Yield Stresses in Dispersions of Swollen, Deformable Cornstarch Granules[1]

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ABSTRACT

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Dispersions of cornstarch granules were heated in excess water at a temperature of 67–80° C. In Couette flow at 23° C (shear-rate range of 3–500/sec), many of these dispersions showed a yield stress. Yield stresses in cornstarch dispersions are significantly lower than those reported earlier for wheat starch granule dispersions at the same volume fraction. Yield stress values depend on the extent of swelling of the granules and thereby increase with the temperature of the dispersion preparation. For example, a 9% dispersion prepared at 75° C gave a yield point of 54 Pa (Pascal, Newton/m^2), whereas a dispersion prepared at 80° C gave a yield point of 120 Pa. These results can be compared to the yield value of the 250 Pa reported earlier for cornstarch heated at 90° C and measured at 60° C. Yield points appear to occur only when the volume fraction of the swollen granules is greater than approximately 0.6—that is, at a volume fraction between cubical (loosest) packing of uniform spheres (0.524) and tetrahedral (tightest) packing (0.74).

Many rheological systems show yield stresses (ie, minimum values of stress necessary to initiate flow). These are frequently seen in such food systems as salad dressings (Elliott and Ganz 1977), in foods modified by the addition of hydrocolloids (Elliott and Ganz 1972, Lang and Rha 1981), and in starch gels (Collison and Elton 1961). The actual evaluation of yield stresses presents difficulties in measurement and interpretation. Elliott and Ganz (1972), for example, differentiated between a moving yield stress and a rest yield stress. Lang and Rha (1981) emphasized that "the experimentally determined yield value is dependent on the method and condition of measurement."

The importance of yield stresses in biofluids, foods, and other systems has resulted in recent studies of the phenomenon by a variety of different methods. DeKee et al (1980) compared data on a variety of foods measured with a cone and plate viscometer, a balance method, a Thomas-Stormer viscometer, and a modified Fisher Autotensiomat. Good agreement among the methods was obtained, with the exception of the Stormer viscometer. Dzuy and Boger (1983) examined the yield stress behavior of bauxite residue suspensions, studying not only various experimental methods but also the usefulness of such models as the Bingham model, the Buckingham-Reiner equation, the Herschel and Bulkley model, and the Casson model. A recent review by Bird et al (1982) summarizes much of the literature dealing with yield stresses in a wide variety of systems.

In food systems, starch granule properties can be of particular significance in determining rheological behavior. Often, however, the starch is heated in water to temperatures of more than 90° C, with resultant partial dissolution of the granules (Doublier 1981). To separate effects of granule swelling from effects of solubilization of the starch itself, Bagley and Christianson (1982) heated wheat starch to 60–75° C, the range in which extensive granule swelling occurs, but the solubles exuded from the granule are of the order of only 5%. Under these conditions, the viscosity, when measured in Couette flow at 60° C, was found to depend (within the accuracy of experiments) only on the volume fraction of the swollen granules and not on the temperature at which the granules were swollen. The viscosity behavior of cornstarch granules, swollen at 67–80° C, followed exactly the same viscous behavior at 60° C as did wheat starch; that is, the viscosity depended on the volume fraction of the swollen granules (Christianson and Bagley 1983, Bagley et al 1983).

As the temperature for the viscosity measurement in Couette flow of the wheat starch dispersions was lowered from 60° C to room temperature and reached 30° C, a yield stress appeared (Bagley and Christianson 1983). These yield stresses were especially evident in plots of apparent viscosity versus shear stress, as might be expected (Mewis 1980). The actual values of the yield stress depended on the detailed history of the sample, and they ranged from 200 dynes/cm^2 (20 Pa) to 3,000 dynes/cm^2 (300 Pa), depending on concentration, heating temperature, time, and cooling history.

The object of this paper is to compare the yield stress behavior of cornstarch dispersions with that observed with wheat starch.

MATERIALS AND METHODS

Globe Pearl Cornstarch 3005, obtained from CPC International, had 11.73% moisture. Dispersions of starch were heated in a Corn Industries Research viscometer (CIV), as described previously (Christianson and Bagley 1983). Apparent viscosities of the dispersions were measured in Couette flow, using a Haake Rotovisco viscometer at 60° C and at room temperature (23° C), over the apparent shear rate range of 3–500/sec. All data were obtained with the MV System Cup (i.d. 4.201 cm) and MV-II Bob (o.d. 3.68 cm and length 6.004 cm). Viscosity-shear rate points were determined in order, starting at the lowest shear rate; measurements were usually completed in approximately 3 min.

RESULTS AND DISCUSSION

In evaluating the yield stresses of their suspensions, Dzuy and Boger (1983) found that direct extrapolation of the flow curve gave adequate results (see their Table VII). However, they had reservations and noted that the accuracy of the direct extrapolation method was "largely dependent on the availability and reliability of the experimental flow data at sufficiently low shear rates." Whether the shear rates are sufficiently low appears to be best resolved on the basis of a double logarithmic plot of apparent viscosity versus shear stress (Bagley and Christianson 1983, Mewis 1980). Figure 1 shows such a plot for cornstarch, with the viscosity measured at 23° C; the dispersions were heated in water at 70° C for 75 min at concentrations of 8, 10, 11, and 12% (db, w/w). As seen in Figure 1, the viscosity is extremely sensitive to concentration. There is also a qualitative difference in the response of the 8 and 10% dispersions on the one hand and the 11 and 12% dispersions on the other. The two lower concentrations are typical shear thinning fluids. The two higher concentrations are also shear thinning but show the typical response expected when yield points exist, with viscosity rising rapidly as the shear stress decreases towards the yield stress. This upward curvature at the two higher concentrations of Figure 1 is conclusive proof of the existence of a yield stress.

The onset and build-up of a yield stress (measured at 23° C) with heating time at 65° C is shown in Figure 2 for a 24% cornstarch dispersion. The original unheated dispersion has a viscosity of the

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[1] Mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

order of only a few centipoise, but after 15 min at 65° C, the granules have swollen enough by imbibing water so that the viscosity has risen to approximately 200 cp. The 15-min curve shows a slight indication of dilatancy, which would imply that the granules are still relatively rigid. This rigidity would be expected at this level of swelling, because only part of the birefringence is lost at this temperature (Leach et al 1959). Note that a 25% dispersion, heated for 15 min at 65°C, clearly shows dilatancy in the flow curve measured at 60°C (Christianson and Bagley 1983).

After 30 min of heating at 65°C, the granules have swollen considerably more, and the viscosity values in Figure 2 are increased by as much as a factor of 10. Furthermore, the 30 min dispersion now shows a yield point at approximately 70 dynes/cm^2. Further granule swelling generated by heating for 45 and 75 min increases viscosity levels still further and simultaneously shifts the yield point up to perhaps 200 and 250 dynes/cm^2, respectively.

Having established the existence of a yield stress from a log η-log τ plot, the actual value is best estimated from the usual linear plots of shear stress versus shear rate using the lower shear rate points (up to 60/sec) from the whole flow curve. As Dzuy and Boger (1983) note, the nonlinear nature of the flow curve makes it necessary to use the lower, more nearly linear points to obtain the yield stress. Figure 3 shows typical results measured at 23° C for a cornstarch dispersion heated at 67° C for either 30 or 75 min for concentrations of 13.7, 14.7, and 16% (db, w/w). Under these temperature and time conditions, yield points develop with change in the concentration of only 1%, from 13.7 to 14.7%. At a dispersion concentration of 14.7%, the yield point is established after 30 min of heating, but it is lower than when the same dispersion is heated for 75 min. The initial slopes of both the 30-min cook and the 75-min plots are the same.

Yield stresses for corn and wheat starches are compared by plotting the observed yield stress versus volume fraction. To obtain volume fractions, the method previously described (Bagley and Christianson 1982) was used; in this method, Q (weight of starch granules, swollen in excess water at temperature T, divided by the initial dry weight of the starch) is plotted against T. (Excess water is used so that the swollen granules filter easily and maximum possible swelling level for the conditions can be determined.) The results are shown in Figure 4; 2% dispersions are heated for 30 and 75 min. Although the curves are similar, swelling equilibrium is not complete at 30 min and may not even be reached after the granules have been heated and mixed in the CIV for 75 min (Bagley and Christianson 1982). At 85° C, the Q drops significantly because of the partial dissolution of granules and loss of solubles in the filtrate.

These data have been used to calculate the quantity CQ, with C being the weight of dry starch in 1 g of dispersion. CQ is then approximately equal to the volume fraction of the swollen starch in the dispersion, uncorrected for the swollen granule density.

In Figure 5, the yield stress obtained at room temperature is plotted against CQ. Curve A shows the previously stated results for wheat starch; curve B is for cornstarch obtained in this study. The cornstarch data, for reasons not fully understood, show more scatter than those for the wheat starch. In spite of the scatter, the yield stresses in cornstarch are significantly lower than those for wheat starch prepared and measured under equivalent conditions.

It appears from Figure 5 that a yield stress exists in these dispersions only when the volume fraction is greater than approximately 0.6. This could be interpreted in terms of general particle-to-particle contact as being a requirement for the existence of a yield stress. The volume fraction for cubical (loosest) packing of uniform spheres is 0.524, and the volume fraction for tetrahedral (tightest) packing is 0.74. The actual volume fraction at which adequate particle-to-particle contacts occur to give a yield will depend on such factors as particle-size distribution, particle rigidity, and the specifics of particle interactions.

No yield stresses were found for wheat starch when the flow curves of the dispersions were measured at 60° C (Bagley and Christianson 1983). No yield points at 60° C for cornstarch were observed in this work, although Evans and Haisman (1979) establish yield points at 60° C for cornstarch dispersions cooked at the higher temperature of 90° C (for 20 min) under static conditions. They extrapolate their data at very low shear rates (0.0007–56/sec) to establish yield stresses at 60° C.

Only small amounts of solubles (4–5%) are leached from either corn or wheat starch at temperatures of 60–80° C. Solubilization increases rapidly at temperatures of more than 80° C (Sandstedt and Abbott 1964). This is made obvious by the dramatic apparent drop in Q values at 85° C (Fig. 4). Yield points could not be accurately established in dispersions heated at this temperature,

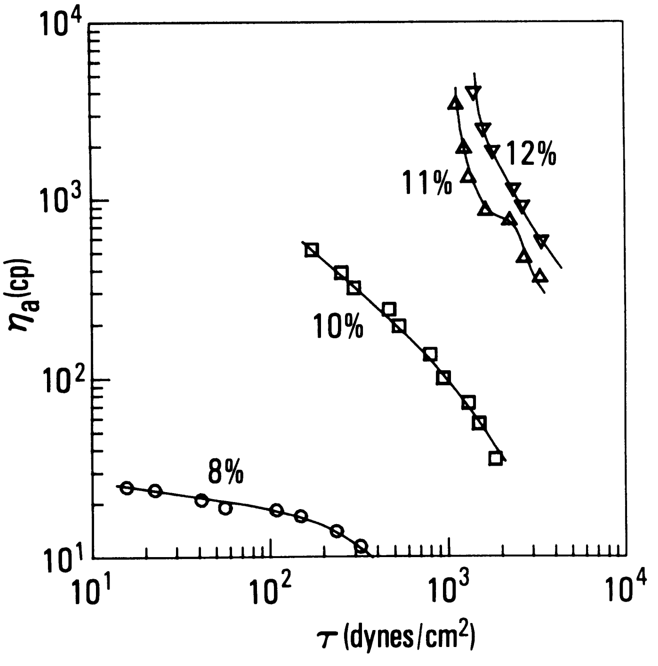

Fig. 1. Apparent viscosity (η_a) versus shear stress (τ) plots for cornstarch dispersions obtained after cooking at 70° C for 75 min in a Corn Industries research viscometer. o, 8%; □, 10%; △, 11%; and ▽, 12%. Viscosity was determined at 23° C over a shear-rate range of 3–500/sec, 2 hr after sample preparation at 70° C.

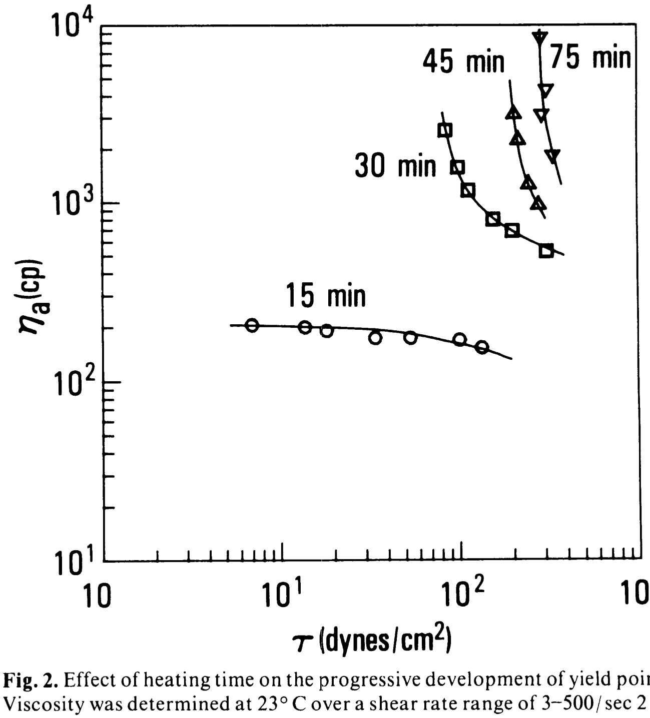

Fig. 2. Effect of heating time on the progressive development of yield point. Viscosity was determined at 23° C over a shear rate range of 3–500/sec 2 hr after sample preparation. Cornstarch dispersions (24%) after heating at 65° C for o, 15 min; □, 30 min; △, 45 min; and ▽, 75 min.

probably due both to the increased amount of solubles and to granule damage and disruption under our mixing conditions.

In attempting to explore alternate procedures for evaluation of the yield stress, the Casson equation was used:

$$\tau^{1/2} = \tau_y^{1/2} + \eta^{1/2}\,\dot{\gamma}^{1/2} \qquad (1)$$

Yield points obtained from Casson plots are in reasonable agreement with values obtained by direct extrapolation of $\tau-\gamma$plots at 23° C for 11, 12, and 13% concentrations. However, a yield stress was also obtainable from the Casson equation for the 10% wheat starch, for which a ln η-ln τ plot indicated that a yield stress did not exist. Subsequently, a Casson plot for 11, 12, 13, and 14% dispersions at 60° C (for which no yield points were expected, based on the ln η-ln τ plots) could just as easily give an extrapolated yield point. We conclude therefore that the use of the Casson equation can be misleading. There is always the lingering suspicion when the equation is used that perhaps the shear rates were not taken low enough. This concern is made obvious when the ln η-ln τ plot is made; but once the existence of a yield point is thus unambiguously established, the shear stress-shear rate plot extrapolation can be made with some confidence. In some cases, as in the work of Dzuy and Boger (1983), the Casson equation does appear very effective in establishing a value of τ_y. Even in their work, the Casson plot at 67% solids (see Fig. 6 in Dzuy and Boger 1983) is ambiguous. Dzuy and Boger effectively resolved the problem by demonstrating that slip occurs at low shear rates and that this leads to incorrect, low values of τ_y if one extrapolates low shear-rate data.

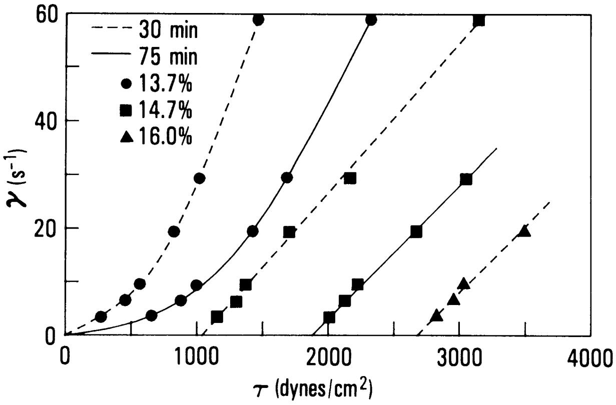

Fig. 3. Shear rate versus shear stress plot for cornstarch dispersions obtained at 23° C after heating at 67° C for either 30 (- - - - -) or 75 (——) min. Dispersion concentrations are 13.7% •; 14.7%, ■; and 16%, ▲.

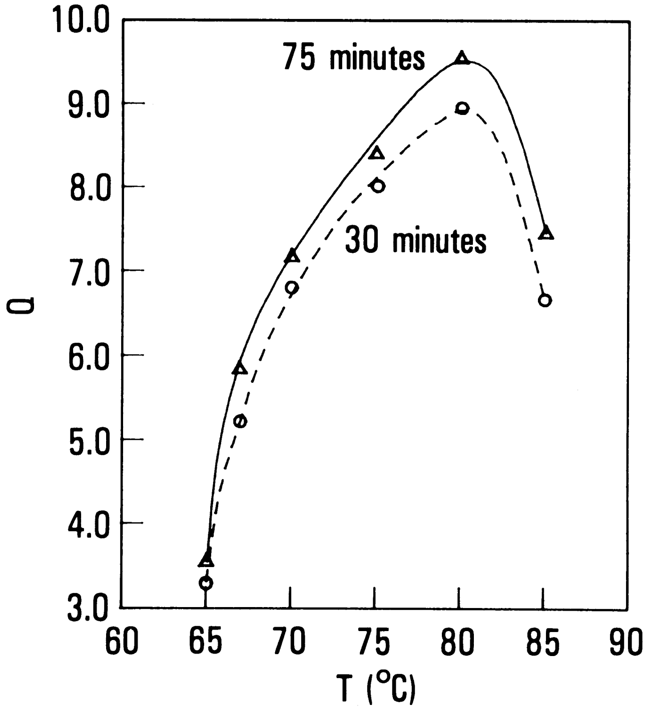

Fig. 4. Grams of swollen starch per gram of dry starch (Q) obtained at various temperatures after 30 (o) and 75 min (△) of heating (Q, grams swollen starch/grams dry starch).

The dependence of yield stress on sample history (Bagley and Christianson 1983; Lang and Rha 1981) makes direct comparison of data in the literature somewhat problematical, but it is of interest to compare recent results of different workers. Evans and Haisman (1979) plotted yield stress at 60° C versus concentration for cornstarch heated for 20 min at 90° C. From their work, an estimate of yield stress at 5% concentration is 25 Pa (250 dynes/cm^2). This can be compared with a yield value for 5% cornstarch obtained by Lang and Rha, which is approximately 20 Pa (200 dynes/cm^2). Further, from their work, 3.25% is the critical concentration below which cornstarch does not show a yield point, again in agreement with Evans and Haisman. Oddly enough, however, the work of Lang and Rha was done at 25° C, but that of Evans and Haisman was at 60° C, which suggests that the yield stress is independent of temperature. In contrast, the work of Bagley and Christianson (1983) shows that a yield stress is not seen at 60° C but is at 25° C. The comparison of the data of Evans and Haisman and of Lang and Rha cannot be taken too seriously, because the actual temperature at which the latter authors prepared their starch dispersions is somewhat ambiguous. According to Lang and Rha, "the suspension was . . . heated to the gelatinization temperature on a hot plate," but actual values of the temperatures reached are not given.

Comparison of the data of Evans and Haisman with our work was rather illuminating. The yield stresses we observed rise rapidly with heating temperature, from 540 to 1,200 dynes/cm^2 at 75 and 80° C, respectively, for a 9% dispersion. From Evans and Haisman's Figure 6, a yield stress of 2,500 dynes/cm^2 is estimated for a 9% dispersion heated at 90° C under static conditions. We examined the flow behavior of a 9% dispersion heated at 85° C under our more vigorous mixing conditions, but the yield stress was actually lower than for dispersions heated at 80° C. We attribute this to the increased fragility of the swollen granules when heated at 85° C, with consequent particle disruption and higher levels of solubles attained by our mixing procedure, as opposed to the static treatment used by Evans and Haisman.

A dispersion that shows a yield stress (ie, a stress below which the dispersion behaves as a solid material and shows no irrecoverable deformation or flow) must have a long-range structure. The present work establishes that this structure is formed only above volume

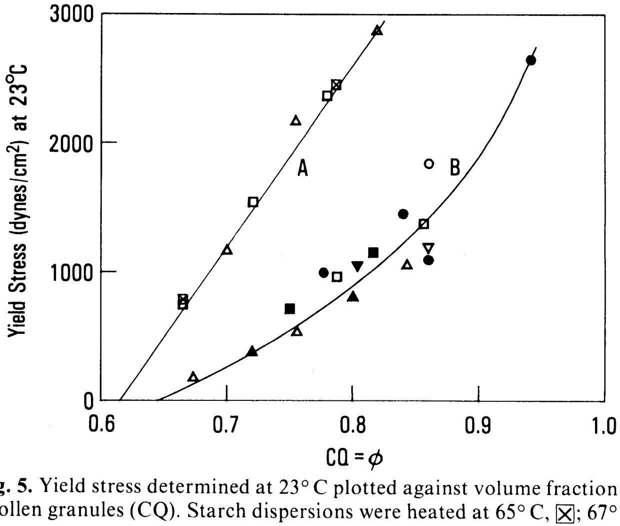

Fig. 5. Yield stress determined at 23° C plotted against volume fraction of swollen granules (CQ). Starch dispersions were heated at 65° C, ☒; 67° C, o; 70° C, □; 75° C, △; and 80° C, ▽ for 30 (solid symbols) or 75 min (open symbols). Curve A = wheat starch; curve B = cornstarch. The two symbols ☒, only for wheat starch (Curve A), refer to samples heated 75 min.

fraction levels of 0.6–0.7. Were the granules monodisperse spheres, this volume fraction range would correspond to something between the loosest (cubical) and tightest (tetrahedral) packing of the spheres. It is certainly interesting that the yield stresses for starch granules also occur in this same range, even though the granules are neither spherical nor monodispersed. In addition, the starch granules are deformable, so that very intimate packing can, in principle, be easily imagined.

For a given volume fraction, Figure 5 further establishes that, at the same volume fraction, wheat starch granule dispersions show higher yield stresses than do cornstarch granules. The exact reasons for this have not been established but must relate to the interactions at the particle/particle contact areas and/or the granule particle-size distribution and granule deformability. One mode of interaction that could vary between wheat and cornstarch is the interdiffusion between touching granules of exuded amylose and/or amylopectin, which can occur at the particle contact points. Such interdiffusion would provide granule-to-granule coupling, which would inevitably lead to structural cohesion for the dispersion as a whole and hence, the observed solidlike behavior. However, it is not clear why this should be more effective at 23° C, where the yield points are very evident, than at 60° C, where we do not observe yield points in these dispersions.

The media in the interstitial spaces between granules can also play a role. Although exudate from granules is minimal at the temperatures used in this work to prepare these dispersions, some amylose undoubtedly enters the interstitial fluid, and amylose-amylose interactions could contribute to the overall structural build-up in these materials. This could be related to the observation of yield stresses at 23° C but not at 60° C. Much remains to be done to clarify the complex but important rheological properties of starch systems.

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