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Comparative study of encapsulation of vitamins with native and modified soy protein

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ABSTRACT

Microencapsulation of hydrophobic (α-tocopherol) and hydrophilic (ascorbic acid) vitamins by native (non-modified) and modified soy protein isolate (SPI) was carried out using a spray-drying technique. Proteins' functional properties were modified by acylation and cationization reactions in aqueous alkaline media. The results obtained demonstrated that SPI modification resulted in decreased emulsion droplet size and viscosity. All preparations with ascorbic acid (AA) had lower viscosity and microparticle size than those with α-tocopherol (T). Moreover, grafting of fatty acid chains to SPI by acylation improved its amphiphilic character and affinity with hydrophobic substances. Thus, the microencapsulation efficiency of T was increased from 79.7% to 94.8% and the microencapsulation efficiency of AA was reduced from 91.8% to 57.3% compared to native SPI. Conversely, attachment of quaternary ammonium cationic groups to proteinic chains by cationization, increased SPI solubility and favored the AA microencapsulation. This study illustrated that an appropriate modification of SPI can improve the microencapsulation efficiency of suitable active cores.

1. Introduction

Over the past decades, environmental requirements have become of great importance. In order to replace synthetic polymers and animal derived products, there is an increasing interest in the industrial use of renewable resources and development of naturally occurring materials for new applications. Natural polymers such as vegetable proteins have attracted considerable research activities because of their availability, biodegradability, renewable character and various interesting functional properties. Among them, proteins extracted from vegetable seeds (soybean, pea, barley, wheat, rice, oat, sunflower) have been reported as having good emulsifying and foaming capacities, water solubility, amphiphilic and film-forming properties (Nunes, Batista, Raymundo, Alves, & Sousa, 2003).

Due to their good physico-chemical properties, vegetable proteins represent a highly suitable wall-forming material for microencapsulation of active components to use in the food industry, pharmaceutics and cosmetics (Nesterenko, Alric, Silvestre, & Durrieu, 2013). Microencapsulation allows the isolation of the active core substance from the surrounding environment within a wall or matrix material. This technique offers benefits for protection of sensitive compounds, controlled release of the core agent, masking of unpleasant taste and odor of the substances or transformation of liquid core into solid powder. Different processes could be used to produce microparticles: spray-drying, spray-cooling/chilling, supercritical fluid expansion, fluidized bed, gelation, solvent evaporation, coacervation and extrusion (Augustin & Hemar, 2009; Dubey, Shami, & Bhasker, 2009; Gouin, 2004).

Spray-drying consists of the conversion of a liquid preparation (containing wall and core material) into a solid powder of microparticles using a stream of heated air. This technology, widely used in industry, is commonly employed for microencapsulation of various active substances with a vegetable protein matrix. Among vegetable proteins, soy proteins, pea proteins, wheat proteins and barley proteins had already demonstrated their effectiveness as carrier materials in microencapsulation by spray-drying (Nesterenko, Alric, Silvestre, et al., 2013).

Soy proteins represent an important component of soy bean seeds (35–40%). Two fractions are mainly present in extracted soy proteins: glycinin (11S globulin) and conglycinin (7S globulin). Soy protein isolate (SPI) showed interesting physico-chemical properties in particular gelling, emulsifying, fat-absorbing and water binding (Caillard, Remondetto, & Subirade, 2009; Hua, Cui, Wang, Mine, & Poysa, 2005; Nunes et al., 2003). The use of SPI as wall

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material in microencapsulation by spray-drying had been reported by various authors. This natural polymer showed a high efficiency for coating different active substances: orange oil (Kim, Morr, & Schenz, 1996), fish oil (Augustin, Sanguansri, & Bode, 2006), stearin/palm oil (Rusli, Sanguansri, & Augustin, 2006), phospholipid (Yu, Wang, Yao, & Liu, 2007), flavors (Charve & Reineccius, 2009), casein hydrolysate (Favaro-Trindade, Santana, Monterrey-Quintero, Trindade, & Netto, 2010; Ortiz, Mauri, Monterrey-Quintero, & Trindade, 2009), paprika oleoresin (Rascon, Beristain, Garcie, & Salgado, 2011) and soy oil (Tang & Li, 2013).

It is widely accepted that the antioxidant properties of α-tocopherol (vitamin E) and ascorbic acid (vitamin C) are responsible in part for their biological activity (Packer, Slater, & Willson, 1979). Nevertheless, environmental factors, such as oxygen, temperature, moisture and UV affect the stability of these compounds and involve their deterioration. Microencapsulation could be an efficient method for the protection and stabilization of α-tocopherol (T) and ascorbic acid (AA). However, the nature of the wall matrix particularly affects the degree of protection of the active core, the microparticles' stability and the retention efficiency.

Modifiable character is one of the important advantages of proteins. Modification of proteinic chains leads to changes in the properties and behavior of this natural polymer and diversification of protein functionalities. In microencapsulation, functionalization of proteinic chains makes it possible to obtain microparticles with new properties, different from those obtained with other wall materials.

Grafting of fatty acid chains to proteins by acylation is well known in order to enhance their hydrophobicity, surface-active functionality and emulsifying capacity (Matemu, Kayahara, Murasawa, Katayama, & Nakamura, 2011; Wong, Nakamura, & Kitts, 2006). In fact, the incorporation of hydrocarbon chains (hydrophobic part) into the protein macromolecules (hydrophilic part) allows the creation of amphiphilic structures with improved surface activity (Rondel, Alric, Mouloungui, Blanco, & Silvestre, 2009). On the other hand, the introduction of quaternary ammonium groups to polysaccharides (Channasanon, Graisuwan, Kiatkamjornwong, & Hoven, 2007; Wang et al., 2012) or to animal derived proteins (Kiick-Fischer & Tirrell, 1998; Zohuriaan-Mehr, Pourjavadi, Salimi, & Kurdtabar, 2009) by cationization is used to enhance their solubility, antibacterial properties as well as their hydrophilic properties (water absorption and swelling capacity). Nevertheless, there is no data in the literature dealing with cationization of vegetable proteins. Both acylation and cationization reactions could be suggested as an effective way to obtain SPI with defined characteristics.

Therefore, the objective of this work was to study the influence of SPI modification by acylation and cationization, on the microencapsulation of hydrophobic (T) and hydrophilic (AA) vitamins by the spray-drying technique. In the context of "green" chemistry (Gałuszkaa, Migaszewskia, & Namieśnik, 2013), modification reactions were carried out without any use of organic solvents and chemical catalysts. The effect of SPI modifications on both solution/emulsion and microparticle properties was also investigated.

2. Materials and methods

2.1. Materials

Soy protein isolate (SPI), 90% pure, was purchased from Lustrel Laboratoires SAS (Saint Jean de Vedas, France). The term 'native SPI' was used in this study for all samples prepared with non-modified commercial soy protein isolate. All other chemicals were of analytical grade. α-Tocopherol, L-ascorbic acid, sodium hydroxide, dodecanoyl chloride, glycidyltrimethylammonium chloride, cyclohexane (HPLC grade), iodine and sodium thiosulfate were purchased from Sigma (Saint-Quentin Fallavier, France).

2.2. SPI modifications

The acylation reaction was carried out on SPI using dodecanoyl chloride (DDC) following the Schotten–Baumann reaction as described previously (Nesterenko, Alric, Silvestre, & Durrieu, 2012). The molar ratio DDC/NH_2 of protein used for the reaction was 0.5/1 and the sample obtained was named SPI-A.

The SPI cationization reaction was carried out in aqueous solution (5% w/w) at 40 °C or 70 °C using glycidyltrimethylammonium chloride (GTMAC). When the SPI solution reached reaction temperature, pH was adjusted to 10.0 with 4 M NaOH and GTMAC was added (molar ratios GTMAC/NH_2 were 1, 2 or 4). The pH of the solution was maintained at 10.0 during the 1 h reaction period. The reaction was ended by adjusting the pH of the solution to 7.0 using 4 M HCl. The mixture of cationized SPI was cooled, freeze-dried at 20 Pa (Cryo-Rivoire equipment, Cryonext, Saint Gely du Fesc, France) and stored at 4 °C. Samples obtained were named SPI-C. The degree of cationization (DC) was evaluated using the o-phtaldialdehyde method (OPA) (Church, Swaisgood, Porter, & Catignani, 1983; Goodno, Swaisgood, & Catignani, 1981) and defined as follows:

$$\mathrm{DC}(\%) = \frac{(n_0 - n_\mathrm{m})}{n_0} \times 100 \quad (1)$$

where n_0 is the molar quantity of amino groups per gram of native SPI, and n_m the molar quantity of amino groups per gram of cationized SPI.

2.3. SPI solubility profiles

Native SPI solubility was compared to the cationized sample (SPI-C) and the blank sample (SPI-C_{blank} treated under cationization conditions without GTMAC). Solubility profiles of SPI were determined as described in a previous study (Nesterenko et al., 2012). Briefly, protein mixtures in deionized water (5% w/w) were prepared at different pH values and stirred at 70 °C for 1 h. Suspensions were centrifuged at 10,000 × g for 15 min (Sigma Laborzentrifugen, Osterode, Germany). The soluble protein fraction in the supernatant was analyzed using the Kjeldahl method and solubility (*S*%, w/w) was calculated from the following equation:

$$S(\%) = \frac{\text{protein content in the supernatant}}{\text{total protein content in solution}} \times 100 \quad (2)$$

2.4. Microencapsulation by spray-drying

Protein based microparticles were prepared using a two-step procedure. An aqueous solution of protein (native or modified) was mixed with active core material. Then a liquid preparation (solution or emulsion) was spray-dried to obtain a microparticle powder.

2.4.1. Solution/emulsion preparation

The wall material (SPI) was dissolved in deionized water (8% w/w) at 70 °C for 1 h under constant mechanical stirring (1000 rpm). In order to allow maximum protein solubilization, the pH of the solution was fixed at 10.5. Active material (T or AA) was then mixed with SPI solution to obtain the preparation in which the protein/