



## Changes Induced by Shear and Gel Formation in the Viscoelastic Behaviour of Potato, Wheat and Maize Starch Dispersions

Karin Svegmark & Anne-Marie Hermansson

SIK, The Swedish Institute for Food Research, PO Box 5401, S-402 29 Göteborg, Sweden

(Received 20 March 1990; accepted 5 April 1990)

### ABSTRACT

*The effect of shear and gel formation on the behaviour of heat-treated wheat, maize and potato starch dispersions was studied using dynamic viscoelastic measurements. The starch types were compared both at a concentration of 10% and at concentrations where the same level of shear forces was applied during the paste preparation procedure (11% wheat, 10% maize, and 4% potato).*

*The cereal and the potato starch pastes initially showed similar viscoelastic properties after gelatinization, but the cereal starch pastes underwent a transition in their viscoelastic behaviour when cooled. This transition was believed to be due to the gelation of amylose. The main changes observed were a sharp increase in the shear modulus and a drop in the phase angle to below 2 degrees. No such transition occurred on cooling the potato starch pastes, at 25°C for 1 h, in the concentration range studied (4–10%). When the warm potato starch pastes were subjected to mechanical treatment, their viscoelastic behaviour changed significantly. Under the shear conditions used, the complex modulus of the 4% potato starch was decreased to as much as 7% of its initial value, and the phase angle was increased. The warm cereal starch pastes were considerably less affected than the potato starch pastes by the shear treatment. The complex shear modulus of the hot cereal starch pastes decreased approximately 50% and the phase angles increased somewhat. The shear-induced changes in the maize starch at 90°C were partly reversible. The gels formed from sheared cereal pastes had a lower complex modulus than those formed from low sheared pastes.*

### INTRODUCTION

The properties of starch systems depend on the type of starch used and the conditions under which they are prepared. The mechanisms by

which the temperature, the rate of heating and the shear in pasting procedure influence starch systems are intricate. In a previous study, it was shown that even moderate shear treatments of potato starch pastes resulted in drastic changes in the viscoelastic behaviour, whereas heating without shear had a negligible effect (Svegmark & Hermansson, 1990). A transition in viscoelastic behaviour, such as seen on shearing potato starch pastes, reflects structural changes. The present study is focused on how the shear in the pasting procedure affects potato, wheat and maize starch systems and how the gel formation behaviour differs according to the type of starch and shear treatment.

The decrease in viscosity on heating and stirring potato starches is believed to be due to the breakdown of granules (von Hofstee, 1962). The texture of potato starch pastes changes on shearing to a more cohesive or long consistency (Osman, 1967). The cereal starches are also affected by shear treatment, but the decrease in viscosity is less extensive than the decrease for potato starch systems. The characteristics of flow curves from wheat and maize starches vary both with the type of mechanical treatment and with the rate of heating (Doublier, 1981; Doublier *et al.*, 1987). Doublier (1981) proposed that small fragments of amylopectin are released on shearing wheat starch granules after the amylose has been leached. A shear-induced fragmentation of the outer layer of wheat starch granules, which occurs at late stages of swelling, has been observed with microscopical techniques (Langton & Hermansson, 1989). The temperature and mechanical treatment used in the pasting procedure have been shown to affect the gel rigidity of cereal starch gels (Collison & Elton, 1961; Christianson *et al.*, 1986; Doublier *et al.*, 1987) and the viscoelastic properties of wheat starch pastes (Wong & Lelievre, 1981).

The dynamic viscoelastic measurement can be performed at such small deformations that it does not cause breakdown of structures or interfere with the formation of a gel network. The shear used in a viscosity measurement may induce structural changes and break elastic network structures such as gels. Dynamic measurements have been used for comparisons of the viscoelastic behaviour of wheat, maize and potato starches during the gelatinization of granules (Eliasson, 1986). Other studies comparing root and cereal starch systems, using small scale deformations, have dealt with the effect of storage times after cooling. Gels formed from cereal starch showed a higher shear modulus than those formed from potato starch, after storage for less than 24 h (Ring, 1985; Orford *et al.*, 1987). During long term storage, up to a week, the shear modulus increased faster for concentrated potato starch systems than for wheat and maize starch (Orford *et al.*, 1987). The changes on

cooling and storage of cereal starch gels were suggested to consist of two kinds of reactions with different rates of increase in shear modulus. The short-term changes, reaching a maximum after about 3 h, were attributed to gelation of solubilized amylose in the continuous phase. The long-term increase was attributed to crystallization involving amylopectin within the granules (Miles *et al.*, 1985*a, b*). Recently, synthetic amylose was shown to exhibit both long- and short-term changes during gel formation and subsequent storage. Studies on the gelation of monodisperse amylose showed that the shorter chains were responsible for the fast increase and the longer chains for the slow increase (Clark *et al.*, 1989). The interaction of amylopectin and amylose in the continuous phase is also a phenomenon which may affect both the rate of gelation and the gel strength (Ott & Hester, 1965; Ciacco *et al.*, 1979; Schierbaum *et al.*, 1986).

The aim of this study was to compare the effect of shear and the gel formation behaviour for cereal and potato starch systems by viscoelastic measurements. The pastes were prepared in a Brabender viscograph prior to viscoelastic measurements. A paste with high viscosity is subjected to higher shear forces than a paste with a low viscosity when stirred in a Brabender viscograph. In order to compare the shear influence for different types of starches at an equal level of applied shear forces, the starches were compared at a fixed level of maximum viscosity. This meant that the concentrations varied, but additional studies were also made at the same level of concentration. The information on shear influence obtained from the viscoelastic measurements is discussed in relation to the changes in Brabender viscosity.

## MATERIALS AND METHODS

### Materials

Native potato starch was produced by Stärkelsen (Kristianstad, Sweden), the wheat starch by CPC-Cerestar (Holte, Denmark) and the maize starch by National Starch (Hamburg, Germany). Specifications were supplied by Stärkelsen and are shown in Table 1. Distilled/deionized water was used in the experiments.

### Sample preparation

A Brabender viscograph was used for preparing the starch pastes. The dispersions were heated from 35°C to 90°C (94°C for the wheat starch)

and then kept at 90°C for 30 min. The heating rate was 1.5°C/min and the stirring rate was 75 rpm. The total weight of the sample was 450 g. The torsion spring used was 700 cmg. The viscosity values in the Brabender viscograph are measured in Brabender Units (BU); these units are empirical since the shear conditions are undefined.

The starch types were studied at concentrations at which they showed the same maximum viscosity. The 4% potato starch, the 11% wheat starch and the 10% maize starch gave pastes with a Peak viscosity of 1200 BU as depicted in Fig. 1.

The starch pastes were transferred for viscoelastic measurements either at Peak viscosity or at Breakdown viscosity, as shown in Fig. 1 by arrows. The samples transferred at the Peak viscosity of 1200 BU were defined as *low sheared*. The 4% potato starch paste was transferred at 73°C, the 11% wheat starch at 94°C and the 10% maize starch at 87°C. Potato starch was also studied at a concentration of 10%. In order to get a low sheared sample from this highly viscous paste a sample was transferred when the viscosity reached 1200 BU, i.e. at 57°C. This is before the Peak viscosity is reached.

At Breakdown viscosity the samples had been stirred during heating at 90°C for 30 min, and these samples were defined as *sheared*.

The samples were kept in a boiling water bath in order to minimize the temperature fall during the rapid transfer from the Brabender viscograph to the Bohlin VOR Rheometer (less than 1 min).

## Rheological measurements

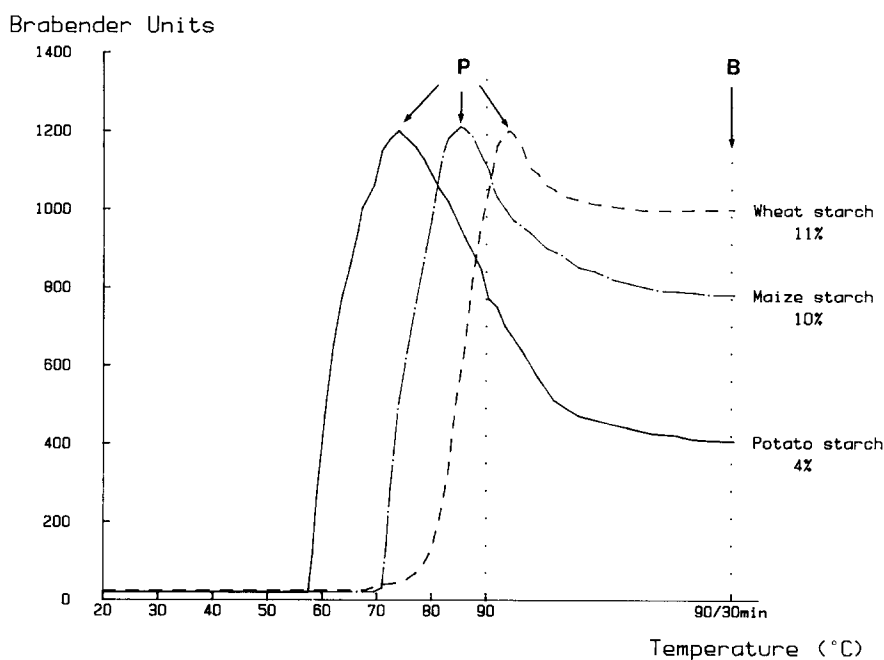
The viscoelastic properties were measured with a small oscillating shear deformation. The results are expressed either as storage ( $G'$ ) and loss modulus ( $G''$ ) or as complex modulus ( $G^*$ ) and phase angle ( $\delta$ ). The complex modulus describes the total shear resistance ( $G^* = G' + iG''$ ). The phase angle gives information of the ratio of the viscous response ( $G''$ ) to the elastic response ( $G'$ ), ( $\tan \delta = G''/G'$ ).

TABLE 1  
Composition of Starches

	Protein (%)	Lipids (%)	Phosphorus (%)	Sodium (%)	Calcium (%)	Water (%)
Potato	0.06	—	0.07	0.01	0.03	20.0
Maize	0.3	0.4	0.04	0.05	0.001	15.0
Wheat	0.1	0.3	0.04	0.03	0.001	15.0

The instrument used was a Bohlin VOR Rheometer. The oscillations were performed at a frequency of 1 Hz and the maximum strain applied was  $1.5 \times 10^{-3}$ . At this deformation all samples were in the linear strain region. Sequential measurements were made every 30 s. A concentric cylinder cup and bob system (C25, DIN 53019) and torque bars of 3.2 gcm and 18 gcm were used. A thin layer of paraffin oil was used to cover the surface of the sample to prevent it from drying out.

The samples were subjected to a temperature cycle during the measurements. The low sheared samples were heated from their temperature of transfer to 90°C, heated at 90°C for 30 min, cooled to 25°C and finally kept at 25°C. The sheared samples were cooled from 90°C to 25°C and then kept at 25°C. The heating and cooling were performed at the rate of 1.5°C/min. The overall temperature cycle when adding the treatments in the Brabender and in the Bohlin rheometer was thus the same for all samples.



**Fig. 1.** Changes in Brabender viscosity on heating and stirring. Points of transfer for viscoelastic measurements, i.e. Peak viscosity (P) and Breakdown viscosity (B) are indicated. The wheat starch was heated to 94°C (the Peak viscosity) prior to the heating at 90°C for 30 min.

## RESULTS AND DISCUSSION

## Changes induced by temperature

The mechanical treatment during the paste preparation procedure was minimal for the pastes defined as low sheared. The changes in the complex shear modulus induced by heating and cooling the low sheared pastes in the Bohlin rheometer are shown in Fig. 2. The structure and properties of heat-treated starch systems before and after cooling are not necessarily related and are therefore discussed separately. The main feature seen in Fig. 2 is the sudden rise in the shear modulus on *cooling* the wheat and maize starch samples. This rise was accompanied by a drop in phase angles to values of about  $1^\circ$ , as shown in Fig. 3, indicating the formation of an elastic network structure. Apparent plateau values in the complex shear modulus were reached when the samples were kept at  $25^\circ\text{C}$ , as can be seen in Fig. 2. The term retrogradation is often used for any of the changes that take place when starch systems are cooled and stored. The word is not used in the present paper since its definitions vary. The changes observed in the viscoelastic behaviour, on cooling the cereal pastes, are typical of gel formation.

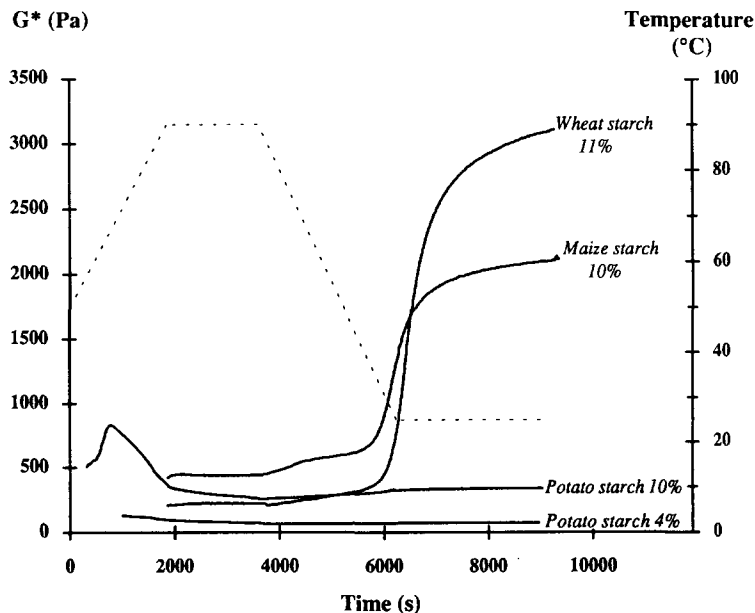
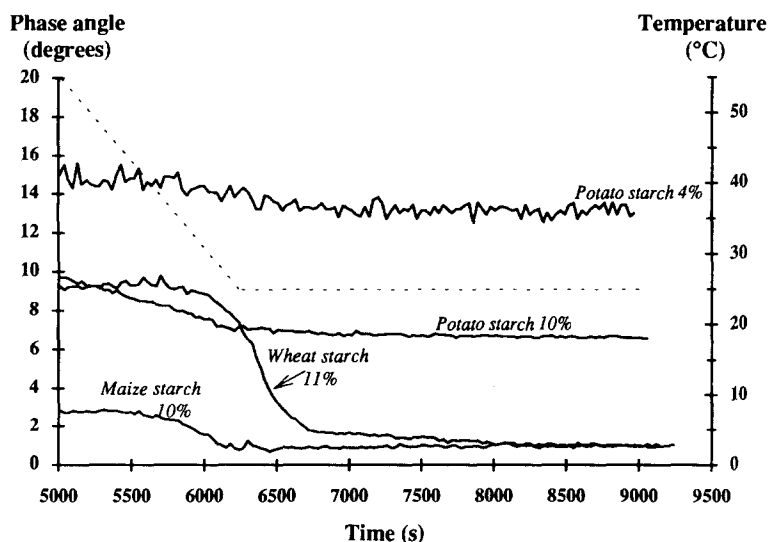


Fig. 2. Influence of temperature on the complex modulus of low-sheared samples. The temperature cycle is shown by the broken line.

As can be seen in Figs 2 and 3, the potato starch pastes did not show a transition on cooling in the time scale studied. When the 10% paste was kept at 25°C for 1 h, the only changes found were a very slow increase in the complex modulus and a decrease in the phase angles from 8 to 7°. No changes were observed when keeping the 4% paste at 25°C for 1 h. In pure amylose systems, a higher concentration has been shown to increase the rate of gelation (Clark *et al.*, 1989; Miles *et al.*, 1985c). Differences in the concentration of amylose might explain why there was no short-term increase in the shear modulus for the potato starch at the 4% concentration and a very slow increase at 10%. Orford *et al.* (1987) showed a slow increase in the shear modulus at 30%. In any case, potato starch pastes form gels after long-term storage (Orford *et al.*, 1987). The lower amylose contents of the potato starch have been suggested to contribute to the slower gelation of potato starch systems (Orford *et al.*, 1987), but a number of other factors may be just as important, such as the size and shape of the amylose molecules and the degree of separation between the amylose and the amylopectin in the system. The mechanisms involved in the gel formation of potato starches and cereal starches need to be studied further.

There is no absolute way of defining a gel and, subsequently, there are no absolute methods of determining the gel point. In polymer science,



**Fig. 3.** Changes in phase angles on cooling the low sheared starch samples from 55°C to 25°C and then keeping the samples at 25°C. The temperature is shown by the broken line.

viscoelastic measurements have been used for determining the gel point as the crossover of the viscous and the elastic response ( $G' = G''$ ), i.e. the phase angle is  $45^\circ$ . The use of the crossover point has been discussed for biopolymers such as gelatin (Djabourov *et al.*, 1988) and for  $\beta$ -lactoglobulins (Stading & Hermansson, 1990). The starch dispersions studied here pass this point when the granules swell during gelatinization and weak gels are formed (Svegmark & Hermansson, 1990). Other methods of determining the gel point of amylose in starch dispersions have therefore to be used. The shift in the phase angle has been used in this study. Phase angles falling to values close to zero imply the formation of an elastic network structure. The onset of the shift in phase angles took place at  $35^\circ\text{C}$  for the wheat starch and at about  $40^\circ\text{C}$  for the 10% maize starch, as depicted in Fig. 3. The low initial values of the phase angles for the maize starch paste make an exact determination of the onset of gelation difficult. The gelation can also be seen from the complex modulus curves in Fig. 2. The complex modulus increases slowly during cooling until the temperature of the wheat starch has decreased to  $40^\circ\text{C}$  and that of maize starch to  $45^\circ\text{C}$ , at which points the shear modulus increases sharply. The onset of the shift in phase angles occurs about  $5^\circ\text{C}$  prior to that of the increase in the complex modulus.

The gel formation of cereal starches was also studied at a lower concentration (8%). The gels formed show a considerably lower complex modulus than those at the 10% concentration, as shown in Table 2. The rate of increase in the shear modulus and the decrease in phase angles was slower than at 10%, especially for the wheat paste. Estimated from the shift in phase angles, the transition began at  $27^\circ\text{C}$  for the 8% maize paste and during the storing at  $25^\circ\text{C}$  for the 8% wheat starch. In pure amylose water systems, the shift in the elastic modulus has been shown to be delayed at lower concentrations (Clark *et al.*, 1989; Miles *et al.*, 1985c). The variation in the complex modulus between replicates is shown in Table 2, as the variation coefficient. The rather poor reproducibility of the results at the lower concentration, i.e. 8%, may be a result of measuring at a concentration and at a temperature close to those critical for gelation. The variation coefficient for the potato starches was less than 10%.

The changes in the complex modulus during *heating* of low sheared samples can be seen in Fig. 2. After transfer from the Brabender viscograph at their Peak viscosity, the complex modulus was 440 Pa for the 10% maize starch, 190 Pa for the wheat starch at 11% and 140 Pa for the potato starch at 4%. The Brabender viscosity of these samples was the same, i.e. 1200 BU as shown in Fig. 1. At the concentration of 10% the potato starch paste showed a higher complex modulus (820 Pa) than



**TABLE 2**  
Complex Modulus for the Cereal Starch Pastes at 90°C and for the Gels Formed After Holding at 25°C for 3 h

	Complex modulus (Pa)			
	90°C		25°C/3 h	
	$\bar{x}^a$	$s/\bar{x} \times 100\%^b$	$\bar{x}$	$s/\bar{x} \times 100\%$
<i>Wheat starch</i>				
11% Low sheared	190	24	3410	11
Sheared	90	20	2240	4
8% Low sheared	27	35	470	28
Sheared	24	35	400	12
<i>Maize starch</i>				
10% Low sheared	440	12	2160	2
Sheared	195	30	1270	4
8% Low sheared	250	13	1000	12
Sheared	80	45	800	20

<sup>a</sup>Mean value ( $\bar{x}$ ).

<sup>b</sup>Coefficient of variation.

The number of replicates is about five.

the warm cereal pastes. The 10% potato starch paste was transferred from the Brabender when the viscosity reached 1200 BU in order to achieve a similar shear treatment as for the other low sheared samples. The sample was thus transferred before the Peak viscosity and gelatinization of granules were completed. Therefore the complex modulus increased during heating as can be seen in Fig. 2. The complex modulus of the potato starch thus differed as much from the cereal starches when compared at a fixed level of viscosity, as when compared at a fixed level of concentration. So there was little correspondence between the complex shear modulus and the viscosity for the warm pastes.

The maximum values of the complex modulus for the potato starches were shown in a previous paper to occur at the same temperature as the maximum in Brabender viscosity (Svegmark & Hermansson, 1990). In the present study, however, the warm wheat starch pastes showed higher complex modulus, at temperatures prior to that of the Peak viscosity temperature as shown in Table 3. The samples transferred at Peak viscosity, i.e. at 94°C had a complex modulus of 190 Pa. Wheat starch pastes transferred before Peak viscosity at 85–88°C had a complex modulus of 450 Pa. In the temperature interval between 85 and 94°C, structural changes such as puckering of the wheat starch granules takes

TABLE 3  
Changes in Rheological Properties of 11% Wheat Starch During Heating to Different Temperatures

	Temperature (°C)	Warm samples			Gels formed on cooling	
		Viscosity (BU)	Complex modulus (Pa)	Phase angle (°)	Complex modulus (Pa)	
Low-sheared	85 <sup>a</sup>	550	450	4	3370	
	90 <sup>a</sup>	1090	340	9	3100	
	94 <sup>a</sup>	1200	190	12	3410	
	90 <sup>b</sup> (30 min)	—	160	8	3410	
	94 <sup>b</sup> (30 min)	—	150	14	2900	
Sheared	90 <sup>a</sup> (30 min)	995	90	23	2240	
	94 <sup>a</sup> (30 min)	950	80	21	2000	

<sup>a</sup>Samples prepared in the Brabender viscometer.  
<sup>b</sup>Samples prepared in the Brabender viscometer to 94°C and then further heated under low shear conditions for 30 min.

place (Bowler *et al.*, 1980). The shear modulus was also decreased on heating from 85°C to 94°C under low shear conditions in the Bohlin rheometer, so the changes can be assumed to be induced by the temperature treatment and not by shear. The changes occurring on heating from 85°C to 94°C do not have any substantial effect on the value of the complex modulus of the gels formed as can be seen in Table 3.

The phase angle of the warm maize starch paste was lower (4°) than those of the potato starches (11° at both concentrations). As shown in Table 3, the phase angle for the wheat starch varied with the temperature in the range of 85–94°C. The low values ( $4 < \delta < 12$ ) of the phase angles shown by the warm low sheared pastes for all starch types investigated reflect the existence of network structures. Low sheared potato starch pastes at 5% were previously shown to have the frequency and strain dependencies typical of a weak colloidal network — a weak gel system (Svegmark & Hermansson, 1990). Such viscoelastic behaviour was also shown by all warm low sheared pastes in this study. The frequency dependencies are not discussed in this paper, since they are highly correlated with the phase angles for the starch systems studied (Svegmark & Hermansson, 1990). The strain sensitivity of the warm low sheared pastes are shown in Table 4. The elastic modulus ( $G'$ ) was independent of the deformation only in a narrow strain region. At deformations above the linear region,  $G'$  was decreased, indicating a structure breakdown. The recovery of this breakdown was studied for the 10% potato starch pastes and for the 11% wheat starch pastes, and the decrease in  $G'$  was found to be reversible and immediately recovered. These features are typical of weak gel systems. A 'true' gel system would have a wider linear strain region and the breakdown of the network should be irreversible (Ross-Murphy, 1984). The weak network character of the warm low sheared pastes may be due to interaction of swollen granules or by temporary networks in the continuous phase.

### The influence of shear

To make a fair comparison of the shear influence of starch pastes of different botanical origins, pastes with the same maximum viscosity were studied at concentrations at which they were subjected to the same level of applied shear forces when prepared in the Brabender viscograph (4% potato starch, 10% maize, 11% wheat).

Since the heat treatment was the same and the effect of shear in the viscoelastic measurement is negligible, the only difference in the treatments of the samples defined as sheared and low sheared was the stirring of the sheared samples in the Brabender viscograph.

### Wheat starch

The shear treatment caused a decrease in the complex modulus both for the warm starch pastes and for the gels formed on cooling, as shown in Fig. 4. The shapes of the complex modulus curves are rather similar for sheared and low sheared pastes, though some small differences can be observed, e.g. prior to the onset of gelation, the rate of increase in the complex modulus was higher for the sheared paste.

The phase angles of the sheared and low sheared samples are shown in Fig. 4(b). The bumps on the phase angle curves are believed to be due to the influence of thermal differences in the cup and bob measuring systems, which may occur when heating and cooling starch pastes at the rate of 1.5°C/min. After the sheared and low sheared samples were kept for more than 10 min and at temperatures close to room temperature, the results obtained were considered to be accurate. This phenomenon has been discussed in a previous paper (Svegmarm & Hermansson, 1990).

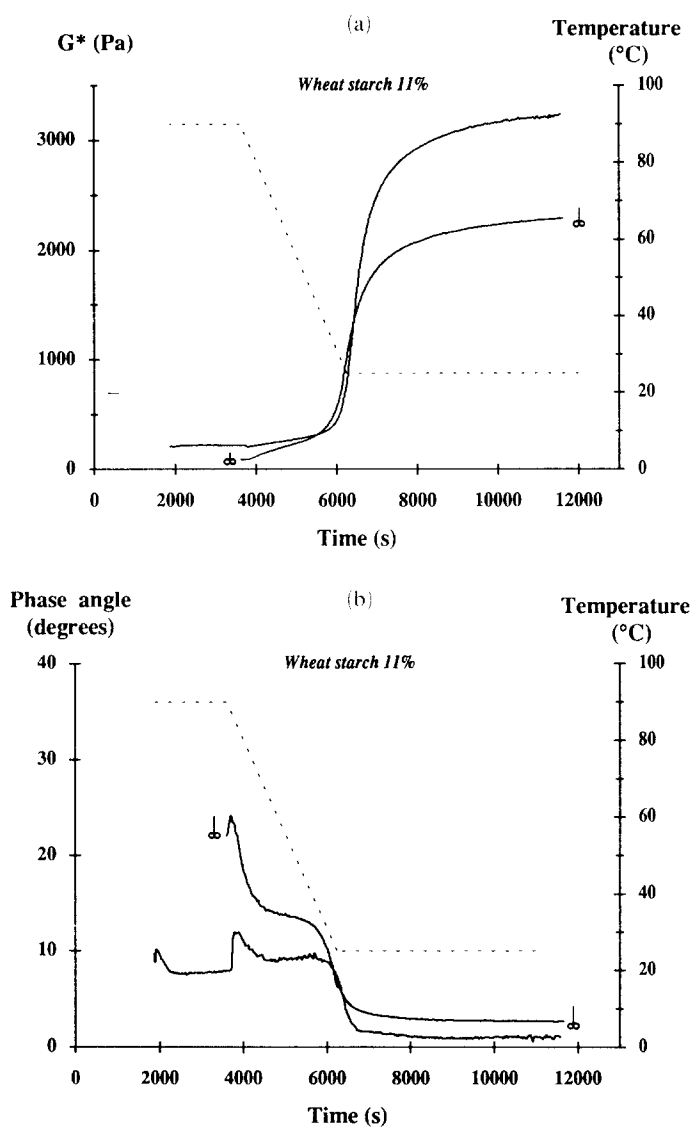
Sheared warm pastes showed significantly higher phase angles than the low sheared pastes, as depicted in Fig. 4(b). The typical shift in the phase angle on amylose gelation was apparent for both types of samples. After amylose gelation, the differences in phase angles between low sheared and sheared systems were not as clearly seen, but there was a tendency towards higher phase angles in the sheared gels. The gel point occurred earlier (at 40°C for the sheared pastes) than for the low sheared pastes, according to the phase angle drop.

The shear influence on the microstructure of wheat starch was investigated in a separate study of the same samples (Langton & Hermansson, 1989). In the continuous phase of the sheared warm pastes and the gels formed, small fragments of amylopectin were observed. The decrease in the complex modulus and the observation of fragments were simultaneous. The fragments were released by disruption of the outer layer of the

**TABLE 4**  
Linear Strain Region of the Storage Modulus ( $G'$ )

	<i>Linear strain region</i>	
	<i>Low sheared</i>	<i>Sheared</i>
Maize 10%	0.050 strain (at 90°C)	0.170 strain (at 90°C)
Wheat 11%	0.020 strain (at 90°C)	0.020 strain (at 90°C)
Potato 4%	0.002 strain (at 73°C)	0.080 strain (at 90°C)
Potato 10%	0.020 strain (at 90°C)	—
	0.005 strain (at 67°C)	—

swollen granule at 94°C. The small fragments might influence the gel strength by weakening the amylose network, or their formation may be associated with some other reaction interfering with the network formation, e.g. release of amylopectin or branched amylose into the



**Fig. 4.** Viscoelastic behaviour of low sheared and sheared ( $\downarrow$ ) wheat starch pastes at 11% during heating and cooling. The temperature cycle is shown by the broken line. (a) Complex modulus; (b) phase angle.

continuous phase. Another result of shearing was shrinkage of granules caused both by fragmentation of the outer layer and by the squeezing out of solubilized amylose from the central zone inside the granules during shearing (Langton & Hermansson, 1989).

### Maize starch

The appearance of the complex modulus curves of sheared and low sheared maize starch pastes, as depicted in Fig. 5, is similar to that of the wheat starch shown in Fig. 4(a). The complex modulus was lower for the sheared systems. The differences in phase angles between the sheared and the low sheared systems were below those of the other starch types examined. A special characteristic of the maize starch was that parts of the shear-induced changes were reversible. The recovery in the phase angle and complex modulus was seen when sheared pastes were heated at 90°C in the rheometer, as shown in Fig. 6. The increase in the phase angle caused by the shear treatment was fully recovered after 1 h, and the loss in the complex modulus was partly recovered. Doublier *et al.* (1987) made a similar observation on the reversibility of the shear-induced changes for maize starches when studying their flow curves, and he proposed that 7.7% maize has a weak structural network, which is destroyed by shear and recovered by decreasing the shear rate.

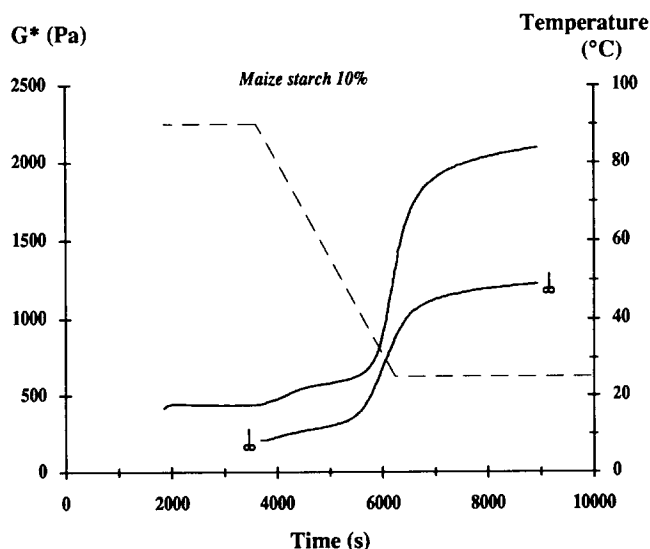


Fig. 5. Complex modulus of low sheared and sheared ( $\downarrow$ ) maize starch pastes at 10% during heating and cooling. The temperature cycle is shown by the broken line.

### Potato starches

The viscoelastic behaviour of sheared and low sheared potato starch pastes at 4% and 10% concentrations is shown in Fig. 7. There was a drastic decrease in the complex modulus on shearing, which was much more emphasized than the corresponding decrease in the cereal starches. To be able to distinguish the curves of the sheared potato starch pastes from the baseline, logarithmic scales were used. The complex modulus of the 10% potato starch decreased to 2.4% of the maximum value and the complex modulus of the 4% paste decreased to 7% of the maximum, as shown in Fig. 7(a). The phase angle increased on shearing to  $32^\circ$  at both concentrations; this can be seen in Fig. 7(b). The 4% paste was subjected to the same degree of shear treatment as the wheat and maize starches. The sheared 10% potato starch paste was subjected to a higher degree of shear treatment since it had a higher viscosity. The shear-induced changes in potato starch systems have previously been discussed in detail (Svegmark & Hermansson, 1990). The viscoelastic behaviour of potato starches changed from a state which was characterized as a weak gel to a more viscous state due to shearing. The sheared potato starch pastes were characterized by a low complex modulus, a rather high phase angle and a significantly wider linear strain region. Two types of

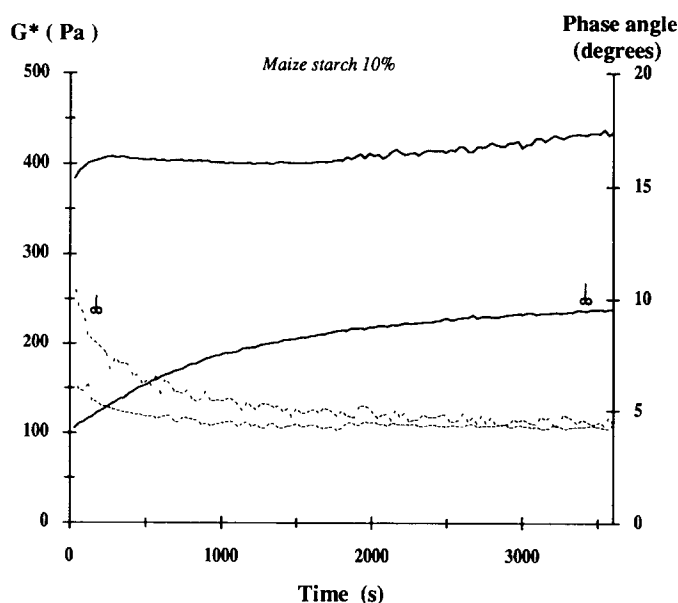
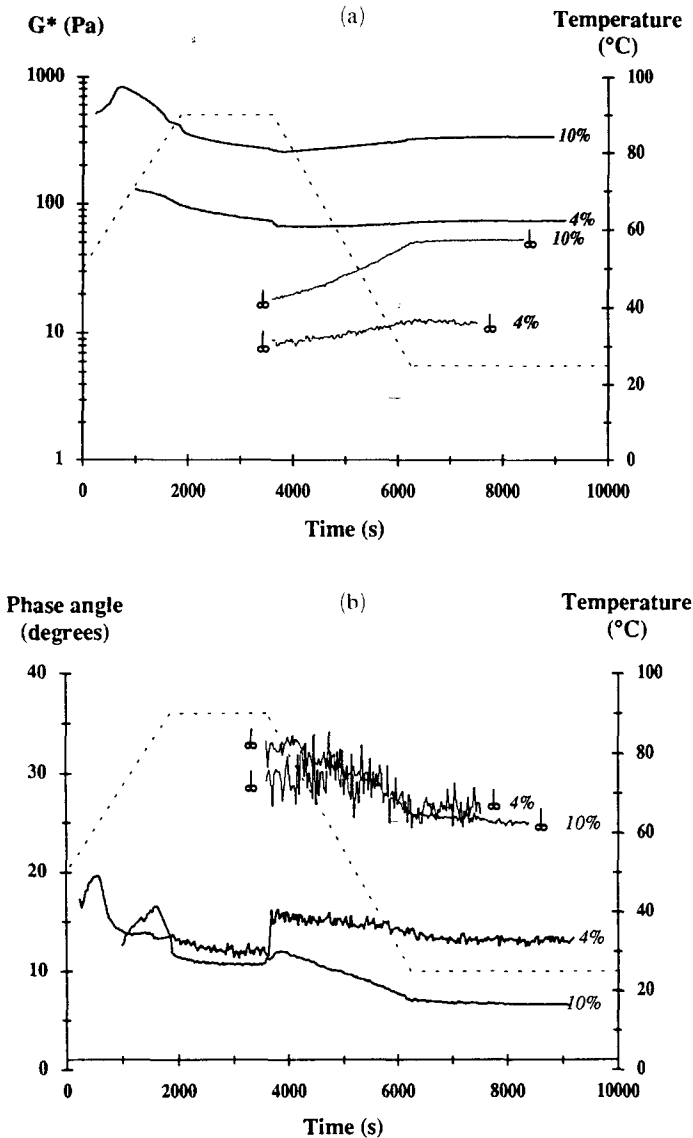


Fig. 6. Changes in phase angles and complex moduli when keeping low sheared and sheared ( $\downarrow$ ) maize starch pastes at  $90^\circ\text{C}$  for 1 h.

viscoelastic behaviour were postulated, type I for the low sheared pastes and type II for the sheared potato starch pastes.

The sheared warm cereal pastes still showed viscoelastic behaviour similar to that of the low sheared warm pastes (type I). Wheat starch



**Fig. 7.** Changes in viscoelastic behaviour of low sheared and sheared (○) potato starch pastes at concentrations of 10% and 4% during heating and cooling. (a) Complex modulus in logarithmic scale; (b) phase angle.



pastes showed a significant increase in phase angles from 12 to 23°, but the complex modulus showed a moderate decrease from 190 Pa to 100 Pa. The strain dependence of the wheat starch was the same for the wheat starch before and after shear treatment, as can be seen in Table 4. When sheared, the cereal pastes did not change their character as drastically as the potato starches did.

Viscoelastic measurements hold several advantages when characterizing starch systems compared to instruments such as the Brabender viscograph. The gel formation of starch systems cannot be studied, since the shear in the viscosity measurement will immediately break a gel structure even though the ability to form gels can be detected by a sudden rise in Brabender viscosity on cooling. In the standard pasting cycle used in a Brabender viscograph, the changes on cooling are studied from 90 to 50°C and then holding at 50°C (Mazurs *et al.*, 1957). The extent of the increase in Brabender viscosity at 50°C, referred to as set-back, is used as a measure of the 'retrogradation' tendency (Mazurs *et al.*, 1957) or the gelling ability (Olkku & Rha, 1978). The actual gel formation ability is measured indirectly. The set-back and retrogradation terms are rather obscure. The shear sensitivity is indicated by the Brabender pasting curve as a decrease in viscosity during heating. The study of the shear-induced changes by viscoelastic measurements gives further information on the differences between the starch types and makes it possible to distinguish between shear- and temperature-induced changes. The changes in viscoelastic behaviour suggest that shear affects potato starch and cereal starch systems in different ways.

## CONCLUSION

Due to the pasting procedure and the type of starch used, three different types of viscoelastic behaviour have been found.

- At the point of gelatinization all the starch types investigated behaved as weak gels.
- On cooling, the cereal pastes formed strong gel systems with pronounced changes in both shear moduli and phase angles. This was not the case for potato starch pastes, which only showed minor changes in viscoelastic properties on cooling.
- Shear had a drastic effect for potato starch pastes, whereas the cereal starch pastes were less affected. On shearing the potato starch changed from a weak gel to a more viscous state. Gel

formation dominated over the shear-induced changes for the cereal starch systems.

## ACKNOWLEDGEMENTS

The authors would like to thank their colleagues at Stärkelsen for financial support and encouragement throughout this work.

## REFERENCES

- Bowler, P., Williams, M. R. & Angold, R. E. (1980). *Stärke*, **32** (6), 186.
- Christianson, D. D., Casiraghi, E. M. & Bagley, E. B. (1986). *Carbohydrate Polymers*, **6**, 335.
- Ciaccio, C. F., Fernandez, J. L. A. & Zoega, R. H. (1979). *An Acad. Brasil Ciênc*, **51**, 250.
- Clark, A. H., Gidley, M. J., Richardson, R. K. & Ross-Murphy, S. B. (1989). *Macromolecules*, **22**, 346.
- Collison, R. & Elton, G. A. H. (1961). *Stärke*, **5**, 164.
- Djabourov, M., Leblond, J. & Papon, P. (1988). *J. Phys.*, **49**, 333.
- Doublier, J.-L. (1981). *Stärke*, **33** (12), 415.
- Doublier, J. L., Llamas, G. & Le Meur, M. (1987). *Carbohydrate Polymers*, **7**, 251.
- Eliasson, A.-C. (1986). *Journal of Texture Studies*, **17**, 253.
- Von Hofstee, J. (1962). *Stärke*, **9**, 318.
- Langton, M. & Hermansson, A.-M. (1989). *Food Microstructure*, **8** (1), 29.
- Mazurs, E. G., Schoch, T. J. & Kite, F. E. (1957). *Cereal Chemistry*, **34** (3), 141.
- Miles, M. J., Morris, V. J., Orford, P. D. & Ring, S. G. (1985a). *Carbohydrate Research*, **135**, 271.
- Miles, M. J., Morris, V. J., Orford, P. D. & Ring, S. G. (1985b). In *New Approaches to Research on Cereal Carbohydrates*, ed. R. D. Hill & L. Munch. Elsevier, Amsterdam, p. 109.
- Miles, M. J., Morris, V. J. & Ring, S. G. (1985c). *Carbohydrate Research*, **35**, 257.
- Olkku, J. & Rha, C. (1978). *Food Chemistry*, **3**, 293.
- Orford, P. D., Ring, S. G., Carroll, V., Miles, M. J. & Morris, V. J. (1987). *J. Sci. Food Agric.*, **39**, 169.
- Osman, E. M. (1967). In *Starch Chemistry and Technology*, Vol. II, ed. R. L. Whistler & E. F. Paschall. Academic Press, New York, p. 163.
- Ott, M. & Hester, E. E. (1965). *Cereal Chemistry*, **42**, 476.
- Ring, S. G. (1985). *Stärke*, **3**, 80.
- Ross-Murphy, S. B. (1984). In *Biophysical Methods in Food Research*, ed. H. W. Chan. Blackwell Scientific Publications, Oxford, p. 138.

- Schierbaum, F., Vorwerg, W., Kettlitz, B. & Reuther, F. (1986). *Die Nahrung*, **30** (10), 1047.
- Stading, M. & Hermansson, A.-M. (1990). *Food Hydrocolloids*, **4** (2), 121.
- Svegmark, K. & Hermansson, A.-M. (1990). *Carbohydrate Polymers*, **13**, 29.
- Wong, R. B. K. & Lelievre, J. (1981). *Rheol. Acta*, **20**, 299.