



Development of thermoplastic starch blown film by incorporating plasticized chitosan



Khanh Minh Dang^a, Rangrong Yoksan^{a,b,*}

^a Department of Packaging and Materials Technology, Faculty of Agro-Industry, Kasetsart University, Bangkok 10900, Thailand

^b Center for Advanced Studies for Agriculture and Food, Kasetsart University, Bangkok 10900, Thailand

ARTICLE INFO

Article history:

Received 29 July 2014

Received in revised form 2 September 2014

Accepted 4 September 2014

Available online 16 September 2014

Keywords:

Thermoplastic starch

Chitosan

Extrusion

Blown film extrusion

Biodegradable film

Bio-based material

ABSTRACT

The objective of the present work was to improve blown film extrusion processability and properties of thermoplastic starch (TPS) film by incorporating plasticized chitosan, with a content of 0.37–1.45%. The effects of chitosan on extrusion processability and melt flow ability of TPS, as well as that on appearance, optical properties, thermal properties, viscoelastic properties and tensile properties of the films were investigated. The possible interactions between chitosan and starch molecules were evaluated by FTIR and XRD techniques. Chitosan and starch molecules could interact via hydrogen bonds, as confirmed from the blue shift of OH bands and the reduction of V-type crystal formation. Although the incorporation of chitosan caused decreased extensibility and melt flow ability, as well as increased yellowness and opacity, the films possessed better extrusion processability, increased tensile strength, rigidity, thermal stability and UV absorption, as well as reduced water absorption and surface stickiness. The obtained TPS/chitosan-based films offer real potential application in the food industry, e.g. as edible films.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

In recent decades, growing environmental consciousness has encouraged the development of biodegradable materials from renewable resources. Among plant-derived materials, starch offers several advantages as a raw material for the plastic industry, including its low cost, non-toxicity, biodegradability, composability, and worldwide availability. Starch granules have been used as a plastic additive, e.g. as reinforcing agent and filler, for many years (Evangelista, Sung, Jane, Gelina, & Nikolov, 1991; Westhoff, Otey, Mehlretter, & Russell, 1974); however, only a small amount of starch could be added without the deterioration of plastic properties. In addition, starch has been transformed into thermoplastic material by applying heat and shear forces together with the incorporation of plasticizers (van Soest, Hulleman, de Wit, & Vliegthart, 1996; Yu, Gao, & Lin, 1996). Although the resulting thermoplastic starch (TPS) can be converted into rigid or flexible packaging using conventional machines as for commodity plastics, its applications are limited due to high moisture absorption which causes surface

stickiness (Thunwall, Kuthanova, Boldizar, & Rigdahl, 2008) as well as poor mechanical and barrier properties (Gáspár, Benkó, Dogossy, Réczey, & Czigány, 2005; Ma, Yu, & Kennedy, 2005; Pelissari et al., 2012; Yu, Prashantha, Soulestin, Lacrampe, & Krawczak, 2013). Blending/mixing TPS with other bio-based polymers such as chitosan (Pelissari, Grossmann, Yamashita, & Pineda, 2009; Pelissari, Yamashita, & Grossmann, 2011; Pelissari et al., 2012), cellulose (Gáspár et al., 2005; Ma et al., 2005), proteins (Gáspár et al., 2005), etc., has been reported to be a good technique for achieving fully bio-based materials and to widen the application window of TPS.

Chitosan, the linear cationic (1-4)-2-amino-2-deoxy- β -D-glucan is industrially produced from marine chitin ((1-4)-2-acetamido-2-deoxy- β -D-glucan) (Muzzarelli, 2012; Muzzarelli et al., 2012). Both of them have attracted attention owing to their superior characteristic properties, among which biocompatibility and absence of allergenicity (Busilacchi, Gigante, Mattioli-Belmonte, & Muzzarelli, 2013; Muzzarelli, 2009, 2010). Chitosan is a non-toxic (Kean & Thanou, 2010) and biodegradable (Bagheri-Khoulenjani, Taghizadeh, & Mirzadeh, 2009) polymer with antimicrobial activity (Cruz-Romero, Murphy, Morris, Cummins, & Kerry, 2013), all of which are important qualities for food packaging purposes. In general, chitosan is insoluble in water, alkali and most common organic solvents, but soluble in aqueous solutions of most organic acids, particularly lactic acid, formic acid and acetic acid with pH less than 6.

* Corresponding author at: Kasetsart University, Faculty of Agro-Industry, Department of Packaging and Materials Technology, 50 Ngamwongwan Rd., Ladyao, Chatuchak, Bangkok 10900, Thailand. Tel.: +66 2 562 5097; fax: +66 2 562 5046.

E-mail addresses: rangrong.y@ku.ac.th, yyrangrong@yahoo.com (R. Yoksan).

Incorporating chitosan into starch-based film has been reported as an alternative to reduce water affinity and improve its mechanical properties, due to the formation of intermolecular hydrogen bonds between amino and hydroxyl groups of chitosan and hydroxyl groups of starch (Xu, Kim, Hanna, & Nag, 2005). However, most previous studies have involved starch/chitosan-based films prepared by a solution casting method, in which the procedure is easy but the scale-up from laboratory to industrial level might be difficult because it is a very time-consuming process. Blown film extrusion is an alternative option to achieve industrial-scale output; however, few research articles have reported the development of starch/chitosan-based film using this method. Pelissari et al. (2009) revealed that starch/chitosan blown film composed of 5% chitosan showed decreased rigidity and water vapor permeability (WVP) as compared with the control, while the thermal stability of the films did not change. The processing parameters, such as die temperature and screw speed, also affect the properties of starch/chitosan blown film (Pelissari et al., 2011). Blow-up ratio and WVP of the film increased, while its opacity, tensile strength and elongation at break decreased with increasing screw speed. Low die temperatures caused decreased tensile properties and reduced WVP of the films. This research group also reported that the presence of a higher relative concentration of chitosan favored the formation of more rigid and opaque and less permeable films (Pelissari et al., 2012). It should be noted that chitosan flakes could not be melted during extrusion (Bonilla, Fortunati, Vargas, Chiralt, & Kenny, 2013; Grande & Carvalho, 2011); hence, homogenous chitosan-based films were acquired only by solvent casting of chitosan from an aqueous organic acid solution (Chillo et al., 2008; Xu et al., 2005). Blown film extrusion of a bio-based material composed of TPS and plasticized chitosan, in which the plasticized chitosan is derived from the protonation in aqueous acetic acid of chitosan followed by the intervention by glycerol, has not yet been reported, although it would be expected for preparing the homogeneous film.

Therefore, the objective of the present work was to develop film from TPS/chitosan-based materials, in which the chitosan was plasticized prior to incorporation into TPS via blown film extrusion.

2. Materials and methods

2.1. Materials

Native cassava starch (Dragon Fish brand) with moisture content of 11% of total weight was purchased from Tong Chan Registered Ordinary Partnership (Thailand). Chitosan (deacetylation degree of 85% and molecular weight of 500 kDa) was supplied by Seafresh Chitosan (Lab) Co., Ltd. (Thailand). Acetic acid (99%) was a product of Merck (Germany). The glycerol used was a commercial grade product.

2.2. Preparation of thermoplastic starch/chitosan-based compound resins by extrusion

Chitosan solutions – 0.37, 0.73, 1.09 and 1.45% – were prepared by dissolving chitosan flakes in an aqueous acetic acid solution (1% v/v, 100 mL), using a magnetic stirrer at 550 rpm until dissolution was complete (typically about 48 h at room temperature). Glycerol (25%) and subsequently starch were added to chitosan solutions and thoroughly mixed by agitation at ambient temperature for 15 min. Each slurry was then poured into a 1.5-cm-high plastic tray and kept in a hot-air oven at 65 °C for 18 h. The resulting dry material, with a moisture content of approximately 20–22%, was ground into powder and then blended using a twin-screw extruder with an L/D ratio of 40 and a screw diameter of 20 mm (LTE-20-40; Labtech Engineering Co., Ltd., Thailand), and with a barrel temperature

profile of 90/95/105/110/115/120/120/120/120/125 °C (from hopper to die) and a screw speed of 170 rpm. The extrudates were cut into 2-mm-long pellets with a pelletizer. Four formulations of thermoplastic starch/chitosan-based compound resins were obtained: i.e. TPS/CTS0.37, TPS/CTS0.73, TPS/CTS1.09 and TPS/CTS1.45, representing thermoplastic starch with a chitosan content of 0.37, 0.73, 1.09 and 1.45%, respectively. TPS without addition of chitosan was also prepared and used as a control.

2.3. Preparation of thermoplastic starch/chitosan-based films by blown film extrusion

The obtained resins were blown into films using a single-screw extruder (LE-25-30/C; Labtech Engineering) – with an L/D ratio of 30, a screw diameter of 25 mm, and four controlled temperature zones – connected to a film-blowing attachment (LF-400; Labtech Engineering) with a ring-shaped die. The barrel temperature profile was maintained at 130/140/140/140 °C (from feed inlet to die) 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.

2.4. Characterization and properties testing of thermoplastic starch/chitosan-based compound resins and films

2.4.1. Melt flow index measurement

Melt flow index (MFI) of the samples was measured according to ASTM 1238-10, with a slight modification. The measurement was performed using an MFI-2 (Custom Scientific Instruments, USA) at 190 °C with a load cell of 3.2 kg, a preheating time of 7 min and a time interval of 6 min. MFI was measured in triplicate for each sample and reported in g/10 min as mean ± SD ($n=3$).

2.4.2. Color measurement

Color of the films was measured using a CR-400 colorimeter (Konica Minolta, Japan). The measurements were performed in triplicate in the CIE 1976 (L^* , a^* , b^*) color space (or CIELAB), where L^* , a^* and b^* indicate lightness, redness and yellowness, respectively.

2.4.3. Measurement of UV absorption and transparency

UV absorption and light transmittance of the films were measured at wavelength ranges of 200 nm to 400 nm and 400 nm to 800 nm, respectively, using a UV-2450 Ultraviolet-visible (UV-vis) spectrophotometer (Shimadzu, Japan).

2.4.4. Fourier transform infrared analysis

Fourier transform infrared (FT-IR) spectra of the samples were recorded in attenuated total reflectance (ATR) mode using a Bruker Tensor 27 FT-IR spectrometer (Bruker, Germany). The spectra were recorded at a wavenumber range from 500 cm^{-1} to 4000 cm^{-1} at temperatures varying from 30 °C to 220 °C, using 32 accumulated scans and a spectral resolution of 4 cm^{-1} .

2.4.5. X-ray diffraction analysis

X-ray diffraction (XRD) patterns of the samples were analyzed by a JEOL JDX-3530 X-ray diffractometer (JEOL, Japan). Samples were scanned at diffraction angles (2θ) from 5 to 40° using a scan rate of 0.02°/s.

2.4.6. Thermogravimetric analysis

TGA thermograms were obtained using a STA PT1000 TG-DSC (Linseis, Germany) with TA evaluation software. Each sample (15–25 mg) was placed in a ceramic crucible and heated from 25 °C to 600 °C at a heating rate of 20 °C/min under a nitrogen atmosphere with a N_2 flow rate of 4 L/h.

Download English Version:

<https://daneshyari.com/en/article/7790590>

Download Persian Version:

<https://daneshyari.com/article/7790590>

[Daneshyari.com](https://daneshyari.com)