Physicochemical properties of starch nanocomposite films enhanced by self-assembled potato starch nanoparticles

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ABSTRACT

The aim of this research was to enhance the physicochemical properties of pea starch-based nanocomposite films by incorporating with different levels of potato starch nanoparticles (SNPs). The SNPs prepared by self-assembly of short amylose were characterized by SEM. The spherical SNPs with a diameter of 15—30 nm were observed. X-ray diffraction results showed that the SNPs displayed higher relative crystallinity than native starch. It was found that the addition of SNPs to starch films enhanced the mechanical properties. With incorporation of 6% SNPs, the tensile strength of film was increased from 8.8 MPa to 15.0 MPa. The nanocomposite films presented reductions in both water vapor permeability and water solubility. Compared with control film, the melting temperature of the nanocomposite films increased with increasing SNPs content, indicating improved thermal stability. The newly developed pea starch films impregnated with potato SNPs could have potential use in degradable packaging applications.

1. Introduction

In recent years, because of grievous resource shortages and environmental pollution, a great number of research studies have focused on obtaining environmentally friendly material in order to solve the problems created by plastic waste (Yasser, 2013). The use of natural polymers is promising for solving resource shortages and minimizing the environmental problems compared with conventional plastics. Some works have studied the possibility of substituting the plastics with natural polysaccharide raw materials with similar properties.

Starch, as a natural, renewable, and biodegradable biopolymer, has been evaluated in its film-forming ability for applications in food packaging (Jiménez, Fabra, Talens, & Chiralt, 2012). It is capable to form a continuous matrix and has low permeability to oxygen (Campos, Gerschenson, & Flores, 2011; Dole, Joly, Espuche, Alric, & Gontard, 2004), lower cost compared to other non-starch films. Films based on starch are transparent (Jiménez et al., 2012; Mali, Grossmann, García, Martino, & Zaritzky, 2004), odorless, tasteless, and colorless. However, when compared to other plastic polymers, films based on starch exhibit several drawbacks, such as their hydrophilic character and poor mechanical property. These problems could be addressed by adding organic or inorganic nanofillers to the starch matrix (Xie, Pollet, Halley, & Averous, 2013). In recent years, the addition of starch nanoparticles (SNPs) to starch matrix to improve the properties of films has aroused the interest of many researchers (Dai, Qiu, Xiong, & Sun, 2015; García, Ribba, Dufresne, Aranguren, & Goyanes, 2011; Jiménez et al., 2012). The unique characteristics—such as biodegradability, impressive mechanical properties, low permeability, and the same chemical structures as the starch matrix—make SNPs an ideal candidate as reinforcement for the fabrication of starch—based nanocomposite films (Lin, Huang, & Dufresne, 2012). In this way, starch films can improve mechanical and barrier properties and act as bioactive packaging. Studies have shown that the tensile strength (TS), Young modulus, and elongation at break (Eb) of the nanocomposite containing starch nanocrystals were improved (Kristo & Biliaderis, 2007; Li et al., 2015). Shi, Wang, Li, and Adhikari (2013) also demonstrated that added SNPs in starch films led to lower water vapor permeability than that of control film.

Potato starch is one of the main commercial starches widely used for sizing paper and textiles and for stiffening laundered fabrics. Potato starch nanocrystals are traditionally prepared by mechanical treatment (Szymońska, Targosz-Korecka, & Krok, 2009) and acid hydrolysis and could serve as an effective reinforcing agent

for natural rubber nanocomposites (Rajisha, Maria, Pothan, Ahmad and Thomas, 2014). Most recently, Sun, Li, Dai, Ji, and Xiong (2014a) proposed a time saving regeneration method that combines enzymolysis with recrystallization to prepare SNPs. Corre and Angellier-Coussy (2014) have stated that this is the most innovative approach proposed in the last years. To our knowledge, nanocomposites impregnated with different levels of potato SNPs fabricated by self-assembly have not yet been reported. Therefore, in this study, potato SNPs were prepared by self-assembly of short amylose debranched from potato starch. The influences of potato SNPs on the physicochemical properties of pea starch-based composite films were evaluated. This will provide the theoretical basis to produce biodegradable starch films that have better mechanical strength, barrier properties, and thermal stability.

2. Materials and methods

2.1. Materials

Pea starch (about 40% amylose) and potato starch (about 31% amylose) were obtained from Tianjin Tingfung Starch Development Co., Ltd (Tianjin, China). Pullulanase (E.C.3.2.1.41, 6000 ASPU/g, 1.15 g/mL) (ASPU is defined as the amount of enzyme that liberates 1.0 mg of glucose from starch in 1 min at a pH of 4.4 and 60 °C) was obtained from Novozymes Investment Co. Ltd. (Beijing, China). All other reagents used were of analytical grade.

2.2. Preparation of potato starch nanoparticles (SNPs)

Potato SNPs were prepared using the method described by Sun et al. (2014a) with some modifications. Potato starch slurry (2.5%, 5%, 7.5%, 10% (w/v)) in pH 5.0 buffer solutions was cooked in boiling water and stirred vigorously for 30 min. The cooked potato starch was adjusted to 58 °C and pullulanase (30 ASPU/g of dry starch) was added. After an 8 h incubation period, the hydrolysate was centrifuged (3000 g, 5 min). The sediment was discarded and the supernatant was heated at 100 °C for 10 min to stop the reaction; the supernatant was then cooled to room temperature. The solution was stored at 4 °C for 8 h for self-assembly of the short amylose. The suspensions were washed several times with distilled water until neutrality and then freeze dried to obtain SNPs.

2.3. Film preparation

Films were prepared according to the procedures used by Shi et al. (2013), with several modifications. Briefly, SNPs were dissolved in 50 mL of distilled water with ultrasonic mixing. The percentage of the SNPs used was set at 0%, 3%, 6%, 9%, and 12% levels on the dry basis of pea starch, respectively. Pea starch (7.5 g) and glycerol (3.0 g) were added to 100 mL of distilled water to obtain composite solutions. The mixture was heated in a boiling water bath with continuous agitation for 30 min to allow full gelatinization of the pea starch. The mixture was cooled to 60 °C. Then 50 mL of the SNPs solution prepared by 5% (w/v) potato starch were added and stirred for 30 min. Thereafter, the composite solutions were degassed under a vacuum, spread evenly over Petri dishes (15 cm in diameter), and dried at 45 °C overnight. All dried films were preserved in a humidity chamber (25 °C, RH = 67%) for further testing.

2.4. Scanning electron microscopy (SEM)

The particle microstructure of the SNPs, the surfaces and fracture surfaces of films were observed using SEM (JSM840, Topcon Corp., Japan). The SNPs suspensions (0.1%, w/v) were deposited on a carbon—coated microscopy grid and freeze dried. The microscopy

grid was then placed on double—sided cellophane tape, coated with a thin film of gold under a vacuum condition, and observed using SEM. The films were frozen in liquid nitrogen and then fractured immediately. The surfaces and fracture surfaces of films were attached to an SEM stub using double—sided cellophane tape, and then the stub and sample were coated with gold-palladium and photographed.

2.5. X-ray diffraction (XRD)

The crystallinity of SNPs was investigated using an X-ray diffractometer (D8—ADVANCE, Bruker AXS Model, Germany) with Cu Kα radiation at a voltage of 40 kV and 30 mA. The samples were scanned between $2\theta = 3-40°$. The area above and under the curve corresponded to crystalline domains and amorphous regions, respectively. The ratio of upper area to total area was taken as relative crystallinity:

$$\text{Relative crystallinity (\%)} = \text{Area under the peaks/Total curve area} \times 100 \tag{1}$$

2.6. Mechanical properties

A TA.XT Plus Texture Analyzer (Lloyd Instruments, West Sussex, England) was used to determine the TS and Eb. Film specimens were tested using the method as suggested by Mehyar, Al-Ismail, Han, and Chee (2012) with several modifications, and the tests were carried out according to the ASTM D828-97 standard test methods. Films were cut into strips (1 cm × 10 cm). The strips were then preconditioned at 67% RH for 48 h inside a sealed desiccator containing saturated sodium chloride solution at room temperature (25 ± 1 °C). At least three replications of each test sample were performed, and average values of the measurements were used. The films were loaded into the testing system, which was set at an initial sample length and grip speed of 2 cm and 100 mm/min, respectively. The TS (MPa) was calculated by dividing the maximum load by cross-sectional areas of the film. Eb was expressed as the percentage of change of the original length of a specimen between grips at breaks.

2.7. Measurement of water vapor permeability (WVP)

Before the tests were conducted, films were conditioned at 25 °C for 48 h in a desiccator with a relative humidity of 67% (saturated solution of sodium chloride). The gravimetric method was used to determine the WVP of the films, as suggested by Sun, Sun, and Xiong (2013), and the tests were carried out according to the ASTM E96-00 methodology. Circular film samples about 30 mm in diameter were placed over the mouth of the test cup and sealed with melted paraffin. The cup was prefilled with anhydrous calcium chloride, leaving 3 mm to the top. After the film specimens were equipped, the assembly was weighed and placed in a chamber conditioned at 25 °C and 100% RH. Weight increments of the cup were measured and plotted at intervals. The slope of the straight line was calculated with a linear regression. The WVP was calculated as follows:

$$WVP = m \times d \: / \: (A \times t \times P) \tag{2}$$

where d is film thickness (m), m is the weight increment of the cup (g), A is the area exposed (m^2), t is the time for permeation (h), and P is the water vapor partial pressure difference across the film (Pa). Three independent films were prepared and three replicates by