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Rheological properties of highly cross-linked waxy maize starch in aqueous suspensions of skim milk components. Effects of the concentration of starch and skim milk components

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The storage modulus of various concentrations of highly cross-linked waxy maize starch was measured in water, a salt solution, a salt solution with lactose, whey, and skim milk. The influence of the skim milk components was deduced from the differences in moduli between these systems. Salts appeared to have no direct influence on the modulus of the starch. Lactose increased the storage modulus, probably due to an increase in the particle rigidity of the swollen starch granules. The whey proteins had only a small effect on the modulus of the starch. However, the concentration of these proteins was very low. Casein micelles increased the modulus of the starch because the swollen starch granules are not accessible to the casein. A model based on the mutual exclusion of swollen starch granules and milk proteins was applied to predict the storage modulus of starch–milk systems as a weighed sum of the moduli of the starch and protein phases. Weight factors were derived from the hydration capacity of starch granules and casein micelles. Although the behaviour of aqueous starch–skim milk systems fell within the boundaries imposed by the model, the predictive power of this model was rather poor. © 1997 Elsevier Science Ltd

INTRODUCTION

Numerous studies have been reported on the rheological behaviour of gelatinised starch in water (Evans & Haisman, 1979; Doublier *et al.*, 1987; Steeneken, 1989). However, starch is often used as a thickening agent in food systems in combination with other ingredients, such as milk in custard. These ingredients may alter the rheological behaviour of starch. The purpose of this study is to predict the mechanical properties of a starch–skim milk system from the component properties.

The viscosity of a certain amount of starch in milk is higher than the viscosity of that same amount in water (Bradley, 1993; Descamps *et al.*, 1987). Some studies describe the influence of the components of skim milk on the rheological behaviour of starch. Sodium caseinate, which is different from the casein micelles in milk, increases the swelling volume of certain starches. This results in an increase of the viscosity (Lelièvre & Husbands, 1989; Marzin *et al.*, 1994). Little is known about the influence of lactose on the rheological properties of starch. The influence of other sugars, such as glucose and sucrose, has been studied. Sugars increase the gelatinisation temperature of starch (Kohyama & Nishinari, 1991; Spies & Hoseney, 1982). The influence of sugars on viscosity is less clear. This depends on the concentrations of starch and sugar used (Savage & Osman, 1978; Cheer & Lelièvre, 1983). Cheer & Lelièvre (1983) found that sucrose increases the viscosity of wheat starch at low concentrations of sucrose. Above a certain concentration, sucrose decreases the viscosity of wheat starch.

It is difficult to distinguish the influences of the different components in skim milk on the rheological behaviour of starch. For example, calcium phosphate strongly affects the behaviour of the casein micelles (Walstra & Jennes, 1984). Therefore, the influence of casein is related to that of calcium phosphate. We have avoided this by studying the influence of several combinations of skim milk components on the rheological properties of starch. The effect of lactose on the rheo-

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logical behaviour of starch was studied by comparing the influence of simulated milk ultrafiltrate (SMUF), a solution of salts present in milk at their proper concentrations, with that of SMUF with lactose. The influence of the whey proteins was studied by comparing the results of whey with those of SMUF with lactose. Comparing the results of whey with those of skim milk allowed the effect of the casein micelles to be elucidated.

The starch used was a highly cross-linked waxy maize starch. In industry, this starch is often used for the production of starch–milk products.

The results from the rheological measurements were evaluated by applying a model developed by Takayanagi *et al.* (1963) and Clark *et al.* (1983), which predicts the modulus of aqueous biphasic gels.

MATERIAL AND METHODS

Materials

Highly cross-linked waxy maize starch was a gift from Cerestar (Sas van Gent, The Netherlands). Skim milk powder (33.6% protein, 47.1% lactose) was supplied by Domo (Beilen, The Netherlands) and low heat whey powder (12.0% protein, 72.9% lactose) by Borculo Whey Products (Borculo, The Netherlands).

Simulated milk ultrafiltrate was prepared according to the procedure described by Jennes & Koops (1962).

Lactose and salts were partly removed from skim milk powder by heating a 20% solution of skim milk powder in water in a round-bottom flask (97 °C). Subsequently, this suspension was centrifuged at 50,000 g for 30 min. After freeze-drying, the resulting powder, denoted as protein-enriched skim milk powder, consists of 64.9% protein and 25.4% lactose.

Analytical methods

The lactose concentration was determined using the anthrone method with lactose as reference. The protein content was measured by the Kjeldahl method ($N\times6.38$).

The swelling capacity of the starch in water, SMUF and SMUF with lactose was measured after gelatinisation at 97 °C with Blue Dextran as an indicator according to Steeneken (1989). In skim milk, the swelling capacity was determined after gelatinisation in skim milk with the milk protein as an indicator.

The gelatinisation temperature (peak temperature) and enthalpy was measured with a Perkin-Elmer DSC-7 in stainless steel pans. The scanning rate was 10 °C min^{-1}. An empty cup was used as a reference.

The hydrodynamic volume of the milk protein was calculated from the intrinsic viscosity ($[\eta]=\lim(c\rightarrow0)\ \eta_{sp}/c$). According to Einstein for a suspension of spheres, η_{sp}/c is equal to $2.5q$, where q is the hydrodynamic volume and η_{sp} is the specific viscosity. η_{sp} was determined by comparing the viscosity of heated skim milk solutions (97°C) with the viscosity of SMUF with lactose in an Ubbelohde viscosimeter at 20°C (Walstra & Jennes, 1984).

Sample preparation for rheological measurements

Suspensions were prepared by weighing skim milk powder or whey powder and adding the appropriate amounts of starch (on a dry basis) and water in a round-bottom flask. SMUF and SMUF with lactose solutions were used instead of water for the rheological measurements of starch in SMUF and in SMUF with lactose. The round-bottom flask was rotated at 180 rpm in a water bath at 97°C for 30 min (Evans & Haisman, 1979).

RHEOLOGICAL MEASUREMENTS

The rheological measurements were made with a Rheometrics RFS II Fluids Spectrometer equipped with cone (0.04 rad) and plate geometry or in a concentric cylinder geometry. The measuring system was filled with the hot paste. A thin layer of paraffin oil of low viscosity was used to prevent loss of moisture. All measurements were done at 15°C. The sample was sheared at a shear rate of 10 s^{-1} for 5 min to reduce effects of small differences in sample preparation. After a 30 min resting time, the viscosity was measured at a shear rate of 1 s^{-1} during 5 min.

Dynamical rheological measurements were done after a 15 min resting time. The modulus (G^*), loss modulus (G''), storage modulus (G'), and phase angle (δ) were determined at a frequency of 1 rad s^{-1} in the linear region (usually below 1% strain). It was ascertained that the moduli before and after shearing at 10 s^{-1} differ by less than 10%.

RESULTS AND DISCUSSION

Swelling capacity of starch

Table 1 shows the swelling capacity of highly cross-linked waxy maize starch in water, SMUF, SMUF with lactose, and skim milk. The concentrations used were comparable with those in skim milk. Considering the

Table 1. Swelling volume (q) of highly cross-linked waxy maize starch in several solutions

Solution	q (ml g^{-1})
Water	10.2±0.6
SMUF	9.3±2.8
SMUF with lactose	10.1±1.1
9.8% skim milk powder	11.2±0.8

large standard deviation of the measurement of the swelling capacity, it can be concluded that the swelling capacity of this starch is approximately the same in the examined solutions. This means that salts, lactose, and milk proteins have no influence on the swelling capacity of the starch. This is only valid for the concentrations used in these swelling experiments. These experiments had to be done with low concentrations of starch. The rheological measurements were performed with higher concentrations of starch. The possibility that the swelling capacity at higher concentrations of starch is influenced by the skim milk components cannot be excluded.

Storage modulus of concentrated milk protein solutions

Figure 1 shows the storage modulus of milk protein solutions with different amounts of added lactose. A lactose concentration of 5.6% corresponds to that in skim milk. At protein concentrations higher than 10%, G' depends strongly on the concentration ($G' \sim c^{18}$). Therefore, the milk protein solution can be described as a suspension of hard spheres.

These measurements were carried out with protein-enriched skim milk powder. The results of these experiments were used for model calculations. To check whether the proteins in enriched skim milk powder are representative of those present in the original skim milk powder, reconstitution experiments were conducted on systems of starch and protein-enriched skim milk powder to which lactose and salts were added to match the composition of the corresponding starch–skim milk systems. From Table 2 it can be concluded that the storage modulus of starch in protein-enriched skim milk powder solution is comparable to G' of starch in untreated powder. So, the extra heating required in the procedure for lowering the lactose and salt concentration does not influence the results of the rheological measurements.

Table 2. Storage modulus of highly cross-linked waxy maize starch in untreated and reconstituted skim milk powder (concentrations two times higher than in skim milk)

Skim milk powder	Conc. starch (g 100 g^{-1})	G' (Pa)
Untreated	4.57	78.1
Untreated	5.07	226.0
Untreated	5.49	528.6
Composite	4.99	143.8
Composite	5.27	316.7

From the intrinsic viscosity of skim milk solutions, the hydrodynamic volume of heated milk protein was calculated to be 5.0 ml g^{-1}. Walstra & Jennes (1984) give values for casein micelles of 3.9 ml g^{-1}. We measured the intrinsic viscosity after heating the milk protein solutions. The heating results in the precipitate of whey proteins on the casein micelles. Therefore, the casein micelles with precipitated whey protein would have a larger hydrodynamic volume than the value mentioned in the literature for pure casein micelles.

Influence of skim milk components on the storage modulus of highly cross-linked waxy maize starch

We measured G' as a function of the concentration of highly cross-linked waxy maize starch in water, in skim milk, and in two and three times concentrated solutions of skim milk powder. The results are shown in Fig. 2. At higher starch concentrations, G' in water is lower than in skim milk at the same concentration of starch. G' in two and three times concentrated skim milk is higher than in water at the same concentration of starch. Therefore, milk components have an influence on the storage modulus of starch. To distinguish between the various components in skim milk we measured the rheological properties of starch in different combinations of skim milk components. The results are described below.

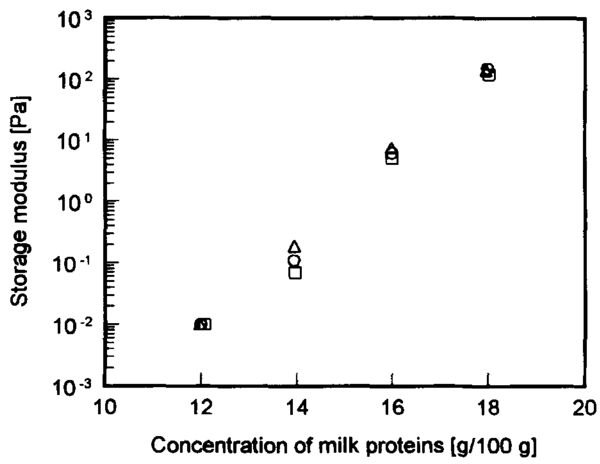

Fig. 1. Storage modulus of milk protein in solutions of 5.6% (□), 11.2% (○), and 16.8% lactose (△).

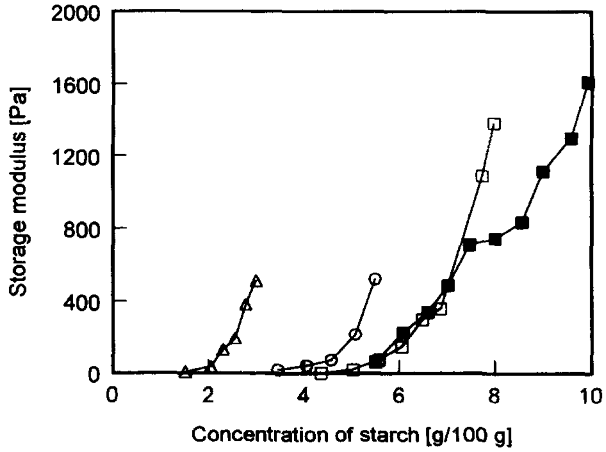

Fig. 2. Storage modulus of highly cross-linked waxy maize starch in water (■), skim milk (□), two times (○), and three times concentrated skim milk (△).

Influence of salts

Figure 3 shows the storage modulus as a function of the concentration of highly cross-linked waxy maize starch in water, SMUF, and SMUF with lactose. The concentrations of the milk components in these systems are comparable with those in skim milk. It can be concluded that G' in water is almost equal to G' in SMUF. This suggests that the salts, in the concentration used in skim milk, have no influence on G' of this starch. On the other hand, the salts in skim milk are important stabilising factors for the casein micelles during heating (Walstra & Jennes, 1984). In that way, they can influence the rheological properties of starch–milk systems.

Influence of lactose

The storage modulus of highly cross-linked waxy maize starch in SMUF with lactose is somewhat higher than G' in SMUF, as can be concluded from Fig. 3. Higher concentrations of SMUF with lactose have an increasing effect of G' of the system (Fig. 4). Explaining this phenomenon is not easy. Table 3 shows that the gelatinisation temperature of the starch is increased by addition of lactose. However, even at high addition levels, these temperatures are far below the temperature used for preparing the samples for the rheological measurements. Hence, it is unlikely that the increase of the gelatinisation temperature is an explanation for the increase of G'. Another explanation could be that lactose is excluded from, or preferentially adsorbed by the swollen starch granules, which could also affect G'. We have investigated this by following the sedimentation under gravity of a heated suspension of known amounts of starch and lactose. After settling for 24 h, the concentration of lactose in the top layer of the solution was measured. Table 4 shows that the concentration in the top layer is equal to the concentration in the total solution. This means that lactose is neither excluded from the swollen starch granules nor preferentially adsorbed.

The concentrations used are expressed in $\mathrm{g\,100\,g^{-1}}$. Because of the presence of lactose, the concentration of starch expressed in $\mathrm{g\,100\,ml^{-1}}$ increased. This could be an explanation for the increase of G' by lactose. However, the effects are small (data not shown).

Steeneken (1989) showed that the rheological properties of starch are determined by the swelling capacity and the particle rigidity. In dilute suspensions the rheological properties are governed by the volume fraction of starch granules. The swelling capacity and the concentration of starch determine the volume fraction. Table 1 shows that lactose has no influence on the swelling capacity of highly cross-linked waxy maize starch. In concentrated solutions, the particle rigidity determines the rheological properties. A measure of the particle rigidity is the storage modulus of starch at the concentration c^* where the swollen granules just fill the

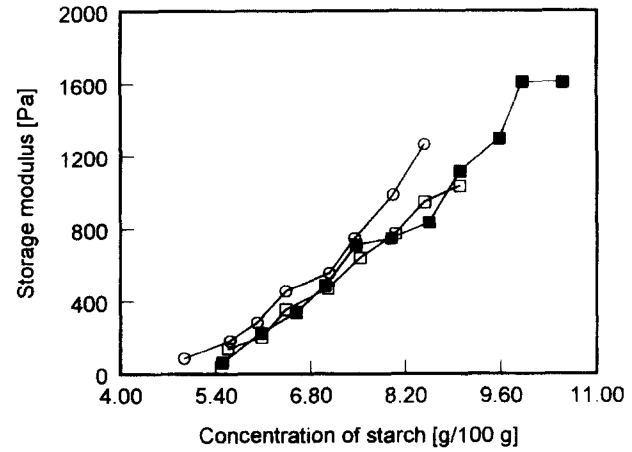

Fig. 3. Storage modulus of highly cross-linked waxy maize starch in water (■), SMUF (□), and SMUF with lactose (○).

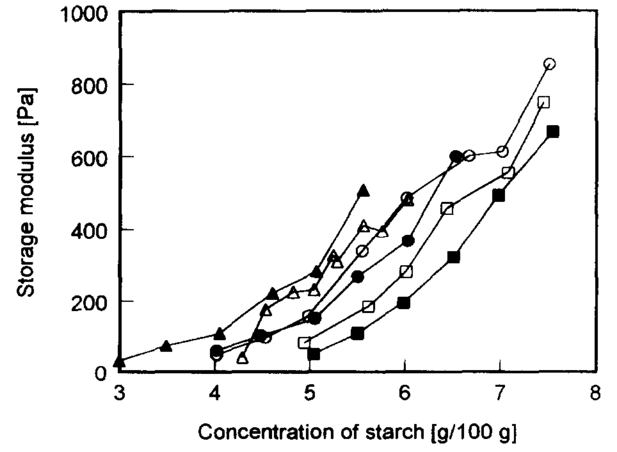

Fig. 4. Storage modulus of highly cross-linked waxy maize starch in SMUF with lactose (□), two times (○), and three times (△) concentrated SMUF with lactose, whey (■), two times (●), and three times concentrated whey (▲).

Table 3. Gelatinisation temperature and enthalpy of highly cross-linked waxy maize starch in water and lactose solutions

Solution	T (°C)	ΔH ($\mathrm{J\,g^{-1}}$)
Water	74.4	19.19
5.6% lactose	75.6	19.53
11.2% lactose	77.0	20.37

Table 4. Lactose concentration in heated solutions of highly cross-linked waxy maize in the total solution and in the top layer after settling under gravity for 24 h

Starch concentration ($\mathrm{g\,100\,g^{-1}}$)	Lactose concentration in total solution ($\mathrm{g\,100\,g^{-1}}$)	Lactose concentration in top layer after settling ($\mathrm{g\,100\,g^{-1}}$)
1	5.6	5.6
2	5.6	5.7
1	11.4	11.3

entire system ($c^* = 1/q = 9.8\%$). From Fig. 3, it can be concluded that the modulus of 9.8% highly cross-linked waxy maize starch is somewhat higher in lactose solutions than in water. This suggests that lactose increases the particle rigidity of this starch. Interaction between starch and sugars could be a cause for this increase in particle rigidity (Chinachoti *et al.*, 1991; Hansen *et al.*, 1989).

Influence of whey proteins

The influence of whey proteins was determined by comparing the storage modulus of highly cross-linked waxy maize starch in whey powder solutions with G' in SMUF with lactose. Figure 4 shows the results for concentrations comparable to those in skim milk and two and three times concentrated solutions. It can be concluded that there is little difference between G' in SMUF with lactose and G' in whey at the same concentration of skim milk components. For concentrations comparable with those in skim milk, G' in whey is somewhat lower than in SMUF with lactose. It is unclear what causes this lowering of G'. A possible explanation is that the swelling capacity of highly cross-linked waxy maize starch decreases at higher concentrations of starch as a result of osmotic deswelling by the proteins. However, this is difficult to examine because the swelling experiments have to be done at low concentrations. Three times concentrated solutions of whey powder gave storage moduli, which are somewhat higher than those in SMUF with lactose. A reason for this could be that the concentration of whey proteins in the solution between the starch granules increases as a result of the exclusion by the swollen granules. The differences are, however, small. It is known that β-lactoglobulin, the major whey protein, can form a gel on heating at concentrations above 5–10% (Stading *et al.*, 1993; Tang *et al.*, 1993). From the swelling capacity of the starch, it is possible to calculate the concentration of starch at which the concentration of whey proteins in the voids between the granules becomes 5%. This concentration will be achieved at a concentration of starch of about 8.5%. However, the measured concentrations of starch were not exceeding 7.5%. So, it is not probable that the whey proteins will form a gel during the measurements.

Influence of casein micelles

Figure 5 shows the storage modulus of different concentrations of highly cross-linked waxy maize starch in suspensions of skim milk and whey powder. Measurements were done in suspensions with concentrations comparable to those in skim milk and two and three times concentrated solutions. It can be concluded that, for concentrations comparable to those in skim milk, the storage modulus of starch is almost equal in skim milk and in whey. However, the storage modulus of starch in concentrated solutions of skim milk powder is considerably higher than in whey powder solutions.

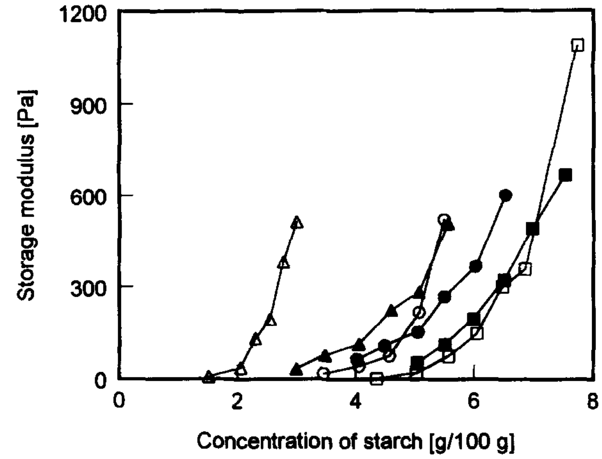

Fig. 5. Storage modulus of highly cross-linked waxy maize starch in whey (■), two times (●), and three times (▲) concentrated whey, skim milk (□), two times (○), and three times concentrated skim milk (△).

From Fig. 1, it can be concluded that the storage modulus of starch in skim milk is not simply the sum of G' of starch and G' of skim milk. The modulus of milk protein solutions in skim milk and two and three times concentrated solutions (respectively 3.3, 6.6 and 9.9% protein) is negligible compared to the G' of starch. However, we assume that the milk proteins will be excluded from the swollen starch granules. As a result, the concentration of the milk proteins in the voids between the granules increases. Figure 1 shows that the milk proteins significantly affect the modulus of starch–skim milk systems at concentrations of 15% or higher, if we assume a G' of 1 Pa s to be the minimum for a significant contribution. This milk protein concentration is reached at a starch concentration of about 7.5% in skim milk. In two and three times concentrated solutions these starch concentrations are 5.3 and 3%, respectively. Above these starch concentrations, the milk proteins will give an important contribution to the rheological properties of the system. The swollen starch granules are excluded from the milk proteins and therefore the starch concentration in the suspension between the milk proteins will increase concomitantly with the increase of the milk protein concentration. This caused an increase in G' of the suspension. This will be significant at the concentrations mentioned above. Figure 5 shows that the modulus of starch in two times concentrated skim milk is higher than in two times concentrated whey above concentrations of about 5%. For three times concentrated solutions this occurs above starch concentrations of 2%. This corresponds with the starch concentrations above at which the milk protein concentration is high enough to cause an increase in the viscosity. For concentrations, which correspond to those in skim milk, only at the highest starch concentration investigated (7.5%) a milk protein concentration between the granules of 15% was reached (Fig. 2).

In short, the above results show that skim milk components have an influence on the storage modulus of highly cross-linked waxy maize starch. Salts do not increase G' of the starch. Nevertheless, the salts have an influence on the heat stability of the casein micelles. Lactose increases G' of the starch dispersion. Lactose diffuses into the swollen starch granules and influences the gelatinisation temperature of the starch. The swelling capacity remains unaffected in the presence of lactose. However, lactose appears to increase the particle rigidity of the starch. This could be the explanation for the increase in the storage modulus.

It can be concluded that the concentrations of whey proteins in our systems were too low to have a noticeable effect on G'. As a result of the swelling of the granules, the concentration of whey proteins between the granules increases from 0.6% in skim milk to 4.2% in the most concentrated systems studied by us. However, the concentration of whey protein remains too low to achieve a concentration where gelling can occur (5%).

Casein micelles contribute significantly to G' of starch–skim milk systems. This is probably caused by the exclusion of the casein micelles from the swollen starch granules. This results in an increase in the concentration of proteins between the swollen starch granules to a sufficiently high level and an increase in the concentration of starch between the milk proteins. This can qualitatively explain the effects of milk proteins on the G' of starch. A model, which is based on these assumptions, is discussed in the following section.

Modelling of rheological data

Takayanagi *et al.* (1963) developed a model to predict the rheological behaviour of a biphasic system from the rheological behaviour and the volumes of the separate phases. The hypothesis is that each phase contains only one of the components. As a result, the concentration of this component in the corresponding phase is higher than in the total solution. The Takayanagi equations provide upper (isostrain) and lower (isostress) bound limits for the value of the storage and loss modulus of the system.

The upper bound limit describes a system of a weak material (x) dispersed in a phase of a stronger material (y). The storage modulus of the system (G'_t) can be calculated by:

$$G'_t = G'_x \phi_x + G'_y \phi_y \tag{1}$$

where ϕ_x and ϕ_y are the volume fractions of each phase ($\phi_x + \phi_y = 1$) and G'_x and G'_y are the storage moduli of each phase.

The lower bound limit describes the reverse situation with a strong filler (y) in a weaker medium (x), and is expressed by:

$$\frac{1}{G'_t} = \frac{\phi_x}{G'_x} + \frac{\phi_y}{G'_y} \tag{2}$$

The upper and lower bound limits for the loss modulus can be calculated in the same manner. The difficulty in this approach is the determination of the volume of the separate phases. If the volumes are known, the effective concentration of a component in that phase can be calculated. The modulus of a phase can be estimated if the relationship between the concentration and the modulus of the component is known. With these data the modulus of the total system can be calculated. For aqueous suspensions, it is necessary to know the distribution of water, the third component, between the phases for determining the volume of the phases. Clark *et al.* (1983) developed a model for dividing the water between the phases by introducing an affinity parameter p of a component for water. A value of $p < 1$ means that component y associates more strongly with water than component x. The fraction of the water α associated with x is:

$$\alpha = \frac{pc_x}{pc_x + c_y} \tag{3}$$

where c_x and c_y are the concentrations in the total system in g g^{-1}. The fraction of water associated to component y is $1 - \alpha$. The volume of phase x is given by:

$$\phi_x = c_x + \alpha c_w \tag{4}$$

where c_w is the concentration of water in the system (g g^{-1}). The volume of phase y is $1 - \phi_x$. The effective concentration of component x in phase x is given by:

$$c_x^{\text{eff}} = \frac{c_x}{\phi_x} \tag{5}$$

The effective concentration of component y is calculated in the same manner.

Clark *et al.* (1983) determined the value of p of agar/gelatin combinations from the best fit of the experimental curve. Svegmark & Hermansson, (1993a, b) estimated the p-value from the microscopic evaluations of the phase volumes or from a shift in the phase angle in dynamic rheological measurements.

We applied the Clark model to the results of the rheological measurements of highly cross-linked waxy maize starch in skim milk. However, the Clark model is developed for dilute biopolymer mixtures assuming that the contribution of the polymer chains to the density of the system is negligible. The starch–skim milk system is a more concentrated system where this assumption is not valid. Therefore, we made a density correction by using the concentrations in g ml^{-1} instead of g g^{-1}. The concentrations in g g^{-1} were converted into g ml^{-1} assuming a density of the starch and the milk protein of 1.5 g ml^{-1}. The concentrations in g ml^{-1} were used for the model calculations. This is comparable to the approach used by Kasapis *et al.* (1993).

For the model calculations the suspension was hypothetically divided in two phases. One phase contains the swollen starch granules and the other phase the hydrated milk proteins. As shown from Table 4, the swollen starch granules take up lactose. This results in an equal distribution of lactose between the phases. The concentration of phosphate in the swollen starch granules in SMUF is the same as the concentration of phosphate in the total solution (results not shown). Therefore, we assume that there is an equal distribution of the salts between the phases. So, the concentrations of salts and lactose in the phases are the same as in the total solution in this model. This results in a distribution of salts and lactose between the phases which is the same as the distribution of water.

Due to this, the starch phase (x) consists of the swollen starch granules in a solution of SMUF with lactose (for skim milk), and two and three times concentrated SMUF with lactose (for two and three times concentrated skim milk). For the calculation of G' of the starch phase, the results of the rheological measurements of starch in solutions of SMUF with lactose are used (Fig. 4). The milk phase (y) consists of the hydrated milk proteins in comparable SMUF solutions. The results of the rheological measurements of these suspensions are shown in Fig. 1.

The p-value is estimated from the best fit of the experimental values. The best fit was achieved with a p-value of 2.3. At that p-value, the measured values of G' lie between the upper and the lower bound limits. The measured values are lower than the lower bound limit if a higher p-value is used. A p-value of 2.3 gives limits which are as close as possible to the measured values. At lower p-values, the limits differ more from the measured values than with a p-value of 2.3. Figure 6 shows the results of the model calculations with a p-value of 2.3. It may be concluded that the measured values cannot be described with either the lower or the upper bound limit. Therefore, there is no phase separation in a weak continuous phase and a strong discontinuous phase or vice versa. A p-value of 2.3 means that the affinity of water for starch is higher than the affinity for milk protein, which is in agreement with the swelling capacity of starch (10.4 ml g^{-1}), and the hydration volume of milk proteins (5.0 ml g^{-1}).

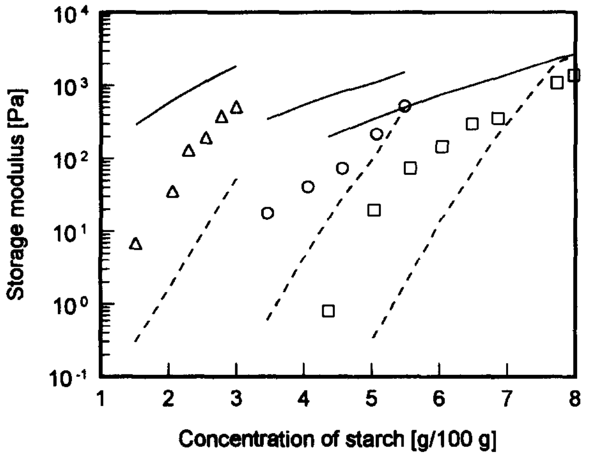

Fig. 6. Storage modulus of highly cross-linked waxy maize starch in skim milk (□), two times (○), and three times concentrated skim milk (△), and upper (sollid lines) and lower bound (dotted lines) calculated with Clark-model with p-value 2.3.

A shortcoming of the Clark model is that the p-value is estimated from the best fit of the experimental curve. We have adapted Clark's model by relating the distribution of the water between the phases to the swelling capacity of the starch (q_s) and the hydrodynamic volume of the milk protein (q_p). There is a difference in the maximum close packing factor (ϕ_{max}) between the starch phase and milk protein phase. Swollen starch granules are deformable and can therefore fill the complete phase. This results in a ϕ_{max} for the starch phase which is equal to 1. The milk proteins will have a ϕ_{max} which is higher than the theoretical value for spheres ($\phi_{max} = 0.74$) because they differ in size from 10 to 300 nm. According to Walstra and Jennes (1984) ϕ_{max} of the milk protein phase is approximately 0.9.

In a system that is just completely filled with swollen starch granules and hydrated milk proteins, the volumes of the phases are:

$$\phi_s = q_s c_s \qquad \phi_p = \frac{q_p c_p}{\phi_{max}} \tag{6}$$

where c_s and c_p are the concentrations of starch and milk protein in the system. In combination with equations (1), (2) and (5), the upper and lower bound limits of the total system can be calculated.

In a diluted system, the swollen starch granules and hydrated milk proteins do not fill the entire available space. A fraction of water is 'left'. We assume that this fraction of water can be divided between the phases according to the ratio of the volume of the starch granules (V_s) to the volume of the milk proteins (V_p).

$$\begin{aligned} V_s &= q_s c_s \\ V_p &= \frac{q_p c_p}{\phi_{max}} \\ \phi_s &= \frac{V_s}{V_s + V_p} \\ \phi_p &= \frac{V_p}{V_s + V_p} = 1 - \phi_s \end{aligned} \tag{7}$$

In a concentrated system, we assume that the milk protein is fully hydrated. By preparing the samples, first a solution of skim milk powder in water is made. This results in complete hydration of the protein. Subsequently, the starch is added and the solution is heated. The starch granules swell just so much that they fill the

Table 5. Calculation of upper and lower bounds for storage (G') and loss modulus (G') of starch–skim milk systems

c_s	c_p	ϕ_s	ϕ_p	c^{eff}_s	c^{eff}_p	G'_s	G'_s	G'_p	G'_p	G'_{tot}		G''_{tot}	
										Upper	Lower	Upper	Lower
4.36	3.3	0.73	0.27	6.11	12.12	281.6	17.5	0.0	0.0	206.1	0.0	12.8	0.1
5.03	3.3	0.76	0.24	6.83	13.50	481.2	28.5	0.1	0.2	364.1	0.1	21.6	0.7
5.57	3.3	0.78	0.22	7.38	14.56	700.9	40.0	0.3	0.6	543.4	1.1	31.2	2.3
6.04	3.3	0.78	0.22	7.91	15.59	984.2	54.5	1.7	1.6	772.3	7.8	43.1	6.9
6.48	3.3	0.80	0.20	8.33	16.38	1261.3	68.2	7.2	3.8	1009.4	35.3	55.3	15.6
6.86	3.3	0.81	0.19	8.72	17.14	1576.7	83.5	28.7	8.5	1279.4	138.7	69.1	30.9
7.73	3.3	0.81	0.19	9.77	18.27	2740.3	137.9	228.2	28.1	2270.5	896.0	117.4	79.7
7.98	3.3	0.82	0.18	9.99	18.27	3040.9	151.6	228.2	28.1	2535.8	946.4	129.4	84.7
3.46	6.6	0.52	0.48	7.06	13.93	717.4	45.6	0.2	0.4	371.7	0.4	23.8	0.8
4.06	6.6	0.56	0.44	7.72	15.21	1063.9	67.2	1.5	1.4	591.8	3.3	37.9	3.1
4.57	6.6	0.58	0.42	8.26	16.24	1427.7	89.6	8.1	4.0	837.9	19.3	54.1	9.1
5.07	6.6	0.61	0.39	8.71	17.10	1793.7	112.2	32.5	9.4	1115.1	81.9	72.6	21.5
5.49	6.6	0.63	0.37	9.17	18.27	2254.7	140.5	221.0	30.4	1507.0	514.6	100.0	60.3
1.52	9.9	0.24	0.76	6.97	13.77	1460.4	74.2	0.2	0.4	346.6	0.2	17.9	0.5
2.06	9.9	0.30	0.70	7.55	14.89	2349.8	113.2	1.1	1.2	697.9	1.5	34.4	1.7
2.30	9.9	0.32	0.68	7.81	15.39	2868.7	135.2	2.4	1.9	920.4	3.5	44.6	2.8
2.55	9.9	0.34	0.66	8.08	15.91	3512.5	161.8	5.5	3.2	1208.9	8.3	57.6	4.9
2.78	9.9	0.36	0.64	8.36	16.43	4274.8	192.7	12.7	5.3	1555.6	19.9	73.2	8.2
3.00	9.9	0.38	0.62	8.59	16.87	5023.6	222.4	26.0	8.2	1925.5	41.9	89.6	12.9

Concentrations (c) in g 100 g^{-1}, moduli in Pa. ϕ is the volume of the phase.
Subscripts are used for starch (s), protein (p), and total system (tot), and for the effective concentration in a phase (eff).

space between the milk proteins. The volumes of the phases are then given by:

$$\phi_p = V_p = \frac{q_p c_p}{\phi_{max}} \qquad (8)$$

$$\phi_s = 1 - \phi_p$$

In our model, density corrections are made in the same manner as in the calculations with the Clark model.

The p-value of the Clark model can be compared with our model by comparing the volume of the starch phase determined by the p-value with the volume determined with our model by combining equations (3), (4) and (7). This results in:

$$p = \frac{q_s - q_s c_s - \frac{q_p c_p}{\phi_{max}}}{\frac{q_p}{\phi_{max}} - q_s c_s - \frac{q_p c_p}{\phi_{max}}} \qquad (9)$$

From this equation it follows that, for low concentrations of starch and skim milk protein, p is equal to $q_s/(q_p/\phi_{max})$ ($= 1.9$). For higher concentrations, p depends on the starch and protein concentrations.

The upper and lower bound limits of the storage and loss modulus of starch–skim milk systems are calculated with this model. The results are shown in Table 5, Fig. 7 and Fig. 8. The figures give also the results of the calculations with the Clark model. Figs 7 and 8 show that the results for both models are almost equal. In Table 6 the p-values of our model are given, calculated with equation (9). The mean value is 2.5. This is close to the p-value determined by the Clark-model. So, it can be concluded that the Clark-model and our model lead to comparable results (Figures 7 and 8). The advantage of our model is that it is based on measurable quantities such as the swelling capacity of the starch and the hydrodynamic volume of the milk proteins, in contrast to the Clark-model, which is based on a best fit.

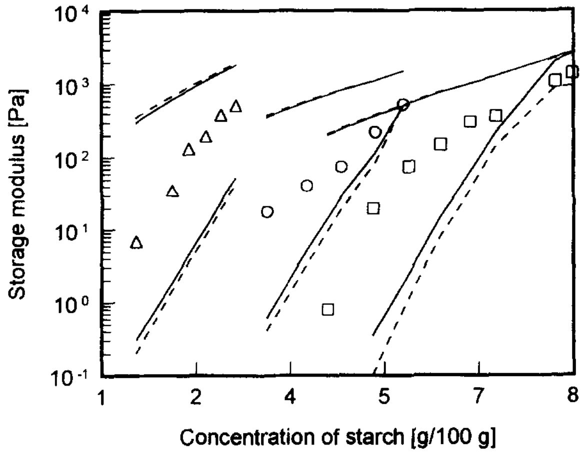

Fig. 7. Storage modulus of highly cross-linked waxy maize starch in skim milk (□), two times (○), and three times concentrated skim milk (△), and moduli calculated with Clark-model with p-value 2.3 (solid lines) and with adapted Clark-model (dotted lines).

In both models, the measured values of the storage and loss moduli lie between the upper and lower bound limits of the model calculations. Moreover, the moduli of the starch and the milk protein phase are sufficiently different to make the use of this model meaningful (Table 5). Therefore, it can be concluded application of the model to starch–skim milk systems is allowed. The upper bound limit describes a phase separated system of a weak material dispersed in a continuous phase of a

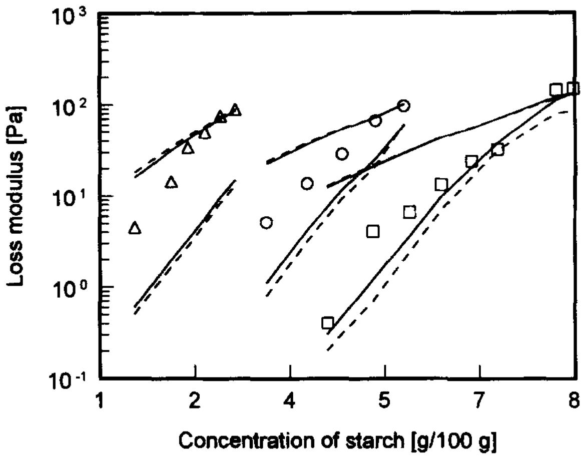

Fig. 8. Loss modulus of highly cross-linked waxy maize starch in skim milk (□), two times (○), and three times concentrated skim milk (△), and moduli calculated with Clark-model with p-value 2.3 (solid lines) and with adapted Clark-model (dotted lines).

Table 6. p-Values calculated with the adapted model of Clark *et al.* (1983)

Solution	p
Skim milk	2.3–2.4
Two times concentrated skim milk	2.4–2.5
Three times concentrated skim milk	2.5–2.6

stronger material. The lower bound limit describes the reversed situation. From Table 5, it can be concluded that the calculated values for G' and G'' are higher for the starch phase than for the milk protein phase at all starch concentrations. Hence, the starch phase is at all concentrations the stronger phase. For most of the starch and skim milk concentrations, the measured values are equal neither with the upper bound limit nor with the lower bound limit. Only at high starch concentrations, the measured values approach the upper (G'') or the lower (G') bound limit. A different limit for G' and G'' is physically not possible. Therefore, it is questionable whether the picture of one distinct phase dispersed in the other one is appropriate to describe starch–skim milk systems. Possibly, these systems may be regarded as bicontinuous. To our knowledge, there are no reports in the literature describing the application of the Takayanagi model to bicontinuous systems.

A major purpose of our study was to develop a model capable to explain and to predict the mechanical properties of aqueous starch–skim milk protein systems from the properties of the individual components. Except for high concentrations, the upper and lower bound limits differ more than one order of magnitude from the measured values. Because the behaviour of our systems falls in between both limits, the predictive value of the model is rather poor for these systems.

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