Rheology of mixed gels of gelatin/whey proteins

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ABSTRACT

Mixed and pure gels of gelatin and whey protein concentrate were investigated by tensile tests and by dynamic oscillatory measurements. The systems were studied at pH 5.4 and 4.6. The results indicate an inversion in rheological properties. Further, it was concluded that the gel formation of whey protein concentrate is unaffected by the presence of gelatin.

INTRODUCTION

Over the years a good deal of research has been performed on pure polymer gels. However, the increased demand for new products with special properties, for example low-fat products, has led the research to mixed gels, as a wider array of textural characteristics and opportunities for engineered products can be obtained.

A need exists for a quantitative approach which would predict the properties of mixed gels, or even of a product based on a mixed gel, from the known properties of the pure individual components[1]. The Takayanagi approach[2], explored by Clark et al.[3], is one of the first and simplest approaches to explain the mechanical behaviour of three-component systems, two polymers and a solvent. Usually, a good fit is achieved where one can use the calculated bounds as an area in which the elastic modulus of the mixed polymer system is placed.

The present paper deals with, gelatin/whey protein concentrate (WPC) mixtures and investigates the fitness of the system to the Takayanagi bounds. The system has previously been discussed in detail[4].

Under the conditions used, one fine-stranded structure, gelatin, is mixed with one particulate structure, WPC. WPC forms a gel network upon heating, while gelatin forms a gel network upon cooling. As the WPC forms its network first, the gelatin network is formed in the pores of the WPC network.

The aim of this study was to elucidate the rheological properties of the mixed gels of gelatin and whey proteins and to relate these to the rheological properties of the pure components and to their different microstructure.

MATERIAL AND METHODS

The WPC used is obtained from Denmark Protein A/S (Lacprodan-95, 240192 s. 1). The gelatin sample are obtained from Extraco, Klippan, Sweden. It is acid-processed and supplied in granular form with nominal strength of 250 Bloom and with a mean molecular weight of 118 kD. It is marked as "lot no 17777 250 Bloom".

The mixed gels have an constant concentration of 8%w/w WPC and varying concentrations of gelatin. For sample preparation see Walkenström and Hermansson[4].

The rheological tecniques used are dynamic oscillatory measurements[5], performed with an Bohlin VOR Rheometer (Bohlin Rheology, Lund, Sweden), and tensile tests[6] until fracture, using an Instron 1122. For more details see Walkenström and Hermansson[4].

THEORY

The modified Takayanagi model

The moduli of the composite gels have been related to the moduli of the pure components with the help of polymer blending laws[2,3]:

$$G_C = \Phi_X G_X + \Phi_Y G_Y \qquad \textit{Isostrain} \qquad (1)$$

$$1/G_C = \Phi_X/G_X + \Phi_Y/G_Y \quad \textit{Isostress} \qquad (2)$$

where Φ_X and Φ_Y are the volume fractions of the two components and G_X and G_Y are their respective mouduli. G_C is the composite modulus.

The effective concentrations were calculated[3] and the effective moduli, G_X and G_Y, were determined by fitting an expression, as given in eq. 3, to experimental data.

$$G = a\ (c_{eff.} - c_0)^b \qquad (3)$$

a and b are constants, c_0 is the critical gel concentration, $c_{eff.}$ is the effective concentration. Φ_X and Φ_Y were calculated[3].

RESULTS AND DISCUSSION

Properties at small deformations

The elastic modulus, E, was measured as the initial slope in a stress-strain curve obtained by tensile tests. In fig. 1, E is plotted against gelatin concentration for mixed gels.

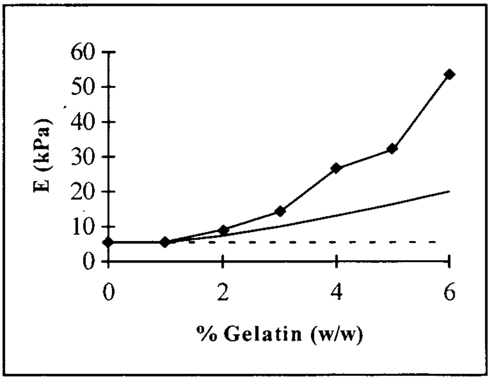

Figure 1. E versus gelatin concentration for mixed gels, pH 5.4. The line corresponds to calculated moduli, see text for further information, and the dotted line corresponds to the modulus of 8% WPC (Walkenström and Hermansson)[4].

The line in fig. 1 corresponds to a calculated modulus for the mixed gels based on the assumption that it is just the sum of the moduli of the pure components, at their respective concentrations. It is clear from the figure that synergistic effects exist and starts to take place around 3%w/w gelatin. Up to around 3%w/w gelatin the increase in E for the mixed gels is small, whereafter it increases with a higher slope. The pH 4.6 gels gave similar results.

Fracture properties

Stress and strain at fracture are shown in fig. 2. The concentration dependence of the fracture propertis is shown for the mixed gel series and for the pure components series.

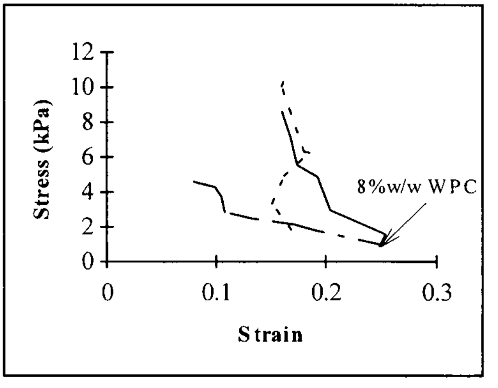

Figure 2. Stress at fracture versus strain at fracture for pure and mixed gels, pH 4.6. --- corresponds to pure gelatin, — - — to pure WPC and —— to the mixed gels (Walkenström and Hermansson)[4].

Pure WPC gels show a decrease in strain and an increase in stress at fracture values as the concentration increases. Strain at fracture for pure gelatin gels is, more or less, concentration-independent while stress at fracture increases with concentration. The mixed gel curves shift to lower strain and higher stress at fracture values as gelatin is added. They show stress and strain at fracture values which fit pure WPC gels at low gelatin concentrations and pure gelatin gels at high gelatin concentrations. The shift takes place between 2-3%w/w gelatin. The pH 5.4 gels gave similar results.

The modified Takayanagi model

The fitness to the modified Takayanagi approach is shown in fig. 3.

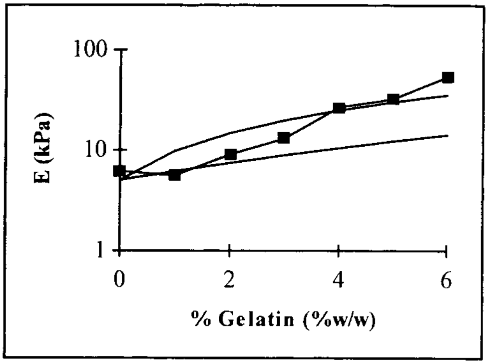

Figure 3. Calculated upper, isostrain, and lower, isostress, bounds, as well as measured data for E versus gelatin concentration. pH 5.4 (Walkenström and Hermansson)[4].

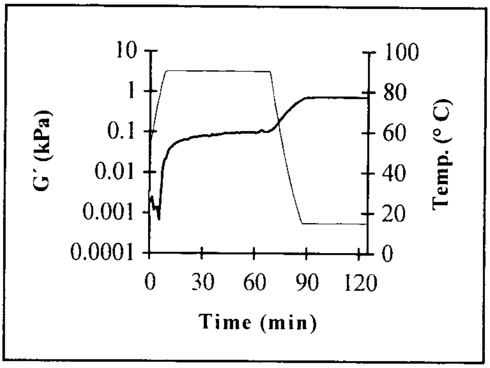

Figure 4. G′ for the gel formation of 8%w/w WPC, full line, and of 8%w/w WPC+3%w/w gelatin, grey line, pH 5.4. The thin line corresponds to time-temperature relations (Walkenström and Hermansson)[4].

At low gelatin concentrations, the mixed gel follow the lower curve, the isostress situation, suggesting that the weaker component is the continuous material, i.e. WPC. As the gelatin concentration increases, a shift takes place and the behaviour of the mixed gel starts to follow the upper curve, the isostrain situation, now suggesting that the stronger component is the continuous material, i.e. gelatin. At pH 5.4, fig. 3, the shift occurs somewhere between 2 and 4%w/w gelatin, and at pH 4.6, not shown, it takes place between 1 and 3%w/w gelatin. A high p-value, around 3, gave the best curve fits, when choosing WPC as the X-component, in both cases. According to theory, this may be interpreted as a phase inversion.

Gel formation

The first increase in G′ in figure 4 shows the gel formation of pure WPC, 8%w/w, and of WPC in a mixed gel, 8%w/w WPC and 3%w/w gelatin, pH 5.4. It is obvious from the figure that the network formation of WPC is more or less independent of the presence of gelatin. Additional studies show that it is independent of the gelatin concentration as well. The decrease in temperature initiates the second increase in G′ in figure 4. This increase is due to the gelation of gelatin and also to a further set in the WPC gel network, which can be seen in both curves. The same behaviour is obtained at pH 4.6.

CONCLUSIONS

- ☺ Rheological results suggest that an inversion in rheological properties takes place in the mixed gels.
- ☺ Microscopy results show that a bicontinuous system is formed throughout the concentration interval studied[4].
- ☺ The network formation of WPC seems unaffected by the presence of gelatin.

ACKNOWLEDGEMENTS

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REFERENCES

1. Ziegler, G. R. and Rizvi, S.S.H. (1989) J. of Food Sci., **54**, no. 2, 430-436.

2 Takayanagi, M., Harima, H. and Iwata, Y. (1963) Memoirs of the Faculty of Engineering, Kyushi University, **23**, 1-13.

3. Clark, A.H., Richardson, R.K., Ross-Murphy, S.B. and Stubbs J.M. (1983) Macromolecules, **16**, 1367.

4. Walkenström, P. and Hermansson, submitted for publication in Food Hydrocolloids.

5. Stading, M. and Hermansson, A-M. (1990) Food Hydrocolloids, **4**, no. 2, 121-135.

6. Stading, M, and Hermansson, A-M. (1991) Food Hydrocolloids, **5**, no. 4, 339-352.