



Effects of cationization of high amylose maize starch on the performance of starch/montmorillonite nano-biocomposites



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ARTICLE INFO

Keywords:

High amylose maize starch

Cationization

Nano-biocomposites

Nanostructure

Rheological properties

ABSTRACT

In the present study, cationized high amylose maize starches (CS) with different degrees of substitution (DS) were prepared. The physical properties and microstructures of CS/montmorillonite (Mt and D1821Mt) films were investigated. Morphological analysis showed stronger intercalations of CS with hydrophilic montmorillonite (Mt) than with hydrophobic montmorillonite (D1821Mt). For CS/Mt nanocomposite films, an increasing exfoliation trend was detected with the increase in DS. On the whole, the tensile strength of CS/Mt nanocomposite films decreased while water vapor permeability increased with an increase of DS. The CS/Mt film with the DS of 0.04 showed the highest tensile strength (14.01 MPa) and lowest water vapor permeability (1.80×10^{-10} g/m² s Pa). Rheological measurements confirmed that the intermolecular forces between CS and Mt decreased with increasing DS. Mt could obviously increase the thermal stability of the films. Overall, CS with lower DS had better compatibility with Mt, which helped improve the properties of CS/Mt nanocomposite films.

1. Introduction

Starch has attracted increasing attention as a substitute for petroleum-based materials due to its inexpensive, reproducible, and biodegradable nature (Dean et al., 2011; Man et al., 2012; Muscat et al., 2012; Ren et al., 2016). However, starch-based films still reveal many disadvantages such as low mechanical properties and high water vapor permeability, which impede its application as a packaging material (Colussi et al., 2017; Zhu et al., 2017). Montmorillonite, a low cost layered silicate, has been extensively reported as a nanofiller to improve the tensile strength, water vapor transmission, thermal stability, etc. of films (Liu et al., 2016; Oleyaei et al., 2016; Romero-Bastida et al., 2016; Zhou et al., 2016). The main challenge is the poor nanoscale dispersion of the clay in the biopolymer matrix.

The dispersion of natural and organic montmorillonites (OMts) in plasticized starch matrices has been widely studied (Huang et al., 2005; Oleyaei et al., 2016; Romero-Bastida et al., 2016; Xie et al., 2013). To improve the exfoliated morphology, efforts have previously been made to modify both the Mt and starch to reduce the shrinkage and brittleness of the film (Dean et al., 2007; Gao et al., 2014). Chivrac et al. (2008) modified Mt with a cationic starch to obtain OMT-CS, which

significantly enhanced the mechanical properties of wheat starch/OMT-CS nanocomposites. OMT-CS also showed a high extent of exfoliation in the starch matrix. However, the influences of cationic starch with different degrees of substitution (DS) on the film properties and compatibility with Mt were not provided. Gao et al. (2014) modified Mt with six quaternary ammonium salts to obtain hydrophobic Mts and found that the modified Mts could significantly increase the tensile strength of starch-based films. However, the compatibility between the modified starches and OMT still remains unsolved.

In the present study, films of cationic high amylose maize starches (CSs)-which simultaneously served as film-forming matrix and intercalation agent for Mt – with different DS were prepared. The compatibility between CS and Mt, as well as the physical properties and microstructure of CS/Mt films were investigated. The main objective is to understand the effects of CS with different DS and types of Mts on the performance of high amylose starch films.

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2. Materials and methods

2.1. Materials

High amylose maize starch (amylose content, 67.41%) was purchased from Shandong Hua-nong Special Corn Development Co. Ltd. (Dezhou, China). The average molecular weight and radius of gyration of high amylose starch were 2.55×10^5 g/mol and 159.8 nm, respectively, determined by static light scattering using a BI-200SM Brookhaven light scattering instrument. Dry high amylose starch (80 mg, dry solids) was dispersed in 20 mL DMSO solution of 50 mmol/L LiCl. The sample was heated for 2 h in a boiling water bath with magnetic stirring. The starch solution was mildly stirred at room temperature for 24 h and then was diluted to seven lower concentrations between 0.1 and 2.0 mg/mL. These solutions were passed through a 0.8 μ m nylon66 membrane and filled into cylindrical vials for light scattering. The refractive index increment of 0.146 mL/g was used for the calculations.

Natural sodium montmorillonite (Mt) was provided by Shou-guang Zhong-lian Fine Montmorillonite Co. Ltd (Wei-fang, China). Dioctadecyl dimethyl ammonium chloride (D1821) was purchased from Sigma-Aldrich (Shanghai, China). Glycerol was purchased from Chemical Reagent Co. Ltd. (Tianjin, China).

2.2. Preparation of organic montmorillonite

The organic Mt (D1821Mt) was prepared using D1821 according to our previous study (Gao et al., 2014). Twenty grams of Mt were dispersed in 100 mL deionized water and magnetically stirred for 2 h at room temperature, followed by sonication for 30 min (intermittent dispersion by pulsing on for 1 s and off for 1 s at a frequency of 20 kHz) to prepare Mt suspension. Ten grams of D1821 were dissolved in 50 mL deionized water at 80 °C and then poured into the Mt suspension followed by mechanical stirring at 80 °C for 3 h. The D1821Mt was collected by centrifugation, washing once with 50% ethanol and washing several times with hot water until the dispersion was free of chloride ions, as determined by the AgNO_3 test. Finally, the D1821Mt was dried in an oven at 80 °C overnight, then ground and sifted to pass through a 200-mesh sieve.

2.3. Preparation of cationic high amylose maize starch

Two kilograms of dried high amylose maize starch were suspended in 5 L absolute ethanol in a 10 L glass reactor. Cationic reagent (3-Chloro-2-hydroxypropyltrimethylammonium chloride, CHPTAC, 65% aqueous solution) was added under constant stirring. The mixture was then adjusted to pH 11.2 with 20% sodium hydroxide solution and reacted for 8 h at 40 °C at continuous stirring. Twelve percent (w/w) hydrochloric acid was added to neutralize the reaction solution to pH 7.0. The product was collected by centrifugation and washed with 70% ethanol until Cl^- could not be detected using AgNO_3 , followed by drying in an oven at 40 °C overnight, grinding, and sifting to pass through a 100-mesh sieve. Four cationic high amylose starches with DS of 0.04, 0.11, 0.16, and 0.20 were obtained by adjusting the amount of CHPTAC. The nitrogen content (N%) of cationic starch was measured by the Kjeldahl method. The DS of cationic starch was determined by nitrogen content (%) and calculated by Eq. (1):

$$\text{DS} = (162.15 \times \text{N\%}) / (1401 - 152.64 \times \text{N\%}) \quad (1)$$

where 162.15 is the molecular weight of anhydroglucose unit, 152.64 is the molecular weight of 3-Chloro-2-hydroxypropyltrimethylammonium ion, 1401 is a constant, and N% is the nitrogen content of cationic starch.

2.4. Preparation of starch film

One gram of Mt or D1821Mt were dispersed in 50 mL deionized water and sonicated for 30 min (intermittent treatment by pulsing on for 1 s and off for 1 s at a frequency of 20 kHz). Ten grams of cationic high amylose starch were dispersed in 250 mL deionized water and gelatinized at 100 °C for 60 min under constant mechanical stirring. The prepared 50 mL montmorillonite dispersion was slowly added into the starch paste and stirred at 100 °C for another 60 min, followed by the addition of 3.6 g glycerol. After homogenization at 13000 rpm using a T18 digital ULTRA TURRAX (IKA, Germany) for 3 min, the mixture was stirred at 100 °C for 30 min to be plasticized. The mixture was then poured onto Teflon-coated glass plates at room temperature for drying. The starch composite films made from CS with DS of 0.04, 0.11, 0.16, and 0.20 incorporated Mt were denoted CS0.04Mt, CS0.11Mt, CS0.16Mt, and CS0.20Mt, respectively. The same rule applied to the starch nanocomposite with both cationic starches and D1821Mt, which were named CS0.04D1821Mt, CS0.11D1821Mt, CS0.16D1821Mt, and CS0.20D1821Mt, respectively. The control films (Blank Control) were prepared by gelatinizing 10 g cationic high amylose starch in 300 mL deionized water at 100 °C for 60 min and plasticizing with 3.6 g glycerol at 100 °C for 30 min. The control films made from cationic starches with DS of 0.04, 0.11, 0.16, and 0.20 were termed CS0.04, CS0.11, CS0.16, and CS0.20, respectively. All films were conditioned at 23 °C and 53% relative humidity (RH) for 72 h prior to testing.

2.5. X-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis

XRD of Mt, D1821Mt, and starch nanocomposites were carried out on a D8 Advance X-ray diffractometer (Bruker-AXS, Germany) with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) over the diffraction angle range from 2 to 40° at a scan rate of 0.02°/s. The basal spacings (d-spacings) of the samples were determined using Bragg's equation ($\lambda = 2d \sin\theta$; θ is the diffraction angle and λ is the wavelength of X-ray radiation). Crystallinity (%) of the films was calculated from the ratio of crystalline area to the total area of the patterns (Müller et al., 2009), which is described by Eq. (2):

$$\text{Crystallinity} = \text{Ac}/\text{At} = \text{Ac}/(\text{Ac} + \text{Aa}) \times 100\% \quad (2)$$

where Ac is the crystalline area, Aa is the non-crystalline area, and At is the total area.

For the TEM test, the starch nanocomposite films were ground in liquid nitrogen and suspended in methanol (Kumar et al., 2010). A drop of ultra-fine suspension was placed on a carbon-coated copper microgrid. After drying, the samples were visualized using a Tecnai 20U-TWIN electron microscope (Philips, the Netherlands) operating at 100 kV.

2.6. Mechanical properties

All films were cut into strips of dimension 120 mm \times 15 mm and equilibrated at 23 °C and 53% RH for 72 h prior to the measurements. Tensile strength (TS, MPa) and elongation at break (E, %) of the samples were determined according to ASTM D882-02 (2002) with a PARAM™ XLW (PC) auto tensile tester (Jinan, China) at 23 ± 2 °C and 53% RH. The initial distance between the grips was 50 mm. The thickness of the samples was measured with a digital micrometer caliper (0–25 mm, 0.001 mm, Guilin, China) at three random positions around the films. The crosshead speed was set at 1 mm/s. Each test was comprised of six replicate measurements.

2.7. Water vapor permeability (WVP)

WVP was measured according to ASTM E96/E96M-16 (2016) with

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