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Comparison of pressure treatment and heat treatment of skim milk with added starch on subsequent acid gelation of milk

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ABSTRACT

Skim milk with added starch (waxy rice starch or potato starch at levels of 0–1.5 g/100 g) was either pressure-treated (500 MPa, 20 °C, 30 min) or heat-treated (80 °C, 30 min) and subsequently acidified (using glucono-δ-lactone) to form acid milk gels. In the second part of the study, the pH of the skim milk samples was adjusted from the natural condition (pH 6.64) to pH 6.5, 6.6 or 6.9 before the pressure or heat treatment and re-adjusted back to pH 6.64 after the respective treatment. The rheological properties of the samples during acidification and of the final acid gels were studied. The storage modulus, G', of the final acid milk gels increased as more waxy rice starch was added to milk before pressure or heat treatment. However, acid milk gels made from pressure-treated milk with added potato starch did not show significant changes in the G' of the final acid gels whereas those made from the heat-treated counterparts showed a marked increase in the final G' as the potato starch level increased. Waxy rice starch was gelatinised in milk by both pressure treatment and heat treatment whereas potato starch was gelatinised by heat treatment only. Increasing the pH of milk before pressure or heat treatment increased the final G' of the acid milk gel produced on subsequent acidification of the milk and the final G' was increased further by the addition of waxy rice starch before the pressure or heat treatment.

1. Introduction

Acid milk gels (AMGs) are particle gels that are formed by aggregation of milk proteins when milk is acidified (Horne, 1999). This gel-forming characteristic of milk proteins is the fundamental basis for making dairy products such as yoghurt and some types of cheese (Lucey & Singh, 1998; van Vliet, Lakemond, & Visschers, 2004). Starch is commonly used as an ingredient in food products and in dairy products, and can be used to modify the product texture (Keogh & O'Kennedy, 1998; Sandoval-Castilla, Lobato-Calleros, Aguirre-Mandujano, & Vernon-Carter, 2004; Williams, Glagovskaia, & Augustin, 2003). Our previous studies have shown that when potato starch (PS) was added to skim milk prior to heat treatment, the firmness of milk gels made on subsequent acidification of heated milk increased due to the gelatinisation of the starch in skim milk during the heat treatment (Oh, Anema, Wong, Pinder, & Hemar, 2007; Oh, Wong, Pinder, Hemar, & Anema, 2007). Similar effects of starch addition on yoghurt gels have been reported in other studies (Keogh & O'Kennedy, 1998; Sandoval-Castilla et al., 2004; Williams et al., 2003). Uptake of water by starch during gelatinisation is proposed to be the primary reason for the increased firmness of AMGs prepared from heated milk with added starch as the effective concentration of proteins increases in the aqueous phase which then resulted in a denser protein network on acidification (Oh, Anema, et al., 2007).

High pressure processing technology has been gaining popularity as a non-thermal method for the manufacture of food products. As well as inactivating pathogenic and spoilage micro-organisms and deteriorative enzymes (Tewari, Jayas, & Holley, 1999), pressure treatment can lead to changes in functional properties of food by affecting the food constituents. Pressure treatment can affect both milk proteins and starch (Balny, Masson, & Heremans, 2002). In some respects, the effects of pressure on starch and globular proteins such as whey proteins are similar to, although not identical to, that of heat (Considine, Patel, Anema, Singh, & Creamer, 2007; Knorr, Heinz, & Buckow, 2006). Globular proteins undergo pressure-induced unfolding of the structures, therefore denaturation, which may be largely attributed to penetration of water into the structure (Balny et al., 2002). Water also penetrates into starch granules, which causes swelling of

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the granules and induces gelatinisation (Rubens, Snauwaert, Heremans, & Stute, 1999).

When heat treatment has been used, milk proteins show different aggregation behaviours on acidification depending on the pH of the milk at heating, and this has resulted in different acid milk gel firmness when the heated milk samples were subsequently acidified (Anema, Lee, Lowe, & Klostermeyer, 2004; del Angel & Dalgleish, 2006; Lakemond & van Vliet, 2005). Compared with samples heated at the natural pH, increasing the pH at heating to about pH 7.1 increased the firmness of the AMGs, whereas decreasing the pH at heating to about pH 6.5 decreased the firmness of the AMGs (Anema et al., 2004; del Angel & Dalgleish, 2006; van Vliet et al., 2004). These results were attributed to the changes in the interaction behaviour of the denatured whey proteins with the casein micelles during heating, since the levels of denatured whey protein associated with the casein micelles decreased as the pH at heating was increased (Anema et al., 2004; Anema & Li, 2003a; del Angel & Dalgleish, 2006; Vasbinder & de Kruif, 2003). Oh, Wong, et al. (2007) showed that the effects of pH at heating and addition of starch were additive and independent of each other up to a starch addition level of 1 g/100 g.

This study examines the AMGs prepared from pressure-treated skim milk with added waxy rice starch (WRS) or PS which has not been studied before. The results are compared to those obtained from AMGs prepared from HT skim milk with added WRS and PS. In the first part of this study, skim milk was used at its natural pH. In the second part of this study, the pH of the skim milk was adjusted to pH values between 6.5 and 6.9 to examine the effect of pH at pressure treatment compared to the effect of pH at heat treatment.

2. Materials and methods

2.1. Materials

WRS was supplied by Remy Industries (Leuven-Wijgmaal, Belgium; 12 g water, 0.05 g protein, 0 g fat and 0.3 g ash per 100 g). PS was supplied by Penford New Zealand Limited (Auckland, New Zealand; 11 g water, 0.07 g protein, 0.06 g fat and 0.08 g ash per 100 g). All starches were used as supplied. Low heat skim milk powder was obtained from Fonterra Co-operative Group – Edendale, New Zealand. Glucono-δ-lactone (GDL) was obtained from Sigma–Aldrich (St. Louis, MO, USA).

Skim milk samples were prepared by reconstituting low heat skim milk powder in purified water (reverse osmosis followed by filtration through a Milli-Q apparatus) to a final concentration of 10 g (total solids)/100 g (milk). The reconstituted skim milk was stirred for at least 1 h and stored overnight at ambient temperature (approximately 20 °C) before use.

2.2. Sample preparation and treatment

In the first part of the study, WRS or PS was added to skim milk at concentrations, 0, 0.5, 1 or 1.5 g (starch)/100 g (suspension) at its natural pH prior to pressure or heat treatment. In the second part of the study, the pH of the skim milk samples was adjusted from the natural condition (pH 6.64) to pH 6.5, 6.6 or 6.9 by the slow addition of hydrochloric acid (1 mol/L) or sodium hydroxide (1 mol/L) while stirring the milk. WRS was then added to the pH-adjusted skim milk at concentrations of 0 or 1 g (starch)/100 g (suspension). All samples were either heat-treated (HT) at 80 °C for 30 min as described by Oh, Anema, et al. (2007) or pressure-treated (PT) at 500 MPa and 20 °C for 30 min as described by Oh, Pinder, Hemar, Anema, and Wong (2008). For the pH-adjusted milk samples, the pH was re-adjusted to the natural pH after pressure treatment and depressurisation or heat treatment and cooling by the slow addition of hydrochloric acid (1 mol/L) or sodium hydroxide (1 mol/L) at room temperature (20 °C) with stirring.

2.3. Acidification and rheology

The samples were acidified by adding 0.1 g of GDL to 4.9 g of each sample. Changes in the rheological properties of the samples during acid gelation were monitored using an AR2000 rheometer (TA Instruments, New Castle, DE, USA) and a cone (4 cm, 4° and 100 μm truncation) and plate geometry as described in Oh, Anema, et al. (2007). To monitor the acid gelation process of milk, the rheological measurements were performed at a frequency of 0.1 Hz, a constant strain of 0.5% and a constant temperature of 30 °C. Once the acid gelation had been completed, the sample was then subjected to a temperature sweep. The temperature of the sample was decreased from 30 to 5 °C at a rate of 0.9 °C min^{-1} and the rheological properties were monitored as the temperature was decreased using a frequency of 0.1 Hz and a strain of 0.5%.

In this study, the term '$G'_{30°C}$' denotes the G' of the milk sample during acidification at 30 °C. The term 'final $G'_{30°C}$' denotes the G' of AMG at 30 °C after 180 min of acidification by GDL and the term 'final $G'_{5°C}$' denotes the G' of AMG when the temperature of AMG formed after 180 min of gelation at 30 °C was subsequently decreased to 5 °C.

All experiments were repeated in duplicate. Analysis of variance (ANOVA) using MINITAB software was conducted where appropriate.

2.4. Microscopy

Birefringence of the starch granules in untreated, PT or HT skim milk was observed prior to acidification, using a polarising light microscope (Nikon Eclipse E600 Pol, Nikon Corporation, Tokyo, Japan) with a 50× or 20× objective.

The microstructure of the final AMGs was observed using a confocal scanning laser microscope (CSLM) by methods described by Oh, Anema, et al. (2007). Fast Green CFC dye was added to the samples prior to acidification to label proteins. The milk samples were then acidified with GDL at 30 °C for 180 min and the AMGs were examined for their microstructures using the CSLM.

3. Results

3.1. Acid gelation of skim milk with added starch after pressure or heat treatment at the natural pH

3.1.1. Acid gelation curves

The milk samples were slowly acidified by GDL after the pressure or heat treatment so that the pH of the samples decreased from the natural pH to pH ~4.2 over a 180 min period. The storage modulus, G', was monitored during acidification and was used to indicate the firmness of the samples during acidification (Fig. 1). Regardless of the treatment the milk samples received, the shapes of the acid gelation curves are typical for the acid gelation of milk as has been previously shown (Lucey, Teo, Munro, & Singh, 1997; Oh, Wong, et al., 2007). The first phase of acid gelation is a lag phase where the G' is low as the milk remains liquid. The length of the lag phase is termed the 'gelation time' in this study. The second phase is a rapid gelation phase in which the increase in G' is almost directly proportional to time.

The gelation times were different between the PT milk with no added starch and the HT counterpart (Table 1, Fig. 1). The gelation time for PT milk was markedly longer than that for HT milk (Table 1). The HT milk sample with no added starch showed a higher final $G'_{30°C}$ value than the PT counterpart. The final $G'_{30°C}$