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Modulating fracture properties of mixed protein systems

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ABSTRACT

To design foods with desired textures it is important to understand structure build-up and breakdown. One can obtain a wide range of structures using mixtures of different structuring ingredients such as for example protein mixtures. Mixed soy protein isolate (SPI)/gelatine gels were analyzed for their linear rheological properties, fracture properties and microstructure. The two ingredients were found to form independent networks despite changes in the SPI microstructure, which were attributed to micro phase separation. It is shown that mixing of SPI and gelatine allows to arrive at a large variety of fracture properties. This provides opportunities for tailoring textures in foods using mixed independent gel networks. The fracture stress of mixed gels corresponded to the fracture stress of the strongest of the two gels. At constant fracture stress, increasing Young's modulus of the mixed independent gels resulted in reduced fracture strain.

1. Introduction

The demand for a sustainable production of protein containing products leads to an increased interest in the use of alternative (mostly plant) proteins. This leads to challenges like employing these proteins in existing foods without changing texture, taste and appearance. Because simple replacement of one protein with another usually leads to different properties one needs to resort to mixtures. Studying the fracture properties of mixed protein systems in which one is of plant origin is therefore essential to gain insight on how textural properties can be modulated when introducing new proteins.

To employ biopolymer mixtures in foods, a basic understanding of their interactions and phase behaviour is important. Thermodynamic (in)compatibility of macro constituents is one of the most important and mostly researched topics in mixed systems. Polysaccharide (PS)/protein mixtures as the most commonly researched biopolymer mixture (Çakir & Foegeding, 2011; Doublier, Garnier, Renard, & Sanchez, 2000; Martínez & Pilosof, 2012; Ould Eleya & Turgeon, 2000; Pires Vilela, Cavallieri, & Lopes da Cunha, 2011; Tolstoguzov, 1991; Turgeon & Beaulieu, 2001; van den Berg, 2008) usually show phase separation at relatively low (total) polymer concentration (Doublier et al., 2000). Protein mixtures, on the other hand, are thermodynamically compatible over a wide concentration range dependent on their Osbourne classification, hydrophobicity and surface charges (Polyakov, Kireyeva, Grinberg, & Tolstoguzov, 1985). However, changes such as denaturation, aggregation and/or coil–helix transitions reduce their compatibility with other polymers and interaction with water (i.e. solubility) drastically. This can induce phase separation and therefore structural changes in single and mixed systems (Ako, Nicolai, Durand, & Brotons, 2009; Fitzsimons, Mulvihill, & Morris, 2008; Polyakov, Grinberg, & Tolstoguzov, 1997).

The rheological properties and microstructure has been described in detail for several polysaccharide/protein (Çakir & Foegeding, 2011; Doublier et al., 2000; Martínez & Pilosof, 2012; Ould Eleya & Turgeon, 2000; Pires Vilela et al., 2011; Tolstoguzov, 1991; Turgeon & Beaulieu, 2001; van den Berg, 2008) and protein/fat (Kim, Renkema, & Van Vliet, 2001; Sala, 2007) mixtures. van den Berg (2008) and Sala (2007) have linked large deformation properties for two examples of the above mentioned mixtures to sensory attributes by mixing whey protein with different polysaccharides (van den Berg, 2008) or using different types of proteins in emulsion filled gels (Sala, 2007). For mixed protein systems, however, these relationships have not yet been established. First steps towards understanding the structure formation and breakdown properties have been

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undertaken for mixed protein systems containing gelatine and a globular protein. Here, gelatine was shown to gel inside existing networks (gels) of globular proteins whereas the reverse situation is more challenging (Walkenström & Hermansson, 1997). Rheological properties of mixed gels ranged from gelatine-like to whey protein (Brink, Langton, Stading, & Hermansson, 2007; Walkenström & Hermansson, 1994, 1996; Walkenström et al., 1997) or egg white-like (Ziegler, 1991). Rheological changes were attributed to segregative phase separation driven by polymerization of one of the two proteins (e.g. aggregation or coil to helix transition (Fitzsimons et al., 2008)). However, these results were only obtained for a limited number of proteins (not including plant proteins), protein concentrations and mixing ratios. Therefore, using plant proteins and at the same time mapping rheological properties at all possible concentrations and mixing ratios provides new insight and opportunities for tailoring mixed gelatine/globular protein systems.

Soy protein is one of the most researched and readily available plant storage proteins and therefore, of high interest for research and industrial applications. Only few related studies on mixed gels including soy protein isolate (SPI) have been published (Chronakis & Kasapis, 1993; Comfort & Howell, 2002). Moreover, the interpretation thereof is often difficult since SPI itself can be considered a mixed system (Kasapis & Tay, 2009; Renkema, Knabben, & van Vliet, 2001; Sok, Kasapis, & Han, 2008). Gelatine, on the other hand, is frequently studied in mixed systems (Alevisopoulos, Kasapis, & Abeysekera, 1996; Almrhag et al., 2012, 2013; Altay & Gunasekaran, 2013; Ares et al., 2007; Fiszman, Lluch, & Salvador, 1999; Fiszman & Salvador, 1999; Fitzsimons et al., 2008; Salvador & Fiszman, 1998; Shrinivas, Kasapis, & Tongdang, 2009; Walkenström et al., 1994, 1996, 1997; Ziegler, 1991; Ziegler & Rizvi, 1989). Gelatine is thermo-reversible and rheologically well distinguishable from heat induced, globular protein gels such as the brittle and weak (tofu-like) SPI gel. Due to its lack of tertiary structure it compares well to many polysaccharides, when in the coil conformation (Doublier et al., 2000). Nevertheless, it is thermodynamically compatible with most proteins over a wider range of concentrations other than most polysaccharides (Tolstoguzov, 1988).

The objective of this study is to map and understand the origin of the fracture properties of mixed gelatine/SPI gels. Differential scanning calorimetry, small deformation measurements and microscopy are combined to gain better understanding of the structure build-up of mixed gelatine/soy protein gels and its relation with fracture properties. These results will help one to employ protein mixtures of plant origin in designing foods.

2. Material and methods

2.1. Material

Defatted soybean flour was obtained from Cargill having ~50% w/w protein. Pork skin gelatine type A was generously provided by Rousselot B.V. (Ghent, Belgium) having a nominal bloom strength of 150 (determined by manufacturer following a standardized procedure), a protein content of 89.6% (Kjeldahl, N-factor 5.5), an isoelectric point around 8 (Isoelectric focussing and QC-RLT) and negligible amounts of salts (ICP-AES). Chemicals were obtained from Sigma Aldrich (St Louis, MO, USA) and were of analytical grade. They were used without any further purification using demineralized water (conductivity 1.5 μS/cm).

2.2. Sample preparation

2.2.1. Soy protein isolate and gelatine stock solution preparation

Soy protein isolate (SPI) was prepared by isoelectric precipitation and subsequent washing steps as described in literature (Urbonaite, de Jongh, Linden, & Pouvreau, 2014). The extracted SPI was kept as solution (pH 7) and had a protein content of 11% (Kjeldahl, N-factor 6.38). For microbiological stability 0.02% sodium-azide was added. Solutions were stored at 4 °C and used within 4 weeks after protein extraction. Within this time no physical changes were observed. Gelatine solutions were prepared by dispersing gelatine granules in demineralized water. For samples with 10% SPI, gelatine was dissolved directly in the SPI solution. Gelatine solutions were heated at 60 °C for 1 h in a water bath and stored at 4 °C overnight.

2.2.2. Sample preparation

All solutions (including demineralized water) were degassed before usage and handling was done at a sample temperature of 40 °C to avoid gelling of the gelatine. Protein stock solutions (12% SPI, 20% gelatine) were mixed with demineralized water, NaCl and Na-azide stock solutions to obtain desired protein concentrations (0–10% SPI, 0–14% gelatine) and constant concentrations of 300 millimolal NaCl and 20 millimolal Na-Azide. MOPS buffer stock solution (1 M, pH 6.8) was added to reach a final buffer concentration of 20 millimolal.

2.3. Rheological techniques

2.3.1. Large deformation

Samples were placed in pre-lubricated (paraffin oil) sealed plastic tubes, tempered for 1 h at 40 °C, heated at 95 °C for 30 min and afterwards stored in an acclimatised room overnight at 25 °C. Gels were cut into cylindrical pieces (2 cm × 2 cm) using a steel wire. For each sample 4 cylindrical pieces were measured and average values are shown. A 90% strain compression test was performed using a texture analyzer (TA-XT plus, Stable Micro Systems Ltd., Godalming, U.K.) equipped with a 500 N load cell. The probe had a much larger diameter than the cylinders and paraffin oil was applied to all surfaces allowing sufficient lubrication. Samples were compressed in a single compression test to 90% of their initial height at a compression speed of 1 mm/s. True stress, true strain and Young's modulus were calculated as described elsewhere (de Jong & van de Velde, 2007).

2.3.2. Small deformation

After preparation, samples were stored in the freezer (−20 °C) and thawed in a water bath prior to analysis at 40 °C for 30 min before rheological measurements (Anton Paar MC502 rheometer Graz, Austria). Gelling behaviour was compared with non-frozen samples and their behaviour did not change significantly upon freezing and thawing. A sand-blasted cup-bob geometry (CC17), a strain of 0.5% and a frequency of 1 Hz were used throughout the experiment. Samples were covered with a thin layer of paraffin oil to prevent evaporation and heated from 40 °C to 95 °C. They were kept at 95 °C for 1 h before cooling back to 15 °C. The temperature was then kept at 15 °C for 1 h before re-heating again to 95 °C. Heating and cooling rates were set at 5 °C/min.

2.4. Differential scanning calorimetry (DSC)

Samples were placed in aluminium pans, equilibrated at 40 °C inside the equipment (TA Instruments DSC Q1000 New Castle, USA) and then cooled to 15 °C before starting the measurements. The samples were heated at 1 °C/min to 110 °C and subsequently cooled