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The effects of ultrasonic/microwave assisted treatment on the water vapor barrier properties of soybean protein isolate-based oleic acid/stearic acid blend edible films

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ABSTRACT

Edible films were prepared using soy protein isolate (4g/100 g), oleic acid (0–2 g/100 g) and stearic acid (0–2 g/100 g). Effects of the ratio of oleic acid to stearic acid and ultrasonic/microwave assisted treatment on the water vapor permeability (WVP) and contact angle of the prepared films were evaluated. Changes in the ratios of oleic acid to stearic acid had significant effects on WVP and contact angle ($p < 0.05$). It was found that the prepared films (oleic acid:stearic acid = 2:3) had the lowest WVP value (0.1×10^{-12} g cm^{-1} s^{-1} Pa^{-1}) and highest contact angle value (135°), when the treatment temperature, time and power were 20 °C, 15 min, and 500 W respectively. Additionally, when OA and SA were added, the peak at 2920 cm^{-1} appeared, indicating a certain degree of interaction between the lipid and SPI.

1. Introduction

The application of edible films and coatings is an innovation in packaging technology aimed at improving the quality and shelf life of food products (Kowalczyk & Baraniak, 2011). Proteins, polysaccharides and lipids are the main components of edible films and coatings (Atarés, De Jesús, Talens, & Chiralt, 2010). Films made from proteins and polysaccharides are excellent barriers to oxygen, because of the tightly packed, ordered structure of their hydrogen-bonded network (Atarés, Pérez-Masiá, & Chiralt, 2011), and films made from lipids have good water vapor barrier properties (Yang & Paulson, 2000). Proteins are generally superior to polysaccharides in their ability to form films with enhanced mechanical and barrier properties (Guerrero, Stefani, Ruseckaite, & de la Caba, 2011), but a limiting factor in the application of protein-based edible films is their reduced barrier to water vapor permeability, because of the hydrophilic property of these macromolecules (Andreuccetti, Carvalho, Galicia-García, Martínez-Bustos, & Grosso, 2011). However, lipids can be added to proteins to improve their barrier water vapor permeability.

Soy protein isolate (SPI), is a protein with reproducible resource, good biocompatibility, biodegradability, processability, and film-forming capacity that has significant potential for use in the food industry, agriculture, bioscience, and biotechnology (Khan, Schutyser, Schroën, & Boom, 2012; Monedero et al., 2010; Song, Tang, Wang, & Wang, 2011). However, the water vapor permeability (WVP) of SPI film is high, which will cause the spoilage of packaged products. WVP values of edible films should be cautiously compared because of the difference in plasticizers, temperature, relative humidity gradient, etc. WVP depends on two factors: (I) film water affinity, water affinity could be attributed to hydrophilic of the film, which controls the partition coefficient of water between air and film; and (II) diffusion coefficient, a higher diffusion coefficient due to increased molecular mobility of plasticizers and polymer chains, thus the edible films often show an increase in WVP with temperature increased. There are two common ways to lower the WVP of edible films, (I) the addition of lipids and crossing-linking agents and (II) film processing (de la Caba et al., 2012; Fabra, Talens, Gavara, & Chiralt, 2012; Guerrero, Beatty, Kerry, & de la Caba, 2012; Keerati-u-rai, Wang, & Corredig, 2011; Yuan, Ren, Zhao, Luo, & Cu, 2012; Zhang, Ma, Guo, & Zhao, 2012). Fatty acids including stearic acid, palmitic acid, oleic acid and

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beeswax are currently used as hydrophobic additives in edible films formulations because of their highly regarded characteristics. It has been reported that the addition of stearic acid-palmitic acid mixtures could lower WVP of the films (de la Caba et al., 2012). Oleic acid, pure or mixed with beeswax, had a plasticizing effect on the films and also reduced WVP of the films (Maria, Fabra, Talens & Chiralt, 2009). The moisture sensitivity of SPI-based films was reduced by incorporation of stearic acid without affecting its biodegradability (Lodha & Netravali, 2005). Films with essential oils could be used to slow down the lipid oxidation process in products high in content with unsaturated fatty acids (Atarés et al., 2010; Liu, Zeng, Deng, Yu, & Yamasaki, 2011; Yang et al., 2000). However, there have been no reports on the addition of oleic acid-stearic acid mixtures into SPI.

Physical, chemical and enzymatic modifications have also been carried out to improve the functional properties of soy proteins. It has been reported that high-pressure homogenization could enhance the interactions between protein molecules and the resulting functional properties (Yuan et al., 2012). More recently, novel methods of modifying the properties of SPI have emerged that use less solvent, are easily automated and high-throughput have been described, including high-pressure homogenization (Zhang et al., 2012). Ultrasonic and microwave treatment has the potential to modify the properties of SPI films, the excellent advantages of the ultrasonic and microwave treatment when compared with the conventional modification methods may derive from the synergistic effect of coupling two energetic radiations (Cheng, Wan, Li, & Qi, 2011). Despite the fact that ultrasonic and microwave treatment are widely studied in extraction and synthesis (Cheng et al., 2011; Sadhana, Praveena, & Murthy, 2011; Saha, Eskicioglu, & Marin, 2011; Yao, Zhang, & He, 2011), its effect on the properties of SPI-based oleic acid/stearic acid blend edible films (SOS) has not been reported.

The objective of this study was to produce SOS films and study the effect the ratio of oleic acid to stearic acid. This characterization included water vapor barrier ability, optical properties, and contact angle on a hydrophobic surface. The films with the lowest WVP value were modified using the ultrasonic/microwave assisted treatment under different treatment time and power. Besides, the microstructures of the films were explored to provide deeper insight on the mechanism of WVP changes.

2. Materials and methods

2.1. Materials

Soy protein isolate (SPI, 90%) was obtained from Gushen Biotechnology Group Ltd. (Shandong, China). Oleic acid (OA) was purchased from Xilong Chemical Group Ltd. (Shantou, China). Stearic acid (SA) was from Guangfu Fine Chemical Research Institute. (Tianjin, China). Distilled water was used for all sample preparations. All other chemicals were analytical grade.

2.2. Film preparation

Soy protein isolate (SPI) was dispersion in distilled water at 4% (w/w), the SPI solution pH = 7, with magnetic stirring, and denatured by heating (80 °C, 35 min). After complete dispersing, glycerol was added at a protein:glycerol ratio of 1:0.3 (w/w) and the mixture was cooled to room temperature. Subsequently, carboxymethyl cellulose (CMC) was added to improve the films strength without significant depressing effect on flexibility, at a protein:CMC ratio of 1:0.1 (w/w). The lipids based on oleic acid (OA) and stearic acid (SA) mixed at different OA: SA ratios (5:0, 4:1, 3:2, 2.5:2.5, 2:3, 1:4, 0:5), were incorporated into the mixture. The ratio of SPI to lipids was 2:1 (w/w). The detailed compositions were listed in Table 1. The mixture was degassed at room temperature using a vacuum pump for 20 min and casted on square plastic dishes (20 × 20 cm^2). The dishes were placed on leveled surfaces to obtain films of homogenous thickness. A volume of 100 mL of film solutions were dried in a drying chamber (PH070A, Shanghai Hengkexue Instruments Co., Ltd., Shanghai, China) at 25 °C for 12 h. The dried films were peeled from the plates and equilibrated at 25 ± 1 °C inside desiccators (50% RH) for 48 h using saturated salt solutions of $MgCl_2$ or $Mg(NO_3)_2$ before testing.

Table 1
Films based on different ratios of SPI to OA and SA content.

Sample	SPI (g)	OA/SA (g)	CMC (g)	Glycerol (g)	Thickness (μm)
SPI (Control)	3	(0:0) 0	0.3	0.9	209 ± 1^{e}
SOS_1	3	(5:0) 1.5	0.3	0.9	267 ± 1^{d}
SOS_2	3	(4:1) 1.5	0.3	0.9	276 ± 1^{d}
SOS_3	3	(3:2) 1.5	0.3	0.9	287 ± 2^{c}
SOS_4	3	(2.5:2.5) 1.5	0.3	0.9	296 ± 2^{bc}
SOS_5	3	(2:3) 1.5	0.3	0.9	311 ± 2^{ab}
SOS_6	3	(1:4) 1.5	0.3	0.9	314 ± 1^{ab}
SOS_7	3	(0:5) 1.5	0.3	0.9	320 ± 1^{a}

a, b, c, d, eFor each measurement, the data marked by different letters in a column indicate significant difference ($p < 0.05$).

2.3. Ultrasonic/microwave assisted treatment

The prepared films (different ratios of OA to SA) are assessed by determining water vapor barrier property. The films which have the best water vapor barrier property will be modified using a microwave and ultrasonic combination reaction system (SL-SM50, Nanjing Shunliu Instruments Co., Ltd, Nanjing, China), at 20 °C, to avoid oleic acid oxidation, and the detailed modification conditions were listed in Table 2.

2.4. Thickness measurements

Film thickness was measured using a manual digital micrometer (Mitutoyo Manufacturing, Tokyo, Japan) with an accuracy of 0.001 mm. Measurements were made in at least ten random locations for each film.

2.5. Opacity measurements

The area under the absorbance curve from 400 to 800 nm was taken as the opacity (O) of the films (Cho, Rhee & Wiss, 2004). Film

Table 2
Ultrasonic/microwave assisted modification conditions.

Sample	Temperature (°C)	Time (min)	Power (W)	Thickness (μm)
SOS_5 (Control)				311 ± 2^{a}
SOS_{053}	20	5	300	321 ± 9^{a}
SOS_{055}	20	5	500	320 ± 1^{a}
SOS_{058}	20	5	800	319 ± 2^{a}
SOS_{153}	20	15	300	321 ± 6^{a}
SOS_{155}	20	15	500	320 ± 14^{a}
SOS_{158}	20	15	800	321 ± 1^{a}
SOS_{303}	20	30	300	321 ± 10^{a}
SOS_{305}	20	30	500	319 ± 8^{a}
SOS_{308}	20	30	800	320 ± 13^{a}

The front number of the samples, 05, 15 and 30, represent the microwave and ultrasonic combination treatment time (5 min, 15 min and 30 min), and the last number, 3, 5, 8 represent the microwave and ultrasonic combination treatment power (300 W, 500 W and 800 W), respectively. For each measurement, the data marked by different letters in a column indicate significant difference ($p < 0.05$).