PHASE SEPARATION IN THE GELATIN–STARCH–WATER SYSTEM

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The gelatin–starch–water system has been studied at different temperatures, at a total biopolymer concentration of 5·0 wt%. The weight ratios (W) of gelatin/starch used were 9:1, 8:2 ········· 2:8, 1:9, with pH values between 5·82 (at W = 9:1) and 6·50 (at W = 9:1). The systems were characterised rheologically and by turbidity measurements, to construct a phase diagram with temperature (T) and composition (W) as variables.

The T, W-quadrant consists of three regions: a single-phase solution region (A) and regions of complete and incomplete phase separation (B and C, respectively). The system in region C is a gel. Region B, lying between A and C, corresponds to a solution with sediment.

The transition from A to C (obtained by cooling the system at constant W) involves intersection with region B. Gel properties depend on the rate of this intersection. For example, the gels formed on rapid cooling have an even distribution of turbidity, whereas slow cooling gives two gel layers of different tubidity. The likely origin of this behaviour, and other properties of the gels, will be discussed.

RHEOLOGICAL PROPERTIES OF HIGHLY CROSS-LINKED WAXY MAIZE STARCH IN SKIM MILK

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In food systems, starch is often used as a thickening agent in combination with other ingredients, like milk in custard. We have measured the rheological behaviour of highly cross-linked waxy maize starch in suspensions of skim-milk powder in water. It was observed that the viscosity and modulus of a suspension of a given concentration of starch are much higher in skim milk than in water.

It is thought that the milk proteins are excluded from the swollen starch granules. This results in a phase separation between the starch and the milk proteins. The concentrations of the components in their phase become higher than in the whole solution. When the concentration of starch is above a critical value, it is possible that the concentration in the milk protein phase became high enough to form a gel of casein or beta-lactoglobulin.

We used a model proposed by Clark to describe the rheological behaviour of the starch–milk system. In this model the rheological behaviour of the combined system is determined by the viscosity and the modulus of a phase and the volume fraction of that phase. The water in the solution is distributed between the two phases by a relative affinity parameter (p). This parameter has to be estimated or measured by comparing the temperatures of the onset of gelation in pure and mixed systems (Svegmark & Hermasson, 1993). We used the volume of the swollen starch granules (Steeneken, 1989) and the hydration volume of the milk proteins (Walstra, 1984). In this manner a model can be made which describes the rheological behaviour of a starch–milk system reasonably well. However, the model needs further refinement.

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EFFECT OF SODIUM CASEINATE ON THE PASTING BEHAVIOUR OF STARCHES FROM DIFFERENT ORIGINS

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A number of food formulations imply the pasting of starch in the presence of casein. We report here some results on the effect of sodium caseinate on the swelling and solubility of starches from different botanical origins (wheat, potato and tapioca) and on the rheology of the pastes. These different starches are known to exhibit a wide range of pasting behaviours and, therefore, of rheological properties. The swelling and solubility patterns of starch during the pasting procedure were established. Meanwhile, the flow properties of the pastes were studied at 60°C and their viscoelastic behaviour characterised at the same temperature by dynamic measurements on the 0·01–10 Hz frequency range. The addition of caseinate decreased by a factor of 2 to 3 the swelling and solubility indices for wheat starch. The decrease was as high as six-fold for potato and tapioca starches. Solubility also was dramatically decreased. These effects result in a large decrease in the volume fraction occupied in the pastes by the swollen starch granules and in the concentration of starch macromolecules (essentially amylose) solubilised in the continuous phase. The rheological properties of the pastes also were strongly influenced by the presence of caseinate. On the basis of the swelling–solubility results, one could expect the caseinate to cause a large drop in the consistency of the pastes. Actually, a decrease in apparent viscosity was seen only in case of casein/tapioca starch mixtures. But, the opposite overall effect was observed with the two other starches, its magnitude depending on starch concentration. In addition, the presence of caseinate tended to reduce the thixotropic character of the pastes. This last effect can be accounted for by the lowering of starch granules deformability and mechanical fragility entailed by the diminution of their swelling. But the interpretation of the consequences of the presence of caseinate on other flow characteristics clearly requires the consideration of the interactions between caseinate and starch macromolecules in the continuous phase. The caseinate also modified the viscoelastic character of the pastes. However, each type of starch yielded a specific result and no clear tendency emerged. The effect of caseinate on starch pasting, particularly the swelling–solubility behaviour, can be discussed as a consequence of thermodynamical incompatibility. However, a clear understanding of the role of caseinate on starch properties requires a more detailed description of starch, and of interactions between caseinate and starch components, in the mixed system.

STRUCTURAL PROPERTIES OF MALTODEXTRIN–SODIUM CASEINATE SINGLE AND MIXED GELS

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Differential scanning calorimetry measurements of Paselli-caseinate preparations demonstrate the denatured coil structure (flat, featureless thermogram) of the protein and the broad melting process (midpoint transition temperature of about 68°C) of the polysaccharide, thus arguing for a non-interactive coexistence of the two components. Centrifugation (up to 3500 *g* for 30 min) of the binary systems at 45°C failed to show signs of bulk phase separation, the two polymers remaining in a single phase. However, dynamic oscillatory data for gelled mixed systems (5°C) indicate that the physical arrangement changes as a function of polymer ratio and overall concentration. Hence, mixed gels containing Paselli at levels above the minimum critical gelling concentration ($C_o \approx 20{\cdot}2\%$) behave similarly to gels of maltodextrin alone, i.e. tan δ values of $\approx 0{\cdot}1$ upon network maturation at 5°C for 3 h and structure disintegration ($G'' > G'$) above 70°C during heating.

At amounts of SA-2 below the C_o, increasing concentrations of caseinate are necessary for gel formation; e.g. 2·5 as opposed to 7·5% protein at initial concentrations of 20 and 15% maltodextrin in the blend, respectively. This pattern of behaviour indicates that the presence of caseinate makes some of the solvent unavailable to maltodextrin, thus raising its effective concentration to at least C_o, with gels then behaving as described above. The viscoelastic properties of mixed systems with a maltodextrin content below 15% change abruptly throughout the experimentally accessible range of protein concentration. The build-up and destruction of structure is reminiscent of the caseinate colloidal assembly with a high loss component (about half of the G' values) and early melting on heating (20–30°C). On the whole, there is clear evidence that at lower concentrations of maltodextrin the sodium caseinate forms a continuous suspension whereas at higher concentrations phase inversion promotes an SA-2 continuous network.

RHEOLOGICAL PROPERTIES OF COMMERCIAL EDIBLE DISPERSIONS

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Several commercial edible dispersions have been evaluated for rheological properties at large and small deformation analysis in an attempt to differentiate, rather empirically at this stage, the viscoelastic and textural properties of these products. Traditionally, compression testing has been used to characterise the properties of firmness and spreadability, which are considered to reflect the consumer's choice on edible fats. It has been proposed that a fair evaluation of firmness and spreadability is obtained by the parameters of maximum stress (σ_m), which is the point where the stress goes through a maximum value, maximum strain (ε_m) whch is the strain at σ_m, and the plastic stress (σ_p) which is the stress at a horizontal or near-horizontal portion of the curve at a strain (ε_p) slightly larger than ε_m (Cain *et al.*, 1989). Conventionally produced samples (80% fat content), require strains (ε_m) from 0·2 to 0·3% to deform, producing σ_p to σ_m ratios between 0·95 and 1. Commercial dispersions with a fat content between 40 and 20% show more pronounced stress maxima resulting in σ_p to σ_m ratios of about 0·8. Obviously, the sharper, more gel-like force-deformation profile in the low fat products is due to the addition of biopolymers (usually starch), used to prevent syneresis of the water phase. Edible dispersions with less than 10% fat in the product employ phase separated mixtures of biopolymers (e.g. gelatin–maltodextrin; Kasapis *et al.*, 1993) to structure the disproportional water phase, thus inheriting the undesirable characteristic of a gel-like structure. Similarly, dynamic oscillatory measurements have characterised low fat spreads (Nielsen & Hansen, 1994) and they have been also used in this investigation to monitor product elasticity. Thus mechanical spectra of spreads with a large aqueous phase ($\geqslant 90\%$) produce storage to loss moduli ratios of two to three times higher than those of the high fat content blends (80%) and strain sweeps demonstrate that the long range deformation in the latter products commences at least an order of magnitude before the destabilisation of the aqueous network in a low fat product.

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DYNAMIC MECHANICAL THERMAL ANALYSIS OF BREAKFAST CEREAL FLAKES AND THEIR COMPONENTS

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In order to understand the textural properties of breakfast cereals it is important to study their mechanical properties as they vary with composition and structure. Cereal flakes comprise biopolymers, principally starch and gluten. The mechanical properties of these polymers are determined to a large extent by their glass transition (Levine & Slade, 1990). The combination of these polymers and the addition of other constituents, such as water and sucrose, alter the glass transition and the final properties of the flakes.

The mechanical properties of hot-pressed specimens of starch and gluten polymers as well as those of two component mixtures with sugars have been recently reported (Kalichevsky and Blanshard, 1992; Kalichevsky *et al.*, 1992*a*, *b*). This study considers the mechanical behaviour of breakfast wheat flake