FLOW BEHAVIOR OF CONCENTRATED STARCH DISPERSIONS USING A TUBE RHEOMETER OF NOVEL DESIGN

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ABSTRACT

A tube rheometer of novel design was used to study the flow properties of starch dispersions with concentration from 7 to 30% w/w at 95C. The flow properties of maize starch dispersions were largely influenced by the time of cooking and shearing that elapsed before the measurements were taken. Viscosity gradually decreased with the time of shearing until it reached a minimum value which then remained constant. Viscosity measurements, taken at 95C and 75C, of dispersions of 10 and 15% w/w starch concentration indicated that the activation energy of the flow was concentration dependent. The flow behavior shown by the starch dispersions was attributed to the presence of the amylose matrix rather than to swollen granules.

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INTRODUCTION

The knowledge of the rheological behavior of biopolymers and their influence on the textural properties of many foods during processing and quality evaluation has increased during the last fifteen years. However, there is still a need for absolute measurements of the flow properties of complex systems such as starch pastes under the conditions normally encountered during the preparation of products in which they are used (Doublier 1989). Hence, it is essential to develop absolute procedures that can simulate the conditions under which complicated food systems are treated in practice so that the measurements of their rheological properties can be directly utilised for process and equipment design.

So far the best method to study the rheological behavior of starch pastes was considered to be the use of a rotational rheometer with concentric cylinders or cone and plate geometry (Doublier 1989). To study concentrated pastes, elevated temperatures must be employed to avoid both gelation and retrogradation. At high temperatures the problem of water evaporation becomes a serious one and this is the reason why virtually no data have been reported at temperatures above 70C.

This paper considers the potential of a new tube rheometer, which was developed to study the flow properties of composite food systems such as concentrated starch dispersions under adverse conditions of elevated temperatures that are often encountered during the processing of starch based food products.

MATERIALS AND METHODS

Materials

Commercial maize starch was purchased from GROUP AMYLUM S.A., Greece, and waxy maize starch was a gift from the same company. The moisture content was 11.5% for the maize starch and 11.05% for the waxy starch. The total amylose content of the maize starch was 26.0 ± 0.3%, determined using the method of Morrison and Laignelet (1983).

The Tube Rheometer

The instrument, coded TR-1 RHEOMETER (Fig. 1) is a multipurpose pneumatic tube rheometer which consists of an air chamber to which compressed air is supplied through an inlet valve. The inlet valve is controlled by a pressure sensor-controller unit so that the pressure in the air chamber is accurately controlled at the set value ranging from 0.010 to 4.000 ± 0.001 bars. A bleed valve is also provided so that the pressure in the air chamber can be set either upwards or downwards. The working principle of the instrument is shown in Fig. 2. The

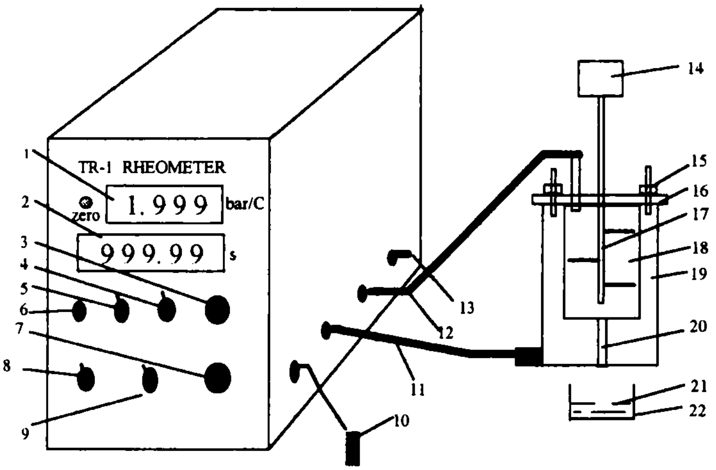

FIG. 1. SCHEMATIC EXPRESSION OF THE TR-1 TUBE RHEOMETER
Numbers denote: (1) Pressure/temperature (P/T) display (2) Time display (3) Temperature setting (4) P/T display selection (5) Pressure setting X1/X2 selection (6) Temperature setting (7) Pressure setting (8) Power switch (9) Valve control, on/off/synchronised with timer (1) Timer switch (11) Temperature control cable (12) Pressurised air outlet (13) Compressed air inlet (14) Motor (15) Lid fastening nut (16) Lid (17) Stirrer (18) Sample (19) Sample vessel (20) Capillary tube (21) Discharged fluid (22) Sample collector.

compressed air from compressor or gas cylinder passes through a filter, a manual regulator and the inlet valve V1 to the air chamber. Inlet valve V1 and bleed valve V2 are controlled by the pressure measurement and control unit. The pressure is applied to the sample container when valve V3 opened. Otherwise the sample container communicates with atmosphere through V3 which is controlled by a switch in three modes, namely on, off or synchronized with the timer. By switching on this valve a controlled air pressure is applied to the fluid and forces it to flow through the capillary tube fixed at the bottom of the sample vessel. The cylindrical sample vessel made of stainless steel, has a capacity of 35 mL and dimensions: height 5.6 cm and internal diameter 3.1 cm. It is equipped with a pin shape stirrer rotating at a fixed speed of 50 rpm. The stirrer is 2.8 cm wide and consists of four rods placed in a row, which have 2 mm thickness and 2.5 cm height. An extra four rods of the same dimensions with the others, are fixed at the bottom of the container in positions that do not restrict the movement of the rods of the stirrer. Preliminary tests of stirring starch dispersions at the concentration range employed in this work, at room temperature, showed that the starch granule damage, due to shearing, was negligible as indicated by the Congo red test. The container is thermostatically controlled at a temperature range from ambient to 130 ± 0.1C, by means of a platinum resistance thermometer

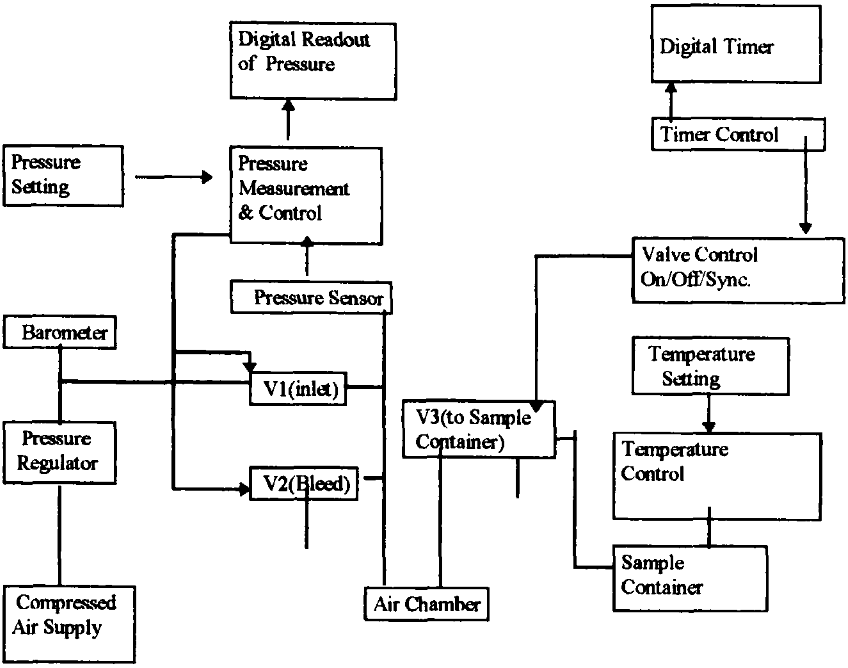

FIG. 2. WORKING PRINCIPLE DIAGRAM OF TR-1 RHEOMETER

— proportional and integral temperature controller. The flow rate can be calculated by measuring the volume or the weight of the discharged fluid at the exit of the tube, and the corresponding time of discharge. By taking flow rate measurements at varying pressures, i.e. shear stresses, a flow curve can be obtained. A wide range of liquids, suspensions and pastes can be measured by selecting tubes of appropriate dimensions. In this work the tube used had a length of 30 mm and an i.d. of 2.05 mm. A metal tube of i.d. 0.975 mm and length 35 mm was used for preliminary experiments. This tube was fixed by inserting it through the 2.05 mm i.d. tube which was permanently attached to the bottom of the container.

Theoretical Considerations

For the tube flow, the viscosity η of a Newtonian fluid is calculated from Hagen-Poiseuille's law

$$\eta = \Pi D^4 \Delta P / 128\ QL \qquad (1)$$

where, D is the diameter of the tube, L is the length of the tube, ΔP is the pressure drop, and Q is the volume flow rate.

For non-Newtonian fluids the apparent viscosity η_a is calculated from the shear stress at wall, τ_w and the corresponding shear rate after the non-Newtonian correction, $\dot{\gamma}$(corr.) which is calculated from the apparent uncorrected shear rate, $\dot{\gamma}$(uncorr.) according to the following equations:

$$\dot{\gamma}(\text{uncorr}) = 32\ Q/\Pi D^3 \tag{2}$$

$$\dot{\gamma}(\text{corr.}) = \dot{\gamma}(\text{uncorr.})\ (3n + 1)/4n \tag{3}$$

$$\tau_w = \Delta PD/4L \tag{4}$$

$$\eta_a = \tau_w/\dot{\gamma}(\text{corr.}) \tag{5}$$

where n is the flow behavior index, calculated from the slope when ln τ_w is plotted versus ln $\dot{\gamma}$(uncorr.) i.e.

$$n = d(\ln \tau_w)/d[\ln \dot{\gamma}(\text{uncorr.})] \tag{6}$$

End Effects. In capillary flow, the converging flow at the entrance and the diverging flow at the exit both cause pressure losses known as end effects. It is customary to treat the end effects in terms of effective capillary length ($L + \zeta D$) and the effective shear stress at wall, τ(eff.), can then be calculated from the following equation:

$$\tau(\text{eff.}) = \Delta PD/4(L + \zeta D) \tag{7}$$

The value of ζ for a particular shear rate is determined by extrapolating the linear relation of ΔP versus L/D ratio measured at that shear rate to $P = 0$. This practice is known as Bagley correction (Bagley 1957). The use of capillary tubes with large L/D ratios is recommended so that end effects are rendered negligible.

Kinetic Energy Correction. (van Wazer *et al.* 1963) When a fluid stream discharges with high speed from the capillary tube into the air, the stream carries a significant amount of kinetic energy. This kinetic energy may represent an appreciable portion of the total applied pressure and should be corrected by the following equation:

$$\Delta P = \Delta P(\text{obs.}) - \rho u^2/\alpha = \Delta P(\text{obs.}) - 16\rho Q^2/\alpha \Pi^2 D^4 \tag{8}$$

where ΔP is the corrected pressure, ΔP(obs.) is the observed pressure, α is the kinetic energy correction factor, ρ is the fluid density.

Factor α is a function of the velocity distribution pattern in a capillary tube set up by a particular fluid. For Newtonian fluids α is equal to unity. For power law fluids α can be calculated from the following equation:

$$\alpha = (4n + 2)(5n + 3)/[3(3n + 1)^2] \tag{9}$$

For treating the data obtained using the TR1 Rheometer, a BASIC language program was constructed which takes into account the above mentioned corrections to calculate the viscosity of a fluid as a function of the shear rate.

Rheological Measurements

Aqueous starch dispersions ranging in starch concentration from 7 to 30% w/w (dry basis) were gelatinised inside the sample vessel of the rheometer at 95 ± 0.2C under continuous stirring. The time needed for the sample to reach the target temperature of heating was approximately 6 min. During the time of heating up and holding the sample at the required temperature, water evaporation was virtually eliminated by sealing the entrance of the compressed air to the sample vessel.

When flow rate was required, the compressed air tubing was connected to the vessel and the time needed to take a number of measurements sufficient to draw a flow curve was 3 to 5 min. Each set of measurements was replicated three times.

Intrinsic viscosity measurements, using an Ubbelohde suspended level viscometer, of 0.5% starch dispersions heated at 95C for time intervals from 15 to 100 min, showed no appreciable changes. This was an indication that starch did not undergo degradation at least within the time scale of the rheological measurements of the present work.

RESULTS

The effects of starch concentration, cooking time, shearing time and temperature on the flow properties of starch pastes were measured.

Effect of Cooking Time

Figure 3 shows the viscosity — shear rate data obtained at 95C for a 20% w/w dispersion of maize starch after 15, 30, 45 and 60 min of cooking under continuous shearing. All flow curves are typical of a non-Newtonian shear-thinning fluid. The value of the flow behavior index (n) increases as the time increases up to 45 min then remains fairly constant. Thus, after 15 min of cooking under continuous shearing the n is 0.498, after 30 min is 0.568, after 45 min is 0.623 and after 60 min is 0.623.

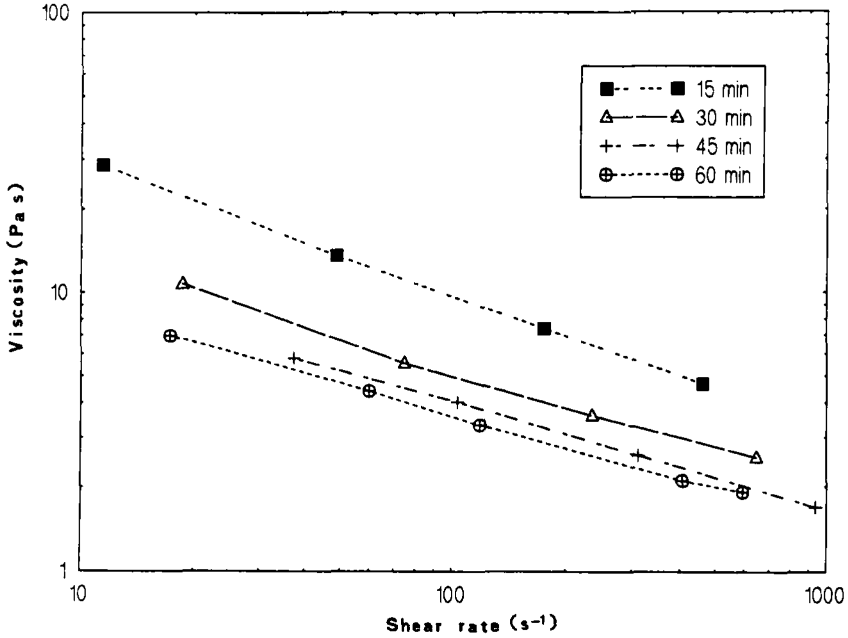

FIG. 3. FLOW CURVES OF 20% MAIZE STARCH DISPERSIONS AT 95C, AFTER 15, 30, 45 AND 60 MIN OF COOKING

At 95C the starch has been fully gelatinised and all the available amylose has been leached out from the granules during the first 10 min. By further stirring some of the amylopectin was also leached out although due to the very slow stirring it is certain that at least the majority of the granules retained their shape. If it is assumed that all amylose has been leached from the granules as soon as the temperature of the dispersion reached 95C then the decrease in viscosity due to prolonged shearing should be primarily attributed to the disentanglement of the molecules of the continuous phase i.e. amylose and to a lesser extent to the softening of the swollen granules due to the leaching of amylopectin molecules. The increase of the flow behavior index supports this assumption as it will be explained below.

Effect of Shearing Time

Figure 4 shows the viscosity change with time under constant stress value of 862.7 Pa at 95C of two starch dispersions at concentrations of 15 and 20% w/w. The viscosity decreased rapidly for approximately 50 min before it leveled off, after which the two curves almost coincide. This provides further evidence that by continuous shearing the amylose molecules which contribute the most to the

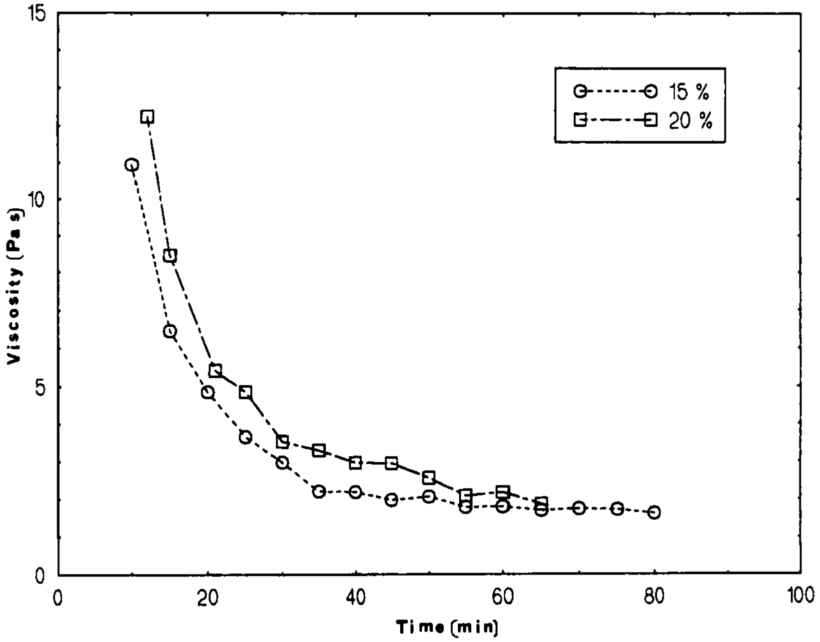

FIG. 4. VISCOSITY AS A FUNCTION OF THE TIME OF SHEARING OF MAIZE STARCH DISPERSIONS OF 15 AND 20% CONCENTRATION, AT 862.7 Pa SHEAR STRESS AND 95C TEMPERATURE

viscosity of the concentrated starch systems are disentangled and the viscosity is due solely to individual amylose molecules and deformed granules whereas possible interactions between the components of the systems are limited to a minimum degree. This behavior supports the microscopic observations of Miller *et al.* (1973) and the postulation of Doublier (1989) that at least in concentrated starch dispersions the main contributor to the viscosity is the continuous (amylose) phase.

Effect of Temperature

Figure 5 shows the effect of temperature on the viscosity shear rate curves of two starch dispersions at concentrations of 10 and 15% w/w. The measurement of viscosity was carried out as follows: The samples were heated from ambient temperature to 95C and for a total time of 30 min (the first 6 min were spent for the temperature to rise to 95C) then the samples were cooled to 75C and viscosity measurements were carried out and then the temperature was raised back to 95C and viscosity measurements were again performed at that temperature. Throughout the cycle of every experiment the samples were continuously stirred.

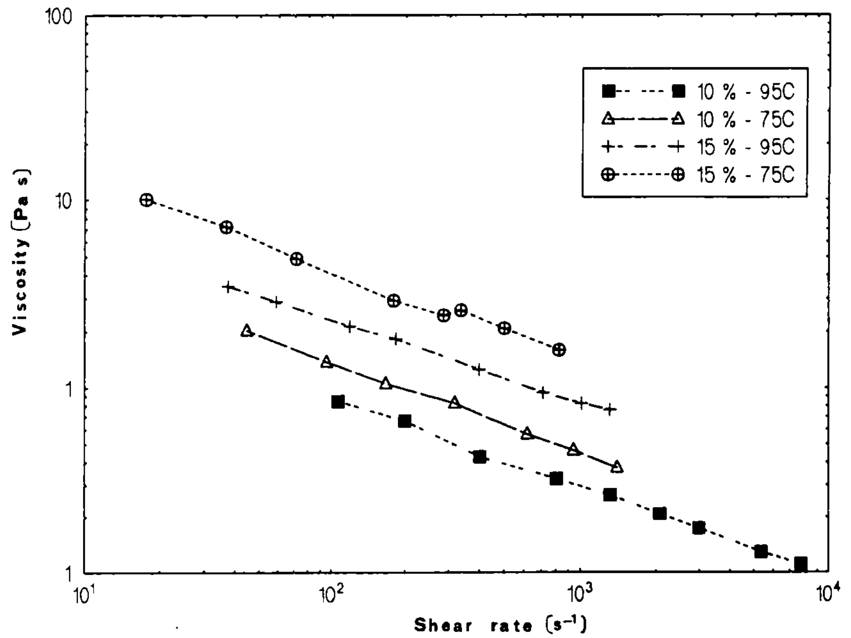

FIG. 5. FLOW CURVES OF MAIZE STARCH DISPERSIONS OF 10 AND 15% CONCENTRATION MEASURED AT 75 AND 95C

The activation energy of flow E_0 was calculated from the Arrhenius equation:

$$\eta = \eta_0 \exp (E_0/RT)$$

where, η is the viscosity, η_0 is the viscosity at a reference temperature, T is the absolute temperature, and R is the gas constant.

The E_0 value calculation was based on the viscosity ratio at shear rate 200 s^{-1}. The E_0 values obtained were 6.2 and 5.86 Kcal/mol for the 15% and the 10% starch dispersions, respectively. These results are higher than the 5.13 kcal/mol reported by Doublier (1981) for 2.6% wheat starch. This is an indication that the activation energy is concentration dependent. Doublier (1989) reported that the activation energy is both concentration and type of starch dependent.

Effect of Starch Concentration

Figures 6 and 7 show the viscosity-shear rate relations to starch concentrations for maize starch and waxy maize starch, respectively. For all flow curves the measurements were taken after 30 min total cooking time (heating up to 95C and holding at this temperature). Maize starch dispersions are more viscous than the

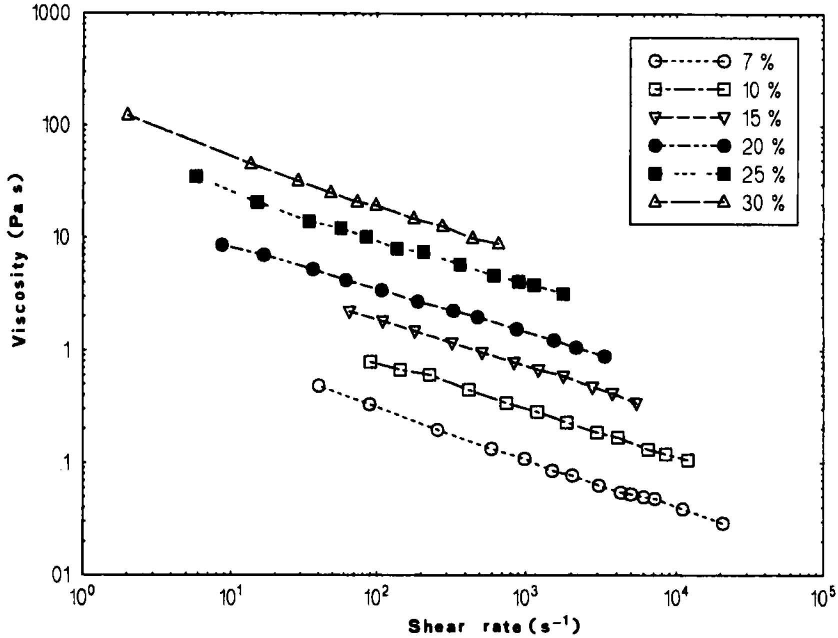

FIG. 6. FLOW CURVES OF MAIZE STARCH DISPERSIONS OF 7, 10, 15, 20, 25 AND 30% CONCENTRATION MEASURED AT 95C

waxy starch by almost an order of magnitude. This is further proof of the significant contribution of amylose matrix to the viscous behavior shown by a starch which consists only of amylopectin. The flow behavior index values for the maize starch are lower (0.53–0.63) than those for waxy starch (0.7–0.8). This can be attributed to the presence in waxy starch dispersions of only individual swollen starch granules with little amylopectin leached out, hence the viscosity exhibited is solely due to the granules which show few interactions between themselves and the behavior of waxy starch dispersions approaches that of a Newtonian fluid. Whereas for the maize starch dispersions the amylose present makes up the continuous phase where many entanglements exist and this causes the development of high viscosity reinforced by the presence of the swollen granules. The pseudoplastic behavior shown by the maize starch dispersions is more pronounced than that of the waxy starch ones and this should be a consequence of the formation of this matrix. That means at high shear rates the amylose molecules separate from each other and the relaxation time elapsed is very short for the junction zones to be reformed.

Comparing the data from Fig. 7, with Fig. 4 shows that after prolonged shearing of maize starch dispersions (50–55 min), the viscosity is comparative to those of waxy starch at the same starch concentrations and for the same shear stress.

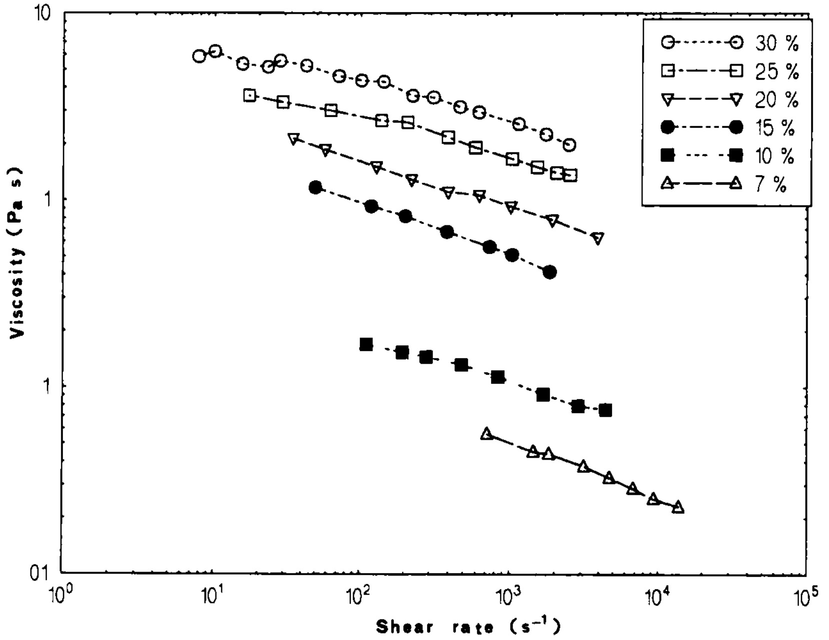

FIG. 7. FLOW CURVES OF WAXY MAIZE STARCH DISPERSIONS OF 7, 10, 15, 20, 25 AND 30% CONCENTRATION MEASURED AT 95C

DISCUSSION

At the beginning of the present work many attempts were made to use either a Rheometrics cone and plate dynamic controlled stress rheometer or an Instron piston capillary rheometer, to study the flow behavior of maize starch dispersions at 15 and 20% w/w concentrations at 90C. All the experiments ended in failure because of the inability to avoid water evaporation.

The claim of Eliasson (1986) that reliable measurements were taken for starch pastes at 95C using a Rheometrics Dynamic Spectrometer, could not be verified because the procedure she used to obtain a uniform sample and to avoid evaporation was not clearly stated.

Another serious problem is the cooking procedure of the starch paste which must be followed. Evans and Haisman (1979) used a rotary evaporator and a water bath to prepare the pastes. Christianson and Bagley (1983) used a Corn Industries Viscometer and Doublier (1981) used the A.F.N.O.R. (French Standards Organisation) procedure which employs a heated vessel equipped with an anchor shape stirrer rotated either at 200 or 750 rpm. The main drawback of all those procedures is that the pastes are prepared separately from where they are measured and during the transfer of the sample to the measuring unit of the rheometer changes caused by evaporation, gelation, or retrogradation is likely to occur. Doublier (1989) clearly stated that it is not possible to measure highly concentrated starch pastes (> 10%) if they are pasted at temperatures over 85C, the temperature of the second starch granule swelling-solubilization stage, since the viscosity is too high for the paste to be transferred from the cooking device to the rheometer. The use of high rotational speeds such as 200 to 750 rpm to stir the starch pastes during preparation possibly promotes, the destruction of a significant number of granules particularly at the stage where all the amylose was leached out and the swollen granules are very soft and prone to rupture.

The rheometer described in this study was designed to overcome all these problems. The on site cooking and measuring of the starch pastes ensures that whatever phenomena observed are exclusively due to the sample itself and not artifacts due to the difficulty of securing controlled conditions of cooking and measuring. The use of a low rotational speed stirrer (50 rpm) is another asset of the instrument which enables both the uniform mixing of the sample and the minimum damage of the starch granules so that good reproducibility of the viscosity measurements (< 5%) can be achieved. This instrument can measure viscosity over a wide range of shear rates, including those encountered in many commercial food processes. Rotational rheometers can not be used to measure viscosity at high shear rates that normally exist in process operations due to the development of secondary flows which lead to serious errors of the measurements (Lammers and Beenackers 1994).

The results of the previously described experiments cannot be compared with those obtained by other workers since the conditions were quite different. Thus, Evans and Haisman (1979) postulated that swollen starch granules significantly contribute to the viscosity of starch dispersions at concentrations up to 10% at 60C. The same opinion was expressed by Christianson and Bagley (1983) for maize starch concentrations up to 26% which had been cooked at temperatures below 85C i.e. the border temperature for effective solubilization of amylose to occur. Thus granules which retained most of their contents and their rigidity were present in the starch pastes they studied and it was obvious that the viscosity shown was almost exclusively due to the presence of these swollen granules. On the other hand Doublier (1981) and Doublier *et al.* (1987) reported that the rheology of starch pastes depends on the pasting procedure. Thus, either the granules or the amylose matrix contribute to the viscosity shown by the pastes. The matrix formed by the amylose seems to play the major role to impart viscosity to a starch paste. Current preliminary experiments with amylomaize, which contained 70% amylose showed that the viscosity values obtained for the same starch concentrations as those used in this work, were much higher than those of the maize starch. This provides further evidence that amylose is the main contributor to the viscosity of a fully gelatinized starch dispersion.

Work is in progress to study the flow properties of concentrated starch pastes of various botanic sources at elevated temperatures.

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