Journal of Dairy Research (2015) **82** 506–512. doi:10.1017/S0022029915000370

The effect of pH on the rheology of mixed gels containing whey protein isolate and xanthan-curdlan hydrogel

Setareh Ghorban Shiroodi* and Y. Martin Lo
Department of Nutrition and Food Science, University of Maryland, College Park, MD 20742, USA

Received 7 February 2015; accepted for publication 23 May 2015; first published online 3 August 2015

The ultimate goal of this work was to examine the effect of xanthan-curdlan hydrogel complex (XCHC) on the rheology of whey protein isolate (WPI) within the pH range of 4–7 upon heating and cooling. Dynamic rheological properties of WPI and XCHC were studied individually and in combination, as a function of time or temperature. For pure WPI, gels were pH-dependent, and in all pH values except 7, gels formed upon first heating from 40 to 90 °C. At pH 7, WPI did not form gel upon first heating, and the storage modulus (G′) started to increase during the holding time at 90 °C. The onset of gelation temperature of WPI was lower in acidic pH ranges compared to the neutral pH. In mixed gels, the presence of XCHC increased the G′ of the gels. The rheological behaviour was pH-dependent and initially was controlled by XCHC; however, after the consolidation of WPI network, the behaviour was led by the whey protein isolate. Results showed that XCHC had a synergistic effect on enhancing the elastic modulus of the gels after the consolidation of WPI network. Based on the results of this study, it is possible to use these biopolymers in the formulation of frozen dairy-based products and enable food manufactures to improve the textural and physico-chemical properties, and as a result the consumer acceptance of the food product.

Keywords: Whey protein isolate, xanthan-curdlan hydrogel, rheology, pH.

The interest for studying the behaviour of mixed gels is increasing due to the improvement of mechanical and structural properties of mixed gels compared to that of pure gels. The use of mixed systems containing protein and polysaccharide renders the opportunity to control or improve the structural and functional characteristics of the food products through their synergistic interactions. Food products are complex systems of hydrocolloids, in which texture is mainly controlled by the presence of proteins and polysaccharides (Turgeon et al. 2003). Studying the interactions between different types of hydrocolloids in aqueous solutions and gels are crucial to develop novel formulated foods.

Mixed gels, obtained from solutions of biopolymers, are either complex (intermolecular attraction) or incompatible (intermolecular repulsion). The macromolecular distribution in solution results in antagonist or synergistic effects on the formation of mixed gels (Bertrand & Turgeon, 2007; Paraskevopoulou et al. 2014). Improvement in the gelling properties of mixed gels has been reported previously (Ould Eleya & Turgeon, 2000; Wang & Qvist, 2000; Shim & Mulvaney, 2001; Bertrand & Turgeon, 2007; Sun et al. 2011).

Gels formed by several gelling agents can be classified into three types: interpenetrating, coupled, and phase-separated networks (Morris, 1986). Interpenetrating (or mixed) gels have independent networks with separate gels, which can form from different types of polymers. It is believed that any interaction between the two networks in mixed gels is mostly topological (Morris, 1986; Zasypkin et al. 1997). Favuorable intermolecular interactions between different types of polymers, result in the formation of coupled (complex coacervate) networks, while in the presence of repulsive interactions, phase-separated gels are formed (Tolstoguzov, 1991, 1995; Beaulieu et al. 2001).

Structural and rheological properties of mixed gel are influenced by internal and external factors such as pH, ionic strength, temperature, polymer concentration, ratio of protein to polysaccharide, the charge of the proteins and polysaccharides (Tolstoguzov, 1991). In mixed systems containing protein and anionic polysaccharide, pH affects both protein self-association and protein–polysaccharide cross-association. Complex coacervation is observed at pH values, where the two polymers carry opposite charges (below the isoelectric point of the protein). At pH values above the isoelectric point of the protein, biopolymers carry similar negative net charges; thus, complex formation is hindered, and thermodynamic incompatibility is supported (Ould Eleya & Turgeon, 2000).

Whey protein, a by-product of cheese production, is widely used as a food ingredient due to its nutritional and

*For correspondence; e-mail: sshiroodi@yahoo.com

useful functional properties. WP is mainly comprised of the globular proteins β-lactoglobulin (β-Lg) and α-lactalbumin (α-La), which are responsible for the hydration capacity, gelling, foaming and emulsifying properties of whey protein (Hongsprabhas & Barbut, 1996; Jara & Pilosof, 2011). Gelling is one of the most important functional properties of whey proteins, which is the result of an aggregation process induced by changing the conditions, usually by increasing the temperature. Gelling properties of whey protein depend on several factors, such as pH, salt concentration, temperature, heating rate, and ionic strength (Stading & Hermansson, 1990; Zayas, 1997). When the electro-static repulsions are strong, gels from globular proteins are transparent with a fine-stranded structure, whereas in conditions of weak electrostatic repulsions, they are opaque with a coarse, lumpy, and particulate structure (Verheul & Roefs, 1998).

Loss of nutrients due to syneresis, the spontaneous expulsion of liquid from a gel, is one of the major concerns in the food industry, which could greatly diminish the nutritional value and the quality of frozen products. Moreover, using different types of polysaccharides, individually or in combination, is one of the useful methods to increase water holding capacity of the food products (Lee et al. 2002).

A previous study showed that a hydrogel complex formed by xanthan, a negatively-charged hydrocolloid, and curdlan gum, a neutral, linear microbial polysaccharide, significantly reduced syneresis (water loss) over five repeated freeze-thaw cycles, while retaining rheological and textural properties (Williams et al. 2009, 2011).

Furthermore, addition of XCHC to WPI solution, showed excellent ability to form a homogeneous and well-structured heat-induced gel, with a significant lower syneresis compared to pure WPI gel over multiple freeze-thaw cycles (Shiroodi et al. 2015).

To test the effects of xanthan-curdlan hydrogel complex (XCHC) in a whey protein isolate (WPI) solution and to further characterise the gelation temperature changes of WPI upon heating and cooling, we have investigated the effects of pH on the rheology of a mixture of WPI and XCHC. Since pH is known to affect the functionality of macromolecules such as proteins (Taulier & Chalikian, 2001), one could expect peculiar properties of pH-treated products. Then, peculiar functional properties of pH-induced biopolymer mixed gels can be expected.

The aim of this study was to investigate the effects of pH on the rheology of a mixture of whey protein isolate and xanthan curdlan hydrogel (WPI-XCHC) upon heating and cooling, and to examine the influence of XCHC on the gelation temperature of WPI gel.

Materials and methods

Material

Odorless, fine, free-flowing white powder curdlan containing a minimum of 90% β-D-glucan and with a maximum of 10% water was used (Takeda Vitamin & Food USA, Orangeburg, NY). Xanthan (TICAXAN®) was kindly supplied by TIC Gums (Belcamp, MD); whey protein isolate (Hilmar 9400) by Hilmar Ingredients (Hilmar, CA). According to the manufacture's information, the whey protein isolate used in this study consisted of 93·4% protein (% dry basis), lactose (0·2%), fat (0·6%), moisture (4%), and ash (2·6%).

Preparation of solutions

Xanthan curdlan hydrogel complex. To prepare xanthan curdlan hydrogel complex (1% w/v) an equal amount of each of the biopolymer powders was weighed and dry blended at ambient temperature and gradually poured to deionised water under constant stirring. Gum solutions were agitated for 15 min to achieve a homogeneous, lump free aqueous solution. The biopolymer solution was magnetically stirred while gradually being heated on a heat plate until the temperature of the solution reached 90 °C. After cooling to room temperature, the pH of the solution was adjusted to 4, 5, 6, and 7 using 0·1 N of HCl or NaOH. Biopolymer solutions were covered and refrigerated overnight at 4 °C to allow complete hydration.

Whey protein isolate solution. Whey protein stock solutions 20% (w/v) were prepared by slowly dissolving the dried powder in deionised water agitated with a magnetic stirrer for 2 h at room temperature to ensure complete dissolution. Solutions were then stored overnight at 4 °C for complete hydration. The pH of WPI solutions was adjusted to 4, 5, 6, and 7 using 1 N of HCl or NaOH.

Mixtures of WPI and XCHC. Mixtures containing XCHC (0·5%) and WPI (10%) were prepared by mixing equal amounts of the stock solutions of WPI and XCHC at desired pH values. The solutions were stored overnight at 4 °C prior to the rheological measurements. Pure WPI and XCHC with the same concentration of 10 and 0·5% were prepared to study the behaviour of individual biopolymers.

Methods

Dynamic oscillatory measurements

Dynamic rheological measurements were performed at a frequency of 1 Hz at a constant strain within the linear viscoelastic region (LVR), using an AR2000 Rheometer (TA Instruments, New Castle DE) with a standard-size DIN geometry. Each sample was poured directly into the measuring system of the rheometer cup at the desired temperature, and left standing for 2 min to allow structure recovery and temperature equilibration. The dehydration of the samples was limited by using a solvent trap. In amplitude sweep tests, the strain was increased from 0·01 to 100% at a constant frequency of 1 Hz to obtain the linear viscoelastic region (LVR). Temperature sweep tests were done at a

https://doi.org/10.1017/S0022029915000370 Published online by Cambridge University Press

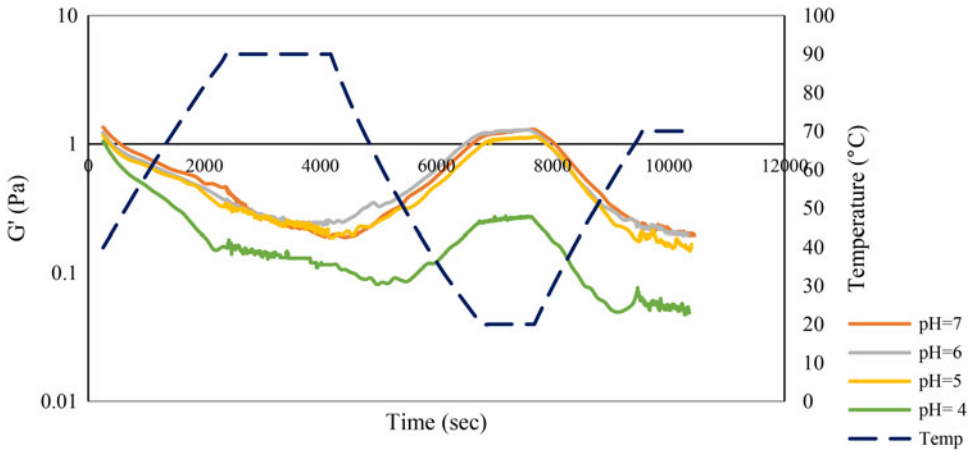

Fig. 1. Time–temperature dependence of G′ for XCHC (0·5%) over the pH range of 4–7 during heating and cooling.

frequency of 1 Hz within the strain of LVR. Solutions were heated from 40 to 90 °C, held at 90 °C for 30 min, cooled to 20 °C, and then kept for 15 min at 20 °C. Finally, samples were heated to 70 °C and held for 15 min. The temperature increment of 2 °C/min was applied for both heating and cooling ramps. At pH 4, WPI and XCHC formed insoluble complexes, which were poured into the geometry cup.

Results and discussions

Effect of pH on XCHC

Figure 1 shows the storage modulus (G′) of XCHC (0·5%) during the temperature treatments at four different pH values from 4 to 7. As seen in Fig. 1, the changes of G′ during the temperature ramps are almost identical for pH values of 5, 6, and 7. As temperature increased from 40 to 90 °C and held at 90 °C for 30 min, the storage modulus of XCHC reduced. Upon cooling from 90 to 20 °C, G′ started to increase and reached close to its initial G′ at 40 °C (≈1 Pa). This can be attributed to the resistance of XCHC structure over the wide range of temperature (Williams et al. 2009), which prevents the structure of the solution from being collapsed at 90 °C and holding for 30 min at this temperature. During the holding time at 20 °C, G′ reached a plateau, and finally reduced during the reheating (from 20 to 70 °C) and holding time at 70 °C. Results show that G′ values varied slightly with decreasing pH from 7 to 5; thus, the rheological properties of XCHC were not pH-dependent, and no significant differences were observed between the storage modulus of hydrogel systems within the pH range of 5 to7. However, G′ of the XCHC was significantly lower at pH 4, indicating less elastic or solid behaviour of hydrogel at this pH. This can be attributed to the partially protonation of anionic carboxylic ($–COO^-$ to –COOH) at pH 4, which is below the PKa of the carboxylic acid (Harnsilawat et al. 2006), and as a result, the higher tendency of the hydrogel to form hydrogen bonds with water molecules at pH values of 5, 6, and 7 rather than that of at pH 4. It should be noted that the trends of G′ changing during heating and cooling of the hydrogel at pH 4 was similar to that at other pH values.

According to the changes of storage modulus as a function of temperature or time, gelation did not occur in XCHC during the applied thermal treatments. Xanthan, widely used in food products as a thickener or stabiliser, has a rigid and rod-like structure and has been reported to form weak gels at concentrations of 0·5% (Carnali, 1991). Moreover, curdlan, having unique thermal gelling properties can form either low-set or high-set gels depending on the temperature (Funami et al. 1999). The results from temperature sweep tests in Fig. 1 revealed that the combination of curdlan and xanthan with total polysaccharide concentration of 0·5% did not form gel upon heating and cooling in the applied thermal treatments.

Effect of pH on gelation of WPI

The effect of pH on gel formation and melting of WPI solution (10%) within pH range of 4–7 is shown in Fig. 2. During the first heating ramp from 40 to 90 °C, G′ did not change significantly up to the point that a steep rise in G′ was observed. This point can be considered as the onset of WPI gelation. The temperature at which G′ started to increase sharply is defined as gelation temperature. As can be seen in Fig. 2, gelation temperature is pH dependent in WPI. The onset of gelation occurred at about 79 °C for pH values of 4 and 5, and 85 °C for pH 6. By contrast, at pH 7, G′ did not change notably during the first heating treatment; therefore, WPI did not form gel upon first heating from 40 to 90 °C. G′ started to increase erratically after the holding time at 90 °C, but not as sharply as the G′ in other pH values. During the 30 min holding time at 90 °C, G′ of the whey protein gels was found to increase. Upon cooling from 90 to 20 °C, the storage modulus of gels increased monotonically. During the 15-min holding time

https://doi.org/10.1017/S0022029915000370 Published online by Cambridge University Press

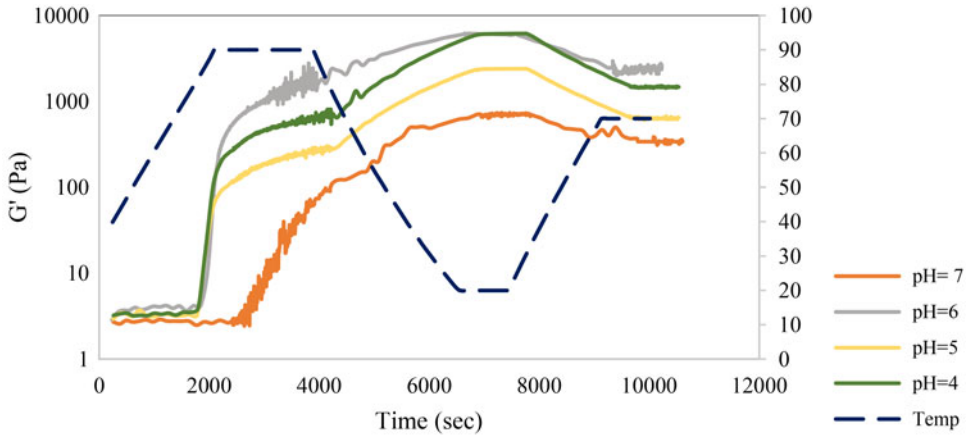

Fig. 2. Time–temperature dependence of G′ for WPI (10%) over the pH range of 4–7 during heating and cooling.

at 20 °C, G′ reached a plateau and then decreased as temperature increased from 20 to 70 °C. During the holding time of 70 °C, G′ reached a second plateau. Previous studies also reported an increase in the magnitude of the gel modulus with decreasing temperature for whey protein gels (Cooney et al. 1993; Manoj et al. 1997; Ould Eleya & Turgeon, 2000); this was attributed to the reinforcement of attractive forces (hydrogen bonding, van der Waals forces) between the protein particles in the gel (Manoj et al. 1997). The gel formed at pH 6 showed the highest G′ among all gels. The second highest storage modulus was observed in the gel formed at pH 4, followed by gel formed at pH 5. The weakest gel with the lowest amount of G′ was seen in the gel formed at pH 7. Ould Eleya & Turgeon (2000) reported a similar trend for changes of G′ during heating and cooling of β-lactoglobulin (10%).

These results are in agreement with previous studies on the changing of gelation temperature of WPI at different pH values, which showed that the onset of gelation of β-lactoglobulin occurred at lower temperatures in the acidic pH range compared to the neutral pH range (Stading & Hermansson, 1990; Ould Eleya & Turgeon, 2000). They also reported that the highest G′ of β-lactoglobulin gel was observed at pH 5·5, which supports the results obtained in this study, with highest G′ seen at pH 6. Figure 3 displays the visual observation of WPI gels at different pH values formed in the rheometer cup after performing thermal treatment. Results from other studies on the microstructure and physicochemical properties of gels formed from thermally-denatured whey proteins support the visual appearance observed in this study. When the electrostatic repulsion between protein molecules is strong, fine-stranded networks are formed (Fig. 3c, d). Whey proteins only have a limited number of hydrophobic patches on their surface, so interactions at other regions on the protein surface are hampered in the presence of strong electrostatic repulsion. On the other hand, near the isoelectric point of protein, where the net charge is relatively low (Fig. 3a, b), gels have a particulate network. The microstructure of whey protein gels affects the optical properties as well; fine-stranded gels are transparent, and particulate gels are opaque. This is due to the low scattering efficiency of thin protein strands, and strong scattering efficiency of the protein particles (Langton & Hermansson, 1992; Doi, 1993; Foegeding et al. 1995; Chantrapornchai & McClements, 2002).

Effect of pH on gelation of mixed gels

The effect of pH on gel formation and melting of the mixture of WPI and XCHC is shown in Fig. 4. As can be seen, gelation temperature and the storage modulus of the gels were strongly pH-dependent. At all pH values except for pH 4, G′ decreased as temperature increased from 40 °C, and reached its minimum level at 76, 79, and 82 °C for pH 5, 6, and 7, respectively, after which drastic increase of G′ was observed. During the holding period at 90 °C, G′ continued to increase. However, at pH 4, G′ was almost constant up to 76 °C, then increased remarkably up to 85 °C. Upon cooling from 90 to 20 °C, G′ in all pH values increased monotonically. During the holding period at 20 °C, G′ reached a plateau, followed by a slight decrease upon reheating to 70 °C. Samples reached a second plateau during the holding period at 70 °C, except at pH 7, where G′ increased during the holding time (15 min at 70 °C).

The trends of G′ changes as a function of time or temperature, in mixed gels, are very similar to those in WPI gels, except for the first step of the temperature sweep test (heating from 40 to 90 °C). During this thermal treatment, G′ of WPI samples was constant at the beginning and then increased, while in mixed WPI-XCHC samples, G′ initially decreased and then increased. The reason that G′ decreased at the beginning of heating was probably because of the heating effect on the XCHC structure, which decreased the storage modulus of the hydrogel (Fig. 1). Furthermore, an increase in G′ was due to the whey protein network consolidation and consequently WPI gel formation. Prior to consolidation of WPI network, the effect of XCHC

https://doi.org/10.1017/S0022029915000370 Published online by Cambridge University Press

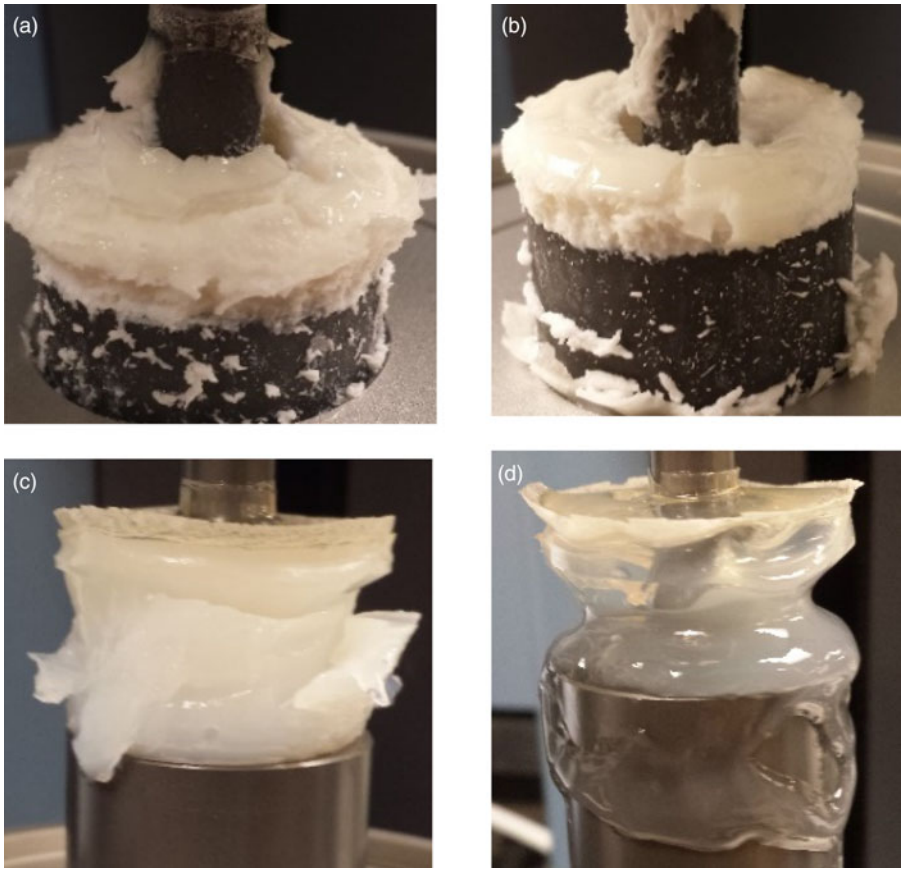

Fig. 3. Visual observation of WPI gels (10%) formed in the rheometer cup after performing thermal treatment; pH 4 (a), 5 (b), 6 (c), and 7 (d).

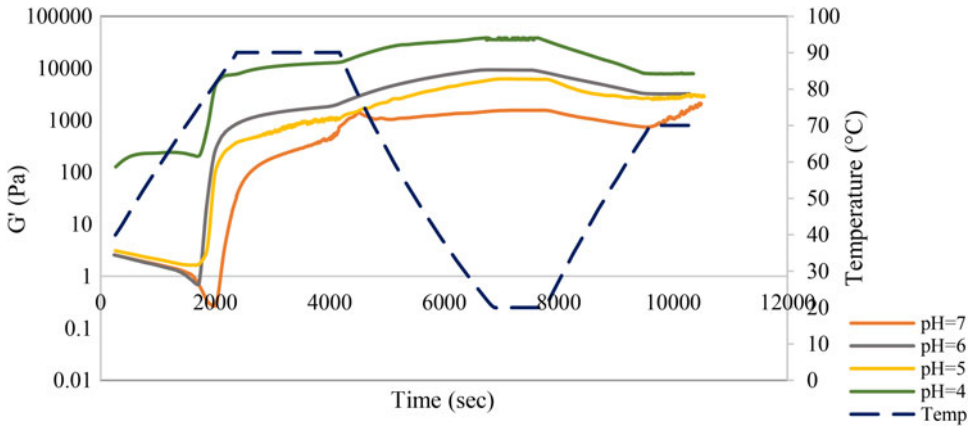

Fig. 4. Time–temperature dependence of G′ for mixed WPI (10%) and XCHC (0·5%) over the pH range of 4–7 during heating and cooling.

dominated the effect of WPI in mixed systems, however, after formation of WPI network whey protein controlled the rheological behaviour of the system. The different behaviour of mixed gel at pH 4, compared to other pH values, can be attributed to the formation of protein-polysaccharide complexes, due to the electrostatic attraction of biopolymers at this pH. As seen in Fig. 4, mixed gel at pH 4 had a significantly higher storage modulus than that of mixed gels over pH 5–7. In contrast, gel formed at pH 7 had the least G′ compared to other pH values. Results showed that pH had a strong effect on the rheological behaviour of WPI and XCHC mixed gels. According to Fig. 4, mixed gels showed two distinct behaviours over the pH range of 4–7: over pH 5–7, and at pH 4.

https://doi.org/10.1017/S0022029915000370 Published online by Cambridge University Press

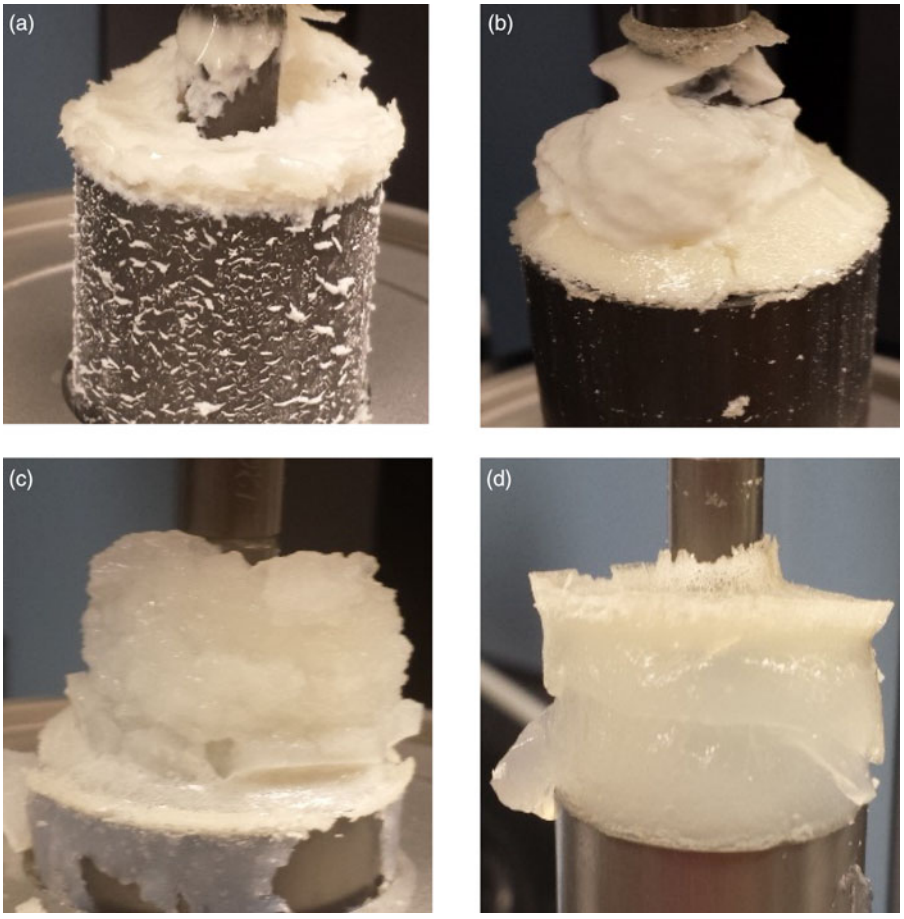

Fig. 5. Visual observation of mixed WPI (10%) and XCHC (0·5%) gels formed in the rheometer cup after performing thermal treatment; pH 4 (a), 5 (b), 6 (c), and 7 (d).

Visual observation of WPI-XCHC mixed gels at different pH values formed in the rheometer cup after performing thermal treatment is shown in Fig. 5. Over pH 5–7, biopolymers are incompatible (they carry a similar negative charge), and phase-separated gels are formed. At pH 5 and 6, around the isoelectric point of WPI, self-association of whey protein is enhanced, and as a result, segregation of protein–polysaccharide is increased. In this situation, thermodynamic incompatibility increases, which inhibits the cross-association of protein and polysaccharide (Fig. 5b, c) (Tolstoguzov, 1991). In contrast, at pH 7 (far from the isoelectric point of whey protein), the protein self-association is reduced, but due to the strong electrostatic repulsive forces, cross-association of WPI and XCHC is also reduced (Fig. 5d). At pH 4, electrostatic complexes between WPI and XCHC are formed prior to protein gelation, which may explain the different behaviour observed for the mixed gel at this pH. Therefore, at pH 4, WPI and XCHC associated, and then formed a coupled or complex coacervate network (Fig. 5a). Previous studies also reported the formation of complex networks for oppositely charged polymer mixtures, such as gum Arabic and gelatin (Peters et al. 1992).

Comparison of the storage modulus as a function of temperature or time in pure WPI and mixed WPI-XCHC, supports the synergistic effects of these biopolymers on increasing the elastic modulus of the gels after the consolidation of WPI network. Mixed protein polysaccharide gels can exhibit improved functionality over protein and polysaccharide gels alone. Manipulating these macromolecular interactions by controlling pH can assist food scientists in gaining new insights into the rheology and microstructure of novel mixed systems in the food industry. Useful knowledge in this area can benefit food manufacturers to create unique and fabricated formulations with superior sensory and physicochemical properties that are more acceptable to consumers.

References

Beaulieu M, Turgeon SL & Doublier JL 2001 Rheology, texture and microstructure of whey proteins/low methoxyl pectins mixed gels with added calcium. *International Dairy Journal* **11** 961–967

Bertrand ME & Turgeon SL 2007 Improved gelling properties of whey protein isolate by addition of xanthan gum. *Food Hydrocolloids* **21** 159–166

https://doi.org/10.1017/S0022029915000370 Published online by Cambridge University Press

Carnali J 1991 A dispersed anisotropic phase as the origin of the weak-gel properties of aqueous xanthan gum. *Journal of Applied Polymer Science* **43** 929–941

Chantrapornchai W & McClements DJ 2002 Influence of NaCl on optical properties, large-strain rheology and water holding capacity of heat-induced whey protein isolate gels. *Food Hydrocolloids* **16** 467–476

Cooney M, Rosenberg M & Shoemaker C 1993 Rheological properties of whey protein concentrate gels. *Journal of Texture Studies* **24** 325–334

Doi E 1993 Gels and gelling of globular proteins. *Trends in Food Science and Technology* **4** 1–5

Foegeding EA, Bowland EL & Hardin CC 1995 Factors that determine the fracture properties and microstructure of globular protein gels. *Food Hydrocolloids* **9** 237–249

Funami Y, Funami M, Yada H & Nakao Y 1999 Rheological and thermal studies on gelling characteristics of curdlan. *Food Hydrocolloids* **13** 317–324

Harnsilawat T, Pongsawatmanit R & McClements DJ 2006 Characterization of β-lactoglobulin–sodium alginate interactions in aqueous solutions: a calorimetry, light scattering, electrophoretic mobility and solubility study. *Food Hydrocolloids* **20** 577–585

Hongsprabhas P & Barbut S 1996 Ca^{2}+-induced gelation of whey protein isolate: effects of pre-heating. *Food Research International* **29** 135–139

Jara F & Pilosof AM 2011 Rheological properties of protein/polysaccharide blends as affected by time-dependent phase separation. In *11th International Congress on Engineering and Food*, Athens, Greece; 22–26 May

Langton M & Hermansson AM 1992 Fine-stranded and particulate gels of β-lactoglobulin and whey protein at varying pH. *Food Hydrocolloids* **5** 523–539

Lee M, Baek M, Cha D, Park H & Lim S 2002 Freeze–thaw stabilization of sweet potato starch gel by polysaccharide gums. *Food Hydrocolloids* **16** 345–352

Manoj P, Kasapis S & Hember MW 1997 Sequence-dependent kinetic trapping of biphasic structures in maltodextrin-whey protein gels. *Carbohydrate Polymers* **32** 141–153

Morris V 1986 Multicomponent gels. *Gums and Stabilisers for the Food Industry* **3** 87–99

Ould Eleya M & Turgeon S 2000 The effects of pH on the rheology of β-lactoglobulin/κ-carrageenan mixed gels. *Food Hydrocolloids* **14** 245–251

Paraskevopoulou A, Amvrosiadou S, Biliaderis C & Kiosseoglou V 2014 Mixed whey protein isolate-egg yolk or yolk plasma heat-set gels: rheological and volatile compounds characterisation. *Food Research International* **62** 492–499

Peters H, Van Bommel E & Fokkens J 1992 Effect of gelatin properties in complex coacervation processes. *Drug Development and Industrial Pharmacy* **18** 123–134

Shim J & Mulvaney SJ 2001 Effect of heating temperature, pH, concentration and starch/whey protein ratio on the viscoelastic properties of corn starch/whey protein mixed gels. *Journal of the Science of Food and Agriculture* **81** 706–717

Shiroodi SG, Rasco BA & Lo YM 2015 Influence of xanthan–curdlan hydrogel complex on freeze-thaw stability and rheological properties of whey protein isolate gel over multiple freeze-thaw cycle. *Journal of Food Science* **80** 1498–1505

Stading M & Hermansson AM 1990 Viscoelastic behaviour of β-lactoglobulin gel structures. *Food Hydrocolloids* **4** 121–135

Sun WW, Yu SJ, Yang XQ, Wang JM, Zhang JB, Zhang Y & Zheng EL 2011 Study on the rheological properties of heat-induced whey protein isolate–dextran conjugate gel. *Food Research International* **44** 3259–3263

Taulier N & Chalikian TV 2001 Characterization of pH-induced transitions of β-lactoglobulin: ultrasonic, densimetric, and spectroscopic studies. *Journal of Molecular Biology* **314** 873–889

Tolstoguzov V 1991 Functional properties of food proteins and role of protein-polysaccharide interaction. *Food Hydrocolloids* **4** 429–468

Tolstoguzov V 1995 Some physico-chemical aspects of protein processing in foods. Multicomponent gels. *Food Hydrocolloids* **9** 317–332

Turgeon S, Beaulieu M, Schmitt C & Sanchez C 2003 Protein–polysaccharide interactions: phase-ordering kinetics, thermodynamic and structural aspects. *Current Opinion in Colloid and Interface Science* **8** 401–414

Verheul M & Roefs S 1998 Structure of whey protein gels, studied by permeability, scanning electron microscopy and rheology. *Food Hydrocolloids* **12** 17–24

Wang Q & Qvist K 2000 Investigation of the composite system of β-lactoglobulin and pectin in aqueous solutions. *Food Research International* **33** 683–690

Williams PD, Sadar LN & Lo YM 2009 Texture stability of hydrogel complex containing curdlan gum over multiple freeze–thaw cycles. *Journal of Food Processing and Preservation* **33** 126–139

Williams PD, Oztop MH, McCarthy MJ, McCarthy KL & Lo YM 2011 Characterization of water distribution in xanthan-curdlan hydrogel complex using magnetic resonance imaging, nuclear magnetic resonance relaxometry, rheology, and scanning electron microscopy. *Journal of Food Science* **76** 472–478

Zasypkin D, Braudo E & Tolstoguzov V 1997 Multicomponent biopolymer gels. *Food Hydrocolloids* **11** 159–170

Zayas JF 1997 *Functionality of Proteins in Food*, pp. 310–358. New York: Springer.