CATHERINE LOISEL[1], ALBERTO TECANTE[2], JEAN-LOUIS DOUBLIER[3]

RHEOLOGY AND STRUCTURE OF CROSS-LINKED STARCH DISPERSIONS

S u m m a r y

The rheological properties of chemically cross-linked waxy maize starch (CWMS) dispersed in water has been studied in relation to its swelling behaviour. The main parameters that were considered were starch concentration (2–4%), pasting temperature (96°C–136°C) and shear conditions ($\sim 10^5$ s^{-1}). The swelling behaviour was assessed by means of swelling experiments and by a measure of the size distribution of the swollen particles. The rheological study was performed by means of steady shear measurements (viscometry) and in oscillatory shear (viscoelasticity). In all conditions, starch dispersions exhibited the behaviour of suspensions of swollen particles as assessed from viscosity measurements. The flow behaviour of the dispersions was shear-thinning and a yield stress was clearly evidenced when the concentration was high enough. The viscoelastic behaviour became measurable as soon as the volume fraction of starch swollen particles was high enough for them to fill a large part of the available volume. This was typical of a gel-like system with G' > G" and a flat frequency dependence of G'. All these properties strongly depended upon the pasting temperature with an optimum determined by the degree of cross-linking of starch granules. Sensitivity of starch granules to shear also was strongly dependent upon the pasting temperature. When starch granules were undercooked, their swelling properties, and hence their rheological properties, were reinforced by high shearing. In contrast, when the starch granules were over-cooked the rheological properties were depressed by shearing as a result of their high fragility. These overall results allow ways to evaluate the swelling behaviour of crosslinked starch in the formulation of starchy products according to processing conditions.

Introduction

Cross-linked starch is a widely used food ingredient because chemical modification makes it resistant to thermal and mechanical treatment. Therefore, it is possible to use conditions that promote granule swelling without destruction and it can be reasonably considered that swelled granules are dispersed in a phase constituted only by

[1] *LGPA-ENITIA, BP 82225, 44322 Nantes Cedex 3 (France)*
[2] *Depto. Alimentos y Biotecnologia, FQ-" E ", UNAM, México, D.F., 04510, México*
[3] *INRA-UPCM, BP 71627, 41316 Nantes Cedex 3 (France)*

water. Rheologically speaking, such a system can be regarded as consisting of swollen gelled particles, the properties of which are mostly governed by the phase volume occupied by the swollen starch granules and their deformability. This has been clearly evidenced at temperature lower than 100°C and under moderate shearing [1, 3, 6, 11]. However, these conditions are far removed from the usual industrial conditions in terms of temperature and shear treatments. Actually, quite few studies have been devoted to the rheological description of dispersions of cross-linked starch in conditions that are close to the industrial ones, that is at temperature higher than 100°C and under strong shearing [7]. The present paper reports some recent investigations dealing with the properties of cross-linked waxy maize starch (CWMS) with the pasting temperature ranging from 96°C and 136°C and in different shearing conditions. The aim was to describe how the extent of swelling as well as the 'fragility' of starch granules influence the properties of the suspensions.

Materials and methods

Materials

Two CWMS samples were adipate/acetate starch supplied by Roquette Frères : Clearam® CH10, lot E9887 and Clearam® CH20, lot 61546). Both samples are devised to resist to high temperature treatment without being disrupted. They differ by their degree of cross-linking. CH 10 being less reticulated than CH 20 swells to a larger extent but is more susceptible to shearing under heat treatment.

Pasting procedure

Starch at 3, 3.5 or 4% (w/w) was slurried in water at room temperature under mechanical stirring to avoid settling. Then the suspension was poured into a jacketed vessel (capacity 2l, stirring rate 500 rpm) inside which gradual heating (5°C/min) was applied from 20°C to the upper pasting temperature (98 to 136°C); this temperature was maintained for 20 minutes and was followed by a cooling step (1.5°C/min) down to 70°C before sampling. Three pasting temperatures were compared to define three swelling degrees of the starch granule: 'undercooked' (90 and 110°C), 'well cooked' (120–125°C) and 'overcooked' (130°C).

Particle size determination of swollen starch granules

Particle size determination was performed at room temperature using a Malvern Master Sizer (Malvern Instruments, Ltd) laser scattering analyser with a 300 mm Fourier cell (range 0.05 to 879μm) as described in Loisel et al. [9]. The starch dispersion was first diluted (1/10) with water at 20°C immediately after the pasting procedure,

then dispersed in the sample dispersion unit (1 ml/100 ml water) and fed into the measuring cell. Volume distribution was obtained using the Mie scattering theory which requires refractive index of the media to be specified: we used, 1.529 and 1.33, respectively for starch and liquid phase and 0.1 for the starch granule absorption. From each distribution a median volume diameter D(v, 0.5) was calculated.

Swelling determination

Swelling was estimated after centrifugation of a starch suspension diluted at 0.5% at 700 g for 15 min [8] using the dye exclusion technique as described by Dengate et al [5] with Blue Dextran as the dying agent. From the absorbance at 630 nm of the supernatant, after dilution of starch suspension by a Blue Dextran solution (0.1%) the amount of water absorbed by the swollen starch granules is given by:

$$W_{abs}=W_0(1-C_1/C_2) \tag{1}$$

with:

W_{abs}, amount of water absorbed by starch granules (%, w/w),

W_0, total amount of water in the starch suspension (%, w/w),

C_1, concentration of the added Blue Dextran solution,

C_2, concentration of the solution in Blue Dextran in the supernatant.

Considering that the solubility of starch can be neglected, the swelling capacity (Q) is given by:

$$Q=(\frac{W_{abs}+(100-W_0)}{100-W_0}) \tag{2}$$

Shearing of starch suspensions

The heated starch suspension was sheared directly out of the reactor after cooling to 70°C by flowing it through a conical contractor (contraction angle = 30°, 10^{-3} m internal diameter). The upper wall shear rate applied was estimated to 10^5 s^{-1}, for a feed rate of 25 L/h.

Rheological measurements

Steady shear tests were carried out at 60°C using a cone-plate measuring device (6 cm/4°) with a controlled stress rheometer (TA Instruments AR 1000). Two consecutive shear scans were performed by programming linearly the shear rate from 0 to 660 s^{-1} and then back to zero. Each cycle was performed for 4 minutes. This was followed by stepwise measurements with a logarithmic programmation of shear rate from 660 to 0.1 s^{-1}.The same device was used to perform oscillatory shear tests on a new aliquot (unsheared sample). A 4% strain amplitude was fixed after determination of the linear

viscoelastic range. Each sample was analysed through a three steps protocol: (1) mechanical spectrum (G' and G'' as a function of frequency) at 60°C to characterize the hot paste, (2) gelling kinetics (at 1 Hz) after rapid cooling of the sample from 60 to 25°C using Peltier effect, (3) mechanical spectrum at 25°C of the gelled system.

Results and and discussion

From the swelling capacity (Q), the volume fraction (Φ) occupied by the swollen particles is obtained by the expression (Φ = c Q). Some values are given in Table 1 corresponding to the concentrations and temperatures that have been studied in the present work. Clearly, the swelling capacity of CH20 was much lower than that of CH10 due to its higher degree of crosslinking. For the examples chosen here, the volume fraction ranged from ~0.50 to ~0.75 depending upon the type of starch, the concentration and, but to a lower extent, the heating temperature. As a result of the different degree of crosslinking, a volume fraction of ~0.50 required a 3% starch concentration in the case of CH10 instead of 3.5% in the case of CH20.

Table 1

Swelling capacity (Q) of two CWMS at different treatment temperatures and corresponding volume fractions (Φ) at different concentrations.

Temperature (°C)	CH10			CH20	
	Q (g/g)	Φ3%)	Φ4%)	Q (g/g)	Φ3.5%)
96	17.0	0.51	0.68	15.1	0.53
112	17.5	0.52	0.70	15.7	0.55
125	18.2	0.55	0.73	16.0	0.56

Note: volume fractions (Φ are obtained from the expression $\Phi = cQ$

Figure 1 shows the typical flow behaviour of a CWMS (CH10) dispersion heated to 96°C. At 3% a shear-thinning behaviour was clearly evidenced. The 'up' curve being superimposed to the 'down' curve, no shear dependency was exhibited. At 4%, the CWMS dispersions exhibited an anticlockwise loop in the first cycle between 0 to 660 s^{-1}. The second cycle then was superimposed to the return curve of the first cycle. Such antithixotropic behaviour has been reported by several authors in the case of crosslinked starches [4, 11, 12].This is indication of a flow-induced structure the origin of which has been postulated from granule rupture and partial leaching of amylopectin [11]. However, as it will be evidenced in the following, starch granules heated at such a low temperature (96°C) are not prone to break down easily and this assumption is far from being proven. As an alternative explanation, it can be suggested that such a be-

haviour in concentrated suspensions is to be ascribed to a rearrangement of the close-packed particles thus yielding a higher organization of the system [2].
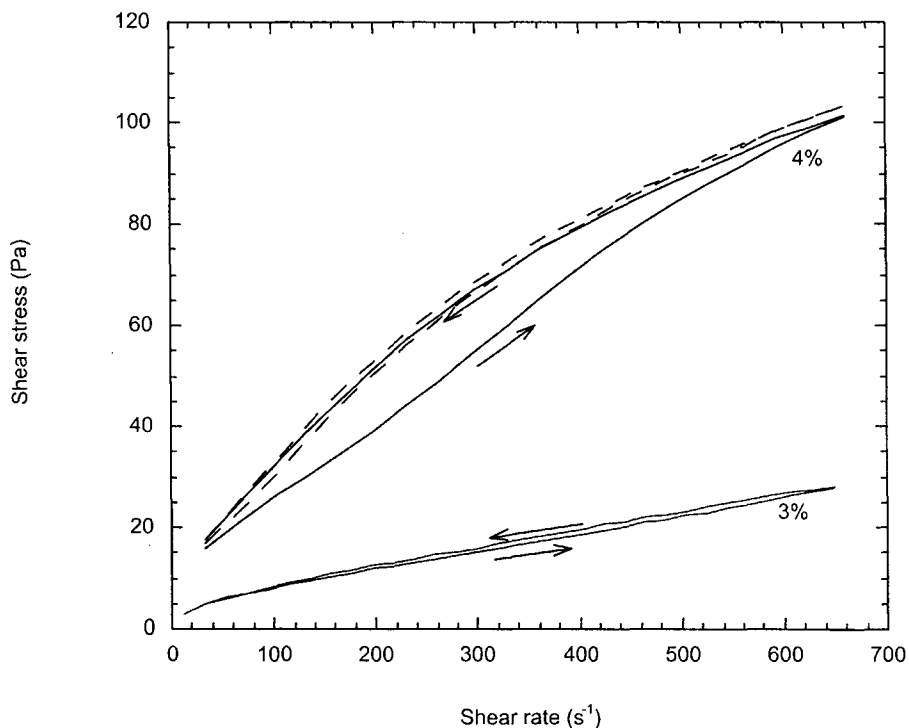

Fig. 1.   Flow curves of 3% and 4% CWMS (CH10) dispersions heated to 96°C. Measurement temperature: 60°C. For the 4% dispersion, two successive cycles are plotted: 1st cycle: continuous line; 2nd cycle: dashed line.

The effect of heating temperature at 96, 112 and 125°C, respectively, on the flow behaviour of a 3% CH10 dispersion is illustrated in Figure 2. As was expected, increasing this temperature above 100°C resulted in an increase of the viscosity. Furthermore, the behaviour was 'antithixotropic' at 112°C and 125°C while not at 96°C. This may be ascribed to an increase of the size of the particles and hence of the phase volume occupied by the swollen particles.
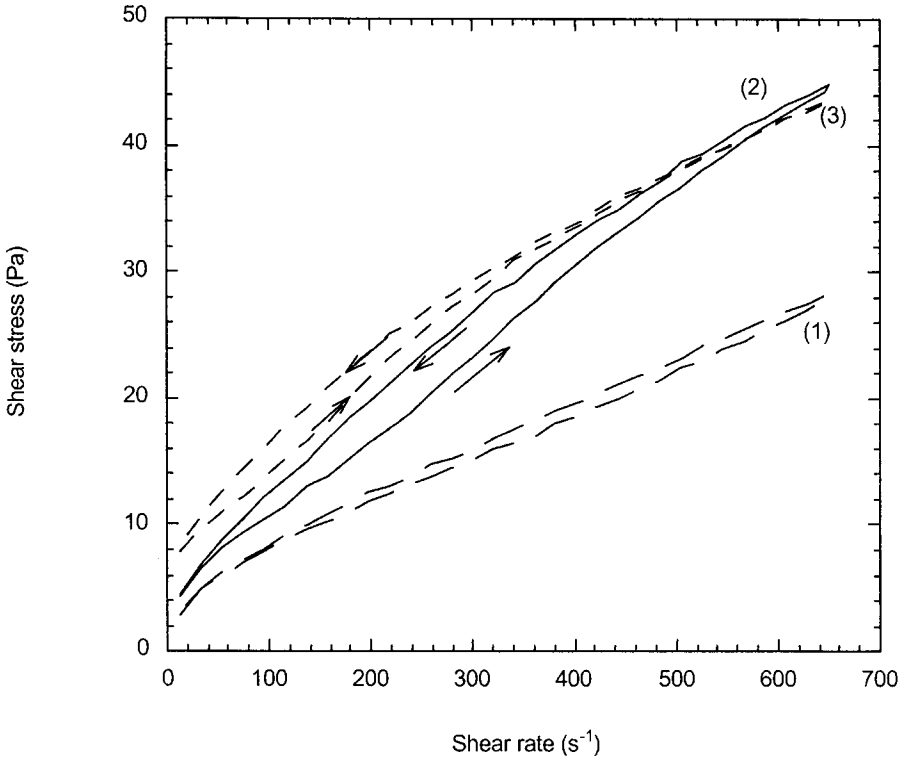
Fig. 2.   Flow curves of 3% (CH10° dispersions heated to 96°C (curve 1), 112°C (curve 2) and 125°C
          (curve 3). Measurement temperature: 60°C.

The viscoelastic behaviour of these dispersions is illustrated in Figure 3. In the present case, measurements were performed at 25°C. Although displaying visually a liquid aspect, all these systems exhibited a solid-like behaviour with G' > G" and G' almost independent of frequency. Since the dispersion is composed of swollen starch granules, this clearly indicates that the dispersion is concentrated enough to develop viscoelastic properties. In other terms, the swollen particles are close-packed which makes them to govern the rheological properties. In these experiments, Φ ranged from 0.50 to 0.55. These observations are consistent with those of Evans et Lips [6] who found that a volume fraction of 0.4–0.5 is required for noticeable elastic properties to be developed in the case of waxy cross-linked maize starch. Although the moduli differed quite significantly between the different temperatures, the shape of the curves were similar suggesting a comparable structure. It can also be noticed that a higher G' value was obtained after treatment at 112°C than at 125°C and 96°C. The optimum swelling temperature should be close to 120°C, starch granules being 'overcooked' at 125°C and 'undercooked' at 96°C.
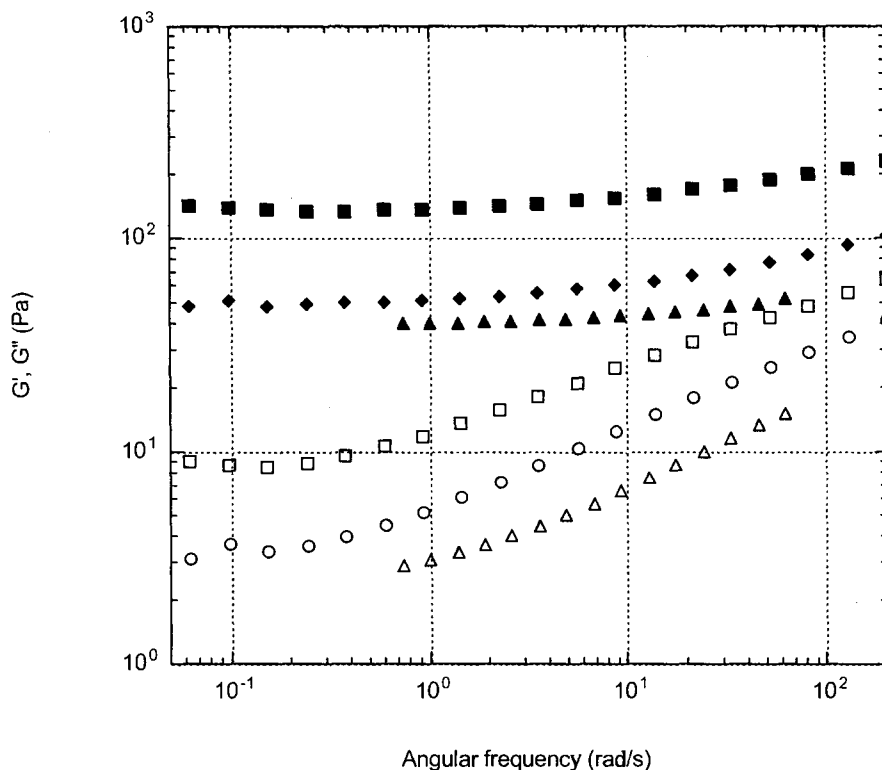
Fig. 3. Mechanical spectra (G' and G" as a function of frequency) of 3% dispersions (CH 10). Filled symbols: storage modulus (G'); empty symbols: loss modulus (G"). Triangles, heating temperature: 96°C; squares, heating temperature: 112°C; lozenges, heating temperature: 125°C. Measurement temperature: 25°C.

The flow curves of 3.5% WMCS dispersions (CH20) at different heating temperatures in the range 98–136°C are illustrated in Figure 4. Again, viscosity measurements were performed at 60°C. In the present case, the curves were plotted in log scales allowing one to visualise the low shear range. Clearly, the curves displayed a shear-thinning behaviour with a yield stress at low shear rate. This is the expected behaviour of suspensions of deformable particles and has already been reported for starch dispersions. The yield stress was strongly dependent on the pasting temperature with a maximum at 129°C: around 0.7 Pa at 98°C, 1.2 Pa at 115°C, 2 Pa at 122°C, 3 Pa at 129°C and less than 1 Pa at 136°C. These overall results clearly illustrate the effect of the pasting temperature around the optimum swelling temperature. In the present case, the optimum was close to 130°C to which the maximum viscosity the highest yield stress were reached. The shape of the curve for a treatment at 136°C differed significantly from the other results. This is clear illustration that the structure of

the suspension is noticeably different since starch granules are overcooked and proba-
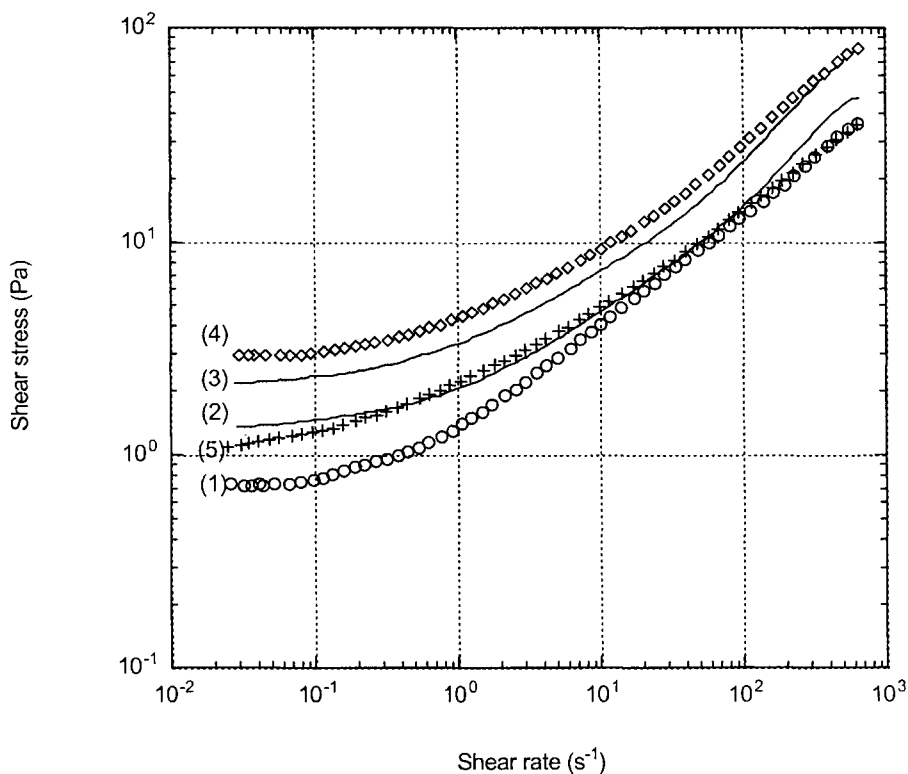bly more easily broken down.

Fig. 4.   Flow curves of 3.5% CWMS (CH20) dispersions. Heating temperatures: 98°C (curve 1), 115°C
(curve 2), 122°C (curve 3), 129°C (curve 4) and 136°C (curve 5). Measurement temperature:
60°C.

Sensitivity of these starch dispersions to shearing as a function of treatment tem-
perature is illustrated in Figure 5. The dispersions have been prepared in the same way
as in Figure 4 but an additional shearing step has been applied at 70°C (see methods).
For treatments between 98°C and 129°C, the flow curves were almost superimposed.
The yield stress was of the order of 2 Pa. From the comparison with Figure 4, the
curve at 122°C was the same while those at 98°C, and 115°C were shifted towards
higher shear stress values. The curve for 129°C was slightly shifted downwards (the
shear stress was depressed from 3 to 2 Pa) but was superposed to the previous curves.
Inversely, the dispersion heated to 136°C experienced a dramatic downward shift. This
indicates that the additional shear process imposed to starch granules can either in-
crease the overall viscosity (< 120°C), probably by improving the swelling pattern of

the starch granules, or decrease the overall viscosity (at 136°C) suggesting their shear sensitivity in these conditions. At 122°C, the shearing process did not yield any significant change in the properties. These observations suggest that the optimum swelling can be achieved by combining treatment temperature and high shearing, with the provision that starch granules have not been 'overcooked'. If the optimum temperature is exceeded the swollen particles become susceptible to shearing; as a result, the granules can be broken down and the viscosity is depressed.
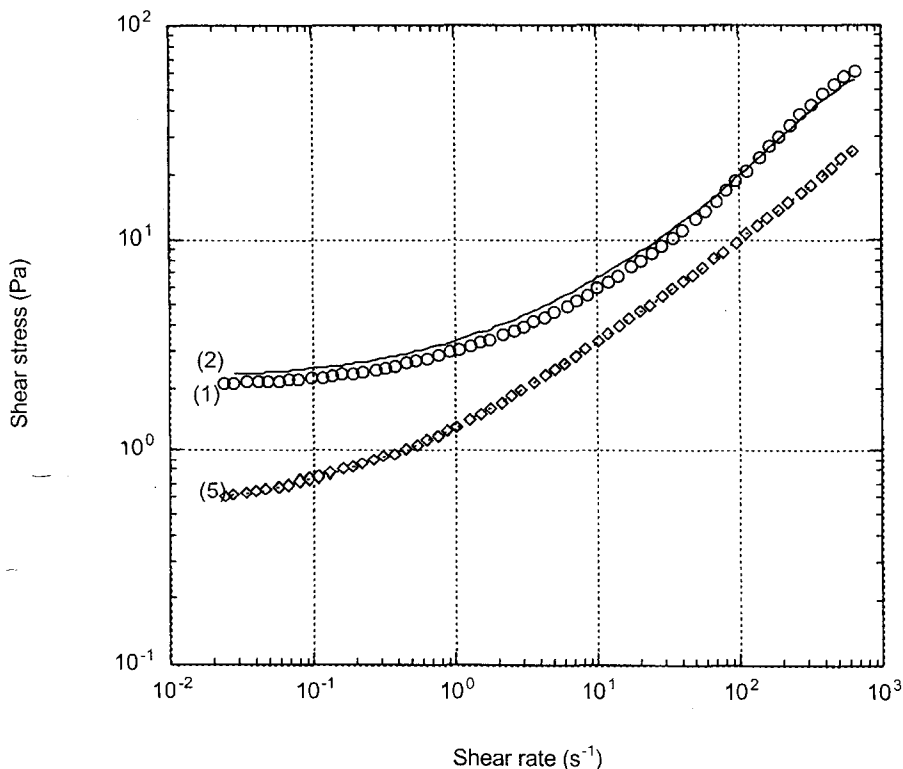

Fig. 5. Flow curves of 3.5% CWMS (CH20) dispersions submitted to strong shearing. The numbers correspond to the same heating temperature as in the previous figure. The results for 122°C (curve 3) and 129°C (curve 4) were superimposed to curve 2 and are not showed.

In order to better understand these effects, we determined the particle size distribution after heat treatment. Figure 6 shows the distribution as a function of the diameter. The median volume diameter at 98°C was increased from around 39 μm without shearing up to ~43 μm upon shearing. Also a slight increase was experienced at 117°C from ~42 μm down to ~44 μm. Figure 7 shows the overall results obtained between 98°C and 136°C. While the median diameter increased continuously from 39 at 98°C to 47

µm at 127°C and then slightly decreased down to 44 µm at 136°C for the unsheared samples, the variations were different when shearing was applied: the diameter was almost constant (at ~43–44 µm) up to 122°C and then dramatically dropped to reach ~26 µm at 136°C. This is clear indication that swollen starch granules of CH20 CWMS become highly susceptible to shearing if treated at temperature higher than 122°C but are highly resistant if the treatment temperature is lower than 122°C. Moreover, the effect of shear on the size of swollen starch granules is beneficial if the treatment is applied at temperature lower than ~125°C. These overall observations are fully consistent with the rheological data (Figures 4 and 5).
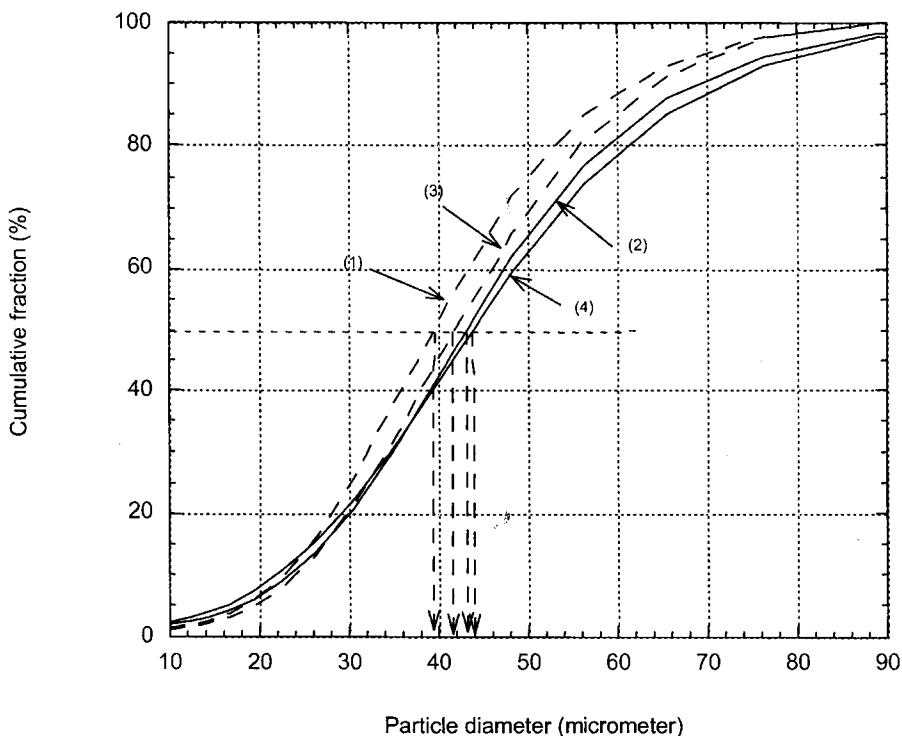

Fig. 6.   Size distribution of swollen starch granules (CH20). Heating temperature 98°C; curve 1: unsheared; curve 2: sheared. Heating temperature: 117°C; curve 3: unsheared; curve 4: sheared.
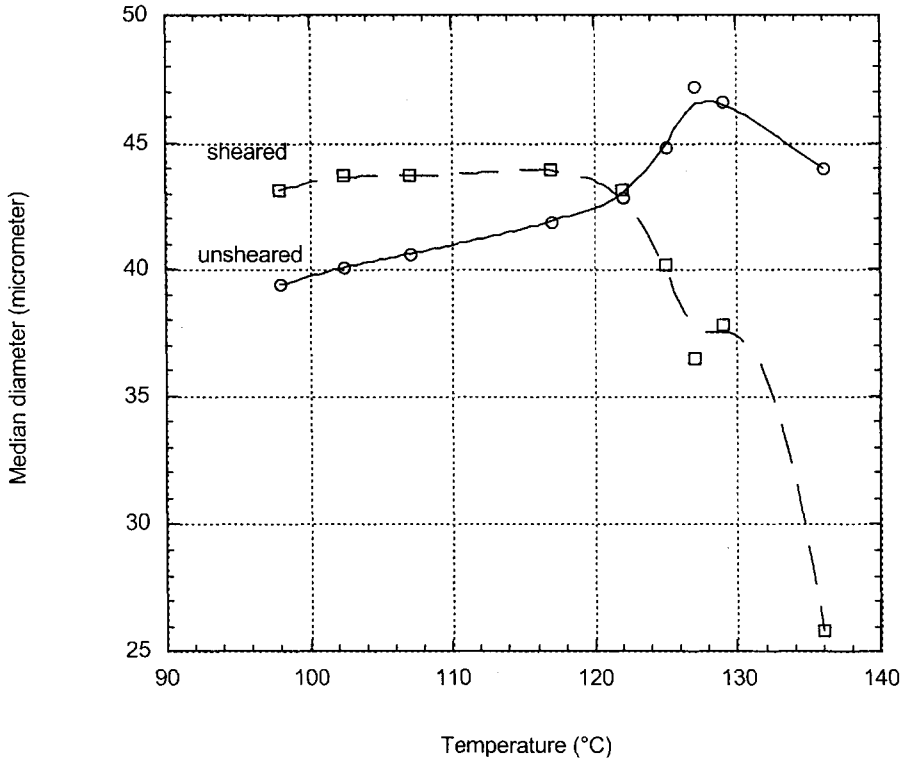
Fig. 7.   Median diameter as a function of heating temperature. Comparison of sheared and unsheared samples (CH20).

Conclusions

All these rheological results correspond to starch suspensions with a volume fraction higher than 0.50 (Table 1). The present observations are consistent with those of Steeneken [10] on the basis of viscosity measurements who found that a volume fraction of 0.4–0.5 is required for viscosity development. This author also reported that within the concentration range 0.50–0.70, it is the volume fraction which determines the viscosity of the suspension. However, it is likely that the deformability of the particles should also be taken into account. This is shown by the solid-like behaviour as evidenced by the viscoelastic properties (G' > G") as well as by the flow behaviour at low shear rate (yield stress). A decrease in G' or in the yield stress would reflect an increase in the deformability of the particles. This is clearly illustrated in Figures 3 and 4 which show large differences as a function of the heating temperature while the volume fraction remains almost constant.

References

[1]   Bagley E.B., Christianson D.D.: J. Texture Studies, 1982, **13**, 115-126.

[2]   Barnes H.A. J.: Rheol., 1989, **33**, 329-366.

[3]   Colas B.: LWT, 1986, **19**, 308-311.

[4]   Da Silva P.M.S., Oliviera J.C., Rao M.A.: J. Texture Studies, 1997, **28**, 123-138.

[5]   Dengate H.N., Baruch D.W., Meredith P.: Starch/Stärke, 1978, **30**, 80-84.

[6]   Evans I.D., Lips A.: Journal of Texture Studies, 1992, **23**, 69-86.

[7]   Lagarrigue S. & Alvarez G.: The rheology of starch dispersions at high temperatures and high shear
       rates: a review. J. Food Engng, 2001, **50**, 189-202.

[8]   Leach H.W., McCowen L.D., Schoch T.J.: Cereal Chem., 1959, **36**, 534-544.

[9]   Loisel C., Tecante A., Cantoni P., Doublier J.L.: Les Cahiers de Rhéologie, 1998, **16**, 152-158.

[10] Steeneken P.A.M.: Carbohydrate Polymers, 1989, **11**, 23-42.

[11] Tattiyakul J., Rao M.A.: Carbohydrate Polymers, 2000, **43**, 215-222.

[12] Tecante A., Doublier J.L.: Carbohydrate Polymers, 1999, **40**, 221-231.

REOLOGIA I STRUKTURA ZAWIESIN SIECIOWANYCH SKROBI

Streszczenie

Badano pęcznienie chemicznie sieciowanych woskowych skrobi kukurydzianych (CWMS) zawie-
szonych w wodzie. Głównymi parametrami branymi pod uwagę były stężenie skrobi (2–4%), temperatura
żelowania (96–136°C) i warunki ścinania (~10^5 s^{-1}). Pęcznienie obserwowano doświadczalnie oraz przez
pomiar rozkładu rozmiaru spęczniałych gałeczek. Pomiary reologiczne wykonano wiskozymetrycznie i
metodą oscylacyjną (lepkosprężystość). W każdym przypadku zawiesiny skrobi wykazywały pęcznienie z
rozrzedzaniem spowodowanym ścinaniem. Zachowanie się zawiesin spęcznionej skrobi było typowe dla
pseudożelowanych układów z G' > G" i płaskim przebiegiem zależności częstość – G'. Właściwości te
zdecydowanie zależały od temperatury kleikowania z maksimum zależnym od stopnia usieciowania gałe-
czek skrobiowych. Przy niezupełnym skleikowaniu gałeczek obserwowano wysoką wartość ścinania. Po
nadmiernym gotowaniu lepkość kleików spadała. ▨