance shelf-life for food products while maintaining quality and safety (Tiwari et al., 2009). Low molecular antiseptics (metal ion metallic oxide), such as Ag nanoparticles, SiO_2, and TiO_2, have been used as antimicrobial agents for food preservatives (Mukhopadhyay et al., 2010; Costa, Conte, Buonocore, & Del Nobile, 2011). However, many studies have demonstrated that they might have residual toxicity that might release into food (Reijnders, 2009; Alkan & Yemenicioglu, 2015). The use of natural antimicrobial

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compounds provides a promising alternative method to extending the application of antimicrobial packaging while maintain human health. Chitosan (CHT) is a non-toxic, biodegradable, and biocompatible polymer industrially produced from chitin and the second most abundant polysaccharide in nature. Chitosan has shown antimicrobial activity against several food pathogens and has remarkable film-forming ability and oxygen and moisture permeability (Rabea, Badawy, Stevens, Smagghe, & Steurbaut, 2003). Sébastien, Stéphane, Copinet, & Coma (2006) prepared a chitosan/PLA composite film by solution casting method in which PEG400 was added as a plasticizer. They reported that the resulting composite film had an inhibitory activity against three fungal strains. Bie et al. (2013) developed a PLA/starch/chitosan blends antimicrobial material by the melting- extrusion process. This material exhibited an effective and long lasting antimicrobial property against *E. coli* and *S. aureus*, which could be used as a potential packing material for fresh meat.

Rosin is a natural product of pine resin. Rosin and its derivatives have been used as stabilizers (Jimenez, Lopez, Iannoni, & Kenny, 2001), plasticizers (Moustafa, Kissi, Abou-Kandil, Abdel-Aziz, & Dufresne, 2017; Arrieta, Samper, López, & Jiménez, 2014) due to their highly hydrogenated phenanthrene ring structures. Additionally, rosin exhibits nontoxic and antimicrobial characteristics, which makes it a potential addictive for food packaging application. Fabrication of ecofriendly rosin/PLA (Narayanana, Loganathanb, Valapac, Thomasb, & Vargheseca, 2017) and rosin/PLA/PBAT (Moustafa et al., 2017) biocomposite films have been reported in literature. Recently, researchers reported using rosin to surface modify cellulose nanocrystals (CNC) and the resulting rosin modified CNC showed antibacterial activity against Gram-negative bacteria and Gram-positive bacteria (Castro, Bras, Gandini, & Belgacem, 2016). In this study, rosin was employed to surface modify CNF to improve its compatibility and dispersion in PLA. Modified CNF worked as a reinforcement and a co-antimicrobial agent to prepare a composite film with PLA and CHT. To the best of our knowledge, such approach has not been reported before. The resulting CNF/PLA film was combined with chitosan to form a ternary composite film using layer-by-layer (LBL) method. The mechanical property and morphology of the composite films were characterized by tensile test and scanning electron microscope (SEM). The antimicrobial properties of the composite films were also evaluated.

2. Experimental

2.1. Materials

Cellulose nanofiber aqueous suspension (0.5%) was purchased from Yu Yue Nano-technology (Shanghai, China). PLA (2003D) was purchased from Nature Works LLC (Minnetonka, MN, USA). Rosin was supplied by Sigma-Aldrich (colophony rosin, gum, St. Louis, MO, USA). Chitosan powder(molecular weight from 600 to 800 kDa, DDA ≥ 90%) was purchased from Acros Organics Co (Waltham, MA, USA). Ethanol, dichloromethane, glacial acetic acid, and hydrochloric acid were obtained from Sinopharm Chemical Reagent Co.Ltd. (Shanghai, China). All chemicals were used without further purification.

2.2. Modification of CNF by rosin

CNF was modified with rosin by means of a SolReact process following the method used by Castro et al., (2016). In brief, 15 g CNF suspension (0.5 *wt*%) was added to a three-neck flask and adjusted the pH to 4.0 with 1 *wt*% HCl in dropwise. The flask was equipped with a condenser and connected to a closed water distillation system. The flask with CNF suspension was heated in an oil bath to 130 °C under magnetic stir. Rosin powder (10/1 to CNF, *wt/wt*) was then directly added to the CNF suspension. The reaction temperature was 130 °C and the reaction was performed for 24 h under continuous stir and in nitrogen ambient. After the reaction, the resulting rosin modified CNF (R-CNF) was washed with ethanol several times to remove the excess rosin and then collected by centrifugation. Finally, R-CNF was solvent-exchanged to dichloromethane for further characterization and preparation of composite film.

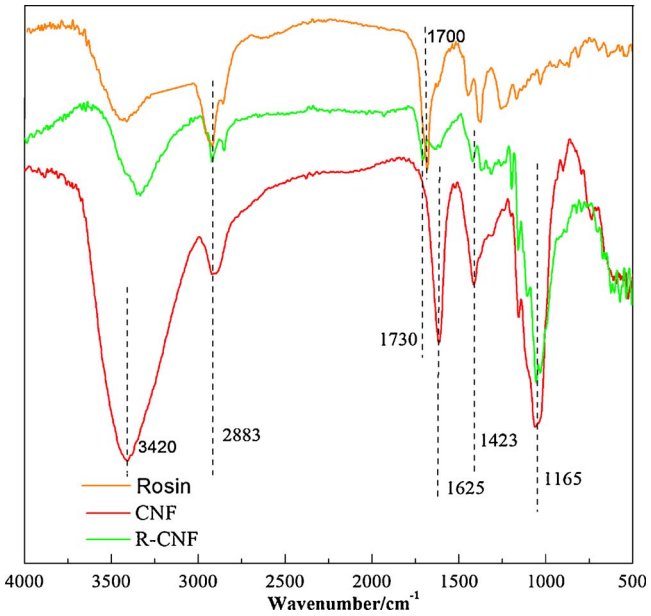

Fig. 1. FTIR spectra of R-CNF and CNF.

2.3. Preparation of CNF reinforced PLA/CHT composite film

The layer of chitosan film was prepared by dissolving chitosan powder (3 g) in 100 mL aqueous glacial acetic acid solution under room temperature for 12 h to make a 3% chitosan solution (Broek, Knoop, Kappen, & Boeriu, 2015). This clear viscos solution (10 mL) was then casted onto a flat glass and dried at 80 °C. The prepared chitosan layer on the glass was then put into a desiccator for further use.

PLA in pellet form was dissolved in dichloromethane at room temperature at a concentration of 6 mg/mL. The obtained solution was mixed with CNF or R-CNF at designed loadings (0 *wt*%, 2 *wt*%, 5 *wt*%, 8 *wt*%, and 10 *wt*%) and sonicated in an ice bath under 100 w for 10 min to degas as well as enhance the dispersion of CNF. The mixture (10 mL) was then cast onto the chitosan layer and dried in a fume hood at room temperature overnight. The PLA/CHT composite films without reinforcement filler were prepared in a similar manner. To remove the residue solvents, all composite films were vacuum dried at 40 °C for additional 24 h after dried in the fume hood and then put in a desiccator before further use. The thickness of the composite films were estimated by measuring 10 random points on each film using a digital vernier caliper and the average value was adopted. All obtained two-layer composite films were controlled having a thickness around 50 μm.

2.4. Characterization of CNF and R-CNF

The morphology of CNF and R-CNF was investigated by means of transmission electron microscopy (TEM, JEM-1400, JEOL, Toyko, Japan). To prepare the TEM samples, a drop of diluted CNF/R-CNF suspension (0.1 *wt*%) was placed on a 400 square mesh copper grid with Formvar carbon film and dried at room temperature. The grid was then floated in phosphotungstic acid for negative staining before subjected to TEM characterization.

The changes in chemical structure of CNF before and after rosin modification were characterized by Fourier transform infrared spectrometer (FT-IR). Freeze-dried CNF/R-CNF powder were mixed with KBr to produce tablets for FT-IR measurement. FT-IR spectra were