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Mixed gels made from protein and κ-carrageenan

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The rheological behavior of mixed gels made from soy or pea protein concentrates with the addition of κ-carrageenan was investigated using uniaxial compression and dynamic measurements. Pea protein concentrate (PPC) exhibited greater synergy with κ-carrageenan than soy protein concentrate (SPC) in relation to gel strength, gel stiffness and pH stability. A modified Takanayagi treatment of dynamic measurements indicated a shift in the continuous phase from protein to κ-carrageenan at concentrations of 4–8% κ-carrageenan in the total solids. This shift occurred at lower concentrations when PPC was used compared to SPC. Copyright © 1996 Elsevier Science Ltd.

INTRODUCTION

A number of proteins are used in food products in order to provide increased functionality (water binding, gelation, emulsion stability etc.). Such functional proteins are often part of food systems, where hydrocolloids are also used, and a synergistic effect can be obtained (Marrs, 1989; Tokaev *et al.*, 1987; Tolstoguzov, 1991).

The present investigation was undertaken in order to map the optimum physico-chemical conditions for a synergistic effect between the commonly used food proteins (soya protein and pea protein) and κ-carrageenan.

MATERIALS AND METHODS

Two pea protein concentrates (P 2000 and P 2100 from Nutrio A/S, Haderslev, Denmark) were compared with a soy protein concentrate (Purina 500 E, SFK, Hvidovre, Denmark). Gels were made to final total solids of 18%, by the addition of κ-carrageenan (Grindsted Products, Århus, Denmark) to 0–8.3% of the total solids.

Suspensions with varying amounts of protein (16.5–18% w/w) and κ-carrageenan (1.5–0% w/w) were made using demineralized water and the pH was adjusted from 6.2 to 7.4 using 0.1 N HCl or NaOH. The suspensions were de-aerated overnight at 5°C, filled in cans, heat-treated at 125°C for 1 h, maintained at 5°C for 24 h and analyzed. Compressive measurements were made on five cylinders (height 21.45 mm, diameter 24 mm) from each can, using a plate with a diameter of 35 mm and a crosshead speed of 100 mm/min. The plates were lubricated with oil before each test and the response was recorded as σ (stress) vs γ (strain). Young's modulus was calculated as the slope of the first linear part of the plot of σ (stress) vs γ (strain).

Dynamic measurements were made using a Bohlin VOR rheometer with a cup and bob measurement system (C25). The pH was maintained at 6.8 with a phosphate buffer. Gelation was followed using oscillatory measurements in the linear viscoelastic region (5.0 Hz, amplitude 0.5%) during a temperature gradient from 40 to 90°C, followed by relaxation measurements (an amplitude of 5%, with a strain rise time of 2 s and a measurement time of 300 s) and a frequency sweep (0.1–20 Hz, 0.5% amplitude) at 40°C.

Results from the dynamic measurements were treated according to the modified Takanayagi method of Clark *et al.*, (1983), used in several recent studies on mixed systems containing food components (Ziegler & Rizvi, 1989; Svegmark & Hermansson, 1993; Chronakis & Kasapis, 1993; Kasapis *et al.*, 1993).

RESULTS AND DISCUSSION

Compressive measurements indicated that the two pea protein concentrates used exhibited greater synergy with κ-carrageenan than soy protein concentrate. Figure 1 illustrates this using Young's modulus as an indicator of the stiffness of the gels. A similar relationship was found for the compressive force at the breakpoint (i.e. gel strength). The highest gel strength and gel stiffness was found in the pH range 6.4–6.8. Mixes of PPC with κ-carrageenan were influenced less by variations in pH than equivalent gels made with SPC (Fig. 2).

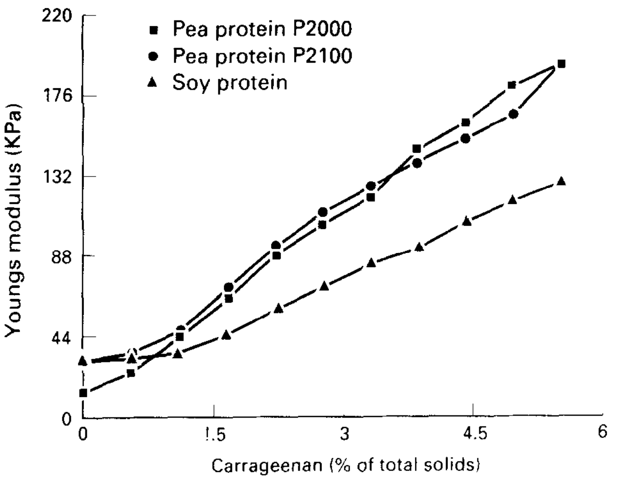

Fig. 1. Young's modulus for gels with 18% total solids made from different proteins with varying amounts of κ-carrageenan added ($n = 6$).

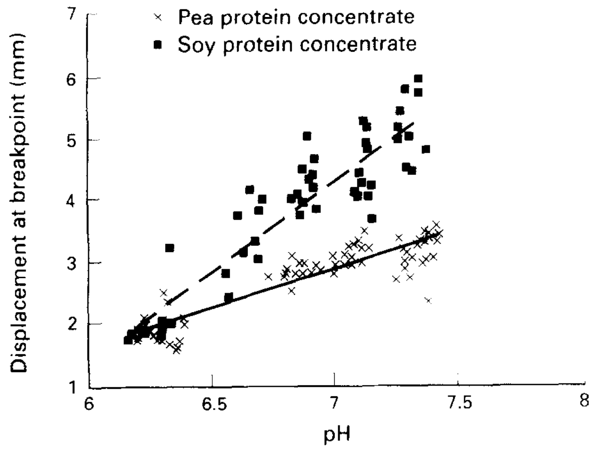

Fig. 2. Displacement at breakpoint vs pH for soy and pea protein concentrates.

Table 1. Concentration dependence of the elastic modulus, G' (5 Hz and 0.5% amplitude)

	a	b	R^2
Pea protein concentrate P 2000	0.0059	4.16	0.96
Pea protein concentrate P 2100	0.00012	5.71	0.98
Soy protein concentrate	0.0014	5.04	0.99
κ-carrageenan	69.4	3.84	0.99

Data were fitted to the power law equation, $G' = a \times C^b$, where C is the concentration of the polymer.

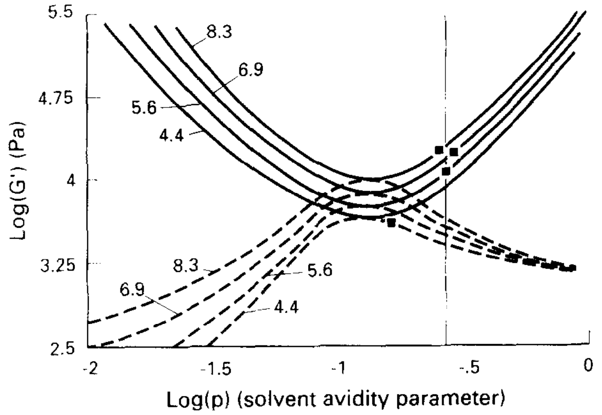

Fig. 3. Calculated upper and lower boundaries for the elastic modulus, G', of pea protein concentrate P 2000 with various amounts of κ-carrageenan added (4.4–8.3% of the total solids) plotted against the solvent avidity parameter, p. Solid lines are upper boundaries, dashed lines indicate lower boundaries. Filled boxes are experimental values.

In order to model moduli of the composite gels it is necessary to know the composition dependence of the moduli. With the present system, it was found that a power law equation gave reasonable fits to the data, when using G', at 5 Hz from the frequency sweep on the finished gel (Table 1). The phase volumes in aqueous binary gels are, however, not only determined by the amounts of polymer present, but also on the partition of solvent between the two phases. Clark (1987), therefore, introduced the so-called solvent avidity parameter, p, as the ratio of solvent to polymer in one phase (i.e. protein), divided by the corresponding ratio in the other phase (i.e. κ-carrageenan). Boundaries for the modulus could then be plotted as a function of p as shown in Fig. 3 for pea protein concentrate P 2000. It can be seen that the experimental values corresponding to 5.6–8.3% κ-carrageenan in the total solids are all located on the upper boundaries, equivalent to a continuous carrageenan phase. The value for 4.4% κ-carrageenan in the total solids is situated very close to the critical point, where the upper and lower boundaries meet, and the experimental values below 4.4% are all on the lower boundaries, equivalent to a continuous protein phase (not shown). The experimental results for the points on the upper boundaries can, with reasonable precision, be fitted to a single value of p. For the systems investigated, the value of p varied from 0.23 to 0.31, indicating that κ-carrageenan is 3–4 times as solvent attracting as the protein concentrates.

Figure 4 shows the experimental values and the calculated lower and upper boundaries using a p value of 4. The indicated change from lower boundary behavior (protein constituting the continuous phase) to upper boundary behavior (a continuous phase consisting of κ-carrageenan) occurs in the mixed gels at concentrations where carrageenan constitutes 2.8–5.6% of total solids. The shift occurs at lower concentrations of κ-carrageenan when PPC is used, compared to SPC.

A similar result (Walkenström & Hermansson, 1994) has been found for a system consisting of whey protein concentrate and gelatin, but it was observed microscopically that a bicontinuous gel formed throughout the concentration interval studied. Phase

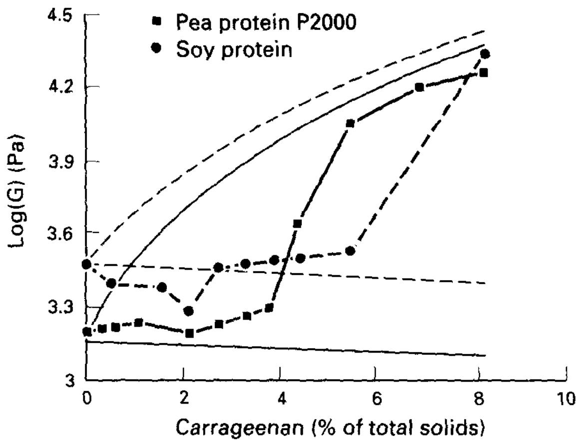

Fig. 4. G'(5 Hz and 0.5% amplitude) for mixed gels made from SPC or PPC and κ-carrageenan. Thin lines represent the upper and lower boundary for $p = 4$ ($n = 3$).

shifts indicated by rheological measurements are thus not necessarily reflected in the actual microstructure observed. Preliminary microscopy of the present system, however, confirmed the indicated phase shifts.

CONCLUSION

Addition of κ-carrageenan to PPC for the formation of mixed gels resulted in gels with higher gel strength and greater stiffness than in equivalent gels made with SPC. The gels made with PPC were also less sensitive to pH than gels made with SPC.

Application of a modified Takanayagi model to oscillatory data indicated a shift in the continuous phase from protein to κ-carrageenan at concentrations of 4–8% κ-carrageenan in the total solids. This shift occurred at lower concentrations when pea protein concentrate was used.

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REFERENCES

Chronakis, I.S. & Kasapis, S. (1993). Structural properties of single and mixed milk/soya protein systems. *Food Hydrocoll.*, **7**, 459–478.

Clark, A.H. (1987). In *Food Structure and Behaviour*, eds J.M.V. Blanshard & P. Lillford. Academic Press, London, pp. 13–34.

Clark, A.H., Richardson, R.K., Ross-Murphy, S.B. & Stubbs, J.M. (1983). Structural and mechanical properties of agar/gelatin co-gels. Small-deformation studies. *Macromolecules*, **16**, 1367–1374.

Kasapis, S., Morris, E.R., Norton, I.T. & Clark, A.H. (1993). Phase equilibria and gelation in gelatin/maltodextrin systems — Part IV. Composition-dependence of mixed-gel moduli. *Carbohydr. Polym.*, **21**, 269–276.

Marrs, W.M. (1989). Protein/polysaccharide interactions and their application in food products. The British Food Manufacturing Industries Research Association, Scientific and Technical Surveys, p. 168.

Svegmark, K. & Hermansson, A-M. (1993). Microstructure and rheological properties of composites of potato starch granules and amylose: a comparison of observed and predicted structures. *Food Struct.*, **12**, 181–193.

Tokaev, E.S., Gurov, A.N., Rogov, I.A. & Tolstoguzov, V.B. (1987). Properties of oil/water emulsions stabilized by casein–acid polysaccharide mixtures. *Nahrung*, **31**, 825–834.

Tolstoguzov, V.B. (1991). Functional properties of food proteins and role of protein–polysaccharide interaction. *Food Hydrocoll.*, **4**, 429–468.

Walkenström, P. & Hermansson, A-M. (1994). Rheology of mixed gels of gelatin/whey proteins. *Ann. Trans. Nordic Rheol. Soc.*, **2**, 53–55.

Ziegler, G.R. & Rizvi, S.S.H. (1989). Predicting the dynamic elastic modulus of mixed gelatin–egg white gels. *J. Food Sci.*, **54**, 430–436.