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A rheological comparison between the effects of sodium caseinate on potato and maize starch

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The differences in response of 1% potato and 4% maize starch pastes to sodium caseinate inclusion were investigated. Pasting of the starches was performed at 95°C for 1 h in a range of concentrations of sodium caseinate. Caseinate levels as low as 0.01% dramatically reduced the swelling volume of potato starch and hence the viscosity of the system. Since sodium chloride addition shows similar effects, it appears that caseinate acts through a non-specific ionic strength effect. The influence of caseinate on maize starch was less clear since it depended on the solvent medium. In distilled, deionized water, there was an increase in viscosity with increasing caseinate concentration, which may simply be explained by a contribution of the caseinate to the viscosity of the continuous phase. However, in 0.1 M, pH 7.0 buffer the results suggest that caseinate may inhibit retrogradation as the viscosity of the system after ageing is reduced by its inclusion. It is suggested that phase separation between starch and caseinate is encouraged at high salt concentrations. As a consequence, both starch granule swelling and subsequent retrogradation are discouraged by caseinate in the buffer system, but not when pasting is carried out in distilled, deionized water. Copyright © 1996 Published by Elsevier Science Ltd.

INTRODUCTION

It is a well-accepted practice in the food industry to utilize the functional properties of starches of various origins together with sodium caseinate. Starches are generally employed for their thickening and stabilizing ability. Sodium caseinate is normally found, in its emulsifying capacity, to result in an overall effect on product body and texture (Mulvihill, 1992).

In systems where these two components occur together, the interactions between them need to be understood if synergistic effects are to be utilized, or antagonistic effects prevented, to provide maximum benefits in new or current food products.

It has previously been reported that the addition of caseinate increases the viscosity of gelatinized maize starch by enhancing the extent to which the granule swells (Lelievre & Husbands, 1989). The suggested mechanism was the limiting of disintegration of the starch granule through either a reduction in the rate of swelling or by limiting the collapse of the swollen granules due to the action of shear during pasting. In contrast, Hermansson (1978) reported a viscosity decrease on caseinate addition and suggested that the formation of an amylose–caseinate complex was responsible. More recently, Doublier *et al.* (1994) have reported the effect of sodium caseinate addition on the behaviour of wheat, potato and tapioca starch. They report a large decrease in the volume fraction occupied in the paste by the swollen starch granules and in the concentration of starch macromolecules solubulized in the continuous phase. Surprisingly, only in the case of tapioca starch did this reduction in swelling volume produce a decrease in apparent viscosity.

It is clearly recognized that the rheological properties of starches depend critically on the volume fraction occupied by the swollen starch granules; Steeneken (1989) has identified domains where the concentration, $c < 1/s$, where s is the volume of solvent associated with 1 g of dry starch following gelatinization in excess water, and the region where c is greater than $1/s$. In the first domain, viscosity at a given concentration increases with s, whereas in the second domain viscosity may decrease with s, since in the regime where the granules are closely packed viscosity will depend on granule rigidity rather than the volume occupied by the swollen granule. In this study we compare the effect of caseinate on the viscosity of maize and potato starch at

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concentrations of 4% and 1%, respectively, which will be slightly above the c^* concentration defined by $c^* = 1/s$. This has been reported to be of the order of 3% for maize starch and 0.6% for potato starch (Evans & Haisman, 1979). In this situation, a reduction in swelling volume would be expected to have the maximum effect on the viscosity of the starch pastes since the resultant reduction of the swelling volume will move the system from the second to the first domain.

MATERIALS AND METHODS

Potato starch was provided by Amylum, Belgium, and maize starch was supplied by Sigma, UK. Sodium caseinate and buffer salts were supplied by St Ivel, UK, and Fisons, UK, respectively. Starch pastes of concentration 4% (w/v) (maize) and 1% (w/v) (potato) were prepared in a range of sodium caseinate solutions in either distilled, deionized water or 0.1 M, pH 7.0 phosphate buffer (8.66 g/l Na_2HPO_4 and 6.084 g/l $NaH_2PO_4.2H_2O$). These concentrations were selected to give roughly equivalent viscosities for the two systems in the absence of the protein. Gelatinization was achieved by preparing 30 ml of the dispersion of starch/caseinate in Universal bottles with screw-top lids. The bottles were shaken manually in a 95°C water bath until gelatinization, to prevent particle settling, and then left for 1 h.

After cooling to ambient temperatures, viscosity measurements were then made using a Bohlin CS Rheometer with cone and plate 4/40 geometry under stress viscometry mode. Viscosity measurements were always reported at a shear rate of 50 1/s and a temperature of 25.0±0.2°C.

Swelling volumes of the granules were obtained by centrifuging a known volume of paste at 2200 rpm for 10 min in graduated centrifuge tubes, allowing direct reading of the pellet volume. Swelling volume is reported as the volume of pellet per dry weight of starch in the centrifuge tube. The soluble solids content of the supernatant was determined gravimetrically for potato starch in the absence of caseinate and up to 0.05% caseinate.

RESULTS AND DISCUSSION

The data in Fig. 1 show that even very small additions of sodium caseinate to a 1% potato starch paste in distilled, deionized water result in a significant decrease in viscosity. The maximum effect is seen when the caseinate concentration approaches 1%. It is apparent that there is an almost parallel decrease in swelling volume observed over the same caseinate concentration range (Fig. 1). Figure 2 shows the increase in apparent solubility of potato starch with increasing low levels of caseinate. Apparent solubility was calculated as the weight of dry solids in the supernatant divided by the total weight of starch in the centrifuge tubes. At the caseinate levels for which the data were reported, the contribution of the caseinate in the granular and supernatant phases was the same. This increase can be ascribed to the caseinate only; that is to say the amount of polysaccharide leaving the granule is low and is not affected by the caseinate concentration.

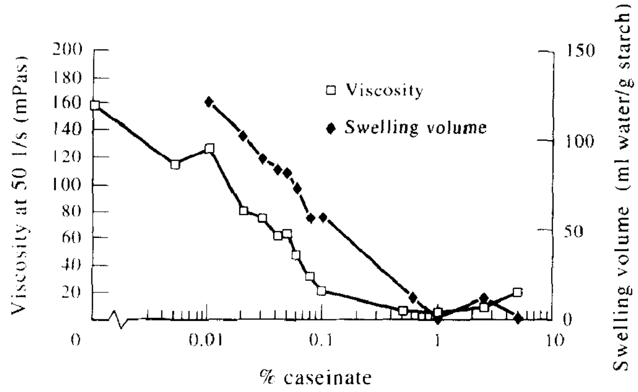

Fig. 1. Effect of caseinate on viscosity and swelling volume of a 1% potato starch paste prepared in distilled, deionized water and measured at a temperature of 25.0±0.2°C. Viscosities relate to a shear rate of 50 1/s.

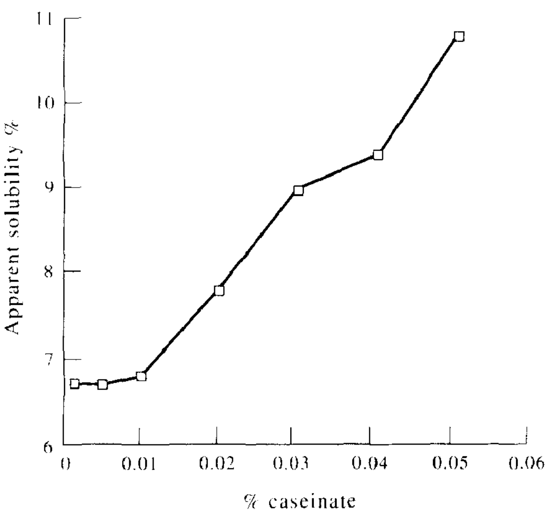

Fig. 2. Effect of caseinate on apparent solubility of a 1% potato starch paste.

It has been reported by Muhrbeck and Eliasson (1987), that low levels of sodium chloride cause a substantial reduction in the viscoelastic properties of potato starch. This effect was not seen for cassava (tapioca) starch. It, therefore, seemed possible that the large effects seen with sodium caseinate could be due to the presence of associated ions. To investigate this possibility, sodium chloride was added to the system. It can be seen that low levels of salt addition (Fig. 3) also caused a large reduction in viscosity, which is consistent with previously reported results on the reduction in swelling volume of potato starch at 0.01% NaCl

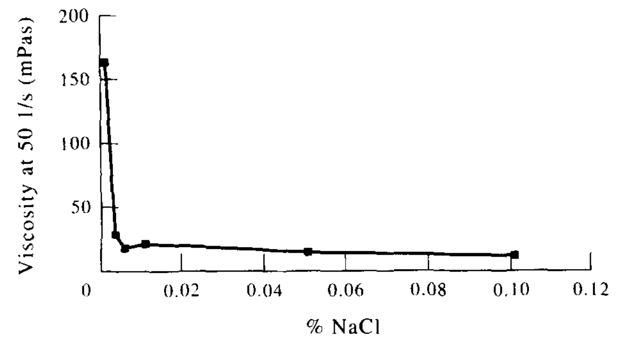

Fig. 3. Effect of sodium chloride on the viscosity of a 1% potato starch paste prepared in distilled, deionized water and measured at a temperature of 25.0±0.2°C. Viscosities relate to a shear rate of 50 1/s.

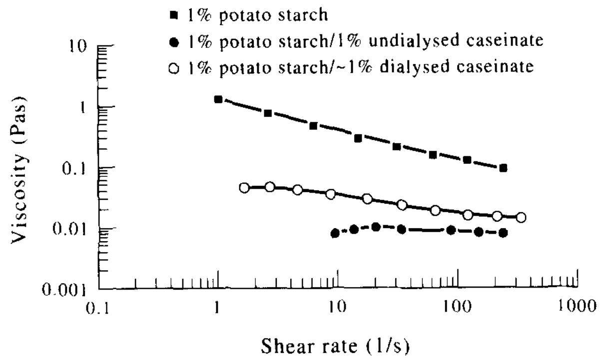

Fig. 4. Flow curves for 1% potato starch alone and in the presence of 1% dialysed and undialysed sodium caseinate.

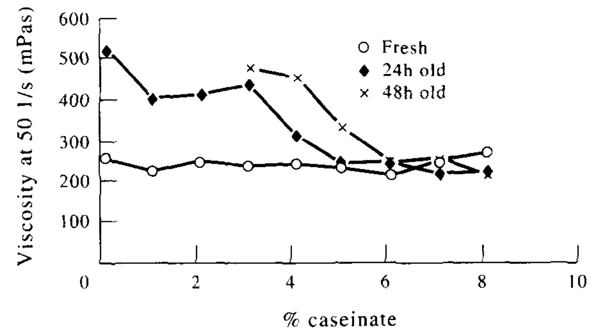

Fig. 5. Effect of caseinate on the viscosity of a 4% maize starch paste prepared in pH 7.0 phosphate buffer. Viscosities were measured within 2 h of obtaining room temperature and after 24 and 48 h ageing. Viscosities were measured at 25.0±0.2°C.

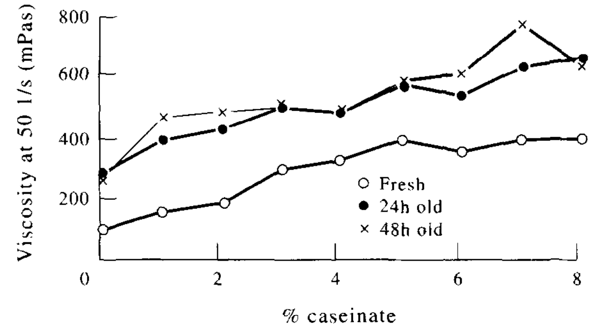

Fig. 6. Effect of caseinate on viscosity of a 4% maize starch paste prepared in distilled, deionized water. Viscosities were measured within 2 h of obtaining room temperature and after 24 and 48 h ageing. Viscosities were measured at 25.0±0.2°C.

(Paterson *et al.*, 1994). Sodium chloride did not have significant effects on the reduction of swelling volume of a range of other starches: cassava, wheat, maize, rice and sago (Paterson *et al.*, 1994). When the caseinate solution was dialysed before being added to the starch, the resultant flow curves were intermediate between the undialysed caseinate control and the potato starch control paste (Fig. 4).

It may, therefore, be concluded that potato starch is unique in its response to low levels of electrolyte and that the very large sodium caseinate effect is related to this rather than a specific protein–starch interaction. Potato starch is known to contain a high level of phosphate groups compared to other starches (see for example Swinkels, 1985; Muhrbeck & Tellier, 1991). It will, therefore, have a significant polyelectrolyte character. It seems probable that the dramatic ionic strength dependence is due to Donnan effects and the gelatinized potato starch granule is behaving as a 'super-swelling' polyelectrolyte gel maintained by a relatively low density of entanglements between amylopectin molecules.

The effect of caseinate on maize starch is less clear. The large viscosity lowering seen with potato starch was not repeated and the solvent medium seemed to play an important part in determining the effects observed. There was a higher viscosity in buffer than in the water in the absence of caseinate, suggesting that the extent of granule swelling was greater in buffer. This could reflect the lower pH (5.2) of starch alone pasted in water. In addition, in the pH 7 buffer (Fig. 5) sodium caseinate addition had no apparent effect on fresh paste viscosity. In distilled, deionized water (Fig. 6), however, viscosity of the fresh system increased steadily with increasing caseinate concentration.

The lack of change in viscosity with increasing sodium caseinate in buffer may reflect a slight decrease in starch swelling volume (Fig. 7), in contrast to the data reported by Lelievre and Husbands (1989). This decrease in swelling volume would compensate for the increase in viscosity of the continuous phase with increasing caseinate concentration. On ageing, maize starch will retrograde far more readily than potato starch. Figures 5 and 6 show the viscosities of the starch after 24 h and 48 h ageing at ambient temperature. As expected, the viscosity of the water-pasted system increased. This increase occurred at all sodium caseinate concentrations. In contrast, in the buffer system high levels of sodium caseinate appeared to prevent the viscosity increase. This different behaviour is unlikely to be due to pH since even after low levels of caseinate

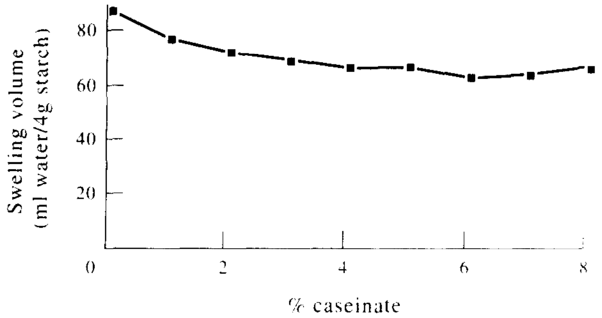

Fig. 7. Effect of caseinate on swelling volume of maize starch paste pasted in pH 7.0 phosphate buffer. Results refer to the volume occupied by the granules in a 4% maize starch paste.

addition, the water–paste system has a pH value very close to 7.0.

A possible explanation for the lack of retrogradation in buffer is phase separation at high concentrations of caseinate, giving a casein continuous phase in the intergranular space that prevents the formation of an amylose continuous network. Such an effect would also be expected to cause a reduction in the swelling volume of starch with increasing caseinate concetration, as is observed in this study. Phase separation between a non-polyelectrolyte (starch polysaccharides) and a polyelectrolyte (caseinate) is encouraged by high salt concentrations, since this reduces the unfavourable entropy change, which would result from the difference in counter-ion concentration occurring on phase separation. It is possible that the postulated effect of ionic strength on phase separation for the starch caseinate system could explain some of the conflicting reports in the literature. Clearly, further work is required to confirm this idea. Microscopy would be particularly useful.

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REFERENCES

Doublier, J.L., Marzin, C., Visdeloup, S. & Lefebvre, J. (1994). Effect of sodium caseinate on the pasting behaviour of starches from different origins. *Carbohydr. Polym.*, **25**, 228–229.

Evans, I.D. & Haisman, D.R. (1979). Rheology of gelatinised starch suspensions. *J. Texture Studies*, **10**, 347–370.

Hermansson, A-M. (1978). 'Protein/Starch Complex'. US Patent No. 4 159 982.

Lelievre, J. & Husbands, J. (1989). Effects of caseinate on the rheological properties of starch pastes. *Starch/Stärke*, **41**, 236–238.

Muhrbeck, P. & Eliasson, A-C. (1987). Influence of pH and ionic strength on the viscoelastic properties of potato and cassava starches. *Carbohydr. Polym.*, **7**, 291–300.

Muhrbeck, P. & Tellier, C. (1991). Determination of starch from native potato varieties by ^{31}P NMR. *Starch/Stärke*, **43**, 25–27.

Mulvihill, D.M. (1992). Production, functional properties and utilization of milk protein products. In *Advanced Dairy Chemistry—1: Proteins*, ed. P.F. Fox. Elsevier Applied Science, London, pp. 369–404.

Paterson, L.A., Mat Hashim, D.B., Hill, S.E, Mitchell, J.R. & Blanshard, J.M.V. (1994). The effect of low levels of sulphite on the swelling and solubility of starches. *Starch/Stärke*, **46**, 288–291.

Steeneken, P.A.M. (1989). Rheological properties of aqueous suspensions of swollen starch granules *Carbohydr. Polym.*, **11**, 23–43.

Swinkels, J.M. (1985). Composition and properties of commercial native starches. *Starch/Stärke*, **37**, 1–15.