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Emulsifying and physicochemical properties of soy hull hemicelluloses-soy protein isolate conjugates

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ABSTRACT

Protein-polysaccharide conjugates could potentially combine the excellent emulsification properties of the protein with the stabilizing effect of the polysaccharide. The investigation aimed to prepare soy hull hemicelluloses-soy protein isolate (SHH-SPI) conjugates by Maillard reaction in a controlled dry state condition and assess the suitability of the conjugates in stabilizing oil-in-water (O/W) emulsion. Results indicated that Maillard reactions occurred between amino groups and carbonyl, resulting in consumption of some functional groups and the appearance of new groups in the conjugates. The conjugates of SHH-SPI obtained at the SPI content of 30% and 40% exhibited substantially improved emulsification capacity in maintaining the physical stability of O/W emulsions for a prolong storage period at heat treatment, compared with SHH and SPI alone. Overall, these results demonstrated that SHH and SPI could generate novel emulsions with improved physical and chemical stability by Mallsird reaction for application in food and pharmaceutical products.

1. Introduction

Many proteins are highly effective emulsifiers because they contain both charged hydrophilic regions and hydrophobic regions, which lower the surface tension and interact at the emulsion interface (Kasran, Cui, & Goff, 2013). Soy protein is an abundant byproduct of the soybean oil industry, and is commonly used as a nutritional additive in food (Su et al., 2012). Various methods based on enzymatic, chemical, physical, and genetic modifications were investigated to improve the functional properties of proteins (Seo, Karboune, Yaylayan, & L'Hocine, 2012). Among the several methods, a great deal of attention has been focused on the covalent interaction protein/polysaccharide via the Maillard reaction (Corzo-Martínez, Sánchez, Moreno, Patino, & Villamiel, 2012). Protein-polysaccharide conjugates could potentially combine the excellent emulsification properties of the protein with the stabilizing effect of the polysaccharide (Shepherd, Robertson, & Ofman, 2000). The main advantages of covalent protein/polysaccharide conjugates as compared with non-covalent complexes are the retention of molecular integrity and solubility over a wide range of experimental conditions (Dickinson & Galazka, 1991). In addition, the covalent conjugates have been shown to be very stable with the changes of temperature, ionic strength, and pH (Kasran, Cui, & Goff, 2013). Soy hulls, the major byproducts obtained in the soybean processing industry, and the insoluble carbohydrate fraction contains 50% hemicelluloses, 30% pectin, and 20% cellulose (Liu et al., 2013). Hemicelluloses have a very wide variety of applications and can be converted into various biopolymers by modification (Peng, Peng, Xu, & Sun, 2012). Therefore, the soy hulls were potentially inexpensive commercial sources of hemicelluloses. However, to best of our knowledge, there is little work carried out on forming SHH-SPI conjugates to improve the emulsifying properties of soy protein isolate by Maillard reaction.

Maillard reaction is a reaction between the primary amine of proteins and the reducing end of carbohydrates, which generally regarded as an efficient and safe method to improve functional properties of proteins, such as emulsifying properties, heat stability, and antioxidant activity (Guo & Xiong, 2013; Jiménez-Castaño, Villamiel, & López-Fandiño, 2007; Sun, Hayakawa, Puangmanee, & Izumori, 2006). During the reaction, the conjugates of the carbohydrate and protein occur spontaneously under heating conditions without the utilization of toxic chemical products (Chevalier, Chobert, Dalgalarrondo, & Haertlé, 2001). In addition, it is well known that Maillard reaction carried out under dry state and well controlled conditions (such as reaction temperature, rela-

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tive humidity, and reaction time), which is an adequate method to improve functionality of proteins without important structural changes (Corzo-Martínez et al., 2012; Oliver, 2011).

Overall, the objective of this investigation was to assess the suitability of soy hull hemicelluloses-soy protein isolate (SHH-SPI) conjugate prepared by controlled dry heating of SPI and SHH mixtures in stabilizing O/W emulsion. The effect of SPI and SHH weight ratios before conjugation on the emulsion stability were investigated by droplet size analysis and visual observation of these stabilizing O/W emulsions. Further, the conjugations were characterized by FT-IR, TGA, amino acid analysis, and color analysis to help understand the emulsification properties of the complexes from the structural perspective.

2. Materials and methods

2.1. Materials

Soy hulls were obtained from Henan Sunshine Oils and Fats Group CO., Ltd. (Xingyang, China). The soy hulls were firstly ground by using a high-speed rotary cutting and then sieved though 40 mesh. The powder was dewaxed with toluene/ethanol (2:1, v/v) in a Soxhlet for 6 h. The dewaxed sample was dried at 60 °C for 24 h and kept in desiccators at room temperature before used. Soy protein isolate (SPI) was purchased from Beijing Aoboxing Bio-Tech CO., Ltd. (Beijing, China). The protein, water, and ash contents of the SPI sample were 85%, 7%, and 3.2%, respectively. All chemicals and solvents used were analytical grade and used without further purification. Deionized water was used throughout.

2.2. Isolation of soy hull hemicelluloses

Soy hull hemicelluloses were extracted from the soy hulls powder by hydrothermal treatment as described previously (Liu, Wang, & Liu, 2016). Briefly, a pressure glass reactor (volume 100 ml) was loaded with soy hulls and water with a solid to liquid ratio of 1:10. Agitation was set at 500 rpm and kept constant for all experiments. The reactor was heated up to the setting temperature by a magnetic heating stirrer (IKA, Germany) at a heating rate of approximately 3 °C/min, and the temperature was maintained constant at the setting temperature for the desired holding time. After the extraction was complete, the reactor was cooled down to room temperature by air. When the reactor was opened, the solid and liquid mixture was removed for separation. The mixtures were separated by filtration though filter paper under vacuum, and 200 ml of deionized water was used for washing the solid products. The filtrate was concentrated to approximately 30 ml on a rotary evaporator under reduced pressure at 45 °C. The water-soluble fraction was then recovered by precipitation of the concentrated water extracts in 3 vols of 95% ethanol. The precipitates formed were recovered by filtration, washed with acidified 70% ethanol, and obtained soy hull hemicelluloses. The soy hull hemicelluloses were stored in desiccators at room temperature.

2.3. Preparation of conjugates

The SHH-SPI conjugates were prepared by the method of described previously (Kasran, Cui, & Goff, 2013) with some modifications. Briefly, soy protein isolate (10%, w/w) and soy hull hemicelluloses (10%, w/w) were dispersed in water with stirring for 4 h at room temperature, respectively, followed by pH adjustment to 7.0 and storage at 4 °C overnight. The SPI and SHH solutions were then mixed at SPI:SHH ratios of 1:9 (SPI content of 10%), 2:8 (SPI content of 20%), 3:7 (SPI content of 30%), 4:6 (SPI content of 40%), 5:5 (SPI content of 50%), and 6:4 (SPI content of 60%), respectively (g:g, dry weight basis). The mixed solutions were freeze dried and milled to make a powder (60 m), to yield SPI and SHH mixture. A desiccators containing saturated NaCl was placed in the oven at 60 °C for 30 min to achieve an equilibrium temperature and relative humidity. And then the SPI and SHH mixture was placed in the desiccators in the presence of saturated NaCl, heated at 60 °C for seven days, to induce Maillard reaction. The reaction mixture of SHH and SPI was collected and defined as SHH-SPI conjugate. The conjugates were sealed and stored at 4 °C until further use.

2.4. Emulsion preparation

For the preparation of O/W emulsions, samples of SPI, SHH, or SHH-SPI conjugate (0.5%, w/w) were dissolved in 1 mol/l sodium dihydrogen phosphate solution with stirring at 500 rpm for 3 h at room temperature. And then 10 ml of soy oil was added gradually to 40 ml 0.5% (g/l, w/v) amount of samples in 1 mol/l sodium dihydrogen phosphate solution and homogenized for 2 min at 10000 rpm by using a high-shear homogenizer (FA 25 model, Fluko Equipment Co., Ltd., Shanghai, China) at room temperature.

2.5. Droplet size measurement

The droplet size distribution and volume-average droplet size of various O/W emulsions were determined by a laser light scattering technique, using a Zetasizer Nano (Malvern Instruments Ltd, Worcestershire, UK). The process underlying the operation of this instrument was detailed previously (Xu, Wang, Jiang, Yuan, & Gao, 2012). Distilled water was used as the dispersant and the relative refractive index of the emulsion was 1.59, i.e. the ratio of the refractive index of soy oil (1.496) to that of the aqueous medium (1.33). Emulsions were diluted to a final oil droplet concentration of 0.005% wt% with buffer solution (pH 7.0) and filtered prior to each measurement to minimize multiple scattering effects. The measurements for each emulsion were performed on at least two separately preparedly prepared samples, with each sample measured repeated at least three times. The results were described as cumulants mean diameter (size, nm) for droplet size, polydispersity index (PdI) for droplet size distribution.

2.6. Optical microscopy

The microscopic observations were performed using optical microscopy (BT-1600, Dandong Bettersize Instruments Ltd., China) to compare the microstructure difference among SHH-SPI conjugates stabilized emulsions. A drop of emulsion sample was placed on a microscope slide, covered with a cover slip. Images were made immediately after preparation of emulsion.

2.7. Color analysis

The method of color analysis was the same as those used by previously (Díaz, Candia, & Cobos, 2016). Briefly, these samples were conducted at 25 °C using a Color Difference Meter (INESA, Shanghai, China) in the reflectance mode. Color was expressed in L^*, a^* and b^* values. The L^* value is a measurement of lightness and varies from 0 (blank) to 100 (white); the a^* value varies from −100 (green) to +100 (red); and the b^* value varies from −100 (blue) to +100 (yellow). Three measurements were performed and results were averaged. In addition, total color difference ($\triangle E$) was calculated using the following equation:

$$\Delta \mathrm{E} = \sqrt{(L^* - Lo^*)^2 + (a^* - ao^*)^2 + (b^* - bo^*)^2}$$

Where L_o^*, a_o^*, and b_o^* are the values for the SHH and SPI.