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THE EFFECT OF pH AND CARRAGEENAN CONCENTRATION ON THE RHEOLOGICAL PROPERTIES OF WHEY PROTEIN GELS

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Whey proteins and polysaccharides are two gelling biopolymers widely used in the food industry. Gelation of whey protein isolate (WPI), WPI-κ-carrageenan and WPI-λ-carrageenan mixed systems has been investigated. The apparent viscosity of WPI (3%) solutions significantly increased after polysaccharide addition. The highest apparent viscosity was observed at pH 7 and 0.3% κ-carrageenan. The texture properties of WPI and WPI- polysaccharide systems have been investigated in the pH range of 3–10 and κ-carrageenan or λ-carrageenan concentration of 0.1–0.5%. In the absence of polysaccharide, very strong and elastic gels were obtained using 10% WPI at pH 7–8. In the presence of κ-carrageenan, the highest shear stress value was observed at pH 7 and 0.3% polysaccharide concentration. Low κ-carrageenan concentrations have been shown to have a major strengthening effect on WPI gels at pH 3 and 6–8. At pH range of 3–4, the complexes between biopolymers could be formed, however, at pH range of 5–10 the phase separation occurred.

INTRODUCTION

Proteins and polysaccharides are present together in many food systems, and both types of food macromolecules contribute to their structure, texture and stability. The functional and processing properties of food products are determined by the interactions between proteins and polysaccharides [Neiser *et al.*, 2000]. Therefore, understanding these interactions is of a great importance in order to develop novel new food products and ingredients.

The nature of protein – polysaccharide inter-actions in solution has a great effect on their functional properties [Tolstoguzov, 1991]. In two biopolymers mixed systems, three situations may occur: co-solubility, association and incompatibility. Co-solubility is rather rare, however, complexing occurs if biopolymer interactions are favourable, *i.e.* in the case of oppositely charged polyelectrolytes [Syrbe *et al.*, 1998]. Thermodynamic incompatibility is the most usual situation, which occurs when forces between different biopolymers are repulsive [Tolstoguzov, 1991]. The system finally demixes into two phases, each being enriched with one of the two biopolymers.

When gelation occurs, three types of gel networks can be observed: interpenetrating, coupled and phase separated [Morris, 1986]. Interpenetrating networks are formed when two components gel separately and form independent networks. Coupled networks are formed when there are associations between polymers prior to network formation; in the contrary opposite phase, separated gels are formed from incompatible biopolymers [Morris, 1986; Tolstoguzov, 1991].

In the present work, the rheological properties of whey protein solutions and gels were modified by the addition of gelling (k) and non gelling (l) types of carrageenan.

MATERIALS AND METHODS

Materials. In this study, κ-carrageenan (KK), λ-carrageenan (LK) – (Sigma Chemical Co., St. Louis, USA) and whey protein isolate (WPI), (BIPRO, Davisco Foods International, USA) were used.

Preparing of solutions and gels. Stock solutions of WPI and KK were prepared separately. WPI solutions were prepared with 3 or 10% (w/w) protein in 0.1 M NaCl by stirring for 2 h at room temperature. Solutions of KK and LK were prepared in 0.1 M NaCl by stirring for 30 min at room temperature and then heating at 70°C for 15 min. Solutions were mixed at 45°C, and pH was adjusted in the range of 3–10 with 1.0 M NaOH or 1.0 M HCl.

Solutions were placed in 8-mm inner diameter glass tubes lubricated with soya oil, and then were heated in water bath at 85°C for 30 min. After heating, all samples were immediately cooled and kept at 5°C for 24 h.

Methods

Analytical methods. Protein, water, and fat contents were determined by standard AOAC [1984] methods and the content of lactose was determined as described by Bueschel *et al.* [1992]. A Carl Zeiss AAS 3 atomic absorption spectrophotometer was used to determine calcium, sodium, potassium and magnesium.

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Rheological measurements. The rheological properties of whey protein-carrageenan mixed solution were evaluated by a Brookfield DV-II+ viscometer (Brookfield Engineering Laboratories, Inc., Stoughton, MA, USA) equipped with a coaxial system. The temperature was maintained by a Fisherbrand FBH 600 thermostate (Fisher Scientific, Schwerte, Germany). Shear stress *vs*. shear rate measurements were performed at 20°C after heating to 85°C, and kept for 5 min at this temperature and cooled down to 20°C. The shear rate was changed from 0.1 to 25 1/s and from 25 1/s to 0.1 1/s. The apparent viscosity *vs*. temperature measurements were performed at a shear rate 5 1/s. The solutions were heated to 85°C, kept for 5 min, and then cooled to 20°C.

Texture measurements. Whey protein – carrageenan gels were removed from the tubes and cut into 8-mm cylinders using a scalpel. Uniaxal compression to failure was used to measure true shear stress at fracture (stress) and true shear strain at fracture (strain). A TA-XT2i texture analyzer (Stable Micro Systems, Haslemere, UK) was used to compress gels between two parallel plates at a crosshead speed of 1 mm/s. Six samples of gels were evaluated per treatment. Each treatment was completed in triplicate. The gels were treated as incompressible materials, and true shear strain at fracture (ε_{cH}) was calculated as: ε_{cH}=-ln [1-(Δh/h)], where h is the height of the uncompressed sample which fractures after Δh of compression. The compressive stress (σ_c) at fracture was calculated as: σ_c=Force [1-(Δh/h)]/πr^2, where r is the initial gel radius.

Statistical analysis. The data were analyzed using analysis of the Student's *t*-test by Stat 1 (ISK, Skierniewice, Poland).

RESULTS AND DISCUSSION

Flow properties of WPI and WPI-carrageenan mixed solutions

Table 1 shows the composition of WPI powder. The composition was similar to the results obtained for five whey isolates examined by Mleko [2001].

Figure 1 shows the changes of the apparent viscosity of 3% (w/w) WPI solution and WPI-KK mixed solutions during heating from 50 to 85°C and then cooling to 20°C. The apparent viscosity of a 3% WPI solution increased at a temperature of 85°C, which indicated gelation of whey proteins. The WPI–KK blend gelled at 83 and 81°C, at 0.2 and 0.3% carrageenan concentration, respectively. Paulsson and Dejmek [1990] found that the onset of gelation of 4 and 5% β-lactoglobulin varied from 84 to 88°C over the investigated pH range (pH 4–7.5). Cooling down from 85 to 20°C resulted in a constant increase in the apparent viscosity to 800 mPa·s at 20°C. The addition of polysaccharide caused a significant increase in whey protein solutions viscosity at 20°C to 1700 and 2700 mPa·s at a concentration of carrageenan 0.2 and 0.3 %, respectively. This observation is in agreement with the decrease of the gelling time with increasing κ-carrageenan concentration and is probably caused by fastening of the aggregation kinetics [Capron *et al.*, 1999]. Dynamic rheology measurements showed that κ-carrageenan formed stronger gels in the presence of whey proteins [Tziboula & Horne, 1999].

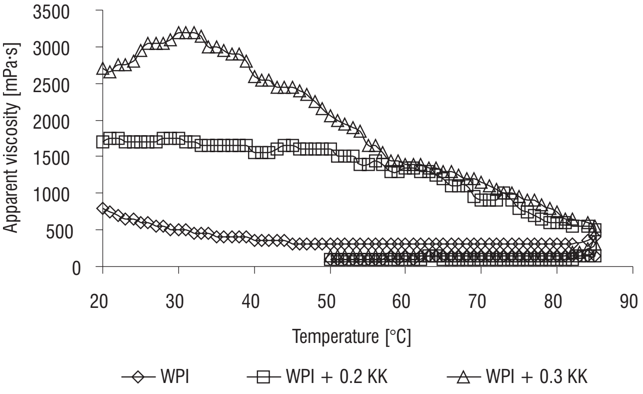

FIGURE 1. Apparent viscosity of WPI (3%) and WPI-κ-carrageenan (KK) mixed solutions (pH 7) as a function of temperature.

Figure 2 shows the effect of pH on changes of the apparent viscosity of WPI-KK (0.3%) dispersions. The dispersion obtained at pH 7 had the highest value of the apparent viscosity. At pH 5, the apparent viscosity of the WPI-KK mixture was lower than that at pH 7. At alkaline pH (10), the protein-polysaccharide mixed system had a very low apparent viscosity in all temperature ranges and did not gel (Figure 2). These observations are in opposition to the results obtained for β-lactoglobulin (10%)-κ-carrageenan (1%) mixed gels, where the highest value of G' was observed at pH 5 [Ould Elaya & Turegon, 2000].

Flow curves of 3% solution of WPI, KK solution at 0.3% concentration and a mixture of 3% WPI and 0.2 or 0.3% KK are shown in Figure 3. When polysaccharide was added to WPI solution, the flow behaviour was strongly modified. A dramatic increase in the shear stress of the systems and histeresis loop area was observed. The highest value of the

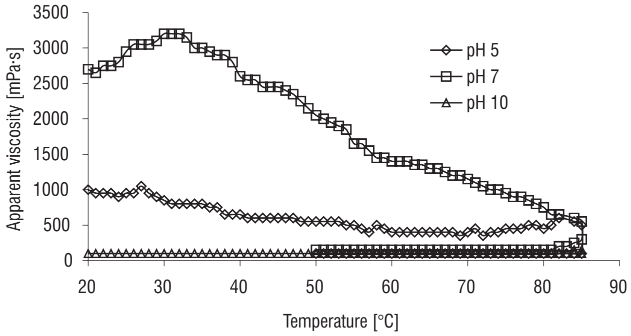

FIGURE 2. Apparent viscosity of WPI (3%) – 0.3% κ-carrageenan (KK) mixed solutions as a function of temperature.

TABLE 1. Composition of whey protein isolate.

	Protein [%]	Lactose [%]	Fat [%]	Water [%]	Ca [%]	Na [%]	K [%]	Mg [%]
WPI	91.9	0.69	0.47	4.25	0.10	0.58	0.0015	0.01

shear stress (25 Pa at shear rate 25 1/s) was observed for mixtures with 0.3% addition of KK.

Figure 4 shows the influence of shear rate on shear stress of the systems prepared by mixing 3% whey protein and 0.3% KK or LK in 0.1 M NaCl. WPI-KK mixed solutions had the highest values of shear stress.

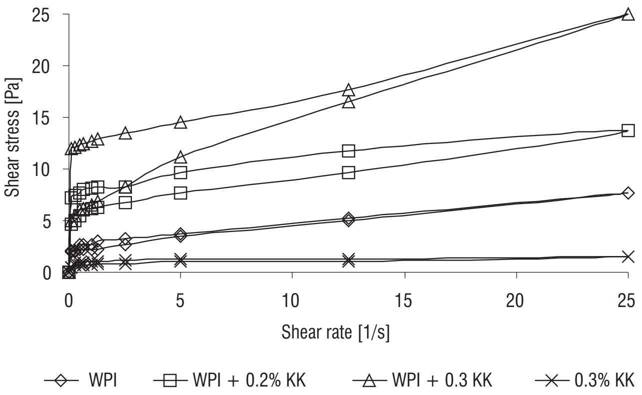

FIGURE 3. Flow behaviour of WPI (3%), κ-carrageenan (KK) and WPI-KK mixed systems at pH 7.

All mixed systems had a yield point. Probably, the mixed systems obtained at this concentration were partly cross-linked, and this structure was caused by the shear forces. The shapes of the flow curves are not characteristic for the tixotropic behavior, but reveal a rheodegradation process.

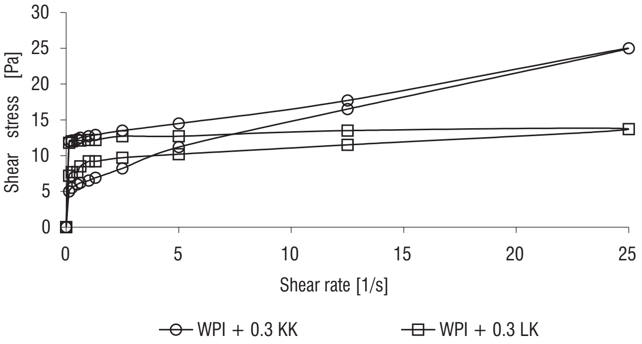

FIGURE 4. Flow behaviour of WPI (3%) – κ-carrageenan (KK) or λ-carrageenan (LK) mixed solutions at pH 7.

Unaxial compression of WPI and WPI-carrageenan mixed gels

The shear stress and strain at a fracture of 10% WPI and WPI-KK mixed systems are shown in Tables 2 and 3, respectively.

WPI gels obtained at pH 3 were weak and brittle, and gels obtained at pH 4–6 were opaque and prone to whey syneresis and did not fracture at 80% deformation. These results are similar to the results noted by Mleko *et al.* [1997], who obtained coagulum at pH 4 and 5.

At pH 7 and 8, very strong gels were obtained, and they were too elastic to fracture. They did not exhibit whey syneresis during compression experiment. Mleko *et al.* [1997] and Pikus *et al.* [2001] observed identical behaviour of whey protein heat-induced gels. The strongest WPI heat-induced gels were obtained by Foegeding [1995] also at pH 7 and 8.

At pH>8 whey protein gels were translucent and homogeneous on a macroscopic scale. Similar gels were obtained at pH 3, but they were more brittle (Table 2).

Referring to a number of sources [Foegeding *et al.*, 1995; Ziegler & Foegeding, 1990; Stading *et al.*, 1993; Mleko *et al.*, 1997; Pikus *et al.*, 2000], WPI gels could be defined as particulate (pH 4–6), fine stranded (pH<4, pH>8), and mixed particulate/fine stranded (pH 7–8). At pH 4–6, near the isoelectric point of whey proteins, the surface charge is low and protein-protein random aggregation is favoured to the detriment of protein-solvent interactions, resulting in a heterogeneous network formed by strands of large aggre-gates. Compression of the gel decreases the volume of pores, which results in whey syneresis. At pH> 8, the surface charge of whey proteins is high and repulsive forces promote ordered aggregation of proteins and formation of long and flexible strands. These gels are less deformable by compression than particulate gels. At pH<4, whey protein gels are also fine stranded, but the strands are rigid and relatively short [Stading *et al.*, 1993].

In gels containing a WPI-KK blend, different textures were observed (Tables 2 and 3). At 0.1 and 0.2% addition of polysaccharide, the texture of all gels, apart from gels obtained at pH 4 and 5, was suitable for compression measurement. At higher carrageenan concentrations (0.3 and 0.5%), gels obtained at pH 5 were also suitable for measurement. An identical behaviour of WPI-KK mixed

TABLE 2. Changes in shear stress at fracture of 10% WPI and WPI-κ-carrageenan (KK) gels at different pH and carrageenan concentration.

	Shear stress at fracture [kPa]							
KK [%]	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9	pH 10
0.0	5.19^{a}	–	–	–	–	–	13.46^{b}	14.25^{b}
	±1.37						±2.69	±3.10
0.1	7.09^{a}	–	–	26.20^{c}	56.22^{f}	43.51^{e}	36.46^{d}	15.92^{b}
	±0.75			±2.15	±4.15	±3.24	±2.31	±1.85
0.2	7.27^{a}	–	–	16.28^{b}	65.46^{f}	35.55^{d}	51.95^{e}	31.84^{c}
	±0.15			±0.52	±2.15	±1.61	±1.00	±1.65
0.3	4.91^{a}	–	7.95^{b}	14.10^{c}	65.43g	35.35^{e}	49.73^{f}	25.11^{d}
	±0.90		±0.49	±1.60	±3.35	±2.12	±2.37	±1.14
0.5	3.19^{a}	–	23.66^{c}	8.41^{b}	9.15^{b}	8.69^{b}	49.85^{e}	28.71^{d}
	±0.29		±1.12	±0.69	±1.00	±0.40	±0.75	±1.54

a–g Means within lines with different superscripts are significantly different at $P<0.05$; (–) texture unsuitable for measurements.

TABLE 3. Changes in shear strain at fracture of 10% WPI and WPI-κ-carrageenan (KK) gels at different pH and carrageenan concentration.

	Shear strain at fracture							
KK [%]	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9	pH 10
0.0	0.16^{a} ±0.01	–	–	–	–	–	0.90^{b} ±0.01	1.10^{c} ±0.08
0.1	0.30^{a} ±0.03	–	–	1.29^{d} ±0.06	0.99^{b} ±0.03	1.07^{bc} ±0.07	1.23^{d} ±0.05	1.14^{c} ±0.06
0.2	0.35^{a} ±0.01	–	–	1.04^{c} ±0.06	1.54^{e} ±0.03	0.94^{b} ±0.05	1.09^{c} ±0.03	1.16^{d} ±0.03
0.3	0.24^{a} ±0.07	–	0.77^{b} ±0.04	1.02^{c} ±0.04	1.57^{d} ±0.08	0.83^{b} ±0.06	1.01^{c} ±0.03	1.04^{c} ±0.03
0.5	0.20^{a} ±0.01	–	0.98^{c} ±0.08	0.87^{b} ±0.06	0.83^{b} ±0.06	0.79^{b} ±0.07	1.01^{c} ±0.05	1.12^{d} ±0.02

a–e Means within lines with different superscripts are significantly different at $P<0.05$; (–) texture unsuitable for measurements.

gels containing 0.5% polysaccharide was observed earlier by Mleko *et al.* [1997]. At pH 3, the stress values of the WPI- KK mixed gels were lower than those for WPI gels at 0.5 and 0.3% carrageenan concentration, however, at lower polysaccharide concentrations (0.1 and 0.2%) the obtained gels were stronger and more elastic (Tables 2 and 3). The highest value of shear stress (23.7 kPa) was observed at pH 5 and a 0.5% addition of KK. Mleko *et al.* [1997] stated that pH 6 created the optimum conditions for obtaining gels from WPI – 0.5% κ-carrageenan mixtures.

The addition of the polysaccharide in the concentration of 0.1–0.3% gave the strongest mixed gels at pH 6–8. A higher KK concentration resulted in a dramatic decrease in the shear stress at fracture of mixed protein-polysaccharide gels. WPI-ι-carragenan mixed gels had similar mechanical properties at pH 7 [Pikus *et al.*, 2001]. Neiser *et al.* [2000] obtained similar results for mixed gels of BSA with κ-carrageenan. At pH 6.9, the strongest gels were observed at low κ-carrageenan concentrations up to 0.3%, however, at pH 5.4 a major strengthening effect of high κ-carrageenan (>0.6%) concentration on BSA gels was shown.

The maximum values of the shear stress were obtained for WPI-κ-carrageenan mixtures at a concentration of KK 0.2 and 0.3% at pH 7. At a higher pH, carrageenan concentrations above 0.1% had a better effect on the mixed gel texture, while at pH 10 and at 0.5% of polysaccharide, gel was obtained at room temperature. Monahan *et al.* [1995] and Mleko [2001] obtained whey protein gels at pH 11 and 12 at room temperature. Extensive unfolding caused sufficient protein-protein interactions, including disulfide bond formation at this pH, which facilitates formation of a gel [Monahan *et al.*, 1995; Mleko, 2001].

The addition of polysaccharide caused a dramatic increase in the shear strain at fracture of whey protein gels, especially at pH 3. The decrease in the elasticity of the mixed WPI-KK gels was observed at higher polysaccharide concentrations (above 0.1%) at pH 3, 6, 8, and 9 (Table 3).

The structures of the three main forms of carrageenan differ only in the number of sulphate groups per disaccharide: κ- has one, ι- has two and λ- has three. In the solutions λ-carrageenan adopts a coil conformation, regardless of the ionic and temperature conditions and is unable to form a gel [Langendorff *et al.*, 2000; Gustaw & Mleko, 1998]. In Table 4, the shear stress values at fracture of mixed gels of 10% WPI with a non-gelling type of carrageenan – LK are shown. At the pH range of 4–6, all mixed gels were unsuitable for compression measurement. At pH 3, the addition of LK caused a weak increase in the strength of WPI gels only at 0.1% polysaccharide concentration. At a higher polysaccharide concentration, shear stress values decreased and were lower than for WPI gel (Table 4). At pH 7, a gel suitable for compression measurement was obtained only at 0.1% LK concentration, but the values of the shear stress were lower than for WPI-KK gel obtained under the same conditions. At an alkaline pH, mixed polysaccharide-WPI gels were stronger than WPI gels and the values of shear stress stabilized at about 32 kPa and 20 kPa at pH 9 and 10, respectively.

The effect of carrageenan on the mechanical properties of WPI-carrageenan mixed gels containing 10% whey protein depended on carrageenan concentration (0.1–0.5%),

TABLE 4. Changes in shear stress at fracture of 10% WPI and WPI-λ-carrageenan (LK) gels at different pH and carrageenan concentration.

	Shear stress at fracture [kPa]							
LK [%]	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9	pH 10
0.1	5.65^{a} ±0.62	–	–	–	49.22^{e} ±1.29	42.65^{d} ±0.75	33.74^{c} ±1.10	24.42^{b} ±0.60
0.2	4.85^{a} ±0.75	–	–	–	–	37.14^{d} ±1.01	32.51^{c} ±1.20	22.18^{b} ±0.85
0.3	4.84^{a} ±0.22	–	–	–	–	–	31.48^{c} ±1.25	20.78^{b} ±1.00
0.5	3.46^{a} ±0.25	–	–	–	–	–	–	27.12^{b} ±1.25

a-g Means within lines with different superscripts are significantly different at $P<0.05$; (–) texture unsuitable for measurements.

carrageenan type (κ or λ) and pH (3.0–10.0). As a general trend, the simultaneous increase in carrageenan concentration and decrease in pH inhibited the gelation of WPI-carrageenan solutions apart from gels obtained at pH 5 from WPI-KK solutions. Below pI of whey proteins, where two polymers (proteins and polysaccharide) carry opposite charges, a complex coacervation was observed [Tolstoguzov, 1991]. At pH 3, mixed gels were similar to those of pure protein gels (translucent and brittle) but significant differences in gel strength were observed. At pH 4 and high KK concentration (0.5%), the formation of coagulum was observed, which resulted from the precipitation of whey proteins – carrageenan complexes. These observations support previous findings on mixtures of whey proteins and anionic polysaccharides at pHs below the pI of the protein [Syrbe *et al.*, 1998; Ould Eleya & Turegon, 2000]. Formation of complexes was observed in the mixtures of BSA with acacia gum at pH 4.2 [Schmitt *et al.*, 2000], BSA with κ-carrageenan [Neiser *et al.*, 2000] and WPI with apple pectin [Zaleska *et al.*, 2000].

In the pH range of 6–10, mixed gels showed two distinct behaviours: one at low polysaccharide concentration (up to 0.3%), and the other under the same conditions but at a higher carrageenan concentration and at pH above 8. At pH 6–8 and a low carrageenan concentration, very strong end elastic gels were formed. Under these conditions, well above whey proteins pI, the protein self-association is reduced and both biopolymers have opposite charges. This could suggest separation under these conditions. It must, however, be mentioned that sulphated hydrocolloids (as carrageenan) can form soluble complexes with proteins at pH above the protein pI [Grindberg & Tolstoguzov, 1997]. κ-Carrageenan interacts with κ-casein by electrostatic interaction even at pH higher than isoelectric point of casein [Snoeren, 1976].

At carrageenan concentrations above 0.3% and at pH range of 6–8, an extensive phase separation between biopolymers was observed. The shear stress values of mixed gels were much lower in these conditions than for mixed gels obtained at lower concentrations of KK. The extensive phase separation between polysaccharide and proteins, that probably occurred during whey protein aggregation, decreased the interactions between protein aggregates and impaired the mechanical properties of the mixed gels. Mleko *et al.* [1997] suggested that at these pH ranges, κ-carrageenan molecules inhibit the aggregation of whey protein molecules which leads to stronger gels.

At alkaline pH (9–10), even though the protein-polysaccharide incompatibility was enhanced, the obtained gels were quite strong and elastic. Mleko *et al.* [1997] and Pikus *et al.* [2001] obtained similar results for WPI-κ-carrageenan and WPI-ι-carrageenan mixed systems, respectively.

A higher content of sulfate in LK and a lack of ability to switch into a rigid helical conformation seems to be crucial for self-association and interaction with whey proteins in mixed gels [Gustaw & Mleko 1998]. These observations are in agreement with the findings of Lin and Hansen [1970], who reported that λ-carrageenan was not a good stabilizer of milk protein. However λ-carrageenan interacts with casein micelles at a broad range of temperatures, whereas κ-carrageenan forms complexes with casein micelles only at temperatures below the coil-helix transition temperature [Langendorff *et al.*, 2000].

The WPI-carrageenan mixed systems can be used in dairy desserts, yogurt and processed cheese [Mleko *et al.*, 1997; Mleko & Gustaw, 2002].

CONCLUSIONS

1. The addition of κ-carrageenan caused an increase in apparent viscosity of 3% WPI solutions, especially at pH 7 and 0.3% carrageenan concentration.
2. The optimum level of κ-carrageenan concentration and pH, which produced WPI gels with the highest shear stress was 0.2% and pH 7.
3. The low κ-carrageenan concentration (up to 0.2%) showed a major strengthening effect on WPI gels at pH 3, 6, 7 and 8. At higher polysaccharide concentrations, the mixed gels obtained at these pHs were weaker than pure WPI gels.
4. Synergistic interactions between λ-carrageenan and WPI were weaker than between whey proteins and κ-carrageenan, probably because of a higher sulfate content in λ-carrageenan.
5. Complexes could be formed in WPI-κ-carrageenan mixed system at pH range of 3–4, however, at pH 5–10 phase separation occurs.

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WPŁYW pH I STĘŻENIA KARAGENU NA WŁAŚCIWOŚCI REOLOGICZNE ŻELI BIAŁEK SERWATKOWYCH

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Białka serwatkowe i polisacharydy są żelującymi biopolimerami szeroko wykorzystywanymi w przemyśle spożywczym. W pracy badano żelowanie izolatu białek serwatkowych (WPI) i mieszanin WPI z κ-karagenem lub λ-karagenem. Po dodaniu polisacharydu do roztworów WPI ich lepkość pozorna znacznie wzrastała. Najwyższą wartość lepkości pozornej zanotowano dla mieszaniny WPI (3%) z κ-karagenem (0,3%) sporządzonej w pH 7 (rys. 1). Właściwości teksturalne żeli WPI i otrzymanych z mieszaniny WPI-polisacharyd badano w zakresie pH 3–10 i przy dodatku κ-karagenu lub λ-karagenu w stężeniach od 0,1 do 0,5%. Roztwory WPI o stężeniu 10% w pH 7 i 8 tworzyły bardzo twarde i elastyczne żele. Najtwardsze żele z mieszanin WPI (10%) z κ-karagenem otrzymano w pH 7 przy 0,3% stężeniu polisacharydu (tab. 2). Małe stężenia polisacharydu miały wyraźny wpływ na wzrost twardości żeli WPI w pH 3, 6–8. Słaby wpływ na twardość żeli WPI lub tworzenie koagulum zaobserwowano przy wyższych stężeniach karagenu w tych samych warunkach. W pH 3–4 pomiędzy polimerami mogły być tworzone kompleksy, natomiast w zakresie pH 5–10 występowała faza separacji.