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Effects of nanoclay type on the physical and antimicrobial properties of PVOH-based nanocomposite films

Guichao Liu [a,b], Ye Song [a,b], Jiamei Wang [a,b], Hong Zhuang [c], Lei Ma [a,b], Can Li [a,b], Yao Liu [a,b], Jianhao Zhang [a,b,*]

[a] National Center of Meat Quality & Safety Control, Nanjing Agricultural University, Nanjing 210095, PR China
[b] Synergetic Innovation Center of Food Safety & Nutrition, Nanjing 210095, PR China
[c] Quality and Safety Assessment Research Unit, Agricultural Research Service, USDA, Athens, GA 30605, USA

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ABSTRACT

Polyvinyl alcohols-based nanocomposite films with four types of montmorillonite (MMT) nanoclay, including 18-amino stearic acid (I.24TL), methyl, bis hydroxyethyl, octadecyl ammonium (I.34TCN), dimethyl, di-hydrogenated tallow ammonium/siloxane (I.44PSS) organically modified MMT and a natural MMT (Na^+-MMT) were fabricated by a solution-intercalation, film-casting method, and effects of the nanoclays were evaluated on physical properties, including transmittance, tensile strength (TS), elongation at break (*E*), water solubility (WS), swelling ratio (SR), water vapor uptake ratio (WVUR), and water vapor permeability (WVP), as well as antimicrobial activity of the polyvinyl alcohols-based films. Transmittance, WS, SR, WVUR, WVP of the nanocomposite films were significantly reduced by nanocomposition compared to a pure polyvinyl alcohols film. The WVP decreased by 11.8–20.7%, and WS, SR and WVUR decreased by 19.9–41.8%, 9.1–26.4%, and 4.8–12.8%, respectively. The extent of changes was dependent on nanoclay type. X-ray diffraction patterns revealed that intercalation was formed in nanocomposite films. Overall among all the tested nanoclays, Na^+-MMT showed more impact on physical properties of polyvinyl alcohols films, and the polyvinyl alcohols film compounded with quaternary ammonium group displayed remarkable antimicrobial activity against Gram-positive bacteria.

1. Introduction

The growth of environmental concerns over non-biodegradable plastic packaging materials has raised interest in the application of biodegradable alternatives that can reduce waste disposal problems. Polyvinyl alcohols (PVOH) are synthetic polymers that are extensively applied in a wide range of industrial, commercial, medical, and food applications including resins, lacquers, surgical threads, and food-contact packaging since the early 1930s because of its biodegradability, resource-saving manufacturing process via non-petroleum route, water-soluble property, chemical resistance and gas barrier properties (DeMerlis & Schoneker, 2003; Sakurada, 1985). However, other properties such as mechanical property, thermal characteristics, and water vapor permeability need to be improved for food-packaging applications.

Nanocomposite is a hybrid material created through dispersing nanoscale particles in polymer matrix to achieve remarkable enhancement of polymer properties (Gaume, Rivaton, Thérias, & Gardette, 2012; Pavlidou & Papaspyrides, 2008; Sinha Ray & Okamoto, 2003; Zhen, Lu, Li, & Liang, 2012), including mechanical performance (Schmidt & Giannelis, 2009), thermal behavior (Chaiko & Leyva, 2004; Ebina & Mizukami, 2007), flame retardation (Kiliaris & Papaspyrides, 2010; Samyn et al., 2008), barrier (Xu et al., 2006), and solvent resistance (Huang, Zhu, Yin, Qian, & Sun, 2001). Since Kojima group developed a montmorillonite reinforced Nylon nanocomposite in 1993 (Kojima et al., 1993), nanocomposite materials have attracted considerable research interest and are widely applied in numerous fields. Nanoscale particles have high aspect ratio (100–1500) and extremely high surface-to-volume ratio (700–800 m^2/g). When completely dispersed in polymer matrix, they could significantly modify some polymer properties, including antimicrobial activity (Rhim, Hong, & Ha, 2009; Rhim, Lee, & Hong, 2006), at even a pretty low level (less than 5% by weight). Results show that the enhancement of polymer properties is not only dependent on nanomaterial type and concentrations, but also dependent on the compatibility between polymer matrix and nanofiller and the nanocomposite preparation methods (Rhim, 2011).

* Corresponding author. National Center of Meat Quality & Safety Control, Nanjing Agricultural University, Nanjing 210095, PR China. Tel./fax: +86 25 84399096.
E-mail address: nau_zjh@njau.edu.cn (J. Zhang).

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Recently, many studies have been performed to enhance the properties of PVOH through distribution of nanoscale particles in PVOH polymer matrix (Gaume, Taviot-Gueho, et al., 2012; Gautam & Ram, 2010; Kokabi, Sirousazar, & Hassan, 2007; Sirousazar et al., 2011; Strawhecker & Manias, 2000; Yu et al., 2003). There are few published studies on the enhancement of water resistance property and antimicrobial activity of PVOH by nanoparticles yet. The main objectives of this study were to fabricate PVOH/clay nanocomposite films through a solvent casting method and to investigate the effect of nanoclay type on the physical properties and antimicrobial activity of the fabricated PVOH-based nanocomposite films.

2. Materials and methods

2.1. Materials

PVOH (a degree of polymerization of 2400 and an alcoholysis degree of 99%) was obtained from the Sinopec Sichuan Vinylon Works (China). Four types of montmorillonite (MMT) nanoclay, including three organically modified MMT (I.24TL, I.34TCN, I.44PSS) and a natural MMT (Na^+-MMT) were purchased from Nanocor Inc. (USA). The general information of these MMT products is listed in Table 1. Alcohol, a solvent, was obtained from Guangdong Guanghua Sci-Tech Co., Ltd. (China).

2.2. Film preparation

PVOH and PVOH-based nanocomposite films were synthesized using a solution-intercalation film-casting method (Strawhecker & Manias, 2000). Five grams of PVOH was dissolved in 100 ml of 20% alcohol aqueous solution by heating to 80 °C for 1 h with constantly stirring, then cooled to 60 °C. The dissolved solution was poured onto a leveled glass plate (180 × 125 mm), the cast plates were dried at ambient conditions (60 ± 2 °C) for 6 h and then the films were peeled off from the glass plate.

For preparation of PVOH/clay nanocomposite films, 0.25 g (5% w/w relative to PVOH on a dry basis) of each type of nanoparticle was dispersed in a 20% alcohol solution by vigorously stirring without heating for 24 h to reach complete swelling of the clay using a magnetic stirrer. The swollen nanoparticles were then sonicated for 30 min at room temperature in a bath-type ultrasound sonicator (Kunshan Ultrasonic Instruments Co., Ltd. China) to obtain nanoclay solution. Five grams of PVOH was then added to the nanoclay solution followed by heating to 85 °C for 1 h to dissolve the PVOH. The mixture was then cooled to room temperature, and the solution was casted following the same procedure as for the preparation of PVOH film.

PVOH and PVOH/nanoclay composite films were preconditioned at 25 °C and 50% relative humidity (RH) in a chamber (STIK Co., Ltd. USA) for at least 24 h before mechanical properties testing.

2.3. Methods

2.3.1. Film thickness

Film thickness was measured before the test of tensile strength (TS) and water vapor permeability (WVP) using a hand-held micrometer (Qinghai Measuring & Cutting Tools Co., Ltd. China) at an accuracy of 0.001 mm.

2.3.2. Transmittance

Optical property of film such as transparency was determined by scanning the percent transmittance in whole visible light region (400–700 nm) using UV/VIS spectrophotometer at a scanning rate of 60 nm/min (Model UV-2600, Shimadzu, Japan).

2.3.3. Mechanical properties

Mechanical properties tensile strength (TS) and elongation at break (E) of films were measured with an Instron tensile testing machine (Style KD-05, Shenzhen Kaiqiangli Mechanical Equipment Co., Ltd. China). According to GB/T 1040.3 (Code of National Standard of China), film samples were punched into dumbbell shapes with a 40 mm × 10 mm square section in the center. The initial gauge length was set at 40 mm and crosshead speed was 50 mm/min.

2.3.4. XRD pattern

The structure of the nanoparticles and their PVOH composite films was characterized by a Rigaku X-ray diffractometer, which is equipped with Cu Ka radiation at a wavelength of 0.1546 nm and a curved graphite crystal monochromator at a scanning rate of 0.4°/min and operated at 40 kV and 40 mA. The d-spacing of the silicate layer (d_{001}) was calculated using the Bragg's equation, $\lambda = 2d \sin\theta$, where λ is the wavelength of the X-ray radiation (0.1546 nm), d is the spacing between diffraction lattice planes and θ is the measured diffraction angle.

2.3.5. Water vapor permeability (WVP)

The WVP of PVOH and PVOH-based nanocomposite films was measured using equation WVP = (WVTR × L)/ΔP, where L was average film thickness (m), ΔP was difference in the partial water vapor pressure (Pa) across the film, WVTR was the measured water vapor transmission rate (g/m^2 s), and could be calculated gravimetrically according to the modified method of Rhim et al. (2009).

Films were cut into 60 × 60 mm samples and mounted horizontally on glass cups filled with distilled water up to 5 mm underneath the film. Then the cups were placed in a chamber with steady condition at 25 °C and 50% RH with constant air current movement. The cups were weighed every 4 h for a period of 24 h. The slopes of the steady state (linear) portion of mass variation versus time curves were used to calculate WVTR. WVTR = K/S, where K was the slope rate of the linear portion of mass variation versus time curves (g/s), S was the area of exposes film (m^2).

Table 1
Characteristics of different commercial montmorillonite-based nanoclays.

MMT type	Characteristics			
	Na^+-MMT	I.24TL	I.34TCN	I.44PSS
Surface modifier	_	18-Amino stearic acid	Methyl, bis hydroxyethyl, octadecyl ammonium	Di-methyl, di-hydrogenated tallow ammonium/Siloxane
Modifier formula	_	$HOOC(CH_2)_{17}NH_3^+$	$CH_3(CH_2)_{17}N(CH_3)[(CH_2CH_2OH)_2]^+$	$[CH_3(CH_2)_{17}]_2N(CH_3)_2^+$
Moisture content	12%	<3%	<3%	<3%
Particle size	16–22 μm	16–22 μm	14–18 μm	14–18 μm
Color	White	White	Off-white	Bright-gray
Specific gravity	2.6 g/cm^3	2.1 g/cm^3	1.9 g/cm^3	1.7 g/cm^3
Relative hydrophobicity	Hydrophilic	Less hydrophobic	Strongly hydrophobic	Strongly hydrophobic