



Improvement of mechanical properties and thermal stability of biodegradable rice starch–based films blended with carboxymethyl chitosan

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ABSTRACT

Biodegradable blend films from rice starch (RS) and carboxymethyl chitosan (CMCh) were produced and characterized. Color, opacity, mechanical properties, thermal properties, swellability, oxygen and water permeability, and biodegradability of the RS–CMCh blend films are reported. Interaction and compatibility of films components were evaluated by using Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction. Increased yellowness, total color difference and transparency, and decreased redness, lightness and whiteness index were observed in the blend films as incorporation of CMCh increased. Addition of 50% w/w of CMCh to the RS matrix increased the tensile strength of the RS–CMCh blend film by 35% and the elongation at break by 28%. Addition of CMCh improved the thermal stability of the RS–CMCh films. Incorporation of 12, 33 and 50% w/w CMCh in the blend films increased the swelling ratio by around 850%, 3985% and 3404% at 24 h, respectively, when compared with the RS film. The oxygen permeability of all the films increased as relative humidity increased. The FTIR spectra suggested that interactions may be present between the –OH groups of RS and the COO– groups of CMCh. Scanning electron microscopy images revealed that the cross-sectional fracture surfaces of all the films were smooth and homogenous. The RS film exhibited a priming effect in the biodegradation study. The addition of 50% w/w CMCh led to a decrease in mineralization of the blend films.

1. Introduction

Among the several types of biomaterials, the polysaccharide starch is an attractive material due to its good film-forming capability, biocompatibility, relatively low cost, renewability and abundance. Rice starch (RS) is a by-product of rice processing. RS is considered to be a relatively cheap source of starch. RS contains around 30% amylose, which is the linear and the more readily crystallizable component of starch compared with amylopectin. RS can be used to produce biodegradable films (Janjarasskul and Krochta, 2010; Wittaya, 2012).

Polysaccharide films are good oxygen barriers with suitable optical properties and moderate mechanical properties at low relative humidity (RH) (Bourtoom and Chinnan, 2008; Laohakunjit and Noomhorm, 2004; Whistler et al., 1984). However, starch-based films are brittle and hydrophilic, which affect and limit their processing and application (Mendes et al., 2016). Plasticizers such as glycerol, sorbitol and polyethylene glycol have been used to overcome the brittleness of starch films (Suppakul et al., 2013; Wittaya, 2012), but their use decreases the tensile strength of the films (Tantala et al., 2012a).

Blending, grafting, and compounding with other materials have been used as the main techniques to overcome this shortcoming (Al-Hassan and Norziah, 2012; Bourtoom and Chinnan, 2008; Dias et al., 2010; Ghanbarzadeh et al., 2010; Mathew et al., 2006; Saberi et al., 2016).

Chitosan is a cationic polysaccharide containing β (1–4)-2-amino-2-deoxy d-glucopyranose repeating units (Wu et al., 2013). Chitosan is a deacetylated product of chitin, and is abundantly available in nature, nontoxic and biodegradable. Chitosan has high quality film-forming capability (Wu et al., 2013); however, it dissolves in acidic water, which affects the finished product by causing a bad odor (Ferreira et al., 2009). Carboxymethyl chitosan (CMCh) is a water-soluble etherified chitosan. Applications for CMCh have been reported for food (Carolan et al., 1991), drugs (Chen et al., 2004), cosmetics (Wannaruemon et al., 2013), and agriculture (Dau et al., 2016). CMCh has the capability to form films and gels, is biodegradable and soluble over a wide range of pH, has high viscosity, biocompatibility and antimicrobial activity, and low toxicity (Bukzem et al., 2016; Tantala et al., 2012b). The introduction of CMCh in blend films can increase water solubility, improve tensile strength, and provide some antimicrobial capability (Fan

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et al., 2006; Tantala et al., 2012b). Previous studies have shown that the incorporation of chitosan or CMCh can improve the mechanical properties of rice starch–chitosan blend films (Bourtoom and Chinnan, 2008), corn starch–chitosan blends (Mendes et al., 2016), and pullulan–CMCh blend films (Wu et al., 2013). Tantala et al. (2012b) showed that CMCh has some antimicrobial capabilities against several strains of lactic acid bacteria but not against foodborne pathogens. Thus, incorporating CMCh into rice starch–based films could provide appealing film properties, and it is the focus of this work.

To the best of our knowledge, there is no published research on the development and characterization of RS-based films that incorporate CMCh, or on understanding their end-of-life scenario and biodegradability. Thus, the purpose of this work was to evaluate the effect of incorporating CMCh on the physical and thermal properties, permeability and biodegradability of RS–CMCh blend films. The interactions and compatibility between these two polysaccharides were also studied by Fourier transform infrared spectroscopy and X-ray diffraction.

2. Materials and methods

2.1. Materials

Native RS powder (Rose 100R) was purchased from Thai Flour Industry Co., Ltd. (Bangkok, Thailand). Shrimp chitosan flake (molecular weight range 900,000–1,300,000 Da; degree of deacetylation 98%) was purchased from Taming Enterprises (Samut Sakhon, Thailand). Sodium hydroxide, glacial acetic acid, isopropanol, ethanol and methanol were purchased from RCI Lab-scan Co., Ltd. (Bangkok, Thailand). Glycerol was purchased from Union Science Co., Ltd. (Chiang Mai, Thailand). Monochloroacetic acid was purchased from Sigma Aldrich (Steinheim, Germany). All reagents were of analytical grade and used as received. Cellulose powder (20-mm grade) was purchased from Sigma Aldrich (St. Louis, MO, USA). Compost was obtained from the Michigan State University commercial composting facility (East Lansing, MI, USA).

2.2. Synthesis of carboxymethyl chitosan

CMCh was synthesized as previously described by Suriyatem et al. (2015). Chitosan powder (25 g), with a particle size less than 60 mesh, was suspended in a medium consisting of NaOH–isopropanol–distilled water at a ratio of 50 g:400 mL:100 mL. The suspension was stirred continuously for 1 h at 50 °C using a hotplate stirrer (IKA C-MAG HS7, Wilmington, NC, USA). Monochloroacetic acid (50 g) was dissolved in isopropanol (50 mL) and gradually introduced to the suspension as an etherifying agent. The mixture was then stirred continuously for 4 h at 50 °C and then held until the two phases separated. The liquid phase was removed, and the solid phase was suspended in methanol and neutralized with glacial acetic acid to stop the reaction and then filtered. The residue was washed with 70% v/v ethanol (500 mL) five times to remove the byproduct NaCl and then washed once with 95% v/v ethanol (500 mL). The final product, CMCh, was dried in an oven at 55 °C for 18 h and then stored in a high-density polyethylene container containing silica gel packs. The degree of substitution of CMCh was measured by the potentiometric titration procedure as detailed elsewhere (Jaidee et al., 2012).

2.3. Preparation of films

Film-forming solutions (3% w/v) with different RS and CMCh contents were prepared to yield five different blend films. The RS/CMCh ratios (wt/wt) of the blend films were 100:0 (RS film), 88:12 (RS/12CMCh film), 67:33 (RS/33CMCh film), 50:50 (RS/50CMCh film) and 0:100 (CMCh film), indicating g CMCh/100 g solid. To prepare the solutions, RS was dispersed in distilled water; the mixture was heated at 85–90 °C with constant stirring using a magnetic stirrer (IKA C-MAG HS7) for 15 min. CMCh was dissolved in distilled water and heated to

80 °C using a magnetic stirrer for 15 min. The various combinations of RS and CMCh solutions were mixed for 30 min using a magnetic stirrer, and glycerol (25% wt of solid content) was added as a plasticizer. Each solution was degassed, cooled to 25 °C and poured onto an acrylic casting plate (0.15 m × 0.15 m). To form and dry the film, the plate was placed in a control room at 25 ± 1 °C and 55% ± 5% RH for 36 h. The films were peeled from the plates, placed in sealed aluminum bags, and stored in an environmental chamber at 25 ± 1 °C and 55% ± 2% RH until use. Selected samples were stored at –20 ± 1 °C and removed for conditioning before testing for mechanical, thermal and barrier properties, swelling and biodegradation. All the films were pre-conditioned at 23 ± 2 °C and 50% ± 10% RH for 48 h before testing.

2.4. Film color and opacity

Lightness (L^*) and chromaticity parameters, a^* (redness) and b^* (yellowness), of the films were measured using a colorimeter (CR-10, Minolta, Japan). A white standard (tile: $L^* = 98.35$, $a^* = 0.00$, and $b^* = 1.08$) was used to calibrate the color reader before measurements were taken. Samples were tested in triplicate. Total color difference (ΔE) and whiteness index (WI) were calculated using Eqs. (1) and (2), respectively:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

$$WI = 100 - \sqrt{(100 - L^*)^2 + a^{*2} + b^{*2}} \quad (2)$$

where ΔL^* , Δa^* and Δb^* are the differences between the color parameter of the samples and of the RS film.

Film opacity (Op) was evaluated by measuring the absorbance at 550 nm (A_{550}) (Al-Hassan and Norziah, 2012) using a Spectro SC spectrophotometer (Labomed, Los Angeles, USA). The Op of the films was calculated using Eq. (3):

$$Op = A_{550}/x \quad (3)$$

where x is the film thickness (mm). According to this equation, a higher value of Op indicates a lower degree of transparency. All tests were run in triplicate.

2.5. Tensile tests

Tensile properties of the films (i.e., tensile strength, break elongation and modulus of elasticity) were measured using a universal testing machine (United Calibration Corp. and United Testing Systems, Huntington Beach, CA, USA). The measurements were conducted according to ASTM-D882-12 (2012). Five rectangular specimens (0.025 m × 0.100 m) were cut from each film. A load cell of 5 kN and a cross-head speed of 0.050 m/min were used. The initial grip separation was set at 0.050 m due to the sample size restriction and because we did not find statistically significant differences when testing films with an initial grip separation of 0.050 and 0.100 m. The specimens were conditioned at 23 ± 2 °C and 50% ± 10% RH for 48 h prior to testing.

2.6. Fourier transform infrared (FTIR) spectroscopy

Transmission infrared spectra of films were obtained with a FTIR spectrometer (Equinox 55, Bruker, USA) in the range of 4000–400 cm^{-1} , with a resolution of 4 cm^{-1} using a DTGS detector and Omnic software. The film was mounted directly in the sample holder.

2.7. X-ray diffraction (XRD)

X-ray diffraction patterns of the powders (RS, CMCh and chitosan) and films (RS, CMCh and RS–CMCh blends) were recorded in the reflection mode on a X-ray diffractometer (MiniFlex II, Rigaku, Japan). The scattering angle (2θ) was from 5 to 60° at a scan rate of 5°/min.

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