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Influence of drying conditions on the gelling properties of the 7S and 11S soy protein fractions

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ABSTRACT

Soy protein fractions rich in β-conglycinin (7S) or glycinin (11S) were freeze dried or spray dried at temperatures of 120, 150 or 180 °C. The fractions were characterized for their particle size distribution, sorption isotherms and by scanning differential calorimetry. The gelling capacity of the protein fractions was studied at pH values of 3 and 7 using oscillatory measurements, mechanical properties and water holding capacity. The rheological measurements showed that viscous modulus (G'') predominated at low temperatures and the elastic modulus (G') at high temperatures. At pH 3, the G'–G'' crossover occurred at lower temperatures when compared to pH 7. This behaviour was more accentuated for the 11S fractions due to its capacity to form stronger gels. An increase of drying temperature led to a displacement of the gel point to higher temperatures and decreased the elasticity modulus or gelling capacity of protein fractions. These results were confirmed by the mechanical properties, since at higher temperatures the gels were more fragile and brittle, especially when formed at pH 7.

Keywords: β-Conglycinin; Glycinin; Denaturation; Disulphide bridges; Mechanical properties

1. Introduction

Soy proteins are the most attractive vegetable proteins for human and animal nutrition due to their optimal nutritional and technological properties (Keerati-u-rai and Corredig, 2009a). The gelling capacity is one of the most important functional properties of soy protein, making this biopolymer one of the most used for this purpose amongst the vegetable proteins (Hua et al., 2005). Soy shows a protein content of about 50% and the majority of the proteins are globulins. The globulins 7S β-conglycinin and 11S glycinin are the main soy proteins and representing more than 70% of the protein fraction (Beckwith, 1984). The 7S globulins are trimeric glycoproteins composed by six different combinations of three subunits: α (57 kDa), α′ (58 kDa) and β (42 kDa), associated via hydrophobic interactions. On the other hand, the 11S globulins consist of two overlapping hexagonal rings, each containing three hydrophobically associated disulphide pairs, connected to acidic (35–37 kDa) and basic (20 kDa) subunits (Utsumi and Kinsella, 1985). The isoelectric point (p*I*) of the soy globulins is around pH 4.6 (Huíz-Henestrosa et al., 2007).

Gelation is a process that occurs when protein molecules are denatured by an external factor and aggregate to form an orientated tridimensional network. High temperatures, pressures and the addition of salts are denaturing factors, but the most common found in food gelation is heat induction (Matsumura and Mori, 1996). The pH value is a factor that also affects the formation of the gel network, since it modifies molecular interactions (Matsumura and Mori, 1996) and the forces of attraction/repulsion that occurs between adjacent polypeptide chains (Cheftel et al., 1993). At pH values close to the isoeletric point, the attraction forces are favoured, promoting aggregation between the molecules and consequently stronger gel formation (Speroni et al., 2009). Amongst the forces of attraction one can find hydrophobic (favoured at high temperatures), electrostatic (salt addition or pH changes), hydrogen bond (reinforced at low temperatures) and disulphide bridge (mainly at high pressures) interactions (Utsumi and Kinsella, 1985; Nakamura et al., 1986; Damodaran, 1988; Puppo and Añón, 1998). The forces of repulsion occurring especially at pH values far from the p*I* value, enhance water–protein interactions and help to keep the polypeptide

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chains separate, which favour the formation of a homogeneous matrix (Heertje, 1993).

The mechanism of protein gel formation is the same for fractions 7S and 11S, which depends on aggregation of the protein molecules (Kinsella and Soucie, 1989). At neutral pH the 11S fraction forms more elastic, rigid, stronger gels than the 7S fraction, mainly because of the greater number of disulphide bridges formed in the gels made from the 11S fraction (Renkema et al., 2001). This characteristic reflects that the thermal denaturation of the proteins is necessary to promote the formation of the intermolecular bonds for gel formation. At neutral pH without the addition of salts, denaturation of the 11S fraction starts at a temperature (80 °C) higher than that of the 7S fraction (70 °C), and consequently the 11S fraction is more heat-stable than the 7S fraction under the same conditions of pH and ionic strength, making possible to form more heat stable gels (Bainy et al., 2008).

Soy protein is traditionally extracted at alkaline pH values and precipitated at its isoelectric point. The protein precipitate is centrifuged, neutralized and spray dried (Keerati-u-rai et al., 2011). The drying method used to transform the protein into powder is extremely important, since its functional properties can change according to the temperature used. Thus the objective of the present work was to study the gelling properties of fractions rich in the 7S and 11S globulins obtained from freeze-dried soy protein (mild drying conditions) or from spray dried soy protein obtained at different temperatures. The influence of pH on the gel properties was also evaluated for gels formed above and below the p*I* value (pH 3 and 7).

2. Materials and methods

2.1. Materials

Defatted soy flour was obtained from Solae (Esteio, Brazil) and the other reagents were of analytical grade.

2.2. Soy protein fractionation

Defatted soy flour (100 g) was solubilized with deionized water at a 15:1 water-to-flour ratio and the pH adjusted to 8.5 with 2 M NaOH. The solution was stirred for 1 h and centrifuged at 14,000 × *g* and 15 °C for 30 min. This extract was combined with sufficient $NaHSO_3$ and $CaCl_2$ to obtain 5 mM SO_2 and 5 mM Ca^{2+}, and then the pH was adjusted to 6.4 with 2 M HCl. The solution was stirred for 1 h at 25 °C and centrifuged at 14,000 × *g* for 30 min at 25 °C. A glycinin-rich fraction (11S) was obtained as the precipitate, which was dissolved in deionized water and neutralized with 2 M NaOH. The supernatant (second protein extract) was adjusted to pH 4.8 with HCl, stirred for 1 h and centrifuged at 14,000 × *g* and 4 °C for 30 min. A β-conglycinin-rich fraction (7S) was obtained as the precipitate, which was dissolved in deionized water and neutralized (Deak et al., 2007).

Both soy protein dispersions were freeze-dried or spray dried. The freeze-drying process was carried out at −53 °C and 2.7 Pa during 48 h (Model FD3, Heto, Denmark) using Petri dishes with 1–1.5 cm depth. The freeze-dried material was sieved manually with a 30 Mesh sieve (0.595 mm). Spray drying process was performed at three different temperatures (120, 150 and 180 °C) using a laboratory scale spray dryer (model MSD1, Labmaq, Brazil), with a 1.2 mm diameter nozzle and spray chamber of 500 mm × 150 mm. The mixture (at 25 °C) was fed into the chamber through a peristaltic pump, at a feed flow rate of 0.7 L/h. The drying air flow rate was 36 m^3/h, compressor air pressure was 0.25 MPa and compressor air flow rate of 2.4 m^3/h. The outlet air temperature was 65, 90 or 111 °C for inlet air temperatures of 120, 150 and 180 °C, respectively. All the fractions were characterized according to their composition, water sorption, particle size distribution, differential scanning calorimetry and gelling capacity (mechanical and rheological properties).

2.3. Characterization of β-conglicinin and glicinin fractions

2.3.1. Moisture, ash and protein content

The moisture (105 °C under forced air convection) and ash contents of the fractions were determined gravimetrically up to constant weight. The protein content was determined by the Kjeldahl method, using a nitrogen-to-protein conversion factor of 6.25 (AOAC, 1995).

2.3.2. Particle size distribution

The particle size distribution was determined by laser diffraction (Laser Scattering Spectrometer Mastersizer S, model MAM 5005 – Malvern Instruments Ltd., UK), using ethanol as the dispersing medium. The mean surface diameter of the particles was calculated according to Eq. (1). All measurements were carried out in triplicate.

$$d_{3,2} = \sum \frac{n_i d_i^3}{n_i d_i^2} \quad (1)$$

where n_i is the number of particles with diameter d_i.

2.3.3. Water sorption isotherm

The equilibrium moisture content was obtained by the static gravimetric method using saturated salt solutions. For the sorption measurements, 1 g of the samples was placed in hermetic chambers containing oversaturated salt solutions with known water activities (a_w) at 25 °C: LiCl (0.112), CH_3COOK (0.226), $MgCl_2$ (0.328), K_2CO_3 (0.432), $Mg(NO_3)_2$ (0.529), KI (0.689), NaCl (0.753) and KCl (0.840). The samples were periodically weighed until constant weight, which was assumed to be that of equilibrium. Finally, the equilibrium moisture content was determined according to Section 2.3.1. The GAB mathematical model was fitted to the data according Eq. (2) (van den Berg, 1984).

$$X_e = \frac{X_m C_{GAB} K_{GAB} a_w}{[(1 - K_{GAB} a_w)(1 + K_{GAB}(C_{GAB} - 1)a_w)]} \quad (2)$$

where X_e is the equilibrium moisture content (g water/g dry fraction), X_m is the moisture content of the adsorbed monolayer (g water/g dry fraction), C_{GAB} is the constant related to the thermal effects, K_{GAB} is the constant related to the total heat of sorption of the multilayer and a_w the water activity. All measurements were carried out in triplicate.

2.3.4. Differential scanning calorimetry (DSC)

The DSC studies were carried out in a DSC 2920 Modulated DSC differential scanning calorimeter (TA Instruments, USA). Indium and water were used to calibrate the temperature and the enthalpic response of the equipment. A DSC hermetic pan containing about 10–15 mg of sample (20%, w/w, protein dispersed in water) was tightly sealed and placed in the DSC cell. An empty pan was used as reference. The samples were