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Modified SPI improves the emulsion properties and oxidative stability of fish oil microcapsules

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ABSTRACT

Fish oil was encapsulated using the Maillard Reaction Products (HSPI-Md) of hydrolyzed soy protein isolate (HSPI) and maltodextrin (SPI) (DE 8-10) by freeze-drying. Effects of enzymatic hydrolysis and glycosylation of protein on the physicochemical properties of the emulsion and the oxidative stability of the achieved capsules were investigated. Smaller droplet size (194.1–263.2 nm) and polydispersity index (PDI) (0.064–0.167) were achieved in the fish oil emulsions coated by HSPI-Md conjugates. Analysis on the surface and interfacial tension showed that HSPI-Md conjugates had excellent amphiphilic property, which was further confirmed by the excellent emulsion stability during the storage period. The HSPI-Md conjugates based microcapsules were found to have higher encapsulation efficiency (EE), which increased from 63.23% to 87.24% with the increase of reaction time. Furthermore, upon storage, the contents of lipid oxidation products (hydroperoxide and propanal) were found apparently lower (3.65 mmol/kg and 2216.01, respectively for HSPI-Md 270 min), comparing with those stabilized by the SPI hydrolysates (9.14 mmol/kg and 3314.70) or native SPI (7.30 mmol/kg and 2957.92). Additionally, the microcapsule coated by HSPI-Md conjugates (270 min) exhibited favorable thermal stability as well as porous and uniform surface structure as evidenced by the thermal analysis and scanning electron microscope (SEM) micrographs, respectively. Therefore, the modified SPI products in this work can be used as potential wall materials for the microencapsulation of bioactive ingredients.

1. Introduction

Fish oil has a considerable amount of long chain polyunsaturated fatty acids of the omega-3 (n-3) family, which make it an invaluable candidate in food fortification (Drusch, Serfert, Scampicchio, Schmidt-Hansberg, & Schwarz, 2007). However, the main limitation of fish oil application in supplement foods is their low solubility in most food systems and excessive susceptibility to oxidation (Kagami et al., 2003). Especially, hydroperoxides, the primary product of lipid oxidation have been considered to be toxic (Oarada, 1990). Preventing n-3 fatty acids from oxidation is indispensable for allowing them to fulfill their original physiological functions. Microencapsulation is a promising technique to protect unsaturated fatty acids against oxidation, thus increasing their shelf life (Baik et al., 2004; Drusch, Serfert, Van Den Heuvel, & Schwarz, 2006; Heinzelmann, Franke, Velasco, & Márquez-Ruiz, 2000; Kagami et al., 2003). According to Jafari, Assadpoor, Bhandari, and He (2008), the properties of fish oil microcapsules including encapsulation efficiency, oxidation stability, size, shape, density, and moisture content are greatly affected by the composition of wall materials, the properties of core (concentration, volatility) and the characteristics of the emulsion (total solids, viscosity, droplet size) (Jafari et al., 2008). Therefore, the selection of suitable wall materials and appropriate preparing conditions of emulsion are essential for the formation of microcapsules with good properties.

The selection of wall materials is mainly based on their interfacial functionality. The water solubility and amphiphilic properties, the ability to self-associate and interact with variety of substances, as well as the high molecular chain flexibility of modified proteins are proved to be conducive to emulsification (Nesterenko, Alric,

Abbreviations: SPI, soybean protein isolate; Md, maltodextrin; DE, dextrose equivalent; PDI, polydispersity index; SEM, scanning electron microscope; MEE, microencapsulation efficiency; H_0, surface hydrophobicity; DH, degree of hydrolysis; POV, Peroxide value; GC, gas chromatograph; FID, flame ionization detector; TG, thermogravimetric curves; DTG, derivative thermogravimetric curves; DLS, dynamic light scattering.

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Silvestre, & Durrieu, 2012; Zhang, Tan, Abbas, et al., 2014). Kagami et al. (2003) reported that incorporating a highly branched maltodextrin into sodium caseinate matrix of wall improved the oxidative stability of encapsulated fish oil (Kagami et al., 2003), whereas, they cannot be individually used as wall materials due to poor emulsification properties. As there is pressing need for multifunctional materials, different modification techniques were developed to enhance and diversify the protein functionalities, in order to make them more appropriate to current microencapsulation techniques. It was demonstrated that limited enzymatic hydrolysis of proteins was also a powerful tool in the modification of functional properties in food systems, especially emulsifying characteristics, solubility, and surface hydrophobicity (H_0) due to the stretched protein chains (Amarowicz, 2010; Zhao et al., 2012). Nesterenko et al. (2012) reported that, although limited enzymatic hydrolysis of SPI led to fine emulsion, lower encapsulation efficiency was inescapable as compared with the combined modification of acylation and hydrolysis (Nesterenko et al., 2012). This is mainly due to the fact that the insufficient chain length of hydrolyzed proteins can not produce a structural matrix strong enough for α-tocopherol encapsulation. Moreover, Augustin research group confirmed that Maillard reaction products greatly improved the encapsulation efficiency and oxidative stability (Augustin, Sanguansri, & Bode, 2006; Chung, Sanguansri, & Augustin, 2008; Kagami et al., 2003; Augustin, Sanguansri, Margetts, & Young, 2001). It was believed that the improvement in oxygen barrier properties was due to increasing molecular weight of the protein source. Drusch et al. (2009) reported that the Maillard reaction in aqueous solution could lead to an increase in redox active compounds of the caseinate–glucose syrup, thus increasing the oxidative stability of encapsulated fish oil (Drusch et al., 2009).

Recently, the combined modification of controlled enzyme hydrolysis and protein-polysaccharide conjugation on proteins has attracted considerable attention of various researchers. The Maillard reaction products (MRPs) of rice protein hydrolysates (DH 5%) and dextran showed great improvement in the emulsifying properties and solubility (Li et al., 2013). Our research indicated that the conjugates of SPI hydrolysates and maltodextrin have excellent surfactant properties as well as antioxidant properties (Zhang, Tan, Zhang, et al., 2014). We assume that it could be a useful approach for preparing effective encapsulating materials via protein-polysaccharide conjugation and controlled enzyme hydrolysis together.

However, few studies had focused on the application of these combined modified proteins as wall materials for microencapsulation, especially for fish oil. Based on these scientific findings, current research was conducted to investigate the effect of combined modifications of SPI on the emulsion properties as well as the oxidative stability of microencapsulated fish oil. The Maillard reaction products were prepared with SPI hydrolysates and maltodextrin (DE 8–10) under wet reaction conditions. It was expected to get further insights into the structural modifications of wall materials and its influence on the encapsulation properties, thus, serving as a reference for the development of new delivery systems for bioactive compounds in future.

2. Materials and methods

2.1. Materials

The defatted soybean meal was obtained from Anyang Mantianxue Food Manufacturing Company (Henan, China). The maltodextrin (Md) with DE values of 8–10, was obtained from Baolingbao Biology company (Shangdong, China). Neutrase enzyme was obtained from Novozymes (Jiangsu, China). The fish oil contained approximately 70% EPA/DHA (20/50). All other chemicals used in this study were of analytical grade.

2.2. Preparation of the soy protein isolate (SPI)

SPI was prepared according to the method of Petruccelli and Anon (Petruccelli & Anon, 1995). The defatted soybean meal powder was suspended in 15-fold water and adjusted to pH 7 with 2 N NaOH. After stirring for 1 h, the suspension was centrifuged at 8000 g for 30 min and the supernatant was subjected to isoelectric precipitation by adjusting pH to 4.5 with 2 N HCl. The protein precipitate, which was recovered by centrifuging (8000 g, 30 min), was re-suspended in water and adjusted to pH 7 with 2 N NaOH. After removing small amount of insoluble substances by centrifuging at 8000 g for 30 min, the protein solution was freeze dried and ground to yield SPI powder. All procedures were carried out at room temperature. Crude protein content of SPI determined by Kjeldhal method was 96.7% (w/w) (N × 6.25).

2.3. Preparation of the Maillard reaction products after hydrolysis

The 5% (w/v) aqueous solution of SPI was cooled down to 54 °C (pH 7.0) after the preheating treatment (80 °C for 10 min), followed by enzymatic hydrolysis with Neutrase (enzyme/substance (E/S) = 0.3%) for 25 min to DH 2.24% through pH-stat method (Adler-Nissen, 1986). Afterward, the hydrolysates was incubated with maltodextrin at the HSPI/maltodextrin ratio of 6/1 (w/w) at 80 °C, pH 7.0 for 120, 180, 240, 270, and 300 min. These samples were lyophilized and referred as HSPI-Md conjugates.

2.4. Emulsion preparation

The modified products of SPI were initially dispersed in warm (70 °C) distilled water. The pH of the resulting solution was adjusted to 7.0 with 1 M NaOH. The oil phase was heated to 70 °C in a water bath prior to dispersion into the aqueous phase using a homogenizer (ULTRA-TURRAX T-25, IKA, Staufen, Germany) at 10,000 rpm for 2 min. The pre-emulsion was subjected to two-stage homogenization (35 + 10 MPa) using a high pressure homogenizer (NS1001 L2K, An S Co. Ltd., Parma, Italy).

2.5. Particle size measurements

The particle size distribution of the emulsion droplets was measured by using a Malvern Mastersizer 2000 (Malvern Instruments Ltd., Malvern, England). The emulsion was diluted with distilled water. A relative refractive index $\eta_{oil}/\eta_{water} = 1.095$ ($\eta_{oil} = 1.465$ and $\eta_{water} = 1.330$) was used for the calculation of particle size distribution, assuming that all droplets were spherical in shape. A polydisperse model was used to analyze the data, and the intensity of scattered light was taken as an indication of particle size.

2.6. Atomic force microscopy (AFM)

AFM was employed to confirm the size measurement results and determine the shape and surface morphology of the microcapsules. It was performed with Bruker Dimension Icon (Bruker AXS, Germany) AFM in a ScanAsyst mode to record the images of HSPI-Md (270 min) conjugates, HSPI and SPI microcapsules at room temperature by using a silicon tip (TESP, Bruker, nom. freq. 320 kHz, nom. spring constant of 42 N/m). The emulsion samples were diluted with water (1:4000). Diluted samples, 1 μL each, were placed on the clean mica surface and air dried overnight at ambient temperature. The images was obtained at a fixed scan rate