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Research Paper

Preparation and characterization of chitosan film incorporated with thinned young apple polyphenols as an active packaging material

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ABSTRACT

The objective of this study was to characterize the physical, mechanical and bioactive properties of chitosan film incorporated with thinned young apple polyphenols (YAP). The results indicated that the addition of YAP resulted in a significant increase in the thickness, density, swelling degree, solubility and opacity of chitosan film, but the water content, water vapor permeability and mechanical properties of the film were decreased. Besides, the antioxidant and antimicrobial properties of chitosan film were significantly enhanced by YAP. Both the NMR and FTIR spectra indicated the interactions between YAP and chitosan were likely to be non-covalent. Furthermore, the thermal stability of the film was decreased by YAP addition, suggested by DSC. Interestingly, the changing tendency of crystalline degree indicated by X-ray kept pace with that of thermal stability for YAP-chitosan films. Overall, YAP-chitosan film was shown a potential as a bioactive packaging material to extend food shelf-life.

1. Introduction

In recent years, biodegradable and biobased packaging materials have been obtained a widespread interest due to the limited natural resources, food safety and environmental problems caused by the use of petrochemical-based plastics. Some carbohydrate polymers, like starches, cellulose derivatives, chitosan and pectin that are biodegradable and edible substances, have been utilized as packaging materials targeting to extend food shelf-life (Espitia, Du, Avena-Bustillos, Soares, & Mchugh, 2014). Moreover, considerable researches have also focused on the addition of natural antimicrobial agents extracted from agricultural commodities and food product wastes into edible packaging materials (Atarés, Bonilla, & Chiralt, 2010).

Chitosan (the degree of deacetylation is 90% in this study), the most abundant biopolymer second to cellulose, is a low acetyl substituted form of chitin and a natural carbohydrate copolymer consisting of β-(1–4)-2-acetamido-D-glucose and β-(1–4)-2-amino-D-glucose units (Shahidi, Arachchi, & Jeon, 1999). It has been proved that chitosan is an excellent film forming material with a selective permeability to gasses and good mechanical properties that can be comparable to many medium-strength commercial polymers (Butler, Vergano, Testin, Bunn, & Wiles, 1996). As microbial spoilage is a major problem affecting food quality, it is promising that antioxidants are incorporated into packaging materials to delay the spoilage. Current researches concerning supplementing natural antioxidants to enhance the antioxidant functions of films include the incorporation of essential oils and the addition of phytochemicals due to their broad antimicrobial activities (Chen, Yue, & Zhong, 2015). Essential oils have been reported to be successfully mixed into chitosan films by means of lamination, dispersion and emulsion (Prodpran, Benjakul, & Artharn, 2007). Films incorporated with cinnamon bark oil and soybean oil were shown a strong antimicrobial activity particularly against Gram-positive *L. monocytogenes* (Ma et al., 2016). The physic-mechanical properties of chitosan films containing carvacrol and grape seed extracts in different proportions showed a high potential to improve food preservation and shelf-life (Rubilar et al., 2013). Although polyphenol, a class of bioactive antioxidant, has been widely applied in food preservative field, the incorporation of it with chitosan film as a new-type and effective bio-preservative film needs to be further shed light on in terms of its structural characterization and bioactivities.

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Apple, very popular and widely available, is a very significant source of polyphenols that show strong antioxidant activity (Vayndorf, Lee, & Liu, 2013). Fruit thinning is one of the most important techniques in apple growing for improving fruit quality and increasing yield (Link, 2000). In China, there are about 1.6 million tons of thinned young apples discarded in apple groves every year (Sun, Guo, Fu, Li, & Li, 2013). Thinned young apples actually are agricultural resource since the content of total polyphenols is approximately ten times higher than that in ripe apples. Furthermore, autotoxicity that plant inhibits the growth of its own kind is the major reason of the replant problem (Singh, Batish, & Kohli, 1999). Previous research suggested that replant disease of apple trees was attributed to the high concentrations of phlorizin in apple roots (Cesco et al., 2012). Thinned young apples are usually abandoned on the ground of the groves, in which the high concentration of polyphenols maybe responsible for apple tree autotoxic behavior. Therefore, it is very important to make use of thinned young apples rather than discard them in the orchard.

Hence, the aim of this work is to prepare and characterize the chitosan film incorporated with thinned young apple polyphenols (YAP) and analyze the effect of YAP on the physical, mechanical and bioactive properties of the film to determine if the YAP-chitosan film has a potential as an active packaging material.

2. Material and methods

2.1. Materials

Chitosan with the degree of deacetylation of 90% and molecular weight of around 91000 Da was supplied by Shanghai Lanji Technology Development Co. Ltd. (China). All the chemicals in this study were of analytical grade.

2.2. Preparation and determination of YAP

YAP was extracted and separated according to our previously reported method (Sun et al., 2013). The determination of the content of individual phenolic compound in YAP was conducted using a Thermo® Ultimate 3000 HPLC system (Thermo Electron Co. USA) and a Thermo® syncronis C18 column (250 × 4.6 mm I.D., 5 μm, USA). Elution with solvent A (30% acetonitrile and 70% methanol) and solvent B (1‰ trifluoroacetic acid and 5% methanol) in a step gradient way was carried out as follows: 0–3 min, 100% B at a flow rate of 0.95 mL/min; 3–19.05 min, 100-60% B at a flow rate of 0.95 mL/min; 19.05–30.1 min, 60% B from a flow rate of 0.95 mL/min to a flow rate of 1 mL/min; 30.1–30.2 min, 60–100% B from a flow rate of 1 mL/min to a flow rate of 0.95 mL/min; 30.2–41 min, 100% B at a flow rate of 0.95 mL/min. During the run, the detection wavelength was 280 nm, and the injection volume was 20 μL.

2.3. Film preparation

Chitosan solution (2%, w/v) was prepared by dissolving into 1.0% (v/v) acetic acid aqueous solution with stirring of 800 rpm for 4 h 30% (w/w) glycerol, as plasticizer, was added into chitosan solution with stirring for 0.5 h. Different concentrations of YAP (0.25%, 0.50%, 0.75%, and 1.0% (w/v)) were added into the polymer solutions. These solutions were vacuum degasified for 1 h to remove air bubbles. Finally, the respective YAP-chitosan solutions (70 mL) were cast over the petri dishes (diameter of 15 cm) for 48 h at 25 °C. The YAP-chitosan films were carefully peeled and stored in the desiccators containing $Mg(NO_3)_2$ saturated solutions (53% relative humidity) at 25 °C for 48 h for further experiments. The film solutions were freeze-dried into powder for antimicrobial assay, in vitro cytotoxicity assay, H^1 NMR and FTIR analysis.

2.4. Physical properties of film

2.4.1. Scanning electron microscopy (SEM)

TM3030 scanning electron microscope (Hitachi Co. Ltd., Kyoto, Japan) was used to observe the surface and cross-section morphology of the films with and without YAP. The films were imaged at a voltage of 15 kV with gold coating.

2.4.2. Thickness and density

The film thickness was measured using a digital micrometer (Mitutoyo Absolute, Tester Sangyo Co. Ltd., Tokyo, Japan). The film density was determined by the film weight and volume. The film volume was calculated according to the area and thickness of the film.

2.4.3. Solubility and swelling degree

The films were cut into 2 cm × 2 cm pieces for the determination of solubility and swelling degree. The pieces were dried at 105 °C to constant weight to obtain the initial dry mass (M_1). Then, they were placed in 100 mL beakers with 50 mL distilled water covered with plastic wraps and stored at 25 °C for 24 h. Next, the films were dried superficially with filter papers and dried at 105 °C to constant weight to obtain the final dry mass (M_2). Then, the solubility was calculated using the following equation:

$$\text{Film solubility} = \frac{M_1 - M_2}{M_1} \times 100\% \quad (1)$$

The films were put into 50 mL beakers with 30 mL distilled water for 24 h at 25 °C after weighing the films (M_1). The wet films were then dried superficially with filter papers, followed by weighing the wet films (M_2). The swelling degree was calculated using the following equation:

$$\text{Film swellng degree} = \frac{M_2 - M_1}{M_1} \times 100\% \quad (2)$$

2.4.4. Water vapor permeability (WVP) and water content

WVP was determined according to the method provided by Talja, Helén, Roos, and Jouppila (2008) with some modifications. The films were cut into pieces (6 cm × 6 cm) before sealed onto a special aluminum cup (internal diameter: 6 cm, external diameter: 9 cm, exposed area: 28.27 cm^2, depth: 1.3 cm) containing anhydrous calcium chloride and ensured that the gap between the film and anhydrous calcium chloride was less than 6 mm. Then the cup was placed into a desiccator with distilled water at room temperature. The cup was weighed every 2 h using an analytical balance with a precision of 0.1 mg (Mettler-Toledo Instrument (Shanghai) Co. Ltd., China). The WVP was determined using the following equation:

$$\text{WVP} = (md)/(At\Delta p) \quad (3)$$

where WVP is the water vapor permeability ($g\,m^{-1}s^{-1}\,Pa^{-1}$), m is the mass increase (g), t is the time of permeation (s), A is the exposed area, d is the film thickness (m^2) and Δp is the saturated vapor pressure of water at the test temperature (25 °C, pa).

The film pieces (2 cm × 2 cm) were prepared and weighed (M_1) for water content according to Jimenez, Fabra, Talens, and Chiralt (2012) Chiralt with some modifications. The pieces were dried at 105 °C to a constant mass (M_2). Then, the water content was determined using the following equation:

$$\text{Water content} = \frac{M_1 - M_2}{M_1} \times 100\% \quad (4)$$