



Preparation and characterization of nanocomposites of polyvinyl alcohol/cellulose nanowhiskers/chitosan



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ABSTRACT

Nanocomposites of polyvinyl alcohol/cellulose nanowhiskers/chitosan (PVA/CNWs/chitosan) were prepared using an environmentally friendly water-evaporation process. The material properties of these “green” hybrid films were characterized extensively using various techniques. Electrostatic interaction between CNWs and chitosan as well as the hydrogen bonds between the three materials played a very important role in determining the properties of the composites. The antimicrobial property, oxygen barrier property and mechanical property of the nanocomposites were all improved owing to the localized aggregations of CNWs and chitosan driven by the electrostatic interactions, thereby making the nanocomposites potentially useful for many applications including food packaging and antimicrobial packaging.

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1. Introduction

In recent times there is growing interest to develop materials with film forming capacity, antimicrobial [1,2] and oxygen barrier properties [3] which improve food safety and shelf-life. Among the packaging systems, PVA is a promising polymer for food packaging, for its good flexibility, transparency, toughness, biocompatibility, barrier properties, nontoxicity, and biodegradability [4]. To bring antimicrobial and improved oxygen barrier properties to PVA is an effective way to expand its applications in food packaging. Chitosan is a biocompatible natural polymer with strong antimicrobial effects [5] and excellent oxygen-barrier properties due to its high crystallinity and the hydrogen bonds between the molecular chains [6,7]. So it is a promising way to introduce antimicrobial and improved oxygen barrier properties to PVA by blending with chitosan.

Although the blends of PVA/chitosan are the promising materials for food packaging owing to the combination of excellent film forming property of PVA and antimicrobial effects of chitosan [8], brittleness are still the main obstacles for its application. Percentage elongation at break of PVA/chitosan blends would drastically decrease with an increase in chitosan content, which has been reported by various researchers [9,10]. Incorporating nanofillers into the PVA/chitosan blended system is one of most facile

methods for dissolving such problems and expanding the applications. George et al. [11] prepared PVA nanocomposites containing cellulose nanocrystals and silver nanoparticles (AgNPs), and they found that the addition of AgNPs increased the elongation properties without compromising on other mechanical properties and at the same time it significantly reduced the moisture sorption. Uddin et al. [12] prepared fibers of PVA/chitin whiskers (ChWs) by gel spinning with outstanding enhancement in mechanical- and anti-creep properties. Pande et al. [13] prepared nanocomposites based on chitosan–PVA and graphene oxide (GO) by casting method, and the composites were mechanically strong and exhibited improved thermal stability. Huang et al. [14] prepared nanocomposite films of chitosan, multiwalled carbon nanotubes (MWCNTs) and PVA by a solution casting method. The results indicated that MWCNTs treated by chitosan dispersed well in the PVA matrix, and the tensile properties and water resistance of nanocomposites were improved greatly compared with neat PVA.

However, with the growing environmental and energy problem, finding completely renewable nanofillers having good compatibility with both PVA and chitosan so as to enhance the properties of their blend still remains a challenge. In this work, we developed a novel strategy for preparing PVA/chitosan based film with good comprehensive performance by introducing cellulose nanowhiskers (CNWs). The extraction of cellulose whiskers from renewable sources has gained much attention in recent years due to their exceptional mechanical properties (high specific strength and modulus), large specific surface area, high aspect ratio,

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environmental benefits and low cost [15,16]. CNWs have already been used as nanofillers for many polymeric nanocomposites including PVA [17,18] and chitosan [19]. Hydrogen bonds and electrostatic interactions between the negatively charged sulfate groups on the whisker surface and the positively charged ammonium groups of chitosan were the driving forces for the good combination of chitosan and CNWs [20–22]. Therefore, incorporating CNWs to PVA/chitosan blends by taking the advantage of interactions between CNWs, chitosan and PVA induced by electrostatic interaction and hydrogen-bond interaction is a feasible and effective method for preparing PVA/chitosan based material with controlled microstructure and enhanced properties.

2. Materials and methods

2.1. Materials

Chitosan sample (DD \geq 90% and molecular weight 5000 Da) was obtained from Golden-Shell Pharmaceutical Co., Ltd, (Zhejiang, China). Ramie was obtained from JB RAMIE Sichuan Co., Ltd, China. PVA (PVA-1799, degree of polymerization 1700, degree of hydrolysis 99%) was obtained from Yunwei Company (Qujing City, Yunnan Province, China) and was rigorously dried at 80 °C in vacuo until a constant weight was obtained, and then stored in a desiccator under vacuum at room temperature over P₂O₅.

2.2. Preparation of CNWs

Sulfuric acid hydrolysis of ramie was performed as described in the literature with minor modifications [23]. Briefly, the ramie fiber was cut into pieces. Then, 10 g of cellulose was added to 200 mL of 64 wt% sulfuric acid under strong mechanical stirring. Hydrolysis was performed at 55 °C for 30 min. After hydrolysis, the suspensions were then washed with deionized water using repeated centrifuge cyclings. The suspensions that could not be centrifuged were collected, which reached pH \sim 5. The final concentration of the CNWs dispersions was about 1 wt%.

2.3. Preparation of PVA/CNWs/chitosan nanocomposites

Chitosan solution (20 wt%) was obtained by dissolving 20 g chitosan powder in 80 g deionized water with continuous stirring at room temperature for 1 h. Acetic acid was not necessary because the low-molecular-weight chitosan was water soluble. PVA solution (5 wt%) was prepared by dissolving 10 g PVA powder in 190 g deionized water with continuous stirring at 90 °C. Then, chitosan and PVA solutions and CNWs dispersions were blended together by a homogenizer to form a homogeneous PVA/CNWs/chitosan suspension. PVA/CNWs/chitosan suspensions with different weight percentages (as indicated in Table 1) were obtained. Then they were poured into a glass plate. After 48 h setting, the PVA/CNWs/chitosan suspensions were de-bubbled and then transferred into a 60 °C oven for about 24 h drying. After that, the blend films were vacuum dried for 24 h at 80 °C in order to remove the residues of water. The PVA/CNWs/chitosan ternary films were marked as PVA/CNWs/chitosan-*x*%, where *x*% is the content of chitosan in PVA/CNWs/chitosan nanocomposite films. As a comparison, PVA/CNWs and PVA/chitosan binary blend films were separately prepared in the same way as described above. For all the PVA/CNWs and PVA/CNWs/chitosan films, the weight content of CNWs is 1%.

2.4. Characterization

The morphologies of CNWs and PVA/CNWs/chitosan composite films were respectively observed by scanning electron microscopy

Table 1

Inhibition of *E. coli* and *S. aureus* growth by films of pure PVA, PVA/CNWs, PVA/chitosan and PVA/CNWs/chitosan with various load of chitosan.

Samples	Inhibition zone (mm) of <i>E. coli</i>	Inhibition zone (mm) of <i>S. aureus</i>
PVA	0	0
PVA/CNWs	0	0
PVA/chitosan-5%	0	0
PVA/chitosan-10%	0.8	1.0
PVA/chitosan-15%	1.4	1.7
PVA/chitosan-20%	2.2	2.5
PVA/chitosan-25%	2.7	2.5
PVA/CNWs/chitosan-5%	0.9	0.3
PVA/CNWs/chitosan-10%	1.3	1.6
PVA/CNWs/chitosan-15%	1.6	2.2
PVA/CNWs/chitosan-20%	2.2	3.3
PVA/CNWs/chitosan-25%	3.0	5.4

(SEM, JSM-5900LV, JEOL, Japan) at an accelerating voltage of 5 kV. CNWs were obtained by evaporating a drop of dilute CNWs aqueous suspensions. Brittle and tensile fracture surfaces were obtained from PVA/CNWs/chitosan films. Before test, all the surfaces were coated with a layer of gold.

The substructural morphology of PVA/CNWs/chitosan deposited from a dilute aqueous suspension was studied by transmission electron microscopy (TEM, Tecnai G2F20 S-TWIN electron microscope, FEI, Holland) at an accelerated voltage of 200 kV. 70–80 nm in thickness from films of PVA/chitosan and PVA/CNWs/chitosan composites were sliced using a RMC cryo-ultramicrotome equipped with a diamond knife and mounted on formvar-coated 200-mesh nickel grids. Ultrathin sections of unstained PVA/chitosan and PVA/CNWs/chitosan as well as uranyl acetate-stained PVA/CNWs/chitosan were separately studied by TEM.

Surface morphology of PVA/CNWs and PVA/CNWs/chitosan nanocomposites was studied by using Nanoscope Multimode and Explore atomic force microscope (AFM, Veeco Instruments, USA). A definite weight of an aqueous suspension of PVA/CNWs and PVA/CNWs/chitosan was spin coated on a mica sheet. Height and amplitude images of the thin layer film were obtained with a tapping mode.

The UV–vis spectra of the aqueous suspensions of PVA/CNWs/chitosan were recorded using a UV–vis spectrophotometer (Varian Cary 50) at a wavelength scan rate of 60 nm/min. And the UV–vis spectra were recorded for every 24 h for 3 days.

Fourier transform infrared (FT-IR) analysis for PVA, CNWs, chitosan and PVA/CNWs/chitosan nanocomposites was conducted with a Thermo Nicolet 670 spectrometer from 4000 to 400 cm⁻¹ at a spectral resolution of 4 cm⁻¹ using KBr method.

X-ray diffraction (XRD) profiles were carried out on a Philips electronic instrument in steps of 0.03° using Cu K α radiation at 40 kV and 150 mA between 5° and 60° (2 θ).

Oxygen permeability measurements were performed by using a gas permeation instrument (VAC-V1, Labthink Instrument Co, China) according to the standard of ASTM standard F2622-08. All samples were cut into circular disks with a diameter of 50 mm and a thickness of 1 mm, and each measurement was continued until a stable oxygen permeability rate was reached.

The antimicrobial activity of PVA/chitosan and PVA/CNWs/chitosan composite films was tested by an inhibition zone method [24]. Two different food pathogenic bacteria including *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) were used for testing the antimicrobial activity of the films. For the qualitative measurement of antimicrobial activity, the film samples were punched to make disks (diameter = 10 mm), and the antimicrobial activity was determined using a modified agar diffusion assay (disk test). The plates were examined for possible clear zones

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