Shear-Thickening and Transient Flow Effects in Starch Solutions*

INTRODUCTION

We observed the unexpected property of shear-thickening and hysteresis loops with solutions of waxy maize starch. These phenomena are well known for concentrated suspensions, including potato starch granules in glycerol–water mixtures. However, to our knowledge, the effects have not been reported previously for moderate concentrations of dissolved starch.

The shear-thickening ("dilatancy") behavior of suspensions has been reviewed in recent years by Hoffman[1] and by Barnes.[2] The explanations offered for dilatant flow in these suspensions involve a transition from an ordered two-dimensional array of particles to a random three-dimensional array; this transition is caused by exposure to increasing shear and leads to an increased, time-dependent, viscosity.

There are few examples in the literature of molecular, rather than particulate, systems exhibiting shear-thickening. Shear-thickening behavior of dilute solutions of ammonium oleate[3] was reported in 1926 and similar behavior of 0.02% solutions of the Cu salt of cetyl phenyl ether sulfonic acid[4] was reported in 1938. The antithixotropic behavior of 5% solutions of rubber in toluene[5] and of polymethacrylic acid in water[6] were noted in the mid-1950s, while in recent years, such behavior has been established for systems of acrylic polymers[7,8] and poly(trimethylamine-*p*-vinylbenzimide).[9] Isotonic solutions of DNA also have been reported to exhibit shear-thickening.[10] Dilatant behavior has been reported for aqueous pastes of crosslinked waxy maize starch by Dail and Steffe.[11,12] Recently, Degner et al. reported anticlockwise hysteresis behavior for pastes of crosslinked waxy maize starch.[13]

EXPERIMENTAL

Two starches were used in this work: Amioca, an unmodified waxy maize starch consisting of about 98% amylopectin, was obtained from American Maize-Products Co., Hammond, IN 46320; and Buffalo® starch 3401, a dent maize starch consisting of about 27% amylose and 73% amylopectin, was obtained from Corn Products Division of CPC International, Summit-Argo, IL 60501. Amylopectins consist of very high molecular weight (5–30 × 10^6), highly branched molecules. Amyloses are of much lower molecular weight (0.2–8 × 10^5), with low degrees of branching.

The starches were dissolved either by initial stirring at room temperature in 1.0*N* KOH and then dilution to 0.2*N* KOH or by cooking in an autoclave at 140°C. The cooking procedure consisted of stirring and heating, in an autoclave, a dispersion, buffered to pH 7.0, for a total of 44 min. Ten minutes was required to heat the sample from 100 to 140°C, after which the dispersion was maintained at 140°C for 15 min. Starch to be dispersed in the base was first mixed thoroughly with 2 mL of distilled water to dampen all granules; then, 20 mL of 1.0*N* KOH was added to the mixture which was stirred vigorously with a spatula for 10–20 min to disrupt all granules and dissolve them. Distilled water (78 mL) was slowly added to the starch with stirring to achieve a uniform solution in 0.2*N* KOH. All samples were centrifuged to remove air bubbles prior to being placed in the viscometer.

Flow measurements were made with a couette-type viscometer (Haake, Rotovisco® RV20, measuring system M). The rotor was accelerated uniformly from rest to a shear rate of 750 S^{-1} over a period of 2 min and then, without pause, uniformly decelerated to rest over the same time period. This cycle was immediately repeated.

RESULTS AND DISCUSSION

In Figure 1 are presented the viscosity vs. shear rate data for two autoclaved starches: waxy maize (closed symbols) and Buffalo (open symbols). The Buffalo starch shows typical polymer solution behavior, the viscosity decreasing with increasing shear rate. The result is the same within experimental error for all up/down cycle runs.

The result for waxy maize is quite different: The first up cycle begins at point A and follows curve 1 of Figure 1. The solution is shear-thinning up to a shear rate of approximately 100 S^{-1} and then the viscosity increases with further increase of shear rate to about 300 S^{-1}. The solution then becomes shear-thinning again down to point B. As the shear rate is subsequently lowered, the viscosity increases steadily along curve 2 to point C. If the shear

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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.

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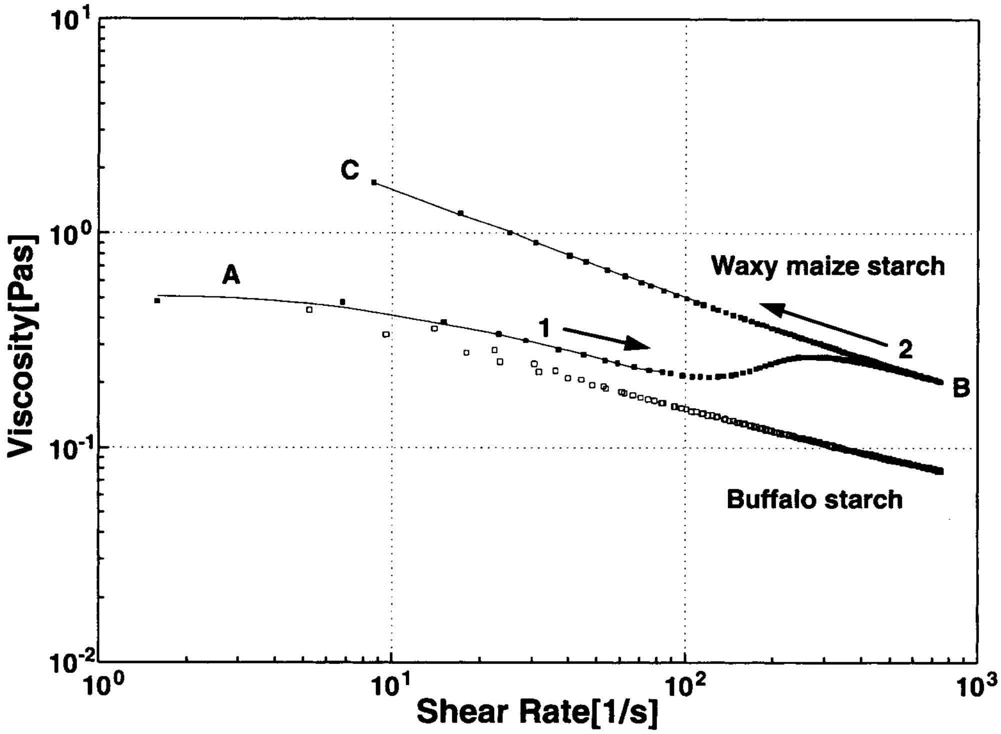

Figure 1 Viscosity vs. shear rate behavior, at 50°C, of 7.7% (wt/vol) autoclaved starch solutions during the first up/down shear rate cycle: (solid symbols) waxy maize starch; (open symbols) dent maize starch. Waxy maize starch data from additional up/down shear rate cycling approximates curve CB. For Buffalo starch, additional cycles replicate the Buffalo starch curve shown.

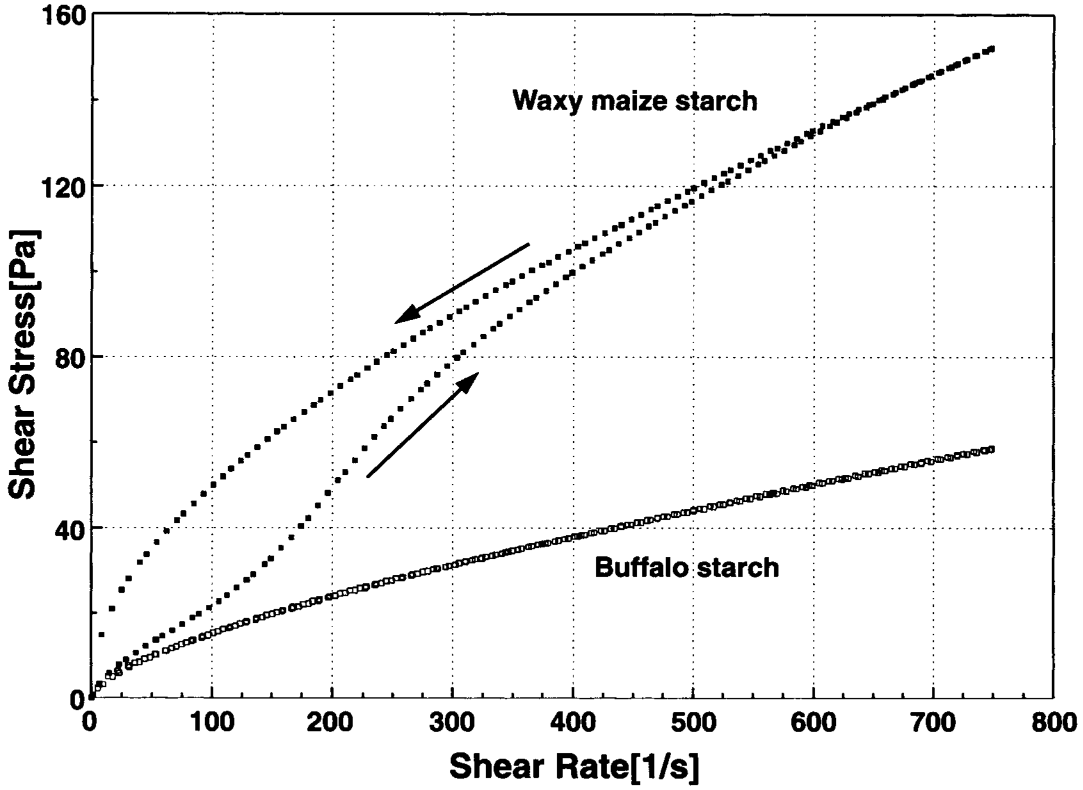

Figure 2 Data of Figure 1 replotted as shear stress/strain rate behavior showing the anticlockwise hysteresis loop exhibited by waxy maize starch.

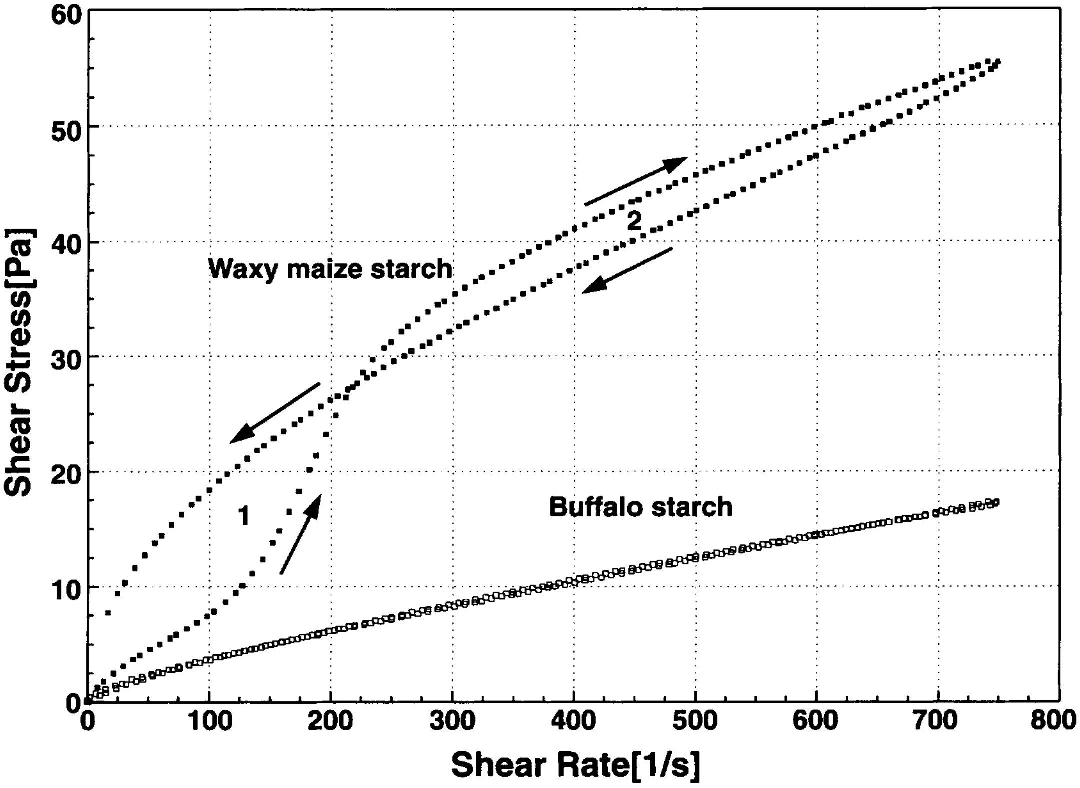

Figure 3 First cycle of shear stress/strain rate behavior of 2.0% (wt/vol) (solid symbols) waxy maize and (open symbols) 2.7% dent maize starch solutions in 0.2*N* KOH at 30°C. The loop designated 1 is anticlockwise; loop 2 is clockwise.

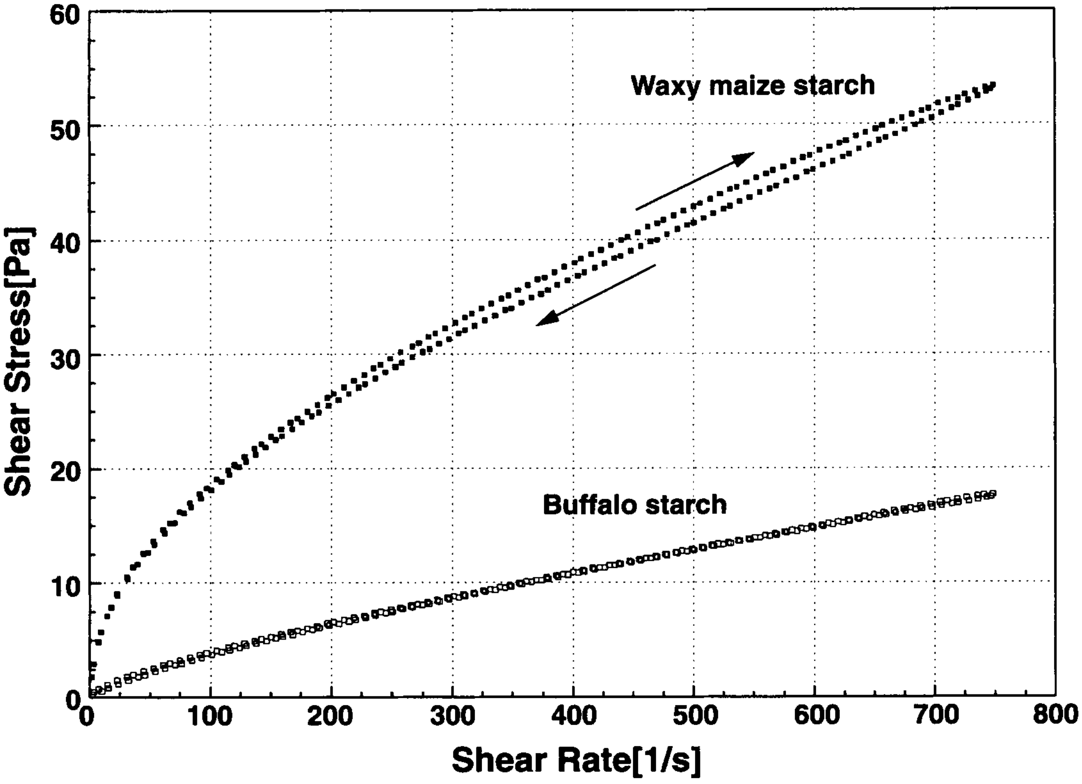

Figure 4 Second cycle of shear stress/strain rate behavior of starch samples from Figure 1. The hysteresis loop of waxy maize starch is now only clockwise; further cycling would eliminate the loop to yield identical up/down data.

rate is immediately increased again, the viscosity decreases from point C along curve 2 to point B. Subsequent cycles follow the path BC along curve 2; curve 1 (A to B) is seen only on the initial up cycle.

The data of Figure 1, are replotted as shear rate vs. shear stress in Figure 2, showing that the stress/strain rate response of waxy maize starch clearly formed a hysteresis loop. The arrows show the anticlockwise order in which the points were obtained, which are opposite to the clockwise direction shown by systems that are thixotropic. (However, the existence of hysteresis loops in itself does not define the property of thixotropy or antithixotropy.) In contrast, no hysteresis loop is observed with the dent maize (Buffalo) starch.

A striking difference in flow behavior of waxy maize compared to dent maize starch solutions occurs also in aqueous base. In Figure 3 is shown the first cycle, and in Figure 4, the second cycle, of shear stress vs. shear rate data for a 2.0 and a 2.7% (wt/vol) solution of waxy maize and dent maize starch, respectively, in 0.2*N* KOH. The concentration of the dent maize starch solution was chosen in order to have samples of approximately equal amylopectin content. No hysteresis loop is associated with the dent maize solution. Two hysteresis loops occur with the waxy maize in the first cycle. The loop at shear rates $< 200\ \mathrm{S}^{-1}$ is anticlockwise; the loop at shear rates $> 250\ \mathrm{S}^{-1}$ is clockwise. Thus, in the first cycle, two distinctly different regions of flow are generated in the waxy maize starch and both are different from that observed in the dent maize starch. In the second cycle, the waxy maize starch exhibits only one clockwise loop and, as before in the first cycle, the dent maize starch exhibits no distinct hysteresis loop. We observed that the behavior of waxy maize starch in dimethyl sulfoxide is similar to that in 0.2*N* KOH.

The differences shown in Figures 1 and 2 between waxy maize starch containing 98% amylopectin and the Buffalo corn starch containing 75% amylopectin and 25% amylose might be attributed to the presence of amylose. However, when dent maize amylose was added to waxy maize starch to obtain a ratio of amylose to amylopectin approximating that of Buffalo starch, a solution prepared from this combination exhibited the same qualitative behavior of dilatancy and anticlockwise stress loops as shown in Figures 1 and 2. The facts that (a) the combination of dent maize amylose added to waxy maize starch yielded a solution that also exhibited dilatancy and an anticlockwise hysteresis loop and (b) dent maize starch exhibited no hysteresis loops or dilatancy leads us to believe that there are highly significant differences between the amylopectin of waxy maize and dent maize. Additional evidence is needed, along the lines discussed by Joye and Poehlein,[14] to confirm that the anticlockwise hysteresis loop behavior of waxy maize starch does represent antithixotropy and structure formation.

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