



Effects of fatty acids with different degree of unsaturation on properties of sweet potato starch-based films

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ABSTRACT

The effect of saturated and unsaturated fatty acids on sweet potato starch and sweet potato starch-based films was studied. Three fatty acids varying in degree of unsaturation were used in the preparation of sweet potato starch-based films; i.e. stearic acid (C18:0), oleic acid (C18:1) and linoleic acid (C18:2). The stearic acid is more strongly bound with amylose than oleic acid and linoleic acid. In differential scanning calorimetry thermograms, both of the sweet potato starch-saturated fatty acid and sweet potato starch-unsaturated fatty acid composites exhibited the melting peak of amylose-lipid complex. The amylose-linoleic acid complex peak was unapparent compared with stearic acid and oleic acid. X-ray diffraction showed that the scattering intensity of amylose-lipid complex decreased with increasing unsaturation. Scanning electronic microscope indicated that the surface of the films became smooth after addition of fatty acids. The sweet potato starch-saturated fatty acid composites films exhibited higher tensile strength, lower elongation at break and lower water vapor permeability than those of the sweet potato starch-unsaturated fatty acid composite films.

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1. Introduction

Over the past decades, packaging industry generates an increasing interest for biopolymer films in order to reduce the environmental impact of plastic waste mainly produced by its huge application area (Colak, Gouanve, Degraeve, Espuche, & Prochazka, 2015). According to previous studies, proteins (Galus & Kadzinska, 2016), and carbohydrates such as cellulose (Bedane, Eić, Farmahini-Farahani, & Xiao, 2015) and starches (Wu, Chen, Lv, Du, & Zhu, 2012) are widely used in the production of biodegradable films. Among these natural biopolymers, starch is one of the most promising candidates for preparing biodegradable films (Maizura, Fazilah, Norziah, & Karim, 2007).

Sweet potato is one of the most common crops and staple food in China, which has the highest production in the world (Shen, Wu, Chen, & Zhao, 2010). As a major source of carbohydrate in the human diet, sweet potato starch plays a very important role in supplying metabolic energy and nutrition for humans (Huang, Zhou, Jin, Xu, & Chen, 2015). Because of storage difficulties and

inefficient processing, up to 15% of sweet potatoes in China are discarded every year (Liu, 2007). The preparation of sweet potato starch-based film is a good way to reduce the waste. But the poor moisture barrier properties of sweet potato starch-based films hinder their extensive application in food packaging. They are sensitive to water and absorb water easily in a high-humidity environment due to the highly hydrophilic nature of starch (Fringant, Rinaudo, & Bardet, 1998).

To expand the application of sweet potato starch-based films, it is necessary to reduce their hygroscopicity. Fatty acids, which are known to exhibit good hydrophobic properties, have been incorporated into the polymer matrix to improve their moisture barrier properties (Zahedi, Ghanbarzadeh, & Sedaghat, 2010). Wong, Gastineau, Gregorski, Tillin, and Pavlath (1992) report that the addition of lauric acid into biopolymer films decreased their water vapor permeability values compared with those of the pure films. In previous researches, fatty acids have been incorporated in hydrophilic films for modulating the moisture barrier properties of starch-based films (Fakhouri, Fontes, Innocentini-Mei, & Collares-Queiroz, 2009; Wu et al., 2012). However, the effects of fatty acids with different degree of unsaturation on the properties of sweet potato starch and sweet potato starch-based films, to the best of our knowledge, have not been investigated, and some

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questions remain unclear concerning the effects of saturated and unsaturated fatty acids on the properties of starch and starch-based films. For instance, which kind of fatty acids (differing in their number of double bonds) has the strongest capacity to bind with amylose? Do saturated fatty acid and unsaturated fatty acid influence sweet potato starch and sweet potato starch-based films in the same way? Which kind of films has better moisture barrier properties (sweet potato starch-saturated fatty acid or sweet potato starch-unsaturated fatty acid composite films)? These questions need to be answered in the future for providing a useful insight into the bonding between fatty acids and amylose.

This paper aims to further the studies reported above and to investigate the effects of saturated fatty acid (stearic acid) and unsaturated fatty acid (oleic acid and linoleic acid) on the properties of sweet potato starch and sweet potato starch-based films.

2. Materials and methods

2.1. Materials

Sweet potato starch (SPS) was provided by Rushan Huamei Starch Products Co., Ltd. (Weihai, China). Glycerol and ethanol were obtained from Kaitong Chemical Reagent Co., Ltd. (Tianjin, China). Saturated fatty acid (SFA) and unsaturated fatty acid (USFA) were purchased from Yuanye Biotechnology Co., Ltd. (Shanghai, China). The SFA used was stearic acid (SA). The USFA used were oleic acid (OA) and linoleic acid (LOA).

2.2. Preparation of the SPS-fatty acid (FA) composites

The SA, OA and LOA (120 mg, 2%, w/w, dry starch base, dsb), dissolved in ethanol, were added to the starch slurry (6 g, 10%, w/w, dsb) before heating. The mixture was stirred (300 revolutions per minute, rpm) at 60 °C for 120 min with the Accura Te Strengthen Electronic Stirrer (Guohua Electrical equipment Co., Ltd., Changzhou, China).

The solvent was evaporated in a drying oven (Jinghong Laboratory Instrument Co., Ltd., Shanghai, China) at 50 °C. The dried samples were then ground into fine powder for further experiments. The SPS without FA addition was used as the control.

2.3. Preparation of the pastes for the SPS inclusion complexes

The SPS-FA composite of 2.5 g was dispersed in 25 ml of distilled water to obtain a smooth dispersion. The dispersion was heated from 50 °C to 95 °C for 30 min, and kept at 95 °C for 30 min. The sample was then cooled to 50 °C (1.5 °C/min) and kept at 50 °C for 5 min. The pastes were analyzed for complexing index (Kaur & Singh, 2000).

2.4. Complexing index (CI) of the samples

The CI of the SPS-FA composite, to represent the complexing degree, was measured by a spectrophotometric method as follows. The iodine solution was prepared by dissolving 2 g of potassium iodide and 1.3 g of I₂ in 50 ml of distilled water and allowing it to dissolve for about 2 h. Then the final volume was made to 100 ml using distilled water. The paste sample (5 g) was mixed with 25 ml of distilled water in a test tube. The tube was vortexed for 2 min and centrifuged for 15 min at 3000 rpm. The supernatant (500 µl) and distilled water were added to iodine solution (2 ml). The capped tube was inverted several times and the absorbance of the samples at 690 nm (A_s) was measured with a UV-Vis spectrophotometer (model UV-8000A, Shanghai Metash Instruments Co., Ltd.,

Shanghai, China). The absorbance of the SPS paste without the addition of fatty acids was used as a control (A₀). To avoid starch retrogradation, the tests were performed within 60 min. CI was calculated using the following equation (Kaur & Singh, 2000; Wu et al., 2012):

$$CI (\%) = (A_0 - A_s) \times 100 / A_0 \quad (1)$$

2.5. Differential scanning calorimetry (DSC)

An examination of the thermal properties of SPS-FA composites were carried out with a DSC 200PC (Netzsch Scientific Instruments, Selb, Germany). Calibration was done on the basis of pure indium, bismuth, tin, and zinc. Then, the samples (5 mg) were weighed in aluminium pans and hermetically sealed. The samples were scanned at a rate of 10 °C/min within a temperature range from 0 to 150 °C for 15 min. The DSC cell was flushed with liquid nitrogen at a flow rate of 20 ml/min to maintain a stable environment (Gao, Dong, Hou, & Zhang, 2012).

2.6. X-ray diffraction (XRD)

The XRD was determined with a D8 Advance X-ray diffractometer (Bruker-AXS, Karlsruhe, Germany). The X-ray diffractometer was operated at 40 kV and 40 mA with Cu K α radiation ($\lambda = 0.15406$ nm; where λ is the wavelength of the X-ray radiation used). Samples were scanned in the range of diffraction angle $2\theta = 5\text{--}40^\circ$ at a step of 0.02° and step time of 1 s. Relative crystallinity of the starch was calculated using the following equation:

$$\text{Relative crystallinity (\%)} = 100 A_c / (A_c + A_a) \quad (2)$$

where A_c is the crystalline area on the X-ray diffractogram, and A_a is the amorphous area (Chang, He, & Huang, 2013).

2.7. Preparation of films

The SPS-FA composites (containing 6 g of SPS and 120 mg of SA, OA or LOA) were dispersed into distilled water (200 ml), and 33% Glycerol (w/w, on the basis of SPS) was then added. The film-forming suspension was heated in a water bath at 90 °C for 90 min through continuous mixing at 350 rpm. The solution was homogenized with an IKA T18 basic Ultra-Turrax (Staufen, Germany) at 14,000 rpm for 4 min. The obtained solutions were filtered through the gauze. A film-forming suspension was poured on 120×240 mm² Teflon-coated glass plates. The SPS-based films were obtained through the evaporation of water in a drying oven at 40 °C. The films were obtained by means of peeling from the Teflon-coated glass plates. The control sample was also used to prepare films in the same way (Yan, Hou, Guo, & Dong, 2012).

All of the tested samples were equilibrated at 23 ± 2 °C and 53% relative humidity in a constant temperature and humidity chamber (Jinghong Experimental Equipment Co., Ltd., Shanghai, China) for at least 2 days before the test.

2.8. Scanning electron microscopy (SEM)

Microstructural analysis of the films was carried out using a Supra 55 (ZEISS, Jena, Germany) electron microscope at an accelerating voltage of 5 kV. All of the films were adhered to a conductive carbon tape, and a sputter coated with Au/Pd (Gao et al., 2012).

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