

Shear-Thickening Behavior and Shear-Induced Structure in Gently Solubilized Starches¹

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ABSTRACT

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The shear-thickening phenomenon was observed with eight unmodified starches that had been gently dissolved and dispersed at 3.0% concentrations in 0.2*N* NaOH. Waxy starches (maize, rice, and barley and potato) showed this phenomenon to a greater extent than did wheat, normal rice, or normal maize starches. Phase-contrast microscopy and circular dichroism measurements confirmed the development of shear-induced structure (incipient phase separation) implied by this shear-thickening behavior. The amylopectin component was responsible for shear-thickening properties and shear-induced structure formation and alteration. These structures were rather stable in 90% dimethyl sulfoxide (DMSO) and H₂O. In this solvent, the intrinsic viscosity was not tightly coupled with

flow behavior in the shear-thickening region. Shear-thickening behavior was influenced by solvent type. The relative abilities of solvent to enhance shear-thickening properties were: 0.2*N* NaOH > 90% DMSO with H₂O ≥ H₂O or 0.5*N* KCl at neutral pH. Shear-thickening properties were extremely sensitive to sample treatment; severe treatment of the sample destroyed the ability of the starch to form shear-thickened fluids. We conclude that dispersed native amylopectins (i.e., the initial higher molecular weight species) are able to form networks that are responsible for the shear-thickening behavior and shear-induced structures observed in granule-free starch solutions and dispersions.

The purpose of this article is to examine the rheological behavior of eight unmodified starches in solution to determine whether they exhibit shear-thickening behavior. Concentrations (2–3%) in the solvents 0.2*N* NaOH or 90% dimethyl sulfoxide (DMSO) and H₂O were examined. Previous studies (Dintzis and Bagley 1995a, Dintzis et al 1995) demonstrated that at low concentrations, waxy maize starches, which are mainly amylopectin, showed marked shear-thickening behavior and that this behavior was associated with flow-induced structure formation that was relatively stable in 90% DMSO and H₂O. Furthermore, this behavior was not observed with normal maize starch, with amylopectin isolated from normal maize starch, nor with severely treated waxy maize starch. Hence, it was concluded that significant structural differences must exist among amylopectins from different botanical sources or processing history.

Shear-thickening, sometimes defined as an increase in viscosity with increasing shear rate (Barnes 1989), often is assumed to be associated with a volume increase under shear. Hence, systems showing these two effects frequently are termed dilatant (Bauer and Collins 1967). During the flow of concentrated suspensions, these two effects can occur in tandem. Tanner (1985), in discussing dilatant fluids, noted that the term dilatant has come to be used for all fluids which exhibit the property of increasing viscosity with increasing rates of shear. However, Tanner emphasized that many systems can show shear-thickening behavior without increasing in volume, that is, without being dilatant. Tanner mentioned starch pastes in this regard, considering them as not true

suspensions and as systems that do not dilate. Hoffman (1982) reviewed the behavior of concentrated particulate systems (suspensions) and produced original observations on flow anomalies in systems containing nongelatinized starch granules, including not merely shear-thickening effects but even discontinuous jumps in viscosity at certain shear-rate levels.

In suspensions of rigid particles of the type discussed by Hoffman, Tanner, and others, shear thickening and dilatancy occur at high concentrations where the rigid particles are so close-packed that flow at increasing shear rates is impossible without development of a stress-generated volume expansion that provides space necessary to allow continued particle movement. Intuitively, this picture of concentrated rigid particle motion makes sense, and detailed models can be developed (as by Hoffman) in which viscosity (and volume) increases can be expected to occur as ordered arrangements of particles are disrupted or rearranged under shear. Shear-thickening behavior, with or without dilatant effects, also occurs in dilute and semidilute polymer systems, but explanations in these cases are more problematical than in the case of rigid particle suspensions. As discussed by Dupuis et al (1994) in their study of polyacrylamide solutions, shear thickening can arise from various mechanisms, and these mechanisms can be quite complex.

We previously have examined waxy maize starches in a variety of solvent systems including: 2–3% starch in 90% DMSO and H₂O, in 0.2*N* NaOH or KOH; 5–10% solutions prepared by autoclaving at pH 7 in H₂O or 0.5*N* KCl. Solutions containing very few, if any, identifiable granules or granule remnants were prepared using comparatively gentle methods and were examined in shear-sweep experiments over the range of 0–250/sec or 0–750/sec. Initially, the viscosity decreased with increasing shear rate following the usual power-law behavior for polymer solutions. However, a shear-rate region was reached, over which the viscosity increased significantly to higher levels. Still further increases in shear rate led to a new power-law region of viscosity versus shear rate. One could observe the development of opalescence in the sheared waxy maize starch with the 90% DMSO and H₂O system, thus indicating either structure formation or phase separation. This new structured polymer system was relatively stable, and the viscosity at low shear rates could be as much as five-fold above that of the original gently prepared solutions (Dintzis et al 1995). Phase-contrast microscopy confirmed the structure formation implied by the shear-induced opalescence.

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Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

We do not use the term dilatant to describe our starch fluids because we do not know whether a volume increase is associated with shear-thickening properties in these systems. The starch-fluid systems we call shear thickening exhibited three characteristics: 1) shear thickening or a decrease in the rate of shear thinning with increasing rate of shear; 2) an initial (presheared) state of lower viscosity; 3) an anticlockwise shear stress and shear strain rate loop. In the unmodified starch-fluid systems investigated here, the granules have been disrupted and the contents dissolved. However, as previously mentioned (Dintzis et al 1995), we are uncertain about the state of the 2–5% concentrations of solute in these fluids. We consider it likely that structures such as clusters of entangled molecules, possibly aggregates, or a volume-filling network exist in the fluid. Thus, within the fluid there may be significant microscale concentration fluctuations. In agreement with earlier works, recent evidence from field-flow fractionation and multiangle light-scattering measurements confirmed the very large molecular weights of amylopectins (Hanselmann et al 1995).

In this article we examine aspects of rheological behavior of some starches of different botanical origin, demonstrate that the amylopectin component of starch, rather than amylose, is responsible for shear-thickening behavior and structure formation, and demonstrate effects of sample treatment on rheological behavior.

MATERIALS AND METHODS

Materials

Normal maize starch (Buffalo starch 3401) was obtained from a commercial supplier (Corn Products Div., CPC International, Summit-Argo, IL). Two waxy maize starches were obtained from commercial suppliers: Amioca (American Maize-Products Co., Hammond, IN) and Staley Waxy No. 1 (A. E. Staley Co., Decatur, IL). Cassava starch was obtained from A. E. Staley Co. Potato and wheat starches were obtained from Sigma Chemical Co. Low-protein normal and waxy rice starches were obtained from a commercial supplier (StarchPlus SPR-LP and SPW-LP, respectively, California Natural Products, Lathrop, CA) Waxy barley starch was obtained from Centennial Foods Inc., (Dillon, MT). Additional potato starch was obtained from fresh white potatoes by the method of Gilbert et al (1964).

Starch Fractionation

Starches were fractionated into two main polysaccharide components: amylose and amylopectin (Gilbert et al 1964). The purity of the two fractions (% amylose content) was determined by the colorimetric method of Knutson (1986).

Chemicals

Except for absolute ethanol, which was purchased in bulk, all other chemicals used were reagent grade.

Methods

Sample preparation techniques, viscosity measurements, and phase-contrast microscopy methods were as previously described (Dintzis and Bagley 1995a, Dintzis et al 1995). Intrinsic viscosities were determined by capillary viscometry in a four-bulb dilution viscometer using the lowest bulb at low shear rates ($<40 \text{ sec}^{-1}$). Flow curves were determined with a rheometer (Carri-Med CSL² 500) in the cone-and-plate mode using a 6-cm, 4° cone. The cone was accelerated uniformly from rest to a maximum shear rate in 2 min and immediately decelerated uniformly back to rest in 2 min. Unless otherwise indicated, values of single experiments are presented. Intrinsic viscosity values are the average of at least two measurements. Flow behavior was sensitive to sample preparation, sample treatment, and sample loading, and clearly was time-dependent in water and in base. Tests rerun on the same stock preparation yielded very good reproducibility. Although it was practically impossible to prepare identical duplicate samples, efforts to do this provided samples with highly similar properties.

Circular dichroism (CD) measurements were made with a spectropolarimeter (J-600, Jasco, Easton, MD) using a cell with a 2.5-cm path length and 2.0% starch solutions in 90% DMSO and H₂O. Nine scans, from 700 to 270 nm, were made on starch solutions at 24°C, followed by nine scans of the solvent. The spectropolarimeter was calibrated with ammonium camphorsulfate solution. The CD of the solvent blank was subtracted from that of the starch solution, and the result was expressed in millidegrees.

A method was devised to disperse and dissolve the starch into the 90% DMSO and H₂O solvent with minimum application of shear. In this technique, a starch sample was placed into a 50-ml glass stoppered Erlenmeyer flask, swirled, and either set aside at room temperature overnight or placed in a warm water bath at 55°C for 6–24 hr. The flasks were then shaken vigorously by hand for several minutes until the fluid containing 2 or 3% starch appeared to be uniform. Samples prepared in 90% DMSO and H₂O by this method are called very gently dispersed.

Because some stirring was required to prepare solutions of starch or starch components in base, we use the term gently dispersed rather than very gently dispersed to describe samples prepared in base by the most gentle treatment. Solutions of amylose and amylopectin in 0.2N NaOH were prepared by first exposing the samples to 5.0 ml of 1.0N NaOH and hand-stirring with a glass rod to dissolve the solid material. When the polysaccharide gel was no longer opaque, aliquots of distilled water were added with minimum continued stirring and shaking by hand until a total of 25 ml of apparently uniform fluid was obtained. The resulting preparation was then wetted and stirred in 2.0 ml of distilled water to increase the access of base to the individual granules. Additional stirring and heating and moderate term storage in base or water had the effect of decreasing the ability of a starch to exhibit shear-thickening properties.

RESULTS

Flow Behavior of Potato Starch and Components

The flow behaviors of potato starch and the amylose and amylopectin isolated from this starch are presented in Figure 1. The arrows show the order of data collection. Potato amylopectin, curve X, displayed a marked degree of shear thickening during the first half cycle at shear rates $>90/\text{sec}$. In contrast, potato starch, curve Y, did not exhibit shear thickening, but had a decrease in the rate of shear thinning starting at $\approx 20/\text{sec}$ during the first half cycle. For the purposes of this article, we refer to both X and Y as shear thickening to contrast the flow behaviors from that of potato amylose (curve Z) in which the up and the down cycles of flow behavior essentially are the same. Figure 1 shows the general

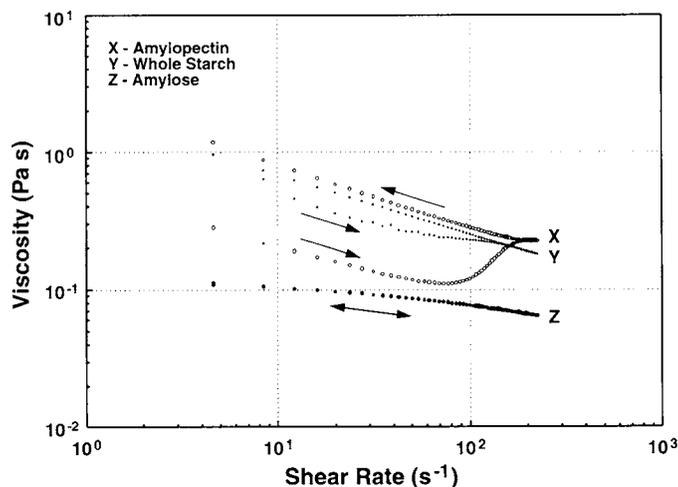


Fig. 1. First cycle viscosity vs. shear rate behavior for 2.8% potato starch and components in 0.2N NaOH at 25°C.

behavior for an amylopectin component with greater viscosity during the second half cycle and greater shear thickening than the whole starch; an amylose component with significantly lower viscosity and no shear thickening also was observed with cassava starch and its components.

Flow Behavior of Rice Starch Treatment

In Figure 2, the first half of the initial shear sweep cycle (when the cone accelerated from rest to maximum shear rate) is indicated as State 1 and the remainder of the cycle is indicated as State 2. State 1 appeared only during the first half of the first cycle. The response obtained from further shear sweeps was similar to that of State 2. However, the additional working of the fluid eventually lowered the viscosity profile of State 2. Although Figure 2 is specific for rice starches, the difference in viscosity levels and shear-thickening behavior between curves *B* (waxy rice starch) and *D* (normal rice starch) may illustrate general differences in rheologi-

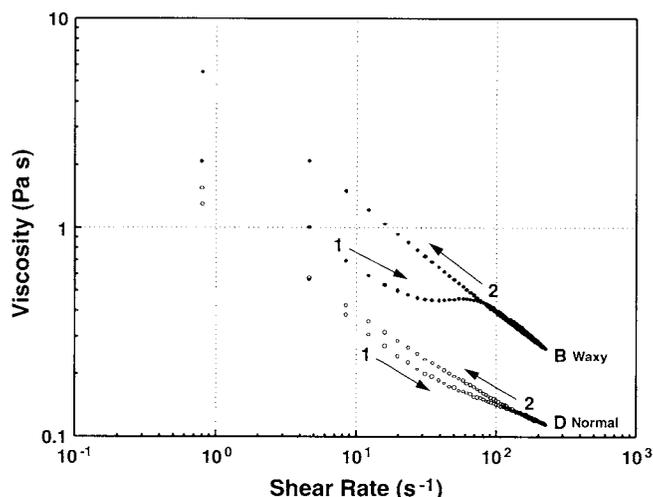


Fig. 2. First cycle data of 3.0% waxy rice starch (*B*) and normal rice starch (*D*) in 0.2*N* NaOH at 25°C plotted as viscosity vs. shear rate curves. Sample treatment details in Figure 3 legend. 1 = first half of cycle, the up-cycle (increasing shear rate, State 1); 2 = second half cycle, the down-cycle (decreasing shear rate, State 2)..

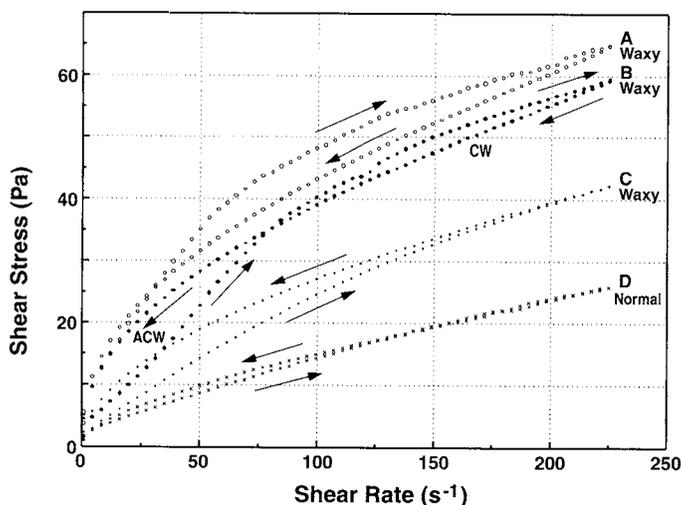


Fig. 3. First cycle shear stress vs. shear rate curves for 3.0% rice starches in 0.2*N* NaOH at 25°C. Arrows indicate sequence of data collection. A Waxy rice starch, fresh sample gently dispersed; B, waxy rice starch treated as in A with additional vigorous stir after 1.5 hr storage at room temperature; C, waxy rice starch treated as in B plus additional 21 hr storage at room temperature; D, normal rice starch, fresh sample gently dispersed. CCW = counter-clockwise loop, CW = clockwise loop.

cal properties between all waxy and normal starches. Curves *B* and *D* in Figure 2 are replotted as curves *B* and *D* in Figure 3 to illustrate some types of shear stress-strain rate loops observed in this work.

First cycle flow curves of shear stress versus shear strain rate for waxy rice and normal rice starches are shown in Figure 3 as functions of sample treatment. All loops in this figure are in the shape of a figure eight; this is most clearly shown by curve *B*. Thus, they are compound loops in which the directions are anti-clockwise (ACW) at lower shear rates and clockwise (CW) at higher shear rates. The ACW loop in *A* is not clearly visible; the CW loops are small and not clearly distinguished in curves *C* and *D*. The most gently treated waxy starch (curve *A*) supported much higher stresses than the most gently treated normal starch (curve *D*). The major loop in curve *A* is CW; the major loops in curves *C* and *D* are ACW. With further exposure to the base and stirring, the waxy starch behavior (curve *A*) was changed to that of curve *B* in which two loops, ACW at low shear and CW at higher shear (per sec > 90), were readily observed. With further exposure to base, the behavior was altered to that of curve *C*, and the ability of the fluid to support stress was greatly decreased.

Viscosity Behavior of Starches

Viscosity values of different starches at 10/sec in 0.2*N* NaOH are compared in Table I. The gently dispersed waxy and potato starches generally exhibited a combination of the highest State 2 viscosity values and the highest values of viscosity increase as measured by the ratio of viscosity in State 2 to viscosity in State 1. For a given starch concentration, the shear-thickening behavior was enhanced in 0.2*N* NaOH when compared to the 90% DMSO and H₂O or to aqueous systems at pH 7. This shear-thickening behavior did not occur in the normal maize or wheat starches in aqueous systems at pH 7 at concentrations where it was observed in base and to a lesser degree in 90% DMSO and H₂O. The shear-thickening properties in starches appeared to be most intense in base and dependent on starch type, sample treatment, starch concentration, and temperature. All starches examined in this study exhibited some degree of shear-thickening behavior in 0.2*N* NaOH (i.e., at least a measurable decrease in the rate of shear thinning with increasing shear rate and a shear stress vs. strain rate

TABLE I
Viscosity of 3.0% wt/vol Starches in 0.2*N* NaOH at 10 sec⁻¹

| Botanical Source and Sample Treatment | Viscosity (Pa) | | |
|---------------------------------------|----------------|---------|----------------------------|
| | State 2 | State 1 | Ratio (State 2 to State 1) |
| Waxy maize | | | |
| Gentle dispersion | 1.6 | 0.45 | 3.6 |
| Waxy rice | | | |
| Gentle dispersion | 1.6 | 1.4 | 1.1 |
| + Additional stirring | 1.4 | 0.64 | 2.2 |
| +21 hr at room temp. | 0.45 | 0.41 | 1.1 |
| Waxy barley | | | |
| Gentle dispersion | 0.71 | 0.48 | 1.5 |
| +45 min at room temp. | 0.68 | 0.45 | 1.5 |
| Potato (laboratory isolated) | | | |
| Gentle dispersion | 0.69 | 0.56 | 1.2 |
| Potato | | | |
| Gentle dispersion | 0.58 | 0.31 | 1.9 |
| Cassava | | | |
| Gentle dispersion | 0.47 | 0.30 | 1.6 |
| Normal rice | | | |
| Gentle dispersion | 0.41 | 0.40 | 1.0 |
| +Additional stirring | 0.40 | 0.28 | 1.4 |
| Wheat | | | |
| Gentle dispersion | 0.23 | 0.16 | 1.4 |
| Normal maize | | | |
| Gentle dispersion | 0.14 | 0.12 | 1.2 |

^a Measurements made with a 6.0 cm, 4.0° cone and plate fixture at 25°C. Samples from commercial suppliers unless otherwise indicated.

loop) (Fig. 3) that was ACW or had an ACW component during the first cycle of a shear sweep test.

Effects of Processing Conditions

In Figure 4, the first cycle viscosity versus shear rate curves are shown for solutions of waxy maize and normal maize starch prepared in three different ways: 1) very gently dispersed; 2) very gently dispersed with moderate heating and stirring; and 3) very gently dispersed with vigorous heating and stirring. To obtain a measure of molecular size as a function of treatment, intrinsic viscosities were determined. Because starches were stable in 90% DMSO and H₂O, this solvent was used for determination of intrinsic viscosities.

The flow behavior (Fig. 4) of waxy maize starch (WM) is more complicated than for the normal maize starch (NM). The viscosity of the very gently dispersed waxy maize starch (WM₁) experiences an increase, starting at ≈20/sec, during the first half of the first cycle, such that the viscosity during remainder of the half cycle is greater than that during the second half of the cycle. In contrast, for the sample treated with moderate severity (WM₂), during the first half cycle, shear-thickening starts at ≈50/sec. The first half cycle viscosity (State 1) is always less than the viscosity in the second half cycle (State 2). The most severely treated sample (WM₃) has a first half cycle viscosity that becomes less shear thinning at ≈70/sec and a lower value of the State 2 viscosity to State 1 viscosity ratio than does WM₂. As indicated previously by steady-state shear measurements (Dintzis et al 1995), the lifetime of State 2 for gently treated waxy maize starch in 90% DMSO and H₂O could be >50 hr at 55°C. The normal maize starch samples are all of lower intrinsic viscosity than the waxy maize starch samples and have essentially the same viscosity in State 1 and State 2, except for sample NM₁ wherein the State 1 viscosity is slightly lower than the State 2 viscosity at shear rates <60/sec.

Induced Structure in Starch Fluids

Previously, phase-contrast microscopy demonstrated that a shear field can generate and perhaps alter structure in waxy maize starch dispersed in 90% DMSO and H₂O (Dintzis et al 1995). Thus, State 2 (Fig. 2, curve B) contained some type of structure that was different than in unsheared State 1. Additional evidence for a shear-induced structure (orientation, phase separation) is presented in Figure 5 where CD is plotted against wavelength for

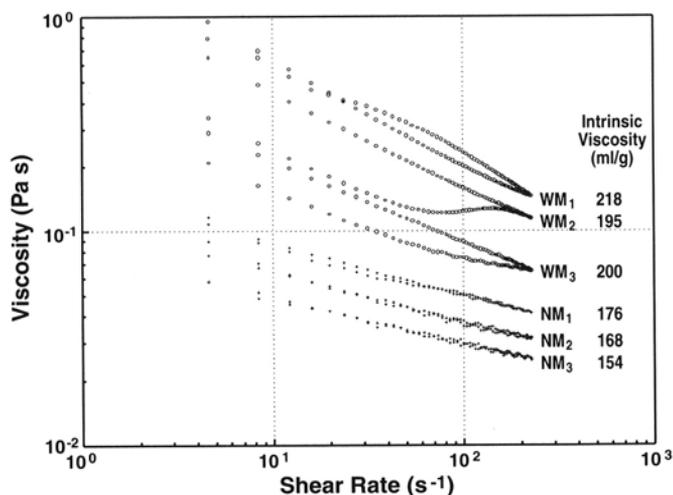


Fig. 4. First cycle shear-sweep behavior of 2.0% maize starches in 90% dimethyl sulfoxide and H₂O at 25°C. WM₁, waxy maize starch, very gently dispersed; WM₂, waxy maize starch, very gently dispersed + additional 6 hr at moderate heat and stirred; WM₃, waxy maize starch, rapidly stirred at 120°C for ≈2 hr; NM₁, normal maize starch, very gently dispersed; NM₂, normal maize starch, very gently dispersed + 6 hr at moderate heat and stirred; NM₃, normal maize starch rapidly stirred at 130°C for 30 min.

a very gently dispersed 2% waxy maize starch in 90% DMSO and H₂O. The dichroism of the sample sheared in a cone and plate fixture is significantly higher than for the not sheared sample. This effect was observed also with waxy barley starch. Figure 6, displays the dichroism difference spectra, samples sheared minus not sheared, for both waxy maize and waxy barley starches. The dichroism induced by the shear field was greater for the waxy maize starch.

An experiment to test whether shear-induced refractive index inhomogeneities also would be generated in 0.2N NaOH, as was seen previously with waxy maize starch in 90% DMSO and H₂O, was performed with laboratory-isolated potato amylopectin and amylose. These fractions were gently dispersed in base over the period of 1 hr and then sheared during four shear-sweep cycles with a 6-cm, 4° cone, collected, and observed by phase-contrast microscopy as described previously (Dintzis et al 1995). Also, potato amylopectin (2.0%) and amylose (3.0%) samples were very gently dispersed in 90% DMSO and H₂O and portions were sheared in the same manner as the samples in 0.2N NaOH.

The potato amylose in 0.2N NaOH (base) bore no discernible structure or mottling, either with or without shearing (Fig. 7A,B). Potato amylopectin solutions in base (Fig. 7C,D) or in 90% DMSO and H₂O (Fig. 7E,F) had a mottled or granular appearance when viewed with phase-contrast optics. In both solvents, the mottling was coarser and had more contrast in sheared samples (Fig. 7C,E) than in the unsheared controls (Fig. 7D,F). Potato amylopectin in both base and 90% DMSO and H₂O was shear thickening; potato amylose was not.

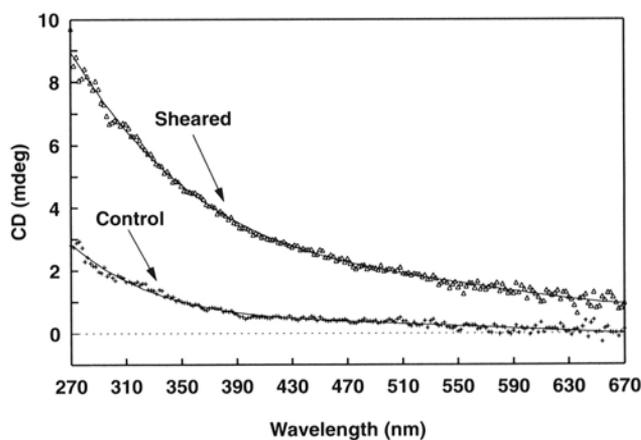


Fig. 5. Circular dichroism (CD) scan of very gently dispersed 2.0% waxy maize starch in 90% dimethyl sulfoxide and H₂O at 24°C. Control, not sheared; sheared, in 6 cm, 4° cone-and-plate fixture.

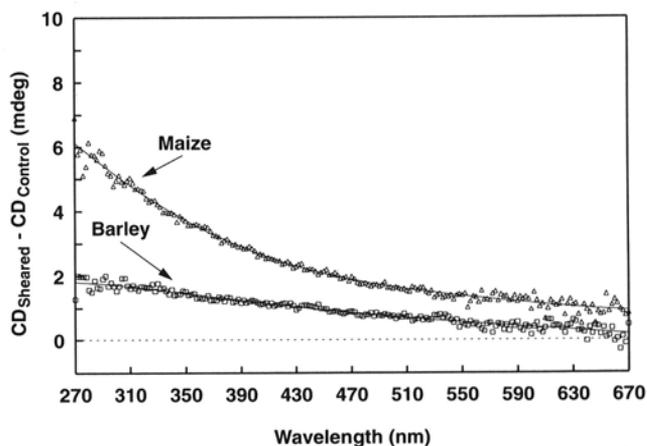


Fig. 6. Circular dichroism (CD) difference spectra, sheared minus unsheared, of 2.0% waxy maize starch and waxy barley starch in 90% dimethyl sulfoxide and H₂O at 24°C.

DISCUSSION

The evidence obtained in this study from starch fluids at low concentrations showed that: a) in 0.2N NaOH, all starches examined at 3.0% concentration exhibited some degree of shear-thickening; b) shear-thickening behavior was dependent on sample treatment, concentration, temperature, shear-sweep regimen, and botanical source; c) the amylopectin component of the starch was responsible for the shear-thickening behavior; d) shear-induced structures or shear-altered structures were associated with the shear-thickening behavior; e) for samples dispersed or dissolved with suitable degrees of severity, the shear-altered state of the starch fluid was of higher viscosity than the presheared state.

The flow data in this report were from shear-sweep experiments. This technique was rapid, simple, and yielded interesting results. A steady flow technique also was examined. A sample of 3% waxy maize starch, gently dispersed in 90% DMSO and H₂O, was tested at 50 sec⁻¹ in the cone-and-plate fixture. The viscosity showed an initial increase with time, thus confirming the two-state viscosity behavior observed in the shear-sweep technique.

The sensitivity of shear-induced behavior to sample preparation and subsequent sample treatment made it tedious to quantitatively compare the effect among different starches.

The viscosity behavior of starches in 0.2N NaOH at 10 sec⁻¹ is listed in Table I in order of the combination of decreasing values of State 2 viscosity and the State 2 to State 1 viscosity ratio. The dependence of behavior in 0.2N NaOH on sample treatment is particularly clear in Figure 3 and when one examines the data for waxy rice and normal rice starches in Table I. Initial gentle dispersion of both starches yielded a fluid that exhibited little viscosity difference between State 1 and State 2, in contrast to the result for waxy maize starch (Table I). After some additional stirring of the waxy and normal rice starches there were significant differences between the viscosities of State 1 and State 2. The additional stirring caused minor decreases in State 2 viscosity, but very signifi-

cant decreases in the viscosity of State 1. This decrease was more pronounced for waxy rice than for normal rice starch. Storage of the waxy rice starch fluid for 21 hr at room temperature caused further major viscosity decreases in both State 1 and State 2, and the ratio of the viscosities returned to 1.1, measured with the original gently dispersed material. It is clear that complex processes must be occurring.

As suggested by the trend to lower viscosity values of waxy barley starch stored at room temperature for 45 min, and the longer term viscosity decrease noted with waxy rice starch, starches were not stable in 0.2N NaOH. We note, also, that the value of the State 2 to State 1 ratio is quite variable and appears to be not well correlated with the viscosity of State 2.

The evidence in Figures 1 and 7 proves that the high molecular weight amylopectin component is the cause of the shear-thickening property arising from shear-induced structure formation, perhaps associated with phase-separation or other structural alterations or alignments. Diffusion and sedimentation measurements on wheat amylopectin indicated that in DMSO, the hydrodynamic configuration was that of a disk-like oblate ellipsoid (Callaghan and Lelievre 1985, Lelievre et al 1986). It seems reasonable to assume that similar structures would exist with amylopectins from other starches. Thus, in our studies the observed shear-induced flow behaviors, refractive index inhomogeneities, and CD could be, in part, the result of orientation or alignment of macromolecular-scale structures that exist in 90% DMSO and H₂O and in 0.2N NaOH. Another possibility is that of incipient stress-induced phase separation. In reviewing literature data, Rangel-Nafaile et al (1984) pointed out that such phase-separation effects can be reversible or irreversible and occur among a wide range of polymers and solvents. Polymer molecular weight, volume fraction in the fluid, hydrodynamic volume, solvent nature, and the shear-sweep regimen are all factors that would influence flow-induced structure and phase separation. We were reminded by I. M. Krieger (*personal communication*) that "linear viscoelastic materials will always yield a clockwise loop in a thixotropic loop test," and that with some materials "the graphs may cross over to produce a figure eight."

Our experience suggests that the effect of solvent on the degree of enhancement of State 2 viscosity values over State 1 in starches follows the order: 0.2% NaOH > 90% DMSO and H₂O ≥ water or 0.5N KCl at pH 7. This also is the order of intrinsic viscosity values of starches dissolved in these solvents. It is tempting to infer that the hydrodynamic volume of the amylopectin is a major factor affecting the shear-thickening property of starches. However, there is the apparently confounding result in Figure 4, that although the flow curves of the pairs WM₂ versus WM₃ and NM₁ versus NM₂ differed significantly, the intrinsic viscosity values were within experimental error of each other. Thus, in 90% DMSO and H₂O there was not a tight coupling between the flow curves and the hydrodynamic volume of the starches at infinite dilution, although there was a trend to lower intrinsic viscosity values as a function of increasing severity of treatment. This result, of course, raises the question of what molecular entities were being measured in the fluid at 2% starch concentration (where C = the concentration, >C* = the overlap concentration) vs. the dilute concentrations (0.06–0.25%) used to obtain intrinsic viscosity values. This question also is relevant to reports of the sensitivity of amylopectin intrinsic viscosity, which we here confirm, to sample preparation (Banks and Greenwood 1975).

We believe that curves, WM₁, WM₂, and WM₃ in Figure 4 may be interpreted as representing different states of an amylopectin network in the fluid. The CW loop in curve WM₁ at shear rates > 20 sec⁻¹ is interpreted as structure breakdown by the shear field (thixotropic behavior) to alter a structure or form a new structure, which then maintained a shear-thinning characteristic on following shear sweeps. Additional moderate stirring (6 hr) of the dispersed sample at 70–80°C eliminated most of the thixotropic behavior (curve WM₂) so that on the initial up-cycle, the fluid was

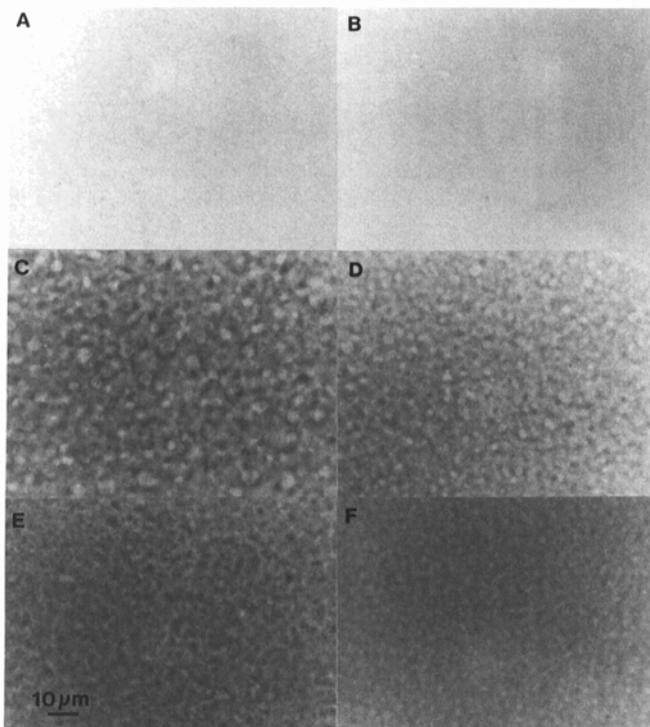


Fig. 7. Phase-contrast micrographs of 2.0% potato amylose and potato amylopectin in 0.2N NaOH and in 90% dimethyl sulfoxide and H₂O. **A**, amylose sheared (0.2N NaOH); **B**, control, amylose not sheared (0.2N NaOH); **C**, amylopectin sheared (0.2N NaOH); **D**, control, amylopectin not sheared (0.2N NaOH); **E**, amylopectin sheared (90% DMSO and H₂O); **F**, control, amylopectin not sheared (90% DMSO and H₂O).

shear-thinning (State 1) until a critical region at about 65 sec^{-1} was entered, wherein the viscosity increased as structure was formed and perhaps oriented. This shear-induced structured fluid, when sheared with several shear-sweep cycles, became entirely shear thinning and of higher viscosity (State 2) than the unsheared fluid. Because the more severely treated starch (curve WM₃) behaved in a similar manner to curve WM₂ and the intrinsic viscosities of both starch samples were the same, we infer that the more severe treatment affected the structures induced by the shear field, but not the hydrodynamic volumes of the smaller molecular entities that contributed to flow in dilute solution. In contrast, since the intrinsic viscosity value of curve WM₁ was significantly higher than for curves WM₂ and WM₃, we infer that both the shear-induced structures of sample WM₁ and the corresponding molecular entities in dilute solution were different than those in samples WM₂ and WM₃. A previous study also demonstrated there could be regions in which there would be a lack of correlation between intrinsic viscosity and flow properties of thermomechanically processed waxy maize starch (Dintzis and Bagley 1995b). Mechanical stress can change the molar mass distribution and rheological properties of polysaccharides (Windhab and zu Höne 1992). We cannot determine from our experiments whether the differences in flow behavior between sample WM₁ and samples WM₂ and WM₃ represent a change in molecular weight distribution, a change in molecular interactions between particles or molecular entanglements, or a combination of these possible changes.

It is conceivable that the amylopectin behaviors demonstrated in Figures 5–7 are associated with phase changes. Experience with synthetic polymers suggests this might be so. McHugh and Edwards (1995) and McHugh (1995) have reviewed shear thickening and structure formation in synthetic polymer systems. In particular, Kishbaugh and McHugh (1993a,b) correlated shear-thickening flows of polystyrene in decalin or bromobenzene with structure formation. The structures they detected “are intermediate in size between a cluster of entangled chains and a completely phase separated liquid.” That shear can also eliminate such structures has been shown by Lyngaae-Jørgensen and Søndergaard (1995), who observed the transition under shear of two amorphous polymers to a homogeneous state from an initially separated blend. Rheo-optical methods have proven valuable in investigating phase-transition phenomena of synthetic polymers. These methods should prove equally valuable for biopolymers like amylopectin. Although amylopectin polymers are vastly different in that their molecular weights and molecular architecture are larger and more complex than for many synthetic polymers, the thermodynamic and kinetic approaches used to analyze phase effects should apply to amylopectins.

CONCLUSIONS

This work has demonstrated that the amylopectin component of starch is responsible for phenomenon of shear thickening and the flow-induced “structure” (incipient phase separation) observed in sheared, essentially granule-free, solutions and dispersions of 2–3% starches in 90% DMSO and H₂O or 0.2N NaOH. Flow data indicated that gently dispersed starches (waxy maize, waxy rice, waxy barley, and potato starch) showed this phenomenon to a greater extent than did wheat, normal rice, or normal maize starches. The relative abilities of solvent to enhance shear-thickening are in the order: 0.2N NaOH > 90% DMSO and H₂O ≥ H₂O or 0.5N KCl at neutral pH. Severe treatments decreased the intrinsic viscosity of the starch, and if continued, would destroy the ability of the sample to display shear thickening and associated flow-induced structure. Therefore, we consider that the native (i.e., higher molecular weight) states of dispersed amylopectins that are able to form a network in the fluid are responsible for the shear-thickening properties and shear-induced structure observed in these starch solutions and dispersions.

NOTE ADDED IN PROOF

The shear-induced behavior described in this article is also shown in the data presented by Ragheb et al (1996).

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