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A Rheological Investigation of Cereal Starch Pastes and Gels. Effect of Pasting Procedures

J. L. Doublier, G. Llamas, and M. Le Meur

Institut National de la Recherche Agronomique,
Laboratoire de Physicochimie des Macromolécules, Rue de la Géraudière,
44072 NANTES, Cedex 03, France

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SUMMARY

Wheat and maize starches have been pasted using four different pasting procedures by varying the heating and stirring rates. The flow behaviour of hot starch pastes was investigated over a wide range of concentrations (~ 3 to 10·5%). For each type of starch each pasting procedure resulted in a specific flow behaviour. Flow curves were tentatively interpreted on the basis of swelling-solubility values, and it was demonstrated that the overall viscosity of starch pastes is primarily governed by a combination of the volume fraction of the disperse phase and the concentration and composition of the continuous phase. For the highest concentration, deformability of swollen particles seems to play a prevailing role. Concentrated starch gels also exhibited different elastic properties, depending upon pasting procedure and type of starch. Wheat starch gels were stiffer than maize gels and it was suggested that the main structural parameters involved are the deformability of the swollen particles and the amylose concentration of the continuous network.

INTRODUCTION

Many investigations have dealt with the rheology of starch pastes. These systems are known to display a specific flow behaviour with a pronounced shear thinning character and a high shear dependency, often referred to as thixotropy (Evans & Haisman, 1979; Doublier, 1981; Wong & Lelievre, 1982; Doublier, 1987). Some studies have also shown that the viscoelastic properties are significant (Myers & Knauss, 1965; Wong & Lelievre, 1981). Interpretation of the rheological behaviour in terms of macromolecular organization has not been fully elucidated. It has been proposed that starch pastes can be described as suspensions of swollen particles dispersed in a macromolecular medium, and several authors have demonstrated that a relationship exists between the overall rheological properties and the swelling capacity of the starch granules (Evans & Haisman, 1979; Wong & Lelievre, 1981, 1982; Bagley & Christianson, 1982). Among the parameters which determine the rheological characteristics of starch pastes it is well known that special attention should be paid to the pasting procedure. Thus, heating and stirring rates must be carefully controlled and large variations have been reported when varying one of these two parameters. This has been illustrated for wheat and maize starch pastes and a relationship between flow behaviour and swelling-solubility parameters has been observed (Doublier, 1981, 1987). Similar observations have been reported by Wong & Lelievre (1981) on the viscoelastic properties of wheat starch pastes when varying the heating rate. These authors also observed a relationship between viscoelastic characteristics and swelling capacity.

The present investigation was undertaken to describe more precisely the effects of the heating and stirring rates on the flow properties. The results were interpreted in terms of the swelling-solubility characteristics, and the implications for the properties of starch gels obtained on cooling were also considered.

MATERIALS AND METHODS

Materials

Prime wheat and maize starches with moisture contents of 13·9 and 12%, respectively, were obtained from Roquette Frères (F 62 136, Lestrem, France).

Preparation of starch pastes

Four pasting procedures were compared with a combination of two heating and two stirring rates, the upper temperature being fixed at 96°C. Weighed amounts of starch were slurried in 200 ml of distilled water in a double-walled round-bottom vessel, stirring being achieved by an anchor-shaped Teflon blade at either 200 rev $\min^{-1}$ (low stirring rate, LS) or 750 rev $\min^{-1}$ (high stirring rate, HS). Temperature control was achieved by means of ethyleneglycol circulating inside the double wall. The first heating rate (1°C $\min^{-1}$, low heating rate, LR), comparable with conditions in the Brabender Viscograph, was achieved by means of a temperature programmer. The high heating rate (HR) was achieved by injecting instantaneously the fluid heated at high temperature (102°–104°C) inside the double wall of the vessel. This resulted in a non-linear temperature increase inside the starch dispersion. The increase from 30°C to 90°C needed about 10 min and 96°C was reached after a further 5 min. This upper temperature was maintained for 30 min. Since water losses due to evaporation could not be controlled easily, concentrations were determined at the end of the pasting period by drying aliquots at 102°C overnight.

Preparation of starch gels

At the end of the cooking period, as previously described, concentrated starch pastes (7·5 and 10·5%) were poured rapidly into cylindrical moulds (diameter: 3·8 cm, height: 3·8 cm) of which the top edge was raised by means of a tape of acetate film. After cooling, the surface of the gels was coated with light oil to avoid dehydration. Gels thus prepared were kept at rest for 24 h at 25°C ± 0.5°C before being measured.

Viscometry

Flow properties were studied with a Rheomat-30 using the A-system of coaxial cylinders (internal radius: 22·9 mm; external radius: 24·2 mm; height: 56·5 mm). Measurements were performed at 70°C as follows:

(1) The shear rate was increased continuously at a constant rate to 6·6 s^{-1} and then decreased continuously to zero. This cycle was completed in 4 min.
(2) Immediately this low shear rate cycle had finished the sample was subjected to two high shear rate cycles both starting at zero and raising the shear rate to 660 s^{-1} at a constant rate and then reducing the shear rate to zero. Both cycles were carried out over a period of 4 min.
(3) Immediately the second of these cycles was completed the shear rate was raised virtually instantaneously to 660 s^{-1} and the equilibrium value of the shear stress was measured. (Equilibration took approximately 0·5 min.) The shear rate was then lowered stepwise and the equilibrium value of the shear stress measured for each shear rate.
(4) Immediately this was completed the shear rate was again cycled from 0–6·6 s^{-1} over a 4-min period as described in (1).

This procedure allowed the starch paste to be characterized before being sheared from the first cycle at a low shear rate, while shear destruction occurred for the cycles at high shear rates, and after shearing from the last cycle. Comparison of the last cycle with the first yielded an estimation of the rheodestruction of the paste. Step-by-step measurements allowed the flow curves to be described at equilibrium after the application of high shear rates and over a wide range of shear rates, from approximately 1 to 660 s^{-1}.

Characterization of gels

After removing the tape, gel in excess above the top edge of the mould was cut off using a thin steel wire. Gel was thereafter removed from the mould and covered again with oil to avoid dehydration during measurement and to eliminate frictional problems as demonstrated by Christianson *et al.* (1985). Compression measurements were performed using an Instron testing machine, at a compression rate of 0·2 cm min^{-1}. The slope of the curve force-displacement was used to calculate the compression modulus (E) of the gel according to the expression:

$$E=\frac{F/A}{\Delta h/h}=\frac{F}{\Delta h}\times\frac{h}{A} \tag{1}$$

where $F/\Delta h$ is from the slope of the compression curve, h is the height of the gel, A is initial cross-section of the gel.

The comparison of the height of the gel, h, with the height of the mould (3·8 cm) yielded the Sag index giving another estimation of gel rigidity.

Swelling-solubility

Swelling-solubility patterns were obtained on 0·5% starch dispersions pasted under the above conditions. Aliquots of the starch dispersion were withdrawn at intervals during the heating period. After rapid cooling, these were centrifuged at 700 g and swelling and solubility values were determined as described by Leach *et al.*, 1959. The supernatant and sediment were characterized by their iodine spectra (Doublier, 1981).

RESULTS

Description of flow curves

Typical flow curves of ~ 5·2% concentrated wheat starch pastes are presented in Figs 1 and 2. Figure 1 shows the results of measurements

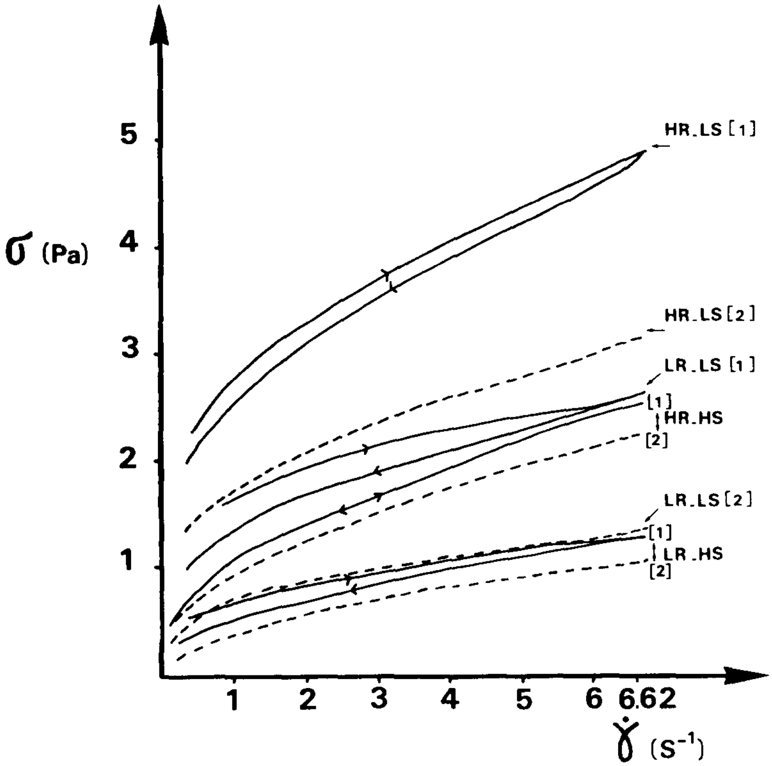

Fig. 1. Flow curves at low shear rates of ~ 5·2% wheat starch pastes. Continuous lines: first cycle; dashed lines: last cycle (see text). The increasing and decreasing portions of the last cycle were always superimposable. Actual concentrations: HR–LS: 5·1%; HR–HS: 5·4%; LR–LS: 5·2%; LR–HS: 5·4%. Temperature: 70°C.

within the low shear rate range performed before the application of high shear rates (first cycle, continuous lines) and afterwards (last cycle of the measuring sequence, dashed lines). In Fig. 2 the flow curves from measurement cycles at high shear rates are plotted. It is clearly seen that each pasting procedure yields specific flow curves. Whatever the pasting procedure, each starch paste displays a pronounced shear-thinning but 'thixotropy' or rheodestruction varies according to the pasting condition. Thus, HR–HS conditions (high heating rate–high stirring rate) result in limited rheodestruction in contrast with the three others. This is clearly seen from Fig. 1 by comparing the flow curves before and after being submitted to high shear rates. When two successive cycles are applied within the high shear rate range, up to 660 s^{-1}, the thixotropic loop between the up and down curves tends to disappear, so that the second loop is a description of the starch paste at equilibrium after

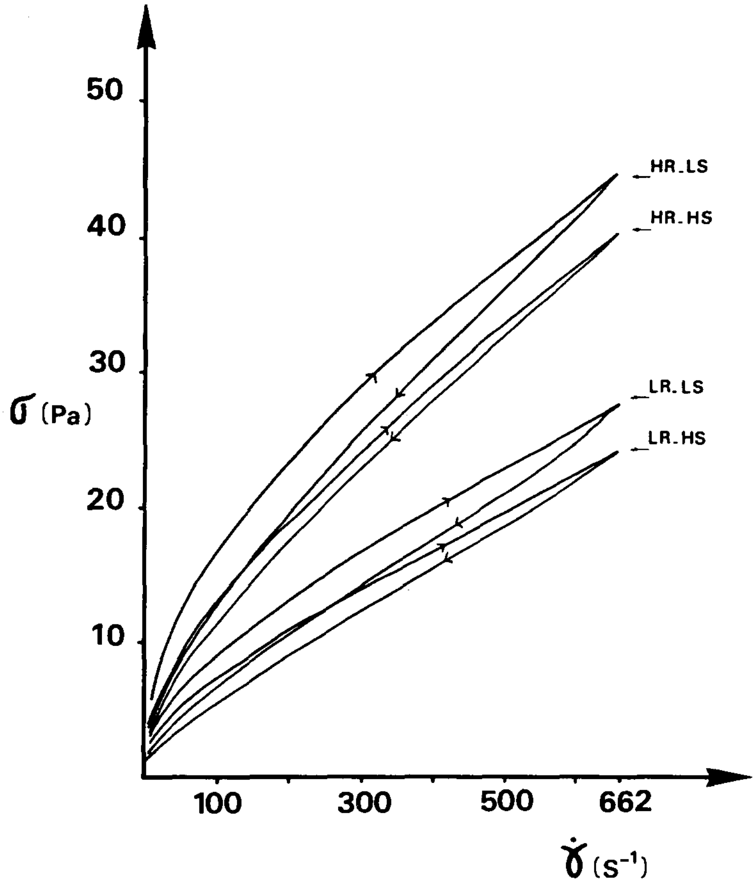

Fig. 2. Flow curves at high shear rates of ~ 5·2% wheat starch pastes. Concentrations as in Fig. 1. Only the first cycle is plotted. The second cycle is superimposed to the down curve of first cycle.

shearing at 660 s^{-1}. This allows pointwise measurements to be performed, yielding the flow curves illustrated in Fig. 3. Different viscosities are obtained with the four different pasting procedures, HR conditions yielding consistencies higher than LR conditions. Moreover, from the comparison of curves at low shear rates, it is seen that the consistency of LR–LS before shearing is higher than in HR–HS conditions, whereas, at high rates (Fig. 2) and after shearing (Fig. 1, dashed lines), the inverse is observed. Shapes of flow curves (Figs 2 and 3) differ also between procedures. From Fig. 3 it is seen that these curves cannot be described by a power-law expression ($\sigma = K\dot{\gamma}^a$ where σ is the shear stress, $\dot{\gamma}$ the shear rate and K and a are constants) because of an upward curvature towards

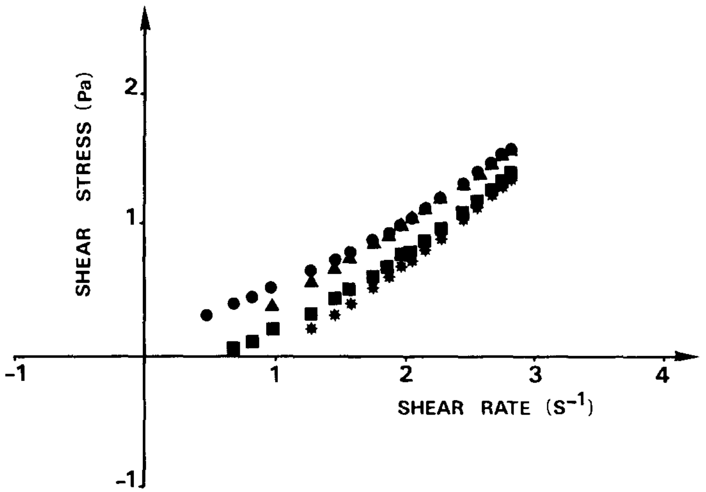

Fig. 3. Plot of flow curves in logarithmic coordinates of ~ 5·2% wheat starch pastes. (●) HR-LS; (▲) HR-HS; (■) LR-LS; (★) LR-HS. Concentrations as in Fig. 1. Temperature: 70°C.

low shear rates. Such tendency, which is generally ascribed to the existence of a yield value, is more pronounced for LR conditions than HR conditions.

Figures 4, 5 and 6 give another example for wheat starch pastes at ~ 7·7%. Here, also, large differences in behaviour are observed depending upon pasting conditions, both for the overall viscosity as well as for thixotropy. The ranking order found for viscosity at ~ 5·5% is not confirmed at the higher concentration where the order is: HR-LS, LR-LS, HR-HS, LR-HS. Another illustration is given in Figs 7 and 8 for ~ 7·7% maize starch pastes. The dependence on pasting procedures is also clearly demonstrated. Unusually shaped curves are observed for the first cycle at low shear rate. A weak structural network seems to exist and is destroyed as soon as a shear deformation is applied. Another peculiarity is seen for the flow curves at HR-HS and LR-HS, where some kind of rheopexy or antithixotropy is evidenced in contrast with HR-LS and LR-LS conditions. This suggests that part of the structural network is rapidly recovered on decreasing the shear rate.

Effect of concentration

The dependence on concentration has been investigated over the concentration range 3–10%. The shear sensitivity, either rheodestruction or

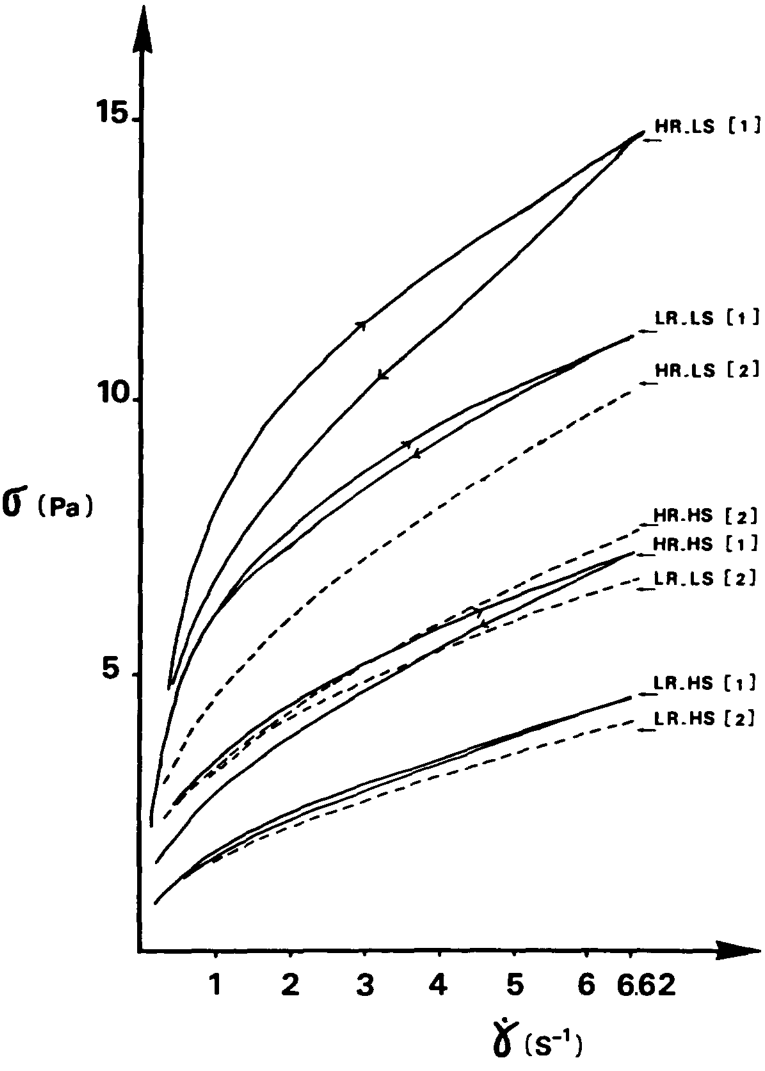

Fig. 4. Flow curves at low shear rates of ~ 7·7% wheat starch pastes. Same legend as in Fig. 1. Actual concentrations: HR–LS: 8·2%; HR–HS: 7·95%; LR–LS: 7·6%; LR–HS: 7·7%. Temperature: 70°C.

rheopexy, was estimated by a comparison of the apparent viscosity at 6·6 s^{-1} before and after application of high shear rates (Tables 1 and 2). A more or less pronounced rheodestruction is observed ($\eta_1/\eta_2 < 1$) but rheopexy ($\eta_l/\eta_2 > 1$) is also seen in some cases for maize starch at HR–HS and LR–HS conditions. For concentrations higher than 5%, $\eta_l/$

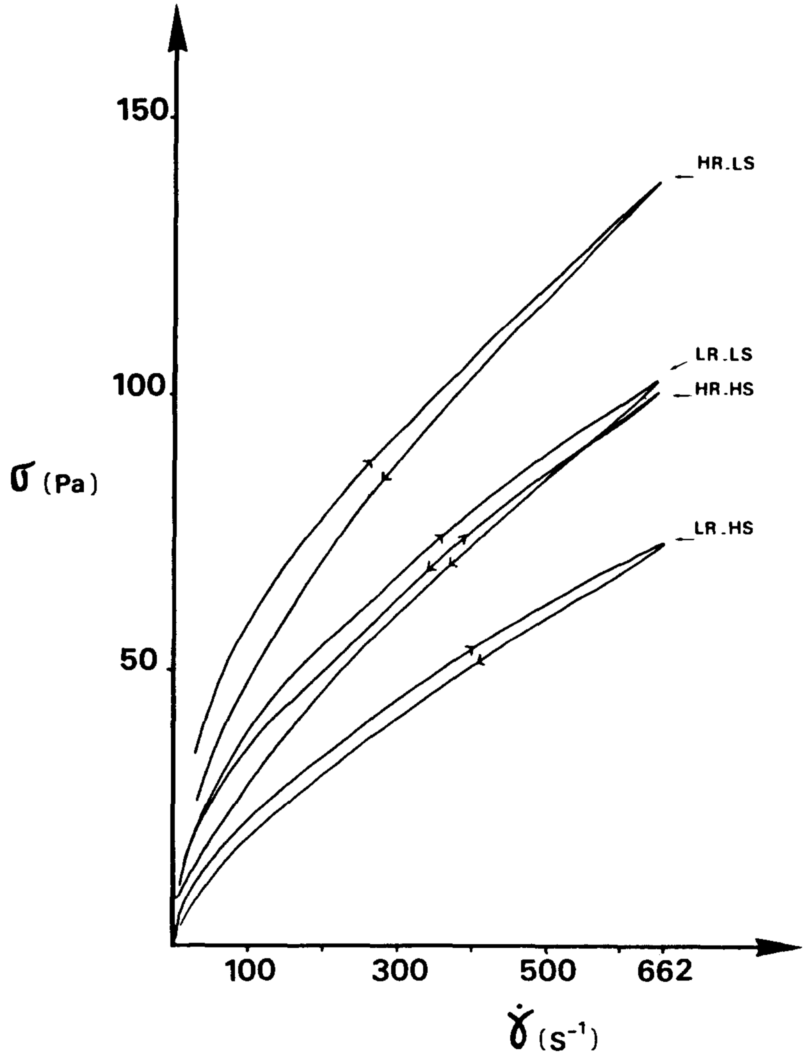

Fig. 5. Flow curves at high shear rates of ~7·7% wheat starch pastes. Legend as in Fig. 2. Concentrations as in Fig. 4. Temperature: 70°C.

η_2 is close to 0·5–0·6 under LS conditions and between 0·8 and 1·3 at the high stirring rate (HS), suggesting that pastes prepared under LS conditions are more susceptible to high shear rates. Moreover, wheat starch pastes display less marked rheodestruction than maize starch pastes whatever the pasting procedure. The concentration dependence is illustrated in Figs 9 and 10 for maize and wheat starch, respectively, by the variations of '*K*' defined as the apparent viscosity at 94·6 s^{-1} and deter-

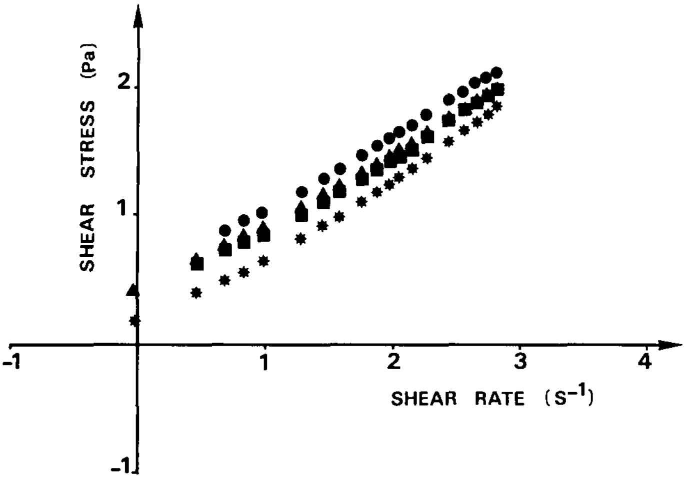

Fig. 6. Flow curves of ~ 7·7% wheat starch pastes in logarithmic coordinates. (●) HR–LS; (▲) HR–HS; (■) LR–LS; (★) LR–HS. Concentrations as in Fig. 4. Temperature: 70°C.

mined as described in step 3 of the viscosity measurements. Although the number of experimental points is limited, these curves show that the variation of K with concentration depends strongly upon the pasting procedure. The stronger dependence is displayed by LR–LS conditions where slopes of log–log plots of K *versus* concentration of 3·6 and 4·2 are observed for maize and wheat, respectively. Wheat starch pastes prepared under LR–HS conditions display a comparable concentration dependence. In contrast, HR–LS for wheat and maize starches and LR–HS for maize starch yield slopes of around 3, and HR–HS conditions result in the smallest dependence with slopes of about 2 for wheat starch and a non-linear variation for maize. An interesting result of these variations is that at the highest concentrations (~ 10·5%) LR–LS conditions yield the more viscous pastes in contrast with the lowest concentrations where the inverse occurs. HR–HS conditions yield the thinner maize starch pastes at high concentrations while at low concentrations these pastes are as thick as those prepared under HR–LS conditions. A practical result of such dependences is that comparable flow behaviours can be obtained for maize and wheat starches at the same concentration by choosing appropriate pasting conditions. For example by using LR–HS conditions for maize starch and HR–LS conditions for wheat starch. Such findings imply that flow properties of starches cannot be predicted using standard procedures unless they correspond to the industrial processes in which starches are to be used.

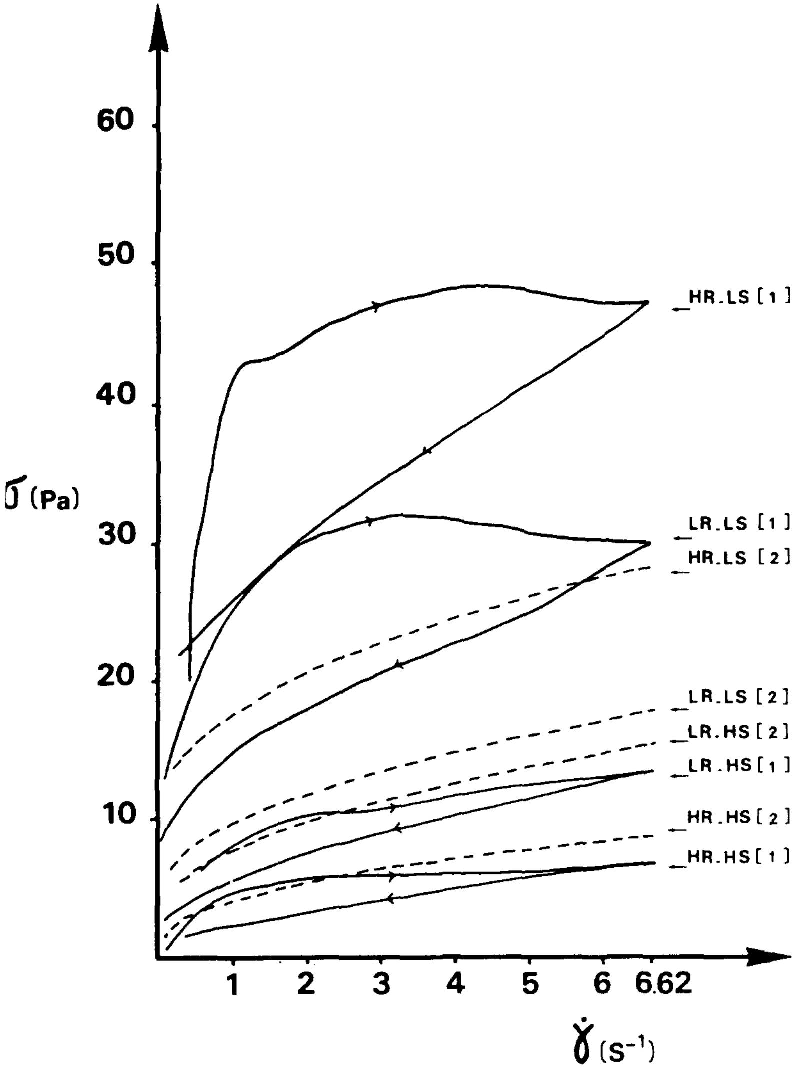

Fig. 7. Flow curves of ~ 7·7% maize starch pastes. Low shear rates. Same legend as in Fig. 1. Actual concentrations: HR–LS: 7·5%; HR–HS: 8·0%; LR–LS: 7·6%; LR–HS: 7·3%. Temperature: 70°C.

Swelling-solubility patterns

The diagrams obtained for maize and wheat starch are shown in Figs 11 and 12, respectively. The classical temperature–dependence of cereal starches is observed, particularly the two-stage swelling and the reduced solubility below 90°C. The first step of the swelling process is observed

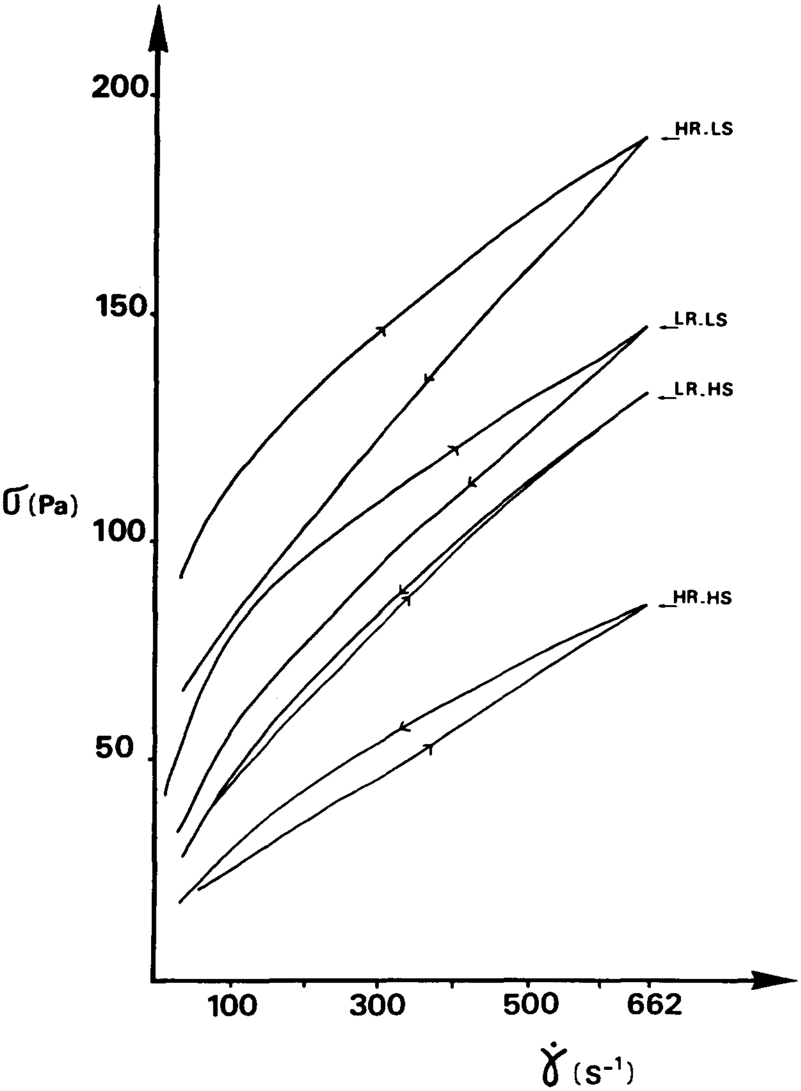

Fig. 8. Flow curves of ~ 7·7% maize starch pastes. High shear rates. Same legend as in Fig. 2. Concentrations as in Fig. 7. Temperature: 70°C.

at about 55°C for wheat starch and 60°C for maize starch, whatever the pasting process. The second step occurs within the same range of temperatures for both starches, between 90°C and 95°C while solubilization occurs. Large differences are observed for the final values of the swelling and of the solubility depending upon the type of starch and the pasting procedure. When a slow temperature increase is applied (LR conditions) the final swelling values are the lowest, i.e. 14–15 g/g for wheat

TABLE 1
Estimation of the Shear Dependence of Maize Starch Pastes

Pasting procedure	*Concentration (%, w/w)*	η_l *Pa.s*[a]	η_2 *Pa.s*[b]	η_2/η_l
HR–LS	3·2	0·273	0·231	0·85
	5·4	2·050	1·079	0·53
	7·5	7·140	4·320	0·60
	10·9	13·200	5·920	0·45
HR–HS	3·6	0·820	0·222	0·27
	5·7	0·860	0·430	0·50
	8·0	0·990	1·310	1·32
	12·3	3·900	3·480	0·89
LR–LS	3·1	0·085	0·038	0·45
	5·7	1·740	0·886	0·51
	7·6	4·500	2·680	0·59
	10·5	20·400	12·300	0·60
LR–HS	3·5	0·338	0·149	0·44
	5·8	0·444	0·507	1·14
	7·3	2·000	2·330	1·16
	9·8	5·550	4·360	0·79

[a] Apparent visocity at 6·6 s^{-1} from the first measuring cycle at low shear rate.
[b] Apparent viscosity at 6·6 s^{-1} from the last cycle at low shear rate.

starch and 22–23 g/g for maize, and independent of the stirring rate. In addition, solubility is low as well but depends on agitation, particularly for maize starch. HR–HS conditions result in the highest swelling values, 36 g/g for maize and 24 g/g for wheat, and the highest solubility, around 90% for maize and 60% for wheat starch. From the iodine spectra it is evident that, with each procedure, leaching of amylose occurs initially and amylopectin can be solubilized only when most of the amylose has been leached out. In all cases the sediment is mainly composed of amylopectin. It is noteworthy that data on the effect of pasting procedures on swelling-solubility patterns are scarce. However, Wong & Lelievre (1981) have reported on wheat starches from different varieties and observed similar differences between HR–LS and LR–LS conditions with comparable final values of swelling and solubility.

Characterization of starch gels

The method used for the characterization of starch gels was applicable only to gels that support their own weight which limited us to the highest

TABLE 2
Estimation of the Shear Dependence of Wheat Starch Pastes

Pasting procedure	*Concentration (%, w/w)*	η_l *Pa.s*	η_2 *Pa.s*	η_2/η_l
HR-LS	3·40	0·218	0·196	0·90
	5·10	0·714	0·477	0·63
	8·20	2·220	1·530	0·69
	11·60	7·440	5·820	0·78
HR-HS	4·39	0·225	0·130	0·58
	5·40	0·375	0·342	0·91
	7·95	1·090	1·150	1·05
	10·50	4·060	3·560	0·88
LR-LS	4·13	0·118	0·092	0·78
	5·20	0·402	0·206	0·51
	7·60	1·680	1·020	0·60
	10·60	7·580	6·120	0·81
LR-HS	4·52	0·088	0·097	1·10
	5·40	0·196	0·162	0·83
	7·70	0·690	0·630	0·91
	10·60	4·060	3·610	0·89

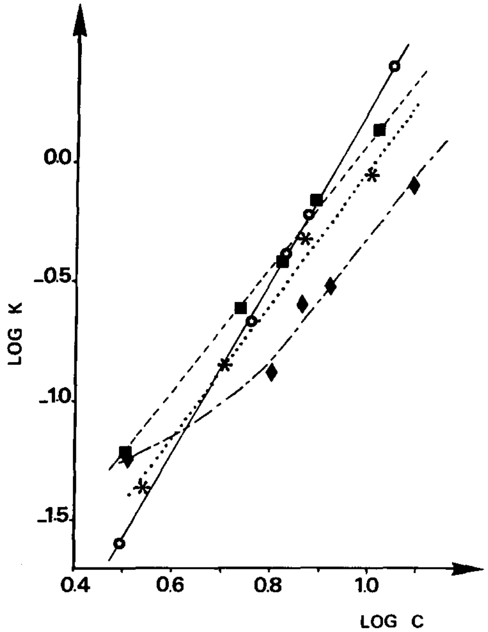

Fig. 9. Variations in logarithmic coordinates of the apparent viscosity at 94·6 s^{-1} as a function of concentration. Maize starch pastes. (O) LR-LS; (✱) LR-HS; (■) HR-LS; (◆) HR-HS. Temperature: 70°C.

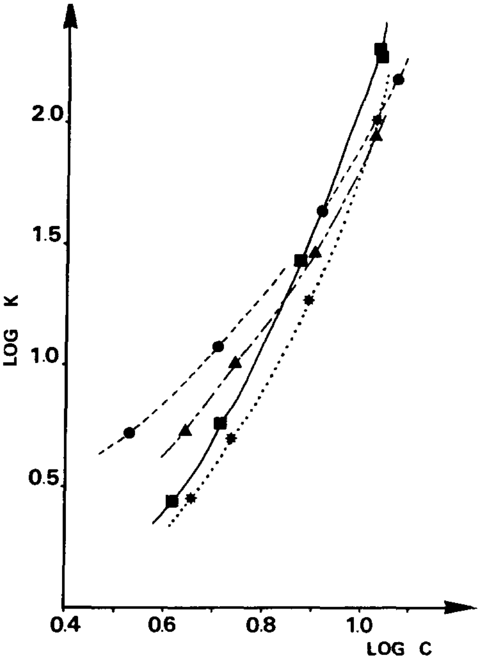

Fig. 10. Same legend as in Fig. 9 for wheat starch pastes. (■) LR-LS; (★) LR-HS; (●) HR-LS; (▲) HR-HS.

concentrations, i.e. 7·5 and 10·5%. Data are summarized in Table 3 where the compression modulus and the sag index are given. There is an evident relationship between these two parameters since sagging is related to the rigidity of gels. A range of values is obtained for each concentration depending upon the pasting procedure and the type of starch. The order of magnitude of the present data is close to values reported by Miles *et al.* (1985*a*) who worked at conditions near those of the HR-LS. These authors reported a shear modulus (G') of 2000 N m^{-2} for 10% wheat starch gels which would correspond to a compression modulus (E') of 6000 N m^{-2} assuming $E' = 3G'$ as for incompressible materials. This value is not too far from the corresponding present data for wheat starch, that is 4200 N m^{-2}, considering that measurements are not performed in the same time-scale conditions, at a high frequency (200 Hz) for G' and at a low compression rate in the present determinations. However, 10·5% maize starch gels prepared in HR-LS conditions were markedly softer, $E = 2500$ N m^{-2}, which is in disagreement with data of Miles *et al.* (1985*a*) who reported comparable values for wheat and maize starch. Data in the last column of Table 3 are given to estimate the concentration dependence of the compression modulus. Wheat starch

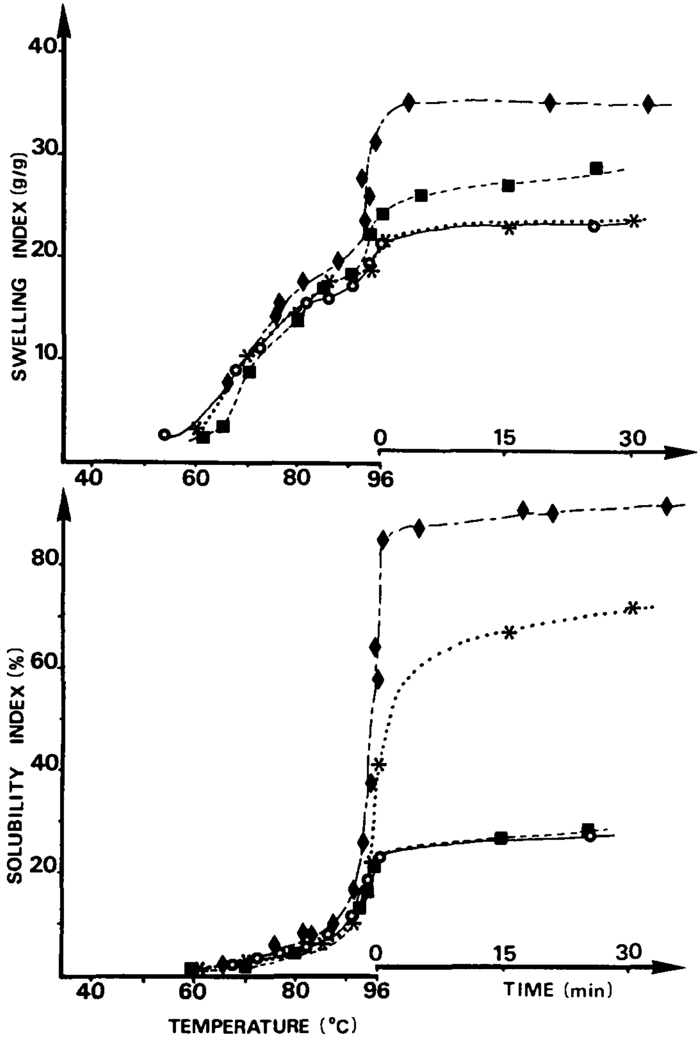

Fig. 11. Swelling-solubility patterns of maize starch. (■) HR-LS; (◆) HR-HS; (o) LR-LS; (✱) LR-HS.

gels display a higher dependence on concentration than maize starch gels, which is evidence for differences in the structure of the gels. Ring (1985) has reported a linear concentration dependence for shear modulus with a slope of 500 N m^{-2}/% for a maize starch gel and 1460 N m^{-2}/% for a pea starch gel, both prepared under HR-LS conditions. There seems to be a good agreement with the present data for maize starch, whereas wheat starch would be a little closer to pea starch.

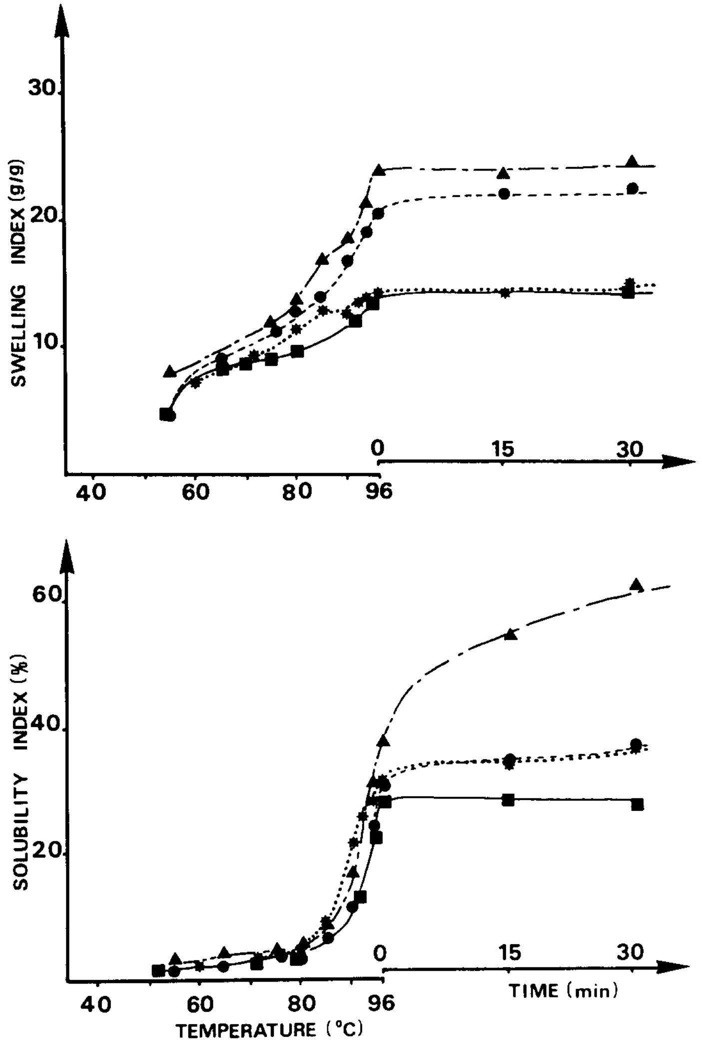

Fig. 12. Same legend as in Fig. 11 for wheat starch. (●) HR–LS; (▲) HR–HS; (■) LR–LS; (★) LR–HS.

DISCUSSION

Interpretation of viscometric measurements

The present work demonstrates that cereal starch pastes of very different consistencies can be obtained depending upon pasting conditions. Furthermore this dependence is influenced by the type of starch and its

TABLE 3
Rheological Characteristics of Wheat Starch Gels

Type of starch	*Pasting procedure*	*Concentration: ~ 7·5%*		*Concentration: ~ 10·5%*		$\Delta E/\Delta C$ $Nm^{-2}/\%$[b]
		E Nm^{-2}[a]	*Sag index*	*E* Nm^{-2}[a]	*Sag index*	
Maize	HR-LS	1630 (1610, 1650)	0·84	2530	0·90	500
	HR-HS	1070	0·78	1820 (1790, 1850)	0·90	250
	LR-LS	2420 (2350, 2490)	0·90	3770 (3620, 3920)	0·95	450
	LR-HS	1530 (1470, 1590)	0·80	2020 (1960, 2080)	0·89	163
Wheat	HR-LS	2090 (1990, 2190)	0·87	4160 (3970, 4350)	0·94	690
	HR-HS	—	—	—	—	—
	LR-LS	2570 (2440, 2700)	0·90	5610 (5380, 5840)	0·97	1000
	LR-HS	1340 (1250, 1430)	0·82	3540 (3470, 3610)	0·94	733

[a] Measurements in duplicate except for LR-LS (6 determinations) and HR-HS (maize) at ~ 7·5% (only one determination).

[b] $\Delta E/\Delta C$: increase of the compression modulus for a concentration increase of 1%.

concentration. It is evident that such a variety of behaviours should be interpreted more accurately on the basis of swelling-solubility data. Thus, if it is assumed that cereal starch granules keep part of their integrity after pasting at 96°C, as suggested by microscopic observations (Bowler *et al.*, 1980, Williams & Bowler, 1982), starch pastes can be described as suspensions of swollen particles dispersed in a macromolecular medium. Swollen particles are composed of remaining swollen granules, and the continuous phase is a solution of macromolecules of the soluble fraction as estimated in swelling-solubility experiments. The rheological behaviour of such a suspension is the result of an inextricable combination of many parameters, i.e. the volume fraction of swollen particles, their deformability, the rheology of the continuous phase which depends among other things upon its concentration and composition, etc. It is not the object of the present investigation to provide a complete description of the role of these different parameters. However, the relationship between viscometric measurements and swelling-solubility values can be dealt with on the basis of some assumptions.

It has been proposed by Bagley & Christianson (1982) that the volume fraction (Φ) of swollen starch in a suspension free of solubilized material can be estimated from the expression CG, C being the starch concentration in the dispersion and G the swelling capacity of granules. Taking into account that part of starch is solubilized, a similar treatment can be applied, resulting in the following expression:

$$\Phi = (1 - S/100)C.G \qquad (2)$$

where S is solubility index expressed in %, C is starch concentration in g/g, G is swelling index in g/g.

This equation assumes that the sediment is fully filled by swollen particles. This is likely to occur if particles are highly deformable so that they are easily close-packed. Furthermore, it is evident that Φ cannot be higher than unity and the proposed treatment is limited to a range of starch concentrations which depends on S and G, that is the pasting procedure and the type of starch. Provided that $\Phi \leqslant 1$, the concentration of the continuous phase can also be predicted from S and Φ:

$$C_S = \left(\frac{1}{1-\Phi}\right)C.S/100 \qquad (3)$$

where $1 - \Phi$ defines the volume available to solubles and the expression $C.S/100$ determines the amount of solubles at a given starch concentra-

TABLE 4
Comparison of Φ and C_S for Maize and Starch Pastes

Type of starch	*Pasting procedure*	*C (g/g)*	*S (%)*	*Concentration: ~ 3·3%*				*Concentration: ~ 5·5%*			
				Actual concentration	Φ	C_S *(g/g)*	η_2 *Pa.s*	*Actual concentration*	Φ	C_S *(g/g)*	η_2 *Pa.s*
Maize	HR–LS	29·8	30	3·2	0·65	0·028	0·230	5·4	> 1	—	1·08
	HR–HS	36·0	90	3·6	0·13	0·037	0·220	5·7	0·20	0·064	0·43
	LR–LS	24·0	27	3·1	0·54	0·018	0·038	5·7	0·99	—	0·89
	LR–HS	24·0	75	3·5	0·21	0·033	0·150	5·8	0·35	0·040	0·51
Wheat	HR–LS	22·7	36	3·2	0·54	0·023	—	5·1	0·79	0·053	0·58
	HR–HS	28·5	62	3·6	0·39	0·036	—	5·4	0·58	0·081	034
	LR–LS	14·2	28	3·1	0·32	0·013	—	5·2	0·53	0·031	0·21
	LR–HS	15·0	36	3·5	0·34	0·019	—	5·4	0·52	0·040	0·16

tion. Application of relations (2) and (3) is illustrated in Table 4 for ~ 3·3 and ~ 5·5% starch pastes. Φ and C_S are compared with the apparent viscosity at 6·6 s^{-1} from Tables 1 and 2. When $\Phi \ll 1$ and provided C_S is above a critical value around 0·02 g/g, the higher C_S the higher is the apparent viscosity. That means that an important contribution is to be ascribed to the continuous phase. When C_S is lower than 0·02 g/g, the overall viscosity is very low. This critical concentration is of the order of magnitude of the overlap concentration of amylose, C^*, as estimated by Ellis & Ring (1985) at around 0·015 g/g depending upon the molecular weight of the macromolecule. Below this critical concentration η varies linearly with concentration whereas, above C^*, η varies as the second or third power of concentration. Thus, it is for $C_S > C^*$ that the continuous phase contributes significantly to the overall viscosity of the suspension.

Relation (2) predicts that Φ should increase linearly with concentration. Table 5 summarizes 'yield' concentrations for which Φ would reach unity. These values give an order of magnitude of concentrations for which the suspension would be a dispersion of close-packed swollen particles. This is not likely to occur because of the presence of the soluble material. In effect, when the concentration increases, the swelling of granules is slowed down owing to the limited amount of water available and solubility is restricted in a similar way. The rheological behaviour of such concentrated systems is not governed by the same rules. This is suggestd by the dependence of K on concentration (Figs 10 and 11) where the gradient at high concentrations is completely different from that found at low concentrations, LR–LS conditions yielding, for

TABLE 5

Estimation of Yield Concentrations for Maize and Wheat Starch

Type of starch	*Pasting procedure*	*G (g/g)*	*S (%)*	*Yield concentration (C_y, %)*	*$1/G \times 10^2$*	*K 10·5% (Pa.s)*
Maize	HR–LS	29·8	30	5·1	3·4	1·34
	HR–HS	36·0	90	28·0	2·8	0·81
	LR–LS	24·0	27	5·7	4·2	2·36
	LR–HS	24·0	75	16·7	4·2	0·92
Wheat	HR–LS	22·7	36	6·5	4·4	1·56
	HR–HS	28·5	62	9·2	3·5	0·91
	LR–LS	14·2	28	9·8	7·0	1·56
	LR–HS	15·0	36	10·4	6·7	1·06

example, the highest viscosity at high concentration in contrast with figures at low concentration. It can be assumed that the rheology of concentrated starch pastes is governed by two main parameters:

(1) Concentration of the continuous phase which is probably very high because of the limited volume available, and
(2) The deformability of the swollen particles in the dispersed phase.

This last parameter is certainly more and more predominant when the concentration increases and is inversely related to the starch concentration inside the swollen particles, as estimated from $1/G$. This qualitative interpretation is supported by the comparison of K at ~ 10·5% and $1/G$ (Table 5) when the concentration is much higher than the yield value C_y. When the concentration is of the order of C_y, corresponding to close-packing of swollen particles, no clear trend can be observed. It can be inferred that three ranges of concentration can be defined depending upon the volume filled by swollen particles:

(1) A dilute and semi-dilute regime with Φ less than about 0·7,
(2) A concentrated regime with Φ between 0·7 and 0·9 defining a definite volume where solubles are concentrated, and
(3) A highly concentrated regime with $C > C_y$ with close-packing of swollen particles and very limited volume available to solubles.

Concentrations corresponding to each of these domains depend upon the type of starch and pasting procedure.

Shear susceptibility is another type of information available from viscosity measurements. Here, also, a wide range of behaviour is apparent with, in most cases, rheodestruction and in some cases rheopexy or shear-induced structure formation. Interpreting on a physical basis such phenomena is not the object of the present investigation. However, it can be mentioned that there seems to be a relationship between swelling capacity and rheodestruction, the more swollen the starch granules, the more shear-sensitive the pastes. An exception is observed for HR–HS conditions where only limited rheodestruction is observed. Cases of rheopexy are also seen in these conditions. More accurate investigations on shear susceptibility are, however, needed. It is a manifestation of viscoelastic properties and related to the existence of a weak structural network. A way to study such viscoelastic properties could be the use of transient methods on application of a shear stress as proposed by Schutz and Tatin (1974).

Description of starch gels

Cooling starch pastes results in a rapid formation of an opaque elastic gel which can be regarded as a composite with swollen granules embedded in a macromolecular matrix (Miles *et al.*, 1984). It is well known that the rheological characteristics of such gels change on ageing and that different mechanisms are involved in the process, i.e. amylose gelation which is complete within about 12 h, and amylopectin crystallization which takes place over much longer time scales (Miles *et al.*, 1985*b*). Characterization was here performed on 24-h old gels so that only amylose gelation occurs. It implies that the only difference between the hot starch pastes and the cold gel is the gelation of amylose in the continuous phase or, possibly, inside swollen granules. As for the viscosity of suspensions, the elasticity of composite gels is a result of a complicated combination of parameters involving the elasticity of the continuous phase, the volume fraction of the dispersed phase and the shape and deformability of the swollen particles. Here, also, deformability can be simply estimated by the inverse of the swelling value, *G*. If swollen particles occur as fillers in the amylose matrix, the elasticity of the continuous network is supposed to be reinforced by such fillers (Ring, 1985). This is illustrated by Fig. 13 where the elastic modulus is plotted as a function of $1/G$ for ~ 10·5% gels and is a confirmation of data by Ring (1985) with pea starch gels. Two types of relationship are observed depending upon the stirring rate. A similar dependence is observed at 7·5% but variations are not linear. Although $1/G$ does not give the actual value of starch concentration inside swollen granules, it is clear that a relationship exists between the degree of swelling at low concentrations and the rigidity of

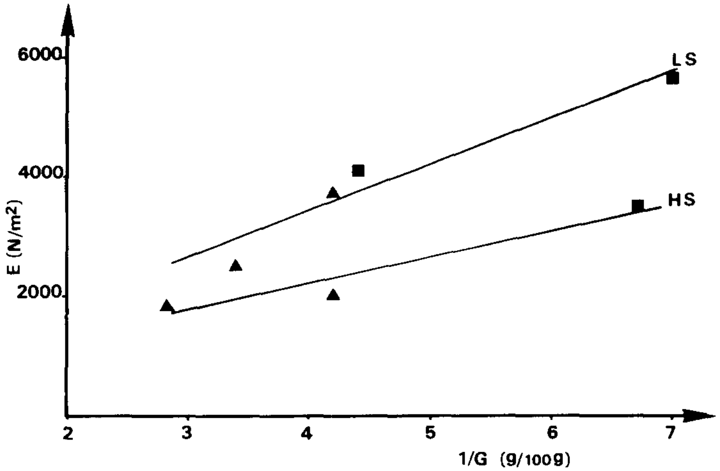

Fig. 13. Variations of the compression modulus of starch gels (concentration: ~ 10·5%) as a function of the inverse of the swelling index. Data quoted are taken from Tables 3 and 5. (▲) maize; (■) wheat.

starch gels. This is also supported by the evidence that wheat starch gels are stiffer than maize starch gels at equivalent concentrations and pasting procedures.

CONCLUSION

The aim of the present work was to describe the effect of different pasting procedures on the characteristics of wheat and maize starch pastes and gels. Each type of starch is shown to behave in specific ways for each pasting condition and a wide range of properties is displayed. It is thus demonstrated that the choice of pasting procedure is of importance for the definition of textural characteristics. It is also confirmed that cereal starch pastes and gels can be regarded as composites and that swelling-solubility determinations provide a basis for the structural description of such systems, particularly within the concentration range where Φ is predicted to be considerably less than unity. For the highest concentrations, when close-packing of swollen particles occurs, the effect of the pasting procedures is also evident but structures are more complicated and further investigations are needed. In this respect, problems which should be investigated concern the deformability of swollen particles, the amylose concentration of the continuous phase and the effect of the remaining amylose inside swollen granules on the overall gelation.

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