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Properties of polyvinyl alcohol/xylan composite films with citric acid

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ABSTRACT

Composite films of xylan and polyvinyl alcohol were produced with citric acid as a new plasticizer or a cross-linking agent. The effects of citric acid content and polyvinyl alcohol/xylan weight ratio on the mechanical properties, thermal stability, solubility, degree of swelling and water vapor permeability of the composite films were investigated. The intermolecular interactions and morphology of composite films were characterized by FTIR spectroscopy and SEM. The results indicated that polyvinyl alcohol/xylan composite films had good compatibility. With an increase in citric acid content from 10% to 50%, the tensile strength reduced from 35.1 to 11.6 MPa. However, the elongation at break increased sharply from 15.1% to 249.5%. The values of water vapor permeability ranged from 2.35 to 2.95 × 10^{-7} g/(mm^2 h). Interactions between xylan and polyvinyl alcohol in the presence of citric acid become stronger, which were caused by hydrogen bond and ester bond formation among the components during film forming.

1. Introduction

Owing to their astatic appearance, light weight, low cost and ease in processing, plastic packaging materials are widely used in the food and preservation fields. However, they are dominated by petroleum-derived polymers. With depleting petroleum resources and increasing environmental concerns, chemically synthesized plastics lacking biodegradability are in direct conflict with the sustainable development needs (Mikkonen & Tenkanen, 2012). Therefore, utilizing biodegradable polymers such as polymers from nature to produce films becomes an inevitable trend in food packaging and technology development (Nakamura, Cordi, Almeida, Duran, & Mei, 2005; Prakash Maran, Sivakumar, Sridhar, & Prince Immanuel, 2013).

Usually films based on single biopolymers are highly sensitive to environmental conditions and generally possess low mechanical resistance (Kanatt, Rao, Chawla, & Sharma, 2012). Films can be produced by chemical cross-linking and physical blending. Polymer blending is an effective approach to endow new material with desired properties (Kanatt et al., 2012). Physically blending biopolymers and synthetic polymers to achieve desired features has received increasing attention in recent years.

Hemicellulose has received an increasing interest especially in the last few decades for the production of biodegradable films and coatings (Hansen & Plackett, 2008; Mikkonen & Tenkanen, 2012). However, free-standing hemicellulose cannot form a continuous film, and several efforts (Goksu, Karamanlioglu, Bakir, Yilmaz & Yilmazer, 2007; Gröndahl, Eriksson, & Gatenholm, 2004; Peng, Ren, Zhong, & Sun, 2011; Saxena, Elder, Pan, & Ragauskas, 2009) have been made to overcome this drawback. One method is to add plasticizer into hemicellulose to enhance its film performance (Gröndahl et al., 2004). However, plasticizers can increase the elasticity of the film, and also lead to an increase in hydrophilicity. As a result, researchers have shifted to examining the films of hemicellulose with other polymers. Goksu et al. (2007) attempted to add lignin into xylan isolated from cotton stalks to produce a film for food packaging applications. The addition of 1% lignin into xylan solution was sufficient for the film formation. The elastic modulus and the hypothetical coating strength of the films obtained by using 8% xylan were 0.11 and 9.45 MPa, respectively. The addition of 7 wt% of sulfonated whiskers into the oat spelt xylan solution was found to increase the tensile energy absorption of xylan films by 445% and the tensile strength of the film by 141% (Saxena et al., 2009). Cellulose nanofibers (CNFs) were found to be a good nanoreinforcement to improve the mechanical properties of xylan films (Peng et al., 2011). At a CNF content of 20 wt%, the tensile stress and Young's modulus of the composite films increased up to 39.5 and 3404 MPa,

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respectively. Strong interactions could be formed between CNFs and xylan.

PVA is a representative water-soluble macromolecular resin and possesses better biodegradability than other resins. Furthermore, it has excellent film forming ability, and emulsifying and adhesive properties. As such, PVA has been used as a component in producing composite films by blending with other polymers from nature, for example PVA/wheat gluten (Dicharry et al., 2006), PVA/collagen hydrolysate (Alexy et al., 2003; Sarti & Scandola, 1995), PVA/chitosan (Kanatt et al., 2012; Naveen Kumar et al., 2010; Park, Jun, & Marsh, 2001), PVA/starch (Yang & Huang, 2008; Yun, Na, & Yoon, 2006), and PVA/carboxymethyl cellulose (Gupta, Agarwal, & Sarwar Alam, 2013). These composite films have potential applications in the packaging industry.

Xylan, as the main component of hemicellulose, has an abundance of hydroxyl groups distributed along the backbone and side chains, and is thus an ideal candidate for the formation of hydrogen bonds when blending with PVA. CA is an inexpensive, non-toxic food additive, which has been used as a cross-linking agent to improve the performance of starch (Ma, Chang, Yu, & Stumborg, 2009; Reddy & Yang, 2010; Shi et al., 2007), cellulose (Coma, Sebti, Pardon, Pichavant, & Deschamps, 2003), and PVA/starch (Shi et al., 2008) films. No information has been reported using CA as a plasticizer or cross-linking agent in PVA/xylan composite films to enhance the mechanical properties. The objective of this paper was to investigate the PVA/xylan composite films in the presence of CA. The impacts of the CA content and weight ratio of PVA and xylan on the mechanical properties, thermal stability, solubility, degree of swelling and water vapor permeability (WVP) of the composite films were comparatively analyzed. Intermolecular interactions and the phase compatibility between PVA and xylan in the composite films were studied by Fourier Transform Infrared (FTIR), and Scanning Electron Microscopy (SEM). Finally, the degree of degradation of the PVA/xylan composite films was examined.

2. Experimental

2.1. Materials

Xylan extracted from beech wood with over 90% residual units being xylose (M_w of 13,000 g/mol) and PVA with a degree of hydrolysis of 99% and a molecular weight average of 14,600–18,600 g/mol were purchased from Sigma Aldrich, USA. Both xylan and PVA were used without any further purification. CA, anhydrous $CaCl_2$ and NaCl were of analytical-reagent grade and bought from Guangzhou Chemical Reagent Factory, Guangzhou. Deionized water was used in all experiments.

2.2. Preparation of PVA/xylan composite films

Composite films were obtained by the casting method. A known weight of PVA was added in a single neck round bottom flask, and was stirred for 30 min at room temperature, then placed in a 95 °C oil bath. After 1 h, PVA formed a homogeneous solution. In succession, xylan and CA were added to the PVA solution at 95 °C and the mixture was stirred for 30 min. The final solution was kept at 75 °C for 4 h. Finally, the solution was poured into a teflon mould. Water was evaporated from the moulds in a ventilated oven at 50 °C overnight. In a typical experiment, the amount of CA was based on the total solids (PVA and xylan) content of the solution, ranged from 0% to 50%. These films obtained above were named non-cross linked films. Cross-linking PVA/xylan composite films were obtained after treating the above film in a hot air oven at 110 °C for 2.5 h. The dried non-cross linked and cross-linked films were stored in a desiccator for at least 48 h prior to all measurements.

2.3. Characterization

FTIR spectra were recorded with a Fourier transform spectrophotometer (Nicolet 750, Florida, USA) appended Attenuated Total Reflectance technique. The samples were thoroughly washed in water to remove unreacted CA, and then dried in an infrared drying oven. The spectra were obtained at a resolution of 4 cm^{-1} with 32 scans in the range from 4000 to 400 cm^{-1}.

Thermal analysis was performed using thermo gravimetric analysis on a simultaneous thermal analyzer (TGA Q500, TA Instruments, New Castle, USA). The composite film (9–11 mg) was cut into pieces and heated at a rate of 10 °C/min from room temperature to 700 °C. Moreover, nitrogen gas was purged at a flow rate of 20 mL/min.

The morphology of the surface and cross-section of the films was observed using a scanning electron microscope (SEM, Hitachi S-4300). The film was cut into smaller pieces, and was stuck on the sample stage by double-sided adhesive tape. For the cross-section of the films, the film was broken using liquid nitrogen, and stuck on the sample stage by double-sided adhesive. The samples were sputter-coated with thin a layer gold prior to the examination in order to make the films conductive. The test was operated in high-vacuum mode at an acceleration voltage of 15 kV.

2.4. Mechanical properties

Tensile testing was conducted on rectangular specimens with a width of 15 mm and a length of 150 mm which were prepared by a paper cutter (FQ-QZD15, Sichuan), using a tensile testing machine (Instron Universal Test Machine Model 5565) fitted with a 100 N load cell. The initial distance between the grips and the cross-head speed was kept constant at 50 mm and 10 mm/min, respectively. The measurements were performed at 23 °C and 50% relative humidity in a constant temperature and humidity chamber. The tensile strength (TS) and elongation at break (EAB) values of the PVA/xylan films were averaged over three specimens. The maximum load and the final extension at break were used for the calculation of TS and EAB, respectively.

2.5. Degree of swelling and solubility of PVA/xylan composite films

Pre-dried PVA/xylan composite films were cut into $2 \times 2\,cm^2$, immersed in 50-mL distilled water at room temperature (25 °C), and were soaked for 24 h. The moisture on the surface of the film was removed slightly by filter paper, and the weight of the films was measured. The degree of swelling (DS) (Yoon, Chough, & Park, 2007) in PVA/xylan composite film was calculated by Eq. (1).

$$DS = \frac{(W_1 - W_0)}{W_0} \tag{1}$$

where W_1 is the weight of PVA/xylan composite film when adsorption equilibrium is reached, g; W_0 is the pre-dry weight of PVA/xylan composite film, g.

Swelled PVA/xylan composite films were dried again for 24 h at 50 °C. And the solubility (S) (Yoon et al., 2007) was calculated by Eq. (2).

$$S = \frac{(W_0 - W_2)}{W_0} \tag{2}$$

where W_2 is the dry weight of the swelled PVA/xylan blend film, g.

2.6. Water vapor permeability

The water vapor permeability (WVP) of PVA/xylan composite films was measured according to an ASTM E96 method (ASTM,