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High performance extrusion blown starch/polyvinyl alcohol/clay nanocomposite films

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ABSTRACT

Starch/polyvinyl alcohol (PVA)/clay nanocomposite films with high mechanical and barrier properties were prepared by extrusion blowing. Based on the starch/clay matrix, the effects of PVA content on the starch/PVA/clay nanocomposite films were investigated. Appropriate preparation conditions were determined by the rheological behavior of the blends. X-ray diffraction and transmission electron microscopy results demonstrated that the starch/PVA/clay nanocomposite films exhibited intercalated structures and the extent of intercalation increased with increasing PVA content. FTIR spectra showed that the molecular interactions were enhanced in the starch/PVA/clay films with higher PVA content. Dynamic mechanical analysis revealed partial miscibility between the starch and PVA in the films and the compatibility was improved when the PVA content was 50%. The maximum tensile strength and elongation at break for the starch/PVA/clay nanocomposite films were 30.18 MPa and 224.40%, respectively. The oxygen permeability of the starch/PVA/clay film with 50% PVA was dramatically decreased by about 210 times compared with that of a starch/clay film. A continuous phase inversion mechanism was proposed to explain the performance improvement of the starch/PVA/clay nanocomposite films. The starch/PVA/clay nanocomposite film is a promising material for high barrier food packaging.

1. Introduction

In the last several decades, the tremendous increase in production and use of petroleum-based plastics has resulted in an immense amount of non-degradable waste and pollution. To solve this problem, much effort has been put forth into developing environmentally friendly materials. Starch has been considered to be one of the most promising renewable polymers to replace petroleum-based plastics (Tian, Yan, Rajulu, Xiang, & Luo, 2017a). Many studies have been reported with regard to the preparation and use of starch-based materials owing to their biodegradability, good transparency, low cost, and easy availability (Khan, Niazi, Samin, & Jahan, 2017; Villa, Barbosa, García, Castillo, & López, 2017). Polyvinyl alcohol (PVA) is a colorless, nontoxic, and widely available biodegradable polymer with excellent film-forming capability (Ismail & Zaaba, 2014; Mittal et al., 2016; Tian et al., 2017a). Starch/PVA blends have great potential for food packaging applications because of their excellent performance and relatively low cost (Tian et al., 2017a; Wang, Zhang, Dai, Hou, & Dong, 2015a).

To improve the processability and performance of starch/PVA blends, many strategies have been developed. For example, it has been shown that adding plasticizers can decrease the melting temperature and increase the flexibility and workability of starch/PVA blends (Tang & Alavi, 2011). The barrier and mechanical properties of starch/PVA blends have also been improved by the incorporation of nanofillers (Tang & Alavi, 2011). Among various nanofillers, layered silicates are the most widely used nanofillers in starch/PVA blends (Tian et al., 2017b). In addition, the content and molecular weight of the PVA has been shown to significantly affect the mechanical and barrier properties of starch/PVA blends (Ali, Alavi, Tang, & Faubion, 2011; Tian et al., 2017a).

Starch/PVA composite films have been primarily produced by solution casting (Tang & Alavi, 2011). However, some researchers

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have prepared samples of starch/PVA blends with higher thicknesses by extrusion (Dean, Do, Petinakis, & Yu, 2008; Zanela, Olivato, Dias, Grossmann, & Yamashita, 2015) or compression molding (Liu, Mo, Pang, & Yang, 2016; Tian et al., 2017a). The above processes are undesirable for industrial scale production primarily owing to the additional high processing cost and low efficiency in comparison with extrusion blowing. Furthermore, the properties of the end products produced by different processing technologies, with the same formulations, varied significantly. Fishman, Coffin, Onwulata, and Willett (2006) compared the processability and properties of pectin/starch/PVA films by extrusion blowing, extrusion casting, compression molding, and solution casting. When the ratio of pectin/starch/PVA/glycerol was 32/14/24/30, the tensile strength (TS) and elongation at break (EB) for extrusion-blown films were 3.59 MPa and 151.8% (transverse direction), respectively. The TS and EB for solution casting films were 7.56 MPa and 26.4%, respectively. Therefore, starch/PVA films produced by extrusion blowing should be further studied, not only for reducing production cost, but also for obtaining the desired properties of the end products used in practical applications.

Our research group has studied the effects of different nanofillers (Wang, Zhang, Dai, Hou, & Dong, 2015b), complex plasticizers (Wang et al., 2015c), and low PVA content (Wang et al., 2015a) on the properties of starch/PVA films by extrusion blowing. However, the mechanical and barrier properties of starch/PVA films are still not comparable with traditional petroleum-based plastics. According to our previous study (Wang et al., 2015b), clay (an organically modified montmorillonite) was an optimal nanofiller to prepare starch/PVA nanocomposite films. In order to obtain starch/PVA nanocomposite films with high performance, the effects of PVA content on starch/PVA/clay nanocomposite films were investigated based on the starch/clay control matrix. The structures, physicochemical properties, and film-forming mechanism of the nanocomposite films were investigated.

2. Materials and methods

2.1. Materials

Hydroxypropyl distarch phosphate (mode HP-CF T0278) is a modified starch from cassava starch and was purchased from Puluoxing Starch Co., Ltd. (Hangzhou, China). The moisture and hydroxypropyl group content of the starch were 13.5% and 3.1%, respectively. PVA was obtained from Sinopec Sichuan Vinylon Works (Chongqing, China), with a degree of polymerization of 1700, alcoholysis degree of 99.0%, and ash of less than 0.6%. Analytical grade glycerol was purchased from Chemical Reagent Co., Ltd. (Tianjin, China). Clay (an organic montmorillonite modified with octadecyl dimethyl benzyl ammonium chloride, average particle size 18.31 μm) was obtained from Zhejiang Fenghong Co., Ltd. (Zhejiang, China).

2.2. Blending and compounding

Starch/PVA (total mass 2000 g, at weight ratios of 100/0, 90/10, 80/20, 70/30, 60/40, and 50/50), glycerol (800 g), and clay (200 g) were thoroughly blended in an SHR50A mixer (Hongji, Zhangjiagang, China) at room temperature for 15 min. The mixtures were then packaged in polyethylene bags and stored for 24 h at room temperature to equilibrate all of the components. The mixtures were then compounded in a laboratory twin screw extruder (Jingrui Plastic Machinery, Laiwu, China) with a screw diameter of 35 mm, screw length of 30 D, and two individually controlled temperature zones. The extruded strands were cut into pellets and conditioned for at least 72 h at 23 ± 2 °C and 53% relative humidity (RH) prior to film blowing.

2.3. Film blowing

The nanocomposite films were prepared by extrusion blowing using a single screw extruder (Jingrui Plastic Machinery, Laiwu, China) with a screw diameter of 35 mm, screw length of 25 D, screw compression ratio of 3:1, and five individually controlled temperature zones. The extruder was equipped with a conventional temperature-controlled film-blowing die with a diameter of 60 mm and a film-blowing tower with a calendering nip and takeoff rolls. The ratio of the diameter of the blown bubble to that of the die was carefully adjusted to 4:1. The ratio of the take-up velocity to the film velocity at the die exit was carefully adjusted to 3:1. The resulting blown films were coded as SxPy, where x and y stand for the weight ratio of starch and PVA, respectively.

2.4. Rheological measurement

An XLY-III capillary rheometer (Jilin University Instrument Factory, Jilin, China) was used to determine the melt viscosity of the starch/PVA mixtures and pellets. The capillary viscometer consisted of a barrel into which material was loaded before being pushed by a plunger through a capillary which was controlled by the surrounding heating unit. The radius of the capillary was 1 mm and the *L/D* was 40. Either 3 g mixtures or 2.5 g pellets were placed into the barrel through a funnel and then packed down with the plunger in order to exhaust all the air in the barrel. The sample was allowed to approach the desired temperature in 10–15 min and then forced through the capillary by the plunger at pre-selected velocities. The load on the plunger and the plunger speed provided the total pressure drop through the barrel and capillary as well as the volume flow rate. The test was set for a temperature range of 60–120 °C for the mixtures and 130–170 °C for the pellets. In the test, the pressure was set at 10 MPa for both the mixtures and the pellets.

2.5. Nanostructure characterization

X-ray diffraction (XRD) was performed with a D8 Advance X-ray diffractometer (Bruker-AXS, Germany). The film samples were previously conditioned at 23 ± 2 °C and 53% RH for at least 72 h prior to testing. The samples were then scanned at diffraction angles (2θ) from 1 to 6° at a speed of 0.02°/s. Transmission electron microscopy (TEM) was performed with a Tecnai 20U-TWIN electron microscope (Philips, the Netherlands) at an operating voltage of 100 kV. Ultrafine grinding samples were placed onto a carbon-coated copper grid by physical grid-powder interactions.

2.6. Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra of the films were obtained using a Thermo Fisher Scientific (USA) Nexus 670 spectrometer attached to universal ATR accessory over a wavenumber range from 4000 cm^{-1} to 550 cm^{-1}. The number of accumulated scans and the scanning rate were 32 and 4 cm^{-1}, respectively. The film was mounted directly in the sample holder and tested.

2.7. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) of the films were performed from −15 °C up to 135 °C in a nitrogen atmosphere using a Netzsch DMA242c (Germany). In all tests, samples with approximate dimensions of 25 mm × 6 mm, were cut from the films. Dynamic temperature spectra of the samples were obtained in tensile mode at a fixed frequency of 1 Hz and a heating rate of 3 °C/min.

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