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Morphological characteristics and barrier properties of thermoplastic starch/chitosan blown film

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ABSTRACT

Fabrication of starch-based edible film using blown film extrusion is challenging and interesting because this process provides continuous operation with shorter production time and lower energy consumption, is less labor intensive, and results in higher productivity than the conventional solution casting technique. Previously, we reported on the preparation and some properties of thermoplastic starch/chitosan (TPS/CTS) blown films; however, their morphological characteristics and barrier properties had not yet been elucidated. The present work thus aims to investigate the effect of chitosan (0.37–1.45%) on morphological characteristics, water vapor and oxygen barrier properties as well as hydrophilicity of the TPS and TPS/CTS films. The relationship between morphological characteristics and properties of the films was also discussed. Scanning electron microscopy (SEM), confocal laser scanning microscopy (CLSM) and X-ray photoelectron spectroscopy (XPS) confirmed the distribution and deposition of chitosan on the film surface. The existence of chitosan on the surface imparted the improved water vapor and oxygen barrier properties and the reduced surface hydrophilicity to the film. The results suggest that this biodegradable bio-based TPS/CTS film could potentially be used as an edible film for food and pharmaceutical applications.

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1. Introduction

For the past decade, there has been a considerably growing interest in developing edible films with high water and gas barrier properties, as they are highly effective in preservation of the structural integrity and the quality of food and pharmaceutical products. In addition, the edible films are biodegradable, free of toxic substances, safe for health, and prepared from low-cost bio-based polymers. Among naturally occurring polymers, polysaccharides such as starch (Al-Hassan & Norziah, 2012; Bonilla, Atarés, Vargas, & Chiralt, 2013; Bonilla, Talón, Atarés, Vargas, & Chiralt, 2013; Laohakunjit & Noomhorm, 2004), chitosan (Dutta, Tripathi, Mehrotra, & Dutta, 2009), cellulose (Park & Chinnan, 1995), alginate (Pranoto, Salokhe, & Rakshit, 2005), plant gums (Aydinli & Tutas, 2000) and their derivatives have been considered to be good raw materials for fabricating edible films and coatings for food packaging and preservation due to their good film-forming ability, possessing appropriate physical characteristics, and being odorless, tasteless, and colorless (Soliva-Fortuny, Rojas-Graü, & Martín-Belloso, 2012). However, the film-formation process of those polymers is often accomplished by a solution casting method, using different solvents according to the polymer type, such as water for starch (Al-Hassan & Norziah, 2012) and diluted aqueous acetic acid solution for chitosan (Dutta et al., 2009). Although this technique is easily performed using low-cost equipment, it is quite time- and energy-consuming, particularly during the solvent removal or drying step. It is also labor-intensive and difficult to apply on an industrial scale due to the use of batch processing, with consequently low productivity (Laohakunjit & Noomhorm, 2004; López, Lecot, Zaritzky, & García, 2011).

Recently, blown film extrusion of polysaccharides, especially starch-based plastic or thermoplastic starch (TPS), has been reported as an alternative to overcome the limitations of solution casting (Dang & Yoksan, 2015; López, Zaritzky, Grossmann, & García, 2013; Thunwall, Kuthanova, Boldizar, & Rigdahl, 2008). Starch granules must be plasticized with plasticizer(s) under the application of heat and shear force to form plastic, which can be continuously melted and subsequently form bubble and film during the blown film extrusion process (Dang & Yoksan, 2015; Thunwall et al., 2008). Starch-based films are known to have excellent oxygen barrier properties, comparable with commer-

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cial ethylene vinyl alcohol film (Forssell, Lahtinen, Lahelin, & Myllärinen, 2002), although they exhibit high water vapor permeability (Bai & Plotto, 2012). The hydrophilic properties of starch films, which strongly depend on the surrounding humidity (Mali, Sakanaka, Yamashita, & Grossmann, 2005), influence the deterioration of other film properties and characteristics such as structural integrity, mechanical properties and oxygen barrier properties; consequently, their applications are narrow and limited. Incorporating chitosan is an interesting approach not only to reduce water sensitivity as well as improve mechanical and barrier properties of starch film (Dang & Yoksan, 2015; Pelissari et al., 2012), but also to provide a fully biodegradable and bio-based film. Until now, only few publications have reported on the preparation and properties of thermoplastic starch/chitosan (TPS/CTS) blown films fabricated using a film blowing machine (Dang & Yoksan, 2015; Pelissari, Grossmann, Yamashita, & Pineda, 2009; Pelissari et al., 2012; Pelissari, Yamashita, & Grossmann, 2011).

Previously, we found that TPS/CTS blown film containing 1.45% of plasticized chitosan showed increased tensile strength (up to 97%), enhanced stiffness (up to 154%), improved extrusion processability and reduced surface stickiness as compared with neat TPS film (Dang & Yoksan, 2015). Nevertheless, two of the most important and useful characteristics of the edible films, i.e. barrier properties and hydrophilicity, for the as-prepared TPS/CTS films have not yet been reported. Therefore, the present work aims to investigate the effect of chitosan on morphological characteristics, water and oxygen barrier properties as well as hydrophilicity of the TPS/CTS film. The relationship between morphological characteristics and properties of the films was also discussed. Advanced techniques, i.e. scanning electron microscopy (SEM), confocal laser scanning microscopy (CLSM) and X-ray photoelectron spectroscopy (XPS), were also applied to determine the distribution and deposition of chitosan in the matrix of starch film.

2. Materials and methods

2.1. Materials

Native cassava starch (Dragon Fish brand, moisture content of 11% total weight and MW of 1.34×10^8 g/mol) was purchased from Tong Chan Registered Ordinary Partnership (Bangkok, Thailand). Chitosan (deacetylation degree of 85% and molecular weight of 500 kDa) was supplied by Seafresh Industry Public Co. Ltd. (Bangkok, Thailand). Acetic acid (99%) and ethanol were products of Merck (Darmstadt, Germany). The glycerol used was a commercial-grade product. Rhodamine B isothiocyanate (RBITC) was purchased from HiMedia Laboratories Pvt. Ltd. (Mumbai, India).

2.2. Preparation of thermoplastic starch/chitosan films by blown film extrusion

Four formulations of TPS/CTS films, i.e. TPS/CTS0.37, TPS/CTS0.73, TPS/CTS1.09 and TPS/CTS1.45, containing different chitosan contents of 0.37, 0.73, 1.09 and 1.45%, respectively, were prepared according to our previous report (Dang & Yoksan, 2015). Briefly, chitosan solution (in 1% v/v of aqueous acetic acid solution, 100 mL), glycerol (25%) and starch were mixed together by agitation at ambient temperature for 15 min and then dried in a hot-air oven at 65 °C for 18 h. The concentration of chitosan was varied as 0.37, 0.73, 1.09 and 1.45%. The resulting dried material was ground into powder and subsequently blended in a twin-screw extruder (LTE-20-40; Labtech Engineering Co., Ltd., Samut Songkhram, Thailand) using a barrel temperature in a range of 90–125 °C and a screw speed of 170 rpm. The extrudates were cut into pellets 2 mm in length. TPS pellets without the addition of chitosan were also prepared and used as a control.

The obtained TPS and TPS/CTS pellets were then blown into films using a single-screw extruder (LE-25-30/C; Labtech Engineering) connected to a film-blowing attachment (LF-400; Labtech Engineering) with a ring-shaped die. The barrel temperature range was maintained at 130–140 °C and the die temperature was set at 150 °C. Screw speed and nip roll speed were adjusted to 35 – 45 rpm and 3 rpm, respectively.

2.3. Characterization and properties testing of thermoplastic starch/chitosan films

2.3.1. Morphological observation by scanning electron microscopy

Microstructures of film samples at both the film surface and the tensile fracture surface were observed using a JSM-6610LV (JEOL, Tokyo, Japan) scanning electron microscope (SEM) at an accelerating voltage of 20 kV. A small piece of each film was placed on a stub using two-sided carbon tape and then coated with a thin layer of gold prior to SEM observation. The tensile fracture surfaces of all film samples were obtained during tensile testing at ambient temperature using an initial grip distance of 100 mm and a crosshead speed of 50 mm/min (Dang & Yoksan, 2015).

2.3.2. Morphological observation by confocal laser scanning microscopy

Rhodamine B isothiocyanate (RBITC)-labeled film samples were prepared using the same method as described in Section 2.2. Briefly, RBITC/ethanol solution (50 mg/mL, 1 μL) was mixed with chitosan solution; starch and glycerol were then added to the chitosan – RBITC mixture and stirred at ambient temperature for 15 min prior to drying, compounding in a twin-screw extruder, and subsequently converting into film by a film blowing machine. TPS film containing RBITC was also fabricated and used as a control.

The structural and morphological characteristics of all film samples were visualized using a $CS2^+$ confocal microscope (Nikon, Japan) with associated filter for simultaneous 543 nm excitation in a C-scan mode. At a magnification of 20×, images with different depths for 40 layers were viewed. Each layer was compiled to obtain a 3D image of the entire functional complex. Micrographs were formatted using an NIS-Elements Viewer v. 4.0 (Nikon).

2.3.3. Surface composition analysis by X-ray photoelectron spectroscopy

Surface elemental compositions of film samples were analyzed by X-ray photoelectron spectroscopy (XPS) using an AXIS Ultra XPS system (Kratos Analytical Ltd., Manchester, UK) with an Al Kα X-ray source (1486.6 eV photons). The X-ray gun setting was 10 mA emission current at an accelerating voltage of 15 kV. The elements were identified from survey spectra recorded at a pass energy of 160 eV. All binding energies were referenced to the C 1s hydrocarbon peak at 284.6 eV. Gaussian–Lorentzian distribution was used for fitting the spectra for each peak, in order to determine the binding energy of the core levels of the different elements. The high-resolution spectra for the N 1s were recorded from individual peaks at a pass energy of 20 eV.

2.3.4. Determination of water vapor permeability

Water vapor transmission rate (WVTR) of film samples was determined using a desiccant method according to ASTM E96. Each film was cut into a round shape with a diameter of 7.5 cm and then placed on the open mouth of a test cup, which had an inner diameter of 6.3 cm and contained dried desiccant (20 mL). The film was then sealed to the cup using paraffin wax. The sample assembly was weighed before placing in an incubator at 25 ± 2 °C and 50 ± 2%

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