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Blend-modification of soy protein/lauric acid edible films using polysaccharides

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ABSTRACT

Different types of polysaccharides (propyleneglycol alginate (PGA), pectin, carrageenan and aloe polysaccharide) were incorporated into soy protein isolate (SPI)/lauric acid (La) films using a co-drying process or by direct addition to form biodegradable composite films with modified water vapour permeability (WVP) and mechanical properties. The WVP of SPI/La/polysaccharide films decreased when polysaccharides were added using the co-drying process, regardless of the type of polysaccharide. The tensile strength of SPI/La film was increased by the addition of polysaccharides, and the percentage elongation at break was increased by incorporating PGA using the co-drying process. Regarding oxygen-barrier performance, no notable differences were observed between the SPI/La and SPI/La/polysaccharide films. The most significant improvement was observed by blending PGA, with the co-dried preparation exhibiting better properties than the direct-addition preparation. Scanning electron microscopy (SEM) revealed that the microstructures of the films are the basis for the differences in the barrier and mechanical properties of the modified blends of SPI, polysaccharides and La.

1. Introduction

Studies investigating the application of protein-based edible film as a preservation coating are constantly emerging due to its good performance in resisting O_2 and CO_2, but few films have been commercialised, which is primarily due to their inefficient water resistance and poor mechanical properties (Krochta & DeMulder-Johnston, 1997). Co-blending a soy protein isolate (SPI) and lipids can improve the physical properties of the SPI film, particularly its water resistance property, but there are still major defects on its mechanical properties, appearance and O_2-resistance property (Turgeon & Beaulieu, 2001). The most common method used to improve the mechanical properties of the SPI/lipid film is crosslinking with crosslinking agents, such as glutaraldehyde. However, the cytotoxicity of glutaraldehyde limits its application in food preservation (Juvonen et al., 2011; Krochta & De Mulder, 1997).

Biological macromolecular materials can be multifunctional and biodegradable; the co-blended composites of different macromolecules developed recently have outstanding advantages and properties compared with other materials, and have become an important subject in current studies of edible film. The represented biological macromolecular materials are proteins and polysaccharides (PS). There are several models of co-drying polysaccharides and proteins that explain the co-blending method and the properties of the co-blended composites using the structural characteristics of polysaccharides and proteins, based on the introduction of several main polysaccharides (starch, cellulose, chitosan) and proteins (collagen, gelatin, silk protein), but reports on the application of edible films are scarce. In the research about edible film solutions, combining compatible protein and polysaccharides creates composites with greatly improve properties because the two components each provide advantages and compensate the other's disadvantages, and furthermore, two components can have synergistic effects, that endow the composite with superior functional features. Moreover, the thickening and gelation functions of polysaccharides in the liquid phase provide additional excellent features to the co-blending film solution and improve its stability (Avena-Bustillos et al., 2011; Zaleska, Ring, & Tomasik, 2000).

Protein/lipid films can be formed using two methods. One method to form emulsions and films is to prepare an emulsion of protein–lipid complexes by a physical treatment (for example, homogenising) and then to create the film by coating and drying. Another method is to form an edible film under different phases. Generally, two-layered or multi-layered films show better mechanical and resistance properties compared with a single-layer film formed from an emulsion (Chen, Kuo, & Lai, 2009; Park, Testin, Park, Vergano, & Weller, 1994). However, the technology of creating two-layered or multi-layered films is more complex and time consuming. The different solvents used and the high temperature

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treatment of the production process increase the cost while decreasing the safety of these films compared with films formed from an emulsion. Furthermore, there is comparatively high surface tension between the different layers, resulting in their separation. Only a single step is required to form an emulsion coating film, and the good emulsifying property of SPI helps to form a film with better qualities at a lower cost. The emulsion can be formed in an aqueous solution and applied at room temperature, which significantly increases its practical value (Atares, De Jesus, Talens, & Chiralt, 2010; Gennadios, McHugh, & Weller, 1994).

In the film mixtures formed with polysaccharides, proteins and lipids, the characteristics of the blended proteins and polysaccharides are critical for the properties of entire system. Phase separation of ternary components in the film liquid is mainly due to the incompatibility of the proteins and polysaccharides. Therefore, when studying a ternary mixed film liquid, the key goal should be to improve the properties of the co-blended films formed by the proteins and polysaccharides. There are few reports concerning modification of the co-blended film with polysaccharides because in the current technology, the polysaccharide is generally directly added, resulting in a less significant improvement in the film properties. This study was divided into the two following projects: (1) modifying the SPI film with polysaccharides and investigating the effect of directly adding the polysaccharide vs. co-drying SPI/polysaccharide films, (2) using the technology of co-blending polysaccharides and the SPI to co-blend SPI and lipids, then add a variety of polysaccharides and form ternary co-blended films, to improve the physical and mechanical properties, appearance, and stability of co-blended SPI/lipid films and provide an experimental basis for the application of macromolecular materials in food preservation.

2. Materials and methods

2.1. Materials

The soy protein isolate (SPI) and aloe polysaccharide (APS) were obtained from Jiangnan University (Wuxi, China). The reagents used for film preparation and testing (lauric acid (La), glycerol, propyleneglycol alginate (PGA), pectin (PEC), carrageenan (CAR), magnesium nitrate, sodium hydroxide, calcium chloride anhydrous) were purchased from Fisher Sci. Ltd. (Shanghai, China).

2.2. Co-dried SPI/PS blended preparation

A solution of SPI/PS at ratio of 20:1 (w/w) was spray-dried using the following method. The SPI was dissolved in distilled water by stirring at 65 °C; the PS solution (PGA, or PEC, or CAR, or APS), prepared in distilled water at 60 °C, was added and the final solution was maintained at 65 °C. The concentration of the solution was adjusted to achieve a viscosity of less than 500 cps, and the pH was adjusted to 9.0 using 2 mol/L NaOH. Spray drying was performed using a BUCHI B-290 Mini Spray Dryer with an atomizer speed of 15,000 rpm, an inlet temperature of 200 °C and an outlet temperature of 95 °C.

2.3. SPI-based film preparation

Different groups of SPI-based films with different blends of La and PS were prepared. One group of films was prepared by adding La, and the other group was prepared with La and PS. The SPI:La ratio selected for the 2 groups of films was 10 parts of SPI to 1 part La. The SPI:PS ratio selected for the co-dried SPI/PGA films was 20 parts SPI to 1 part PS and this ratio was maintained throughout the study.

To produce the SPI-based film containing La, an aqueous solution of 50 g/L SPI (or a co-dried SPI/PGA blends) was prepared and heated in a 250 ml Erlenmeyer flask for 30 min in a 80 °C water bath to denature the proteins. The amount of La required was melted in the hot denatured protein solution, and each solution was homogenised using a high-shear probe mixer (Ultra-Turrax, Model T25, IKA-Works, Inc., Cincinnati, Ohio, USA) for 1 min at 10,000 rpm, followed by 3 min at 20,000 rpm. The homogenisation temperature was 80 °C. The emulsions were then cooled in an ice bath. Glycerol (0.3 g/g SPI) was added in the amount required to achieve the desired final film composition, and the film-forming solutions were de-gassed under vacuum using a vacuum pump (SHZ-D(III), Gongyi City Yuhua Instruments Co. Ltd., China).

Films were prepared by placing an amount of the degassed film-forming solution or emulsion that would provide 3 g of total solids on a smooth high-density polyethylene (HDPE) casting plate resting on a leveled granite surface. The films were dried for approximately 20 h at 53% RH and 25 °C. All 3 dried films could be peeled intact from the casting surface. The films for water vapour permeability (WVP) and mechanical testing were conditioned at 53 ± 1% RH and 25 ± 1 °C by placing them in a desiccator containing a saturated solution of $Mg(NO_3)_2 \cdot 6(H_2O)$ for 72 h or longer.

2.4. Film thickness measurement

The film thickness was measured using a digital micrometer (High-Accuracy Digimatic Digital Micrometer, USA). Film strips were placed between the jaws of the micrometer and the gap was reduced until the friction was minimal. The mean thickness (m) of the films were determined from the average of measurements at 10 locations.

2.5. Water vapour permeability measurement

The water vapour transmission rate (WVTR) of the film specimens was measured according to a modified ASTM E96 method (ASTM, 2002; Gennadios et al., 1994; Ou, Wang, Tang, Huang, & Jackson, 2005). Glass cups with diameter of 3 cm and depth of 4 cm were used. To maintain 0% RH in the cup headspace, 3 g of dried $CaCl_2$ was added to the cup, and then the film was sealed over the rim of the cup by applying molten paraffin. The cups were placed in hermetically sealed jars maintained at 20 °C and 100% RH. The RH was maintained by placing 1000 ml of water in the bottom of the jar. The cups were weighed every 12 h for 1 week. The amount of water that permeated the films was determined from the weight gain of the cups. The WVTR and water vapour permeability (WVP) were calculated using the following equation:

$$\mathrm{WVTR} = \Delta w/\Delta t \times A,\ \mathrm{WVP} = \mathrm{WVTR} \times L/\Delta p$$

where WVTR is expressed in g/h m^2; $\Delta w/\Delta t$ is the rate of water gain in g/h; A is the exposed area of the film in m^2; L is the mean thickness of the film specimens in m; and Δp is the difference between the partial water vapour pressure on the two sides of the film specimens in Pa. The water vapour pressure on the high-stream side of the film was 2.34 kPa (i.e., saturated water vapour pressure at 20 °C), while the low-stream side was assumed to be zero.

2.6. Mechanical properties measurement

Before testing their mechanical properties, film samples were equilibrated for 1 week at 25 °C at 53% RH. Two mechanical properties of the films, the tensile strength (TS) and the elongation at break (E%), were determined using a texture analyser (TA-XT2i, Stable Micro Systems, Surrey, UK). The film samples were cut into 10 mm wide and 800 mm long strips using a sharp razor blade. Ten samples of each film type were tested. The tensile properties of the