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Modulating the aggregation behaviour to restore the mechanical response of acid induced mixed gels of sodium caseinate and soy proteins

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ABSTRACT

Partial replacement of milk proteins with plant proteins is a challenge due to the reported negative effect on physical and sensory properties. Understanding of how the mechanical properties of acidified milk gels can be restored when 30% casein is replaced with soy proteins is therefore explored. Mixtures of sodium caseinate (CAS) and soy proteins (SP) are pre-heated at different conditions (pH, ratio CAS:SP, temperature) prior to acidification with GDL in order to modulate aggregation, structure build-up and final mechanical properties of acidified gels with total protein content of 10% (w/w). Optimal results in mechanical response were obtained when CAS and SP were pre-heated together at a 7:3 protein ratio for 15 min at 95 °C. In addition, heat treatment of CAS-SP mixtures resulted in a shift to higher onset pH and a faster onset gelation as determined by dynamic oscillation rheology. From turbidity measurements a change in aggregation kinetics was observed which can be appointed to the altered aggregation propensity during acidification of the heat induced aggregates. Pre-heating of CAS and SP together resulted in an enhanced increase in aggregate size (as determined with light scattering) compared to unheated mixture or when only SP was heated. By pre-heating mixtures of CAS and SP at the right conditions prior to acidification, the mechanical response of mixed CAS–SP gels can be restored to that comparable with CAS only gels. As a result, 30% CAS can be successfully replaced with SP while maintaining mechanical properties.

1. Introduction

Proteins play an important role in food for their nutritional and texture properties. When mixing proteins, the nutritional value and functional properties of the mixture could surpass those of the individual proteins and hence selective mixing can be of benefit for new product development or reformulation. Designing food products with mixtures of proteins offers a solution to introducing plant proteins in existing formulations and meeting up with the increasing demand for flexibility in the application of protein sources. However, partially replacing animal proteins with plant proteins is a challenge due to the reported negative effect on physical and sensory properties, e.g. when introducing soy proteins to dairy products. For yogurt, an increase in chalkiness and thickness was observed (Drake, Chen, Tamarapu, & Leenanon, 2000), whereas for cheese, the hardness decreased when cow's milk was partially replaced with soy milk (Gökçe & Gürsoy, 2003). Insight into how to improve physical and sensory properties of mixed milk protein – plant protein is therefore essential.

Acidified milk gels, such as yogurt and cheese, are particulate protein gels (Horne, 1999) with casein as major protein contributing to the characteristic mechanical and sensory properties. One of the typical sensory attributes for particulate protein gels is spreadability, which was found to be directly related to the number of pieces in which the product falls apart during oral processing (van den Berg, Carolas et al., 2008; van den Berg, van Vliet et al., 2008). Furthermore, this sensory attribute was found to relate to the fracture behaviour of semi-solids (van den Berg, Carolas et al., 2008; van den Berg, van Vliet et al., 2008; van Vliet & Walstra,

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1995). When applying large deformation to particulate casein gels, their breakdown behaviour is such that most energy applied goes into fracture of the gel, and hence, the falling apart into pieces. To overcome deterioration of sensory and physical properties of acidified casein gels due to introduction of soy proteins, understanding of how to restore the mechanical properties of these mixed gels is essential for consumer acceptability and potential application of plant proteins in dairy products. Although acid-induced gelation by means of addition of glucono-δ-lactone (GDL) has been frequently studied for the individual proteins of casein (Braga, Menossi, & Cunha, 2006; Dalgleish, Alexander, & Corredig, 2004; Horne, 1999; Lucey, Teo, Munro, & Singh, 1997; Vasbinder, Van Mil, Bot, & De Kruif, 2001) and soy proteins (Bi, Li, Wang, & Adhikari, 2013; Campbell, Gu, Dewar, & Euston, 2009; Grygorczyk & Corredig, 2013; Nik, Alexander, Poysa, Woodrow, & Corredig, 2011), only limited studies deal with the gelation and mechanical properties of mixed gels.

In mixtures of soy proteins and casein, both proteins are susceptible to form acid-induced networks. However, the onset of gelation, the gelation kinetics and subsequent microstructure that is formed differ between the two proteins due to differences in isoelectric point, molecular composition and assembly behaviour. Differences in aggregation behaviour during acidification was studied for mixtures of soy protein concentrate (SPC) and proteins from skim milk (SMP) at different ratios. The addition of SPC resulted in gelation at higher pH, and a more particulate network with more branched strands and a larger pore size (Roesch, Juneja, Monagle, & Corredig, 2004). The change in network structure was however not attributed to specific intermolecular interactions between casein and soy proteins as these were not observed (Roesch & Corredig, 2006). A similar conclusion was drawn by Beliciu et al (Beliciu & Moraru, 2011, 2013), who studied the nature of interactions between soy protein and micellar casein upon heating, without subsequent acidification. Complex formation did not occur; on the contrary, they suggested that at intermediate concentration, enhanced incompatibility between casein micelles and denatured soy proteins occurred. In order to have both proteins participate in the network, a combination of acid-induced and rennet-induced gelation was proposed (Grygorczyk, Duizer, Lesschaeve, & Corredig, 2014; Grygorczyk, Lesschaeve, Corredig, & Duizer, 2013; Lin, Hill, & Corredig, 2012). While acid-induced gelation leads to aggregation of soy proteins before milk proteins, the combination of rennet and acid-induced gelation resulted in simultaneous aggregation and hence, a more homogeneous network (Grygorczyk et al., 2013). As it is hypothesized that simultaneous aggregation and network formation is beneficial for physical and sensory properties, the aim of this research is therefore to explore new ways to fine-tune the aggregation, microstructure formation and fracture properties of acid-induced mixed protein gels from sodium caseinate and soy proteins. Especially knowledge on fracture properties of these type of mixed gels is essential to relate to textural properties which has not been given any attention so far. The combination of sodium caseinate (in the absence of whey proteins) with native soy proteins, has not been studied before as all studies on acidified casein-soy protein mixtures used casein micelles as casein source (Grygorczyk & Corredig, 2013; Grygorczyk et al., 2014; Lin et al., 2012; Roesch & Corredig, 2006; Roesch et al., 2004). Furthermore, using sodium caseinate results in a defined model system to study the acid induced gelation of mixtures of these proteins and obtain insight on how to direct the mechanical gel properties when 30% caseinate is replaced with soy proteins. Modulation of the aggregation was done by varying the heat treatment and the pH of mixtures of sodium caseinate and SP before acidification. Aggregation and gelation kinetics are followed during acidification (rheology, turbidity), and combined with large deformation properties and microstructural analysis to relate to textural properties.

2. Materials & methods

2.1. Materials

Defatted soybean flour was purchased from Cargill BV (Amsterdam, The Netherlands). Sodium caseinate was obtained from DMV (Veghel, The Netherlands). Glucono-delta-lactone (GDL) was purchased from Sigma Aldrich (St Louis, MO, USA). All other chemicals were obtained from Sigma Aldrich (St Louis, MO, USA) and were of analytical grade and used without further purification.

2.2. Preparation of protein solutions

Native soy proteins (SP) were prepared by isoelectric precipitation and subsequent washing steps as described in literature (Urbonaite, de Jongh, van der Linden, & Pouvreau, 2014). The extracted SP was kept as solution (pH 7) to maintain its native state, and had a protein content of ~11% (w/w) (as determined by Kjeldahl, N-factor 6.25). As preservative 0.02% (w/w) sodium azide was added. Solutions were stored at 4 °C and used within 4 weeks after protein extraction.

Sodium caseinate (CAS) was dissolved at 11% w/w in demineralized water and stirred overnight at 4 °C for complete hydration. Protein solutions were degassed prior to further use.

2.3. Preparation of protein mixtures and gels

Solutions of CAS and SP were mixed in a 7:3 ratio based on protein content at a total protein concentration of 10% (w/w), having a pH of 6.7. A 10% (w/w) mixed protein solution with a 7:3 CAS:SP ratio therefore contains 3% (w/w) soy protein and 7% (w/w) caseinate. GDL was added to allow acidification to pH 4.8 for 20 h at 25 °C. The amount of GDL needed to reach pH 4.8 was determined by measuring the end pH as a function of GDL concentration for both 10% w/w CAS solution as well as the mixed CAS:SP solution, and was found to be 1.35% in both cases. The choice in this study was made to perform the acidification solely at one GDL concentration to allow us to compare different systems. However, it has to be noted that a change in acidification kinetics would be required to determine if the chosen systems have reached steady state.

After addition of GDL, the samples were either directly used for small rheology and turbidity experiments or placed in prelubricated (paraffin oil) sealed plastic tubes and kept 20 h at 25 °C in a water bath to allow acidification to pH 4.8 and gel formation to measure fracture properties. Variation in sample preparation was obtained by heating mixed protein solutions, prior to acidification, at different CAS:SP ratios (from 0:3 to 7:3 CAS:SP based on protein content) and therefore at different protein concentration (from 3 to 10% (w/w) respectively) at pH 6.5 for 15 min at 95 °C in a water bath. After subsequent cooling, CAS solution was added to these heated solutions to reach a final protein concentration of 10% w/w and a final ratio of 7:3 CAS:SP. For the 7:3 CAS:SP ratio, the pH at which heat treatment took place was varied from 7.2 to 6.0. After heating the pH was reset to pH 6.7 before the addition of GDL.

2.4. Turbidity

Turbidity was followed during acidification for 6 h at 25 °C for 0.2% (w/w) protein solutions at a wavelength of 600–800 nm using a Cary 4000 UV–vis spectrophotometer (Varian, Nederland BV). Cuvettes with a light path of 1 cm were used. Simultaneously, the