Apparent Viscosities of Dispersions of Swollen Cornstarch Granules[1]

D. D. CHRISTIANSON[2] and E. B. BAGLEY

ABSTRACT

Cornstarch granules were dispersed in water at various concentrations and heated to 65, 67, 70, 75, and 80°C for various times. Viscosity shear-rate plots for these dispersions were then determined at 60°C and a shear-rate range of 3–500 sec^{-1} using a rotational viscometer. A variety of viscosity shear-rate curves were observed that varied with concentration, cooking temperature, and cooking time. A very sharp transition in the apparent viscosity behavior occurred between 65 and 67°C with, for example, a viscosity of 2,000 cp observed both at 26% concentration when cooked at 65°C for 15 min and at 15% concentration when cooked at 67°C for 15 min. All apparent viscosity-concentration plots for temperatures from 65 to 80°C could be superimposed by plotting η/CQ vs CQ, where η is the viscosity, C is the concentration in grams of dry starch per grams of dispersion, and Q is the grams of swollen starch divided by grams of dry starch. The quantity CQ is equivalent to volume fraction of swollen starch in the dispersions.

Investigation of the behavior and properties of starch dispersions in water continues to attract attention because of the wide variety of uses of such dispersions. Unambiguous answers to the many scientific and technical questions concerning these systems are not always obtainable. The subject is particularly interesting because of the range of concentrations and temperatures over which starch dispersions are used, from the thickening of soups and sauces to the very concentrated viscoelastic doughs used in baking. Additionally, starch-based food systems can include a wide range of constituents such as gums, proteins, and salts, where strong interactions occur. These interactions are important and complex.

Bean and Yamazaki (1978) and Bean et al (1978) examined the swelling and gelatinization of starch in the presence of various sugars and discussed the consequence of the behavior with respect to cake performance. Christianson (1981) reviewed the effects of hydrocolloid interactions with starch. Christianson et al (1981) investigated the effect of xanthan, guar, and cellulose gums on the gelatinization of starch. Gough and Pybus (1973) examined the effect of metal cations on the swelling and gelatinization of wheat starch granules, and Hizukuri and Takeda (1978) examined the effect of lower alcohols on starch gelatinization. Osman (1975) studied starch interactions with other components in food systems, including surfactants, sugars, salts, and gums, and also examined the effect of protein denaturation. Christianson et al (1974) examined the properties of protein-fortified starch in the presence of xanthan gum. Morris et al (1980) discussed polysaccharide interactions in detail, using various gels as models. This type of information is valuable in providing insight into problems such as bread staling (Kim and D'Appolonia 1977).

The importance of such factors as temperature, mixing rates, energy input, and component interactions on the properties of starch dispersions and gels is well established. To separate the various effects that occur in a specific system, a recurring issue is to determine the contributions due to the swelling, gelatinization, and solubilization of starch granules. Sandstedt and Abbott (1964) summarized methods of following the course of starch gelatinization. However, much of the information they discussed is based on experiments (eg, the amylograph method) in which the temperature is varied continuously; this renders the resulting data difficult to interpret quantitatively, even though the measurements may be useful in a practical sense. On the other hand, some work is available in which this difficulty was avoided. Odigboh and Mohsenin (1975), for example, studied the viscosity of cassava starch pastes as a function of the drying history of the starch as well

as of the cooking and paste temperatures at different paste concentrations. The cook temperature range (65–95°C) was a useful one, although the concentrations were limited (2, 4, 6, and 8%). More recently, Evans and Haisman (1979) examined the rheology of gelatinized starch suspensions, using corn, potato, and tapioca starches, at concentrations up to 10% and at cooking temperatures and times that varied with the starch type. They showed that these gelatinized starch systems comprise a suspension of swollen starch granules in a continuous phase known to contain soluble macroscopic material and that the swollen granules are compressible as well as deformable. Hence, starch suspensions remain "liquid" at concentrations well in excess of the close-packing point of the fully swollen granules.

In the work of Bagley and Christianson (1982) and of Taylor and Bagley (1977), the viscosity data were plotted using the variable CQ. The concentration, C, of the starch dispersion is in units of grams of dry starch per gram of dispersion. Q is a quantity describing the swelling of the granule, determined for the starch systems by swelling of the particle in dilute suspension (2–4%) and subsequent filtration. Q has the units of grams of swollen starch per gram of dry starch. The advantage of plotting rheological properties against the variable CQ is that at CQ, less than unity-free water exists between the swollen granules, whereas at CQ, greater than unity, all the water available is absorbed by the granules, and the system can be considered a close-packed dispersion of gel particles. Starch as a thickening agent in soups and sauces would be used at concentrations for which CQ is less than unity; for doughs, the starch concentration levels could correspond to values of CQ greater than unity.

The dimensional analysis of the quantity CQ shows that the dimensions are grams of swollen starch per gram of dispersion. When CQ is less than unity, CQ is approximately the volume fraction, ϕ, of swollen starch in the dispersion because the density of the swollen starch will be near that of water. When CQ is greater than unity, swelling equilibrium is not reached. The granules could absorb more water, but it is not available.

We present viscosity data on cornstarch dispersions and show that the cornstarch behavior, at the same levels of granule swelling, is identical to the behavior of wheat starch within the precision of our experiments.

MATERIALS AND METHODS

The cornstarch dispersions were cooked in a Corn Industries Viscometer (CIV). A cooking temperature in the range 65–80°C was selected, and the CIV bath temperature was set at the chosen level. A Globe Pearl Cornstarch 3005 from CPC International was dispersed in distilled water at room temperature and then added to the CIV. The concentrations of the starch used depended on the cooking temperature but ranged from 5 to 26%, calculated as grams of dry starch per gram of dispersion. Zero time was taken when the dispersion was within 2°C of the bath (target) temperature.

Samples were removed from the CIV for viscosity determinations at 15, 30, 45, and 75 min.

The mixing pattern in the CIV is excellent, but the large size of the sample relative to the CIV heating bath meant that considerable time was required for the sample to reach the target temperature. This time also depended in part on the level of starch concentration. Normally, the sample temperature was within 2°C of the target within 12–20 min.

Samples were removed from the CIV, and viscosities were determined using a Haake Rotovisco viscometer with a coaxial cylinder design (Haake, Saddlebrook, NJ). The sample was first run at 60°C, and the whole flow curve, from 3 to 500 sec^{-1}, was established within 3–5 min. Measurements were taken progressively from 3 to 500 sec^{-1}. A portion of the sample was cooled, and the viscosity was subsequently remeasured at 23°C. All data were obtained using the MV-I cup (i.d. 4.201 cm) and MV-II bob (diameter 3.680 cm; length 6.004 cm).

The swelling of the starch particles, Q, in an excess of water was separately determined by preparing relatively dilute dispersions (2–4%) in the CIV and cooking at the appropriate temperature for 75 min. The objective in studying swelling in dilute particle suspension was to determine the equilibrium swelling that the granules undergo in an excess of water. This is to give a reference swelling level in considering the flow properties of the more concentrated dispersion in analogy with gel particle systems discussed by Taylor and Bagley (1974, 1977). Since the Q values are determined only within the temperature range 65–80°C, many of the problems associated with starch dispersions cooked at the higher temperature (94°C) at which solubles interfere are minimized. Starch granules can be easily filtered at these low concentrations within the temperature range studied. Excess water was filtered off while hot, and the swollen starch granules were weighed. Q is reported as grams of swollen starch per gram of dry starch. The filtration was carried out with a 4-in. diameter funnel using a water aspirator and no. 54 hardened Whatman filter paper. Only 25 ml of the dispersion is filtered within a 2-min period to minimize water evaporation losses. The results were reproducible to 5%.

Granules were also isolated from the cooked dispersions by low-speed centrifugation. The pastes were washed with water to remove minor exudate. The granules were then dried by lyophilization and sparsely sprinkled on stubs containing double-faced Scotch tape. After the granules were coated with gold-palladium 200–300 Å thick, they were viewed in a Cambridge Stereoscan scanning electron microscope.

RESULTS AND DISCUSSION

Effect of Cooking Time

Figure 1 shows the viscosity shear-rate data obtained at 60°C for a 25% dispersion of cornstarch taken from the CIV after 15, 30, 45, and 75 min at the bath temperature of 65°C. At 15 min, when the sample can be 1–2°C from the target temperature, the cornstarch shows dilatant behavior, with viscosity increasing with increasing shear rate in the range of 10–150 sec^{-1}. This implies that the granules at this stage have swollen enough to crowd one another but are too rigid to flow by particle deformation and can only move under shear by a volume increase and consequent viscosity rise. A referee raised a question as to whether the dilatancy shown in Fig. 1 for 15 min of cook was an artifact due to further cooking of the dispersion during viscosity measurement giving the rise in viscosity at the higher shear rates.

In our view, this contribution of continued swelling during the 2–3 min needed for flow curve measurement is not significant. The same dilatancy is observed in samples measured at 23°C, where the sample has essentially been quenched when transferred from the CIV to the viscometer. Nevertheless, an additional experiment was performed. The sample was transferred from the CIV at 65°C to the viscometer at 60°C. The flow curve was measured six times within a 30-min period going up and down in shear rate without a basic change in the flow curve. Thus, no additional swelling of the granule seems to occur in the rotational viscometer at 60°C.

After 30 min in the CIV, the flow curve is more typical of a non-Newtonian shear thinning material, with the viscosity almost constant in the range of 3–30 sec^{-1} and decreasing thereafter. For the 45- and 75-min samples, the dispersions show non-Newtonian shear thinning behavior over the whole shear-rate range covered. From this, the conclusion can be drawn that the granules after 45 and 75 min are readily deformable under shear.

The rheological details of the viscosity-shear rate curves for these dispersions are very sensitive to temperature in the 65–67°C range. Figure 2 shows viscosity-shear rate plots at 60°C for a 13.7% cornstarch dispersion cooked at 67°C. Here, at 15 min, there is a region from 3 to 80 sec^{-1} where the viscosity is almost constant. Above 80 sec^{-1}, shear thinning occurs. At the other cooking times,
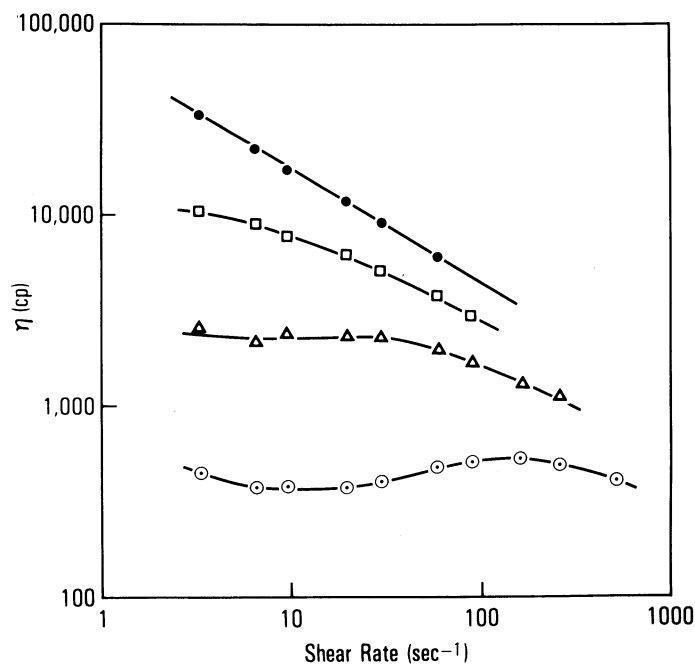

Fig. 1. Viscosity (cp) vs shear rate (sec^{-1}) for a 25% dispersion of cornstarch in water, measured at 60°C after cooking in a Corn Industries Viscometer at 65°C for 15 (⊙), 30 (△), 45 (□), and 75 (●) min.
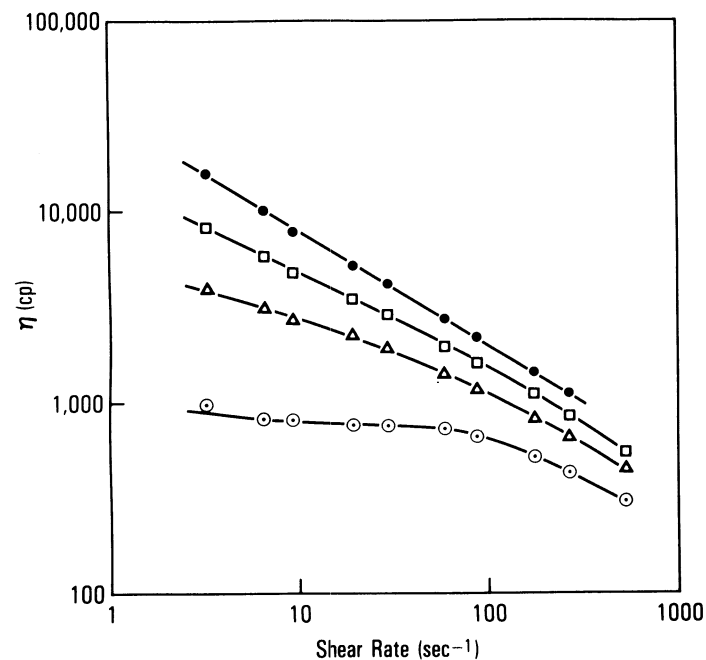

Fig. 2. Viscosities of a 13.7% dispersion of cornstarch in water, measured at 60°C after cooking at 67°C for 15 (⊙), 30 (△), 45 (□), and 75 (●) min.

the dispersions are shear-thinning over the whole shear-rate range, approaching approximately the same slope at shear rates above 100 sec^{-1}. Below that shear rate, the extent of shear thinning is greater at the greater cooking times.

Comparison of Figs. 1 and 2 shows that, at 67° C cook and 13.7% cornstarch, the viscosities are of about the same magnitude as for the 25% dispersion cooked at 65°C. There is a bigger spread of viscosities with cooking time at 65° C than at 67° C. Thus at 10 sec^{-1}, viscosities at the four cooking times are approximately 400, 2,500, 8,000, and 16,000 cp, respectively, at 65°C, whereas at 67°C the corresponding values are approximately 800, 2,800, 4,600, and 8,000 cp.

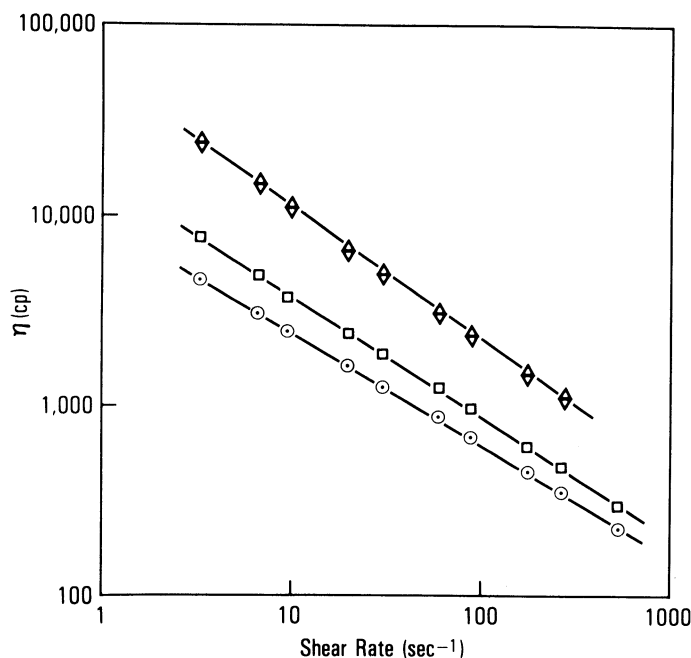At higher CIV cook temperatures, the viscosity shear-rate plots

Fig. 3. Comparison of the viscosities obtained after cooking an 8% and a 9% dispersion at 80° C for 15 and 75 min; 8% at 15 (⊙) and 75 (□) min; 9% at 15 (▽) and 75 (△) min.
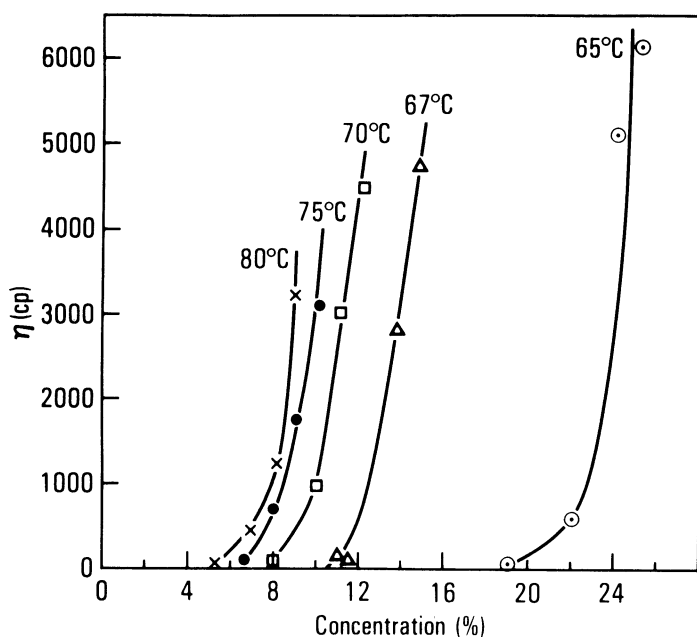

Fig. 4. Viscosity vs concentration plots for cornstarch dispersions in water. The viscosity was determined at 60° C and at a shear rate of 59 sec^{-1}. The curves are for dispersions heated for 75 min at 65 (⊙), 67 (△), 70 (□), 75 (●), and 80°C (✕), respectively.

at different sampling times are brought closer together. This is illustrated by Fig. 3, in which the flow curves for 15 and 75 min cooked at 80° C and 8% concentration are within 40% of each other, whereas at 9% the 15- and 75-min flow curves are almost identical.

A quantitative treatment of the rates at which the viscosities change with time will not be undertaken here because of the time-dependence of the sample temperature at the 30- and 15-min sampling times as discussed.

These results are in harmony with the equivalent data obtained by Bagley and Christianson (1982) for wheat starch dispersions, and the earlier interpretation seems to apply to these cornstarch dispersions. At short cooking times, the granules are only partially swollen and undoubtedly retain considerable rigidity so that dilatancy is observed at concentrations high enough for particle crowding to occur (Morgan 1968). As cooking proceeds, the granules become more swollen, and their volume fraction in the dispersion increases. Additionally, the more swollen granules become more easily deformable in the shear field and hence the dispersion becomes non-Newtonian, showing a degree of shear thinning typical of polymer melts and solutions even though these dispersions consist of large, swollen granules rather than discrete polymer molecules. Polymer scientists recognized early that the response of deformable, elastic particles in suspension should be equivalent in their viscosity shear-rate behavior to the response of discrete molecules, whether in solution or in the melt. This point was discussed by Bueche (1962), and the following quotation from his book illustrates why the apparently dissimilar systems—molecules and discrete particles—show equivalent behavior. Bueche stated that the origin of shear-thinning behavior of melts and solutions is due to the fact that as the molecule rotates in the shear field, its component elements undergo sinusoidal deformation and a resultant drop in viscosity with increasing shear rate. He continued:

> "Another approach to this problem has been taken by Pao, the essence of whose theory is as follows. He considers the rotating body to be a piece of matter having the same retardation spectrum as the gross polymer. The rotating object need not be reduced to molecular terms; it can just as well be a minute particle of polymer. The relation between the frequency response of the polymer and its response to shear rate is completely obvious in a qualitative way. The polymer particle is clearly undergoing oscillatory distortion, and it will evidence the dynamic viscosity one would predict for an oscillating applied force."

Thus, the degree of shear-thinning in these starch dispersions must be directly and simply related to the retardation spectrum of the individual granules. The transition in rheological behavior with cooking time is thus a reflection of the transition from a rigid, unswollen granule to a swollen, elastically deformable gel particle. This is also true for other gel systems such as the highly swellable starch-graft copolymers discussed by Taylor and Bagley (1974, 1977).

Effect of Concentration

Viscosity-concentration curves obtained at 60° C and 58.78 sec^{-1} for samples cooked at various temperatures for 75 min are shown in Fig. 4. The time of 75 min was chosen because all samples then showed only non-Newtonian shear thinning behavior, with none exhibiting dilatancy. The very large change in viscosity between 65 and 67° C is noteworthy. Thus, for these cornstarch samples, a viscosity of 2,000 cp is found at a concentration of about 23% at 65° C and 13% at 67° C. In contrast, wheat starch gives a viscosity of 2,000 cp at approximately 19.5% at 60° C and 14% at 65° C.

Figure 5 shows the swelling of the starch granules for both wheat and cornstarch after 75 min at various temperatures, in grams of swollen starch per gram of dry starch. The rapid swelling of the cornstarch granule between 65 and 70° C mirrors the rapid viscosity changes shown in Fig. 4, in contrast to the less extreme rate of swelling shown by the wheat starch in the 60–70° C range. This is in line with the gelatinization ranges for corn and wheat starch, as indicated by the loss of birefringence given by Osman (1967). Our value for the swelling of the starch granules of wheat and corn

starches are in reasonable agreement with the results reported by Leach et al (1959). They used a centrifugation technique and compared starches with a wide range of swelling values, from potato through milo. They noted that the swelling and solubility curves of corn and wheat starches resembled those of milo both qualitatively and quantitatively. Their Q values, however, were in the range of about 2–10 (estimated from their Fig. 2), as were the values we obtained by the filtration procedure.

The viscosity-concentration curves of Fig. 4 were replotted as η/CQ vs CQ, using the Q values (swelling power) for cornstarch given in Fig. 5. The solid line of Fig. 6 is the curve obtained for wheat starch and reported by Bagley and Christianson (1982); the points are those for cornstarch from Fig. 4.
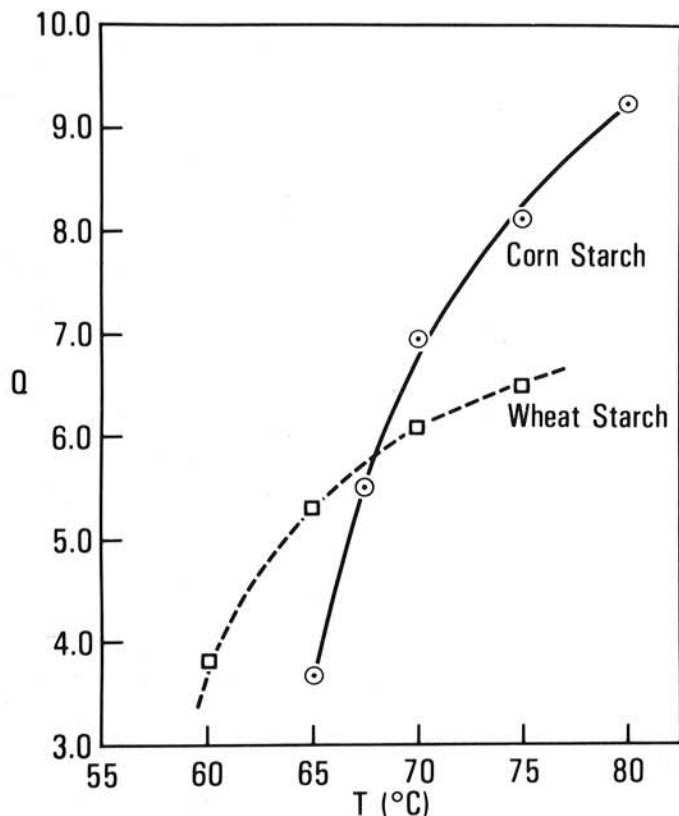

Fig. 5. Grams swollen starch per gram dry starch (Q) obtained at various temperatures after 75 min of cook. ⊙ = Cornstarch, □ = wheat starch.
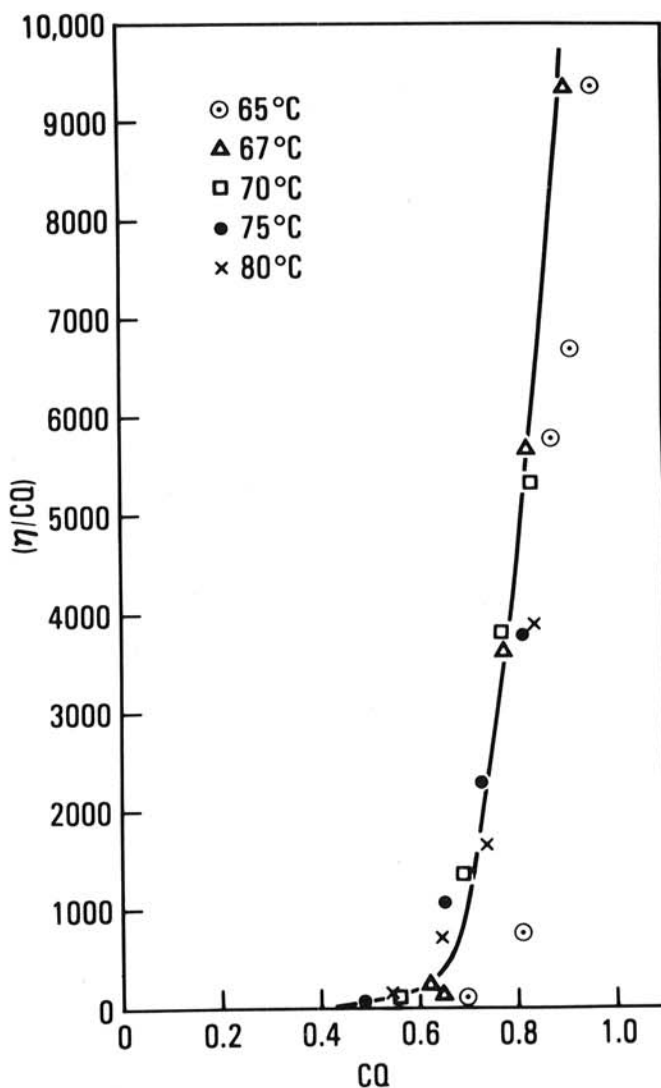

Fig. 6. The data of Fig. 4 replotted as η/CQ vs CQ, where Q is a measure of the swelling of the starch granule, expressed as grams of swollen starch per gram of dry starch. The line curve drawn in is reproduced from a wheat starch plot (Bagley and Christianson 1982).
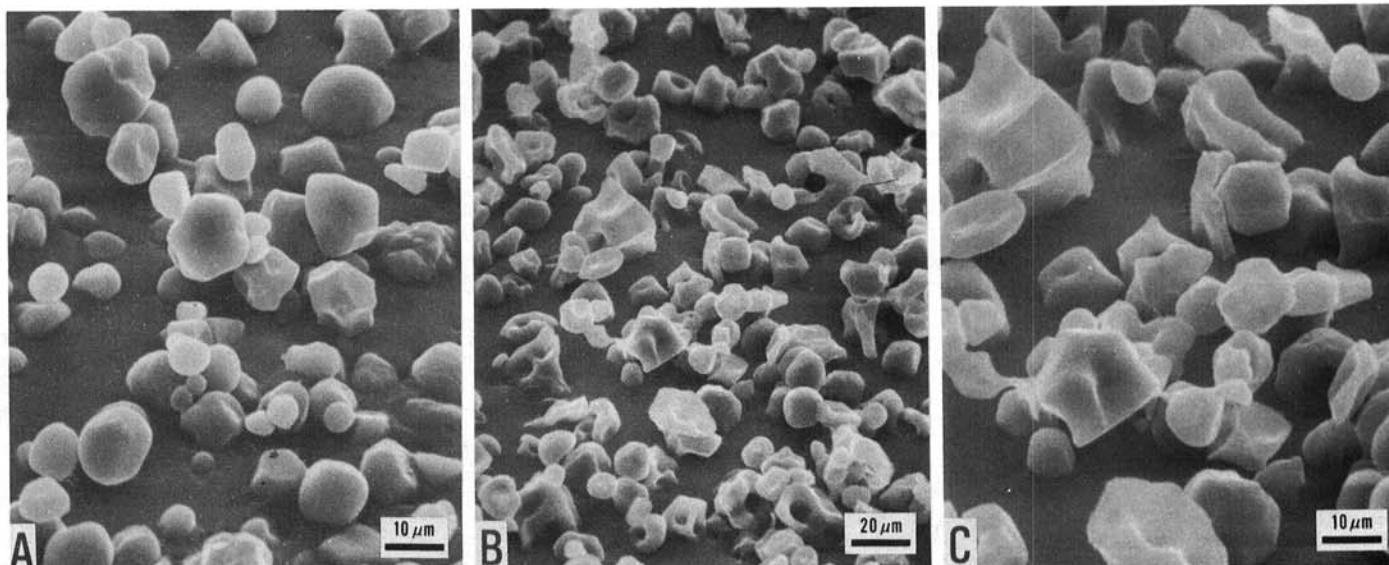

Fig. 7. Electromicrographs of uncooked cornstarch (**A**) ×1,000 and 22% dispersion of cornstarch cooked at 65°C for 75 min; (**B**) ×500; and (**C**) ×1,000.

Although there is some scatter, the cornstarch data for 67, 70, 75, and 80°C agree well with those obtained for wheat starch in the range of 60–75°C. Since CQ is approximately the volume fraction of the swollen starch granules, the superposition of the data indicates that the viscosity depends only on the volume occupied by the swollen granules. In the temperature range studied here, no effect is due to the filamentous starch exudate to which Miller et al (1973) attributed the large viscosity increases developed by a fully heated starch. At higher temperatures, this exudate will certainly play a significant role, as discussed by Miller et al.

There is some scatter of the viscosity data in Fig. 6. This is due in part to the uncertainties in the determination of Q and the very strong dependence of viscosity on cooking time. Thus, there are differences in the rate at which these starch suspensions can be brought to temperature, the times being longer for the more concentrated suspensions. In addition, some cooking occurs during the viscosity measurements at 60°C as discussed by Bagley and Christianson (1982). Nevertheless, the agreement between the corn and wheat starch results is gratifying.

The experimental points for cornstarch cooked at 65°C undoubtedly lie below the master curve of Fig. 6, well beyond the experimental error inherent in these studies. In examining the flow curves for the samples cooked at 65°C, dilatancy is observed even at 75 min of cook time at both 19 and 22% concentrations. This accounts for the low η/CQ values at $CQ = 0.7$ and 0.8. For the three higher CQ points for the 65°C cook, the viscosity shear-rate plots demonstrate shear thinning at 75 min of cook. However, dilatancy is clearly evident at 24 and 25% up to 30 min of cook, but not at all at 26%. Nevertheless, because these points lie below the master curve in Fig. 6, one can conclude that the dynamic losses that occur on shearing these granules are low because the retardation spectrum for the granules is different from the spectrum that describes the granules cooked at 67–80°C (Bueche 1962). A major change in granule properties occurs between 65 and 67°C for the cornstarch.

Scanning Electron Microscopy of Cooked Granules

Figure 7 shows a comparison of uncooked cornstarch (A) with the same cornstarch after cooking at 65°C for 75 min in a 25% dispersion (Fig. 7B,C). Some granule swelling and distortion is apparent as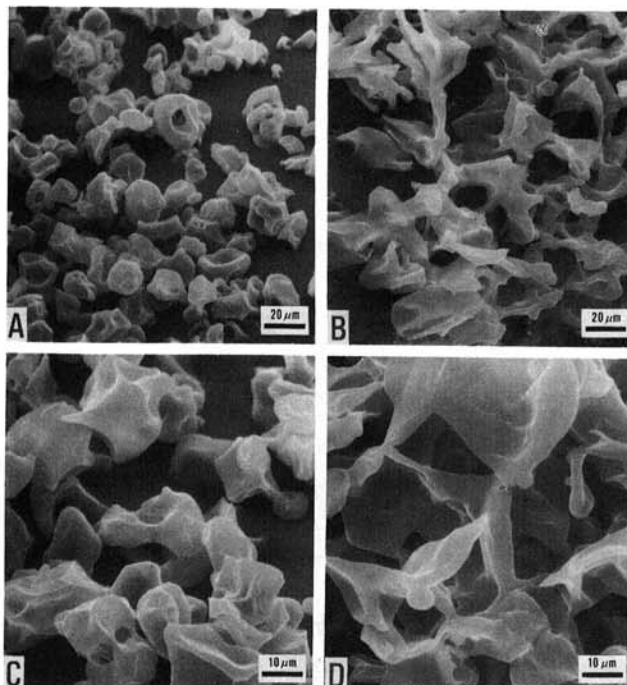 a result of cooking for this length of time, even at this pregelatinization temperature. Further changes in granule morphology can be shown when the starch is cooked at higher temperatures (Fig. 8). The large change in viscosity observed in going from 65 to 67°C (as shown in Fig. 4) is a reflection of the granule changes that occur in this temperature range. Figure 8 shows the granules of cornstarch heated at an 11% concentration at 67°C for 75 min and granules heated at a 9% concentration at 80°C. Not only are the granules more swollen and distorted at 67°C than at 65°C, but few granules appear to be unaffected. Many granules appear to exist in an unswollen or undeformed state at 65°C. Granules heated in a 9% concentration at 80°C for 75 min show the extensive swelling and distortion of the granules; moreover, some evidence suggests that the granules were deformed by shear and may even have fused together in some cases. A great deal of variance occurs in the progressive distortion of the granules as the concentration of the suspension is increased at various cook temperatures.

Morphological changes at different cooking temperature and the correlation with starch paste rheology are discussed in more detail elsewhere (Christianson et al 1982).

SUMMARY

The viscosities of cornstarch dispersions were determined at 60°C over a shear-rate range of 3–500 sec^{-1} as a function of cooking time in a CIV held at 65–80°C. As with wheat starch, cornstarch dispersions showed a strong dependency of the flow curves on sampling time, particularly at the lower temperatures. When the starch granules were swollen enough to result in interparticle crowding, but not yet softened enough to deform under the stresses existing in the shear field, dilatancy effects were observed. Eventually, at long enough cooking times, all concentration levels at all temperatures showed typical shear-thinning behavior. Such viscosity-concentration curves at the various cooking temperatures could be superimposed on each other by plotting the η/CQ vs CQ, where C is the concentration and Q is the grams of swollen starch divided by grams of dry starch used. (CQ is approximately equal to the volume fraction of the starch in the dispersion.) The curve of η/CQ vs CQ was the same, within experimental error, for wheat starch and cornstarch for the longest cook time, independent of cooking temperature.

LITERATURE CITED

BAGLEY, E. B., and CHRISTIANSON, D. D. 1982. Swelling capacity of starch and its relationship to suspension viscosity—Effect of cooking time and temperature and of concentration. J. Texture Stud. 13:115.

BEAN, M. M., and YAMAZAKI, W. T. 1978. Wheat starch gelatinization in sugar solutions. I. Sucrose: Microscopy and viscosity effects. Cereal Chem. 55:936.

BEAN, M. M., YAMAZAKI, W. T., and DONELSON, D. H. 1978. Wheat starch gelatinization in sugar solutions. II. Fructose, glucose, and sucrose: Cake performance. Cereal Chem. 55:945.

BUECHE, F. 1962. Physical Properties of Polymers. Interscience Publ., New York.

CHRISTIANSON, D. D. 1981. Hydrocolloid interactions with starches. Page 399 in: Food Carbohydrates. D. Lineback and G. E. Inglett, eds. Avi Publ. Co., Westport, CT.

CHRISTIANSON, D. D., BAKER, F. L., LOFREDDO, A. R., and BAGLEY, E. B. 1982. Correlation of microscopic structure of corn starch granules with rheological properties of cooked pastes. Food Microstruct. 1:13.

CHRISTIANSON, D. D., GARDNER, H. W., WARNER, K., BOUNDY, B. K., and INGLETT, G. E. 1974. Xanthan gum in protein-fortified starch bread. Food Technol. 28(6):23.

CHRISTIANSON, D. D., HODGE, J. E., OSBORNE, D., and DETROY, R. W. 1981. Gelatinization of wheat starch as modified by xanthan gum, guar gum, and cellulose gum. Cereal Chem. 58:513.

EVANS, I. D., and HAISMAN, D. R. 1979. Rheology of gelatinized starch suspensions. J. Texture Stud. 10:347.

GOUGH, B. M., and PYBUS, J. N. 1973. Effect of metal cations on the swelling and gelatinization behavior of large wheat starch granules. Staerke 4:123.

HIZUKURI, S., and TAKEDA, C. 1978. Studies on the gelatinization of starches. II. Effect of lower alcohols on the gelatinization of cereal

Fig. 8. Electromicrographs of a 11% dispersion of cornstarch cooked at 67°C for 75 min; (A) ×500; and (C) ×1,000; and a 9% dispersion of cornstarch cooked at 80°C for 75 min; (B) ×500; and (D) ×1,000.

starches. Staerke 30:228.

KIM, S. K., and D'APPOLONIA, B. L. 1977. The role of wheat flour constituents in bread staling. Bakers Dig. 51(1):38.

LEACH, H. W., McCOWEN, L. D., and SCHOCH, T. J. 1959. Structure of the starch granule. I. Swelling and solubility patterns of various starches. Cereal Chem. 36:534.

MILLER, B. G., DERBY, R. I., and TRIMBO, H. B. 1973. A pictorial explanation for the increase in viscosity of a heated wheat starch-water suspension. Cereal Chem. 50:271.

MORGAN, R. J. 1968. A study of the phenomenon of rheological dilatancy in an aqueous pigment suspension. Trans. Soc. Rheol. 12:4, 511.

MORRIS, E. R., REES, D. A., ROBINSON, G., and YOUNG, G. A. 1980. Competitive inhibition of interchain interactions in polysaccharide systems. J. Mol. Biol. 138:363.

ODIGBOH, E. V., and MOHSENIN, N. N. 1975. Viscosity characterization of unmodified cassava starch paste. J. Texture Stud. 6:363.

OSMAN, E. M. 1967. Starch in the food industry. Page 165 in: Starch, Chemistry and Technology, Vol. III, Industrial Aspects. R. L. Whistler and E. F. Paschall, eds. Academic Press, New York.

OSMAN, E. M. 1975. Interaction of starch with other components of food systems. Food Technol. 29(4):30.

SANDSTEDT, R. M., and ABBOTT, R. C. 1964. A comparison of methods for studying the course of starch gelatinization. Cereal Sci. Today 9:13.

TAYLOR, N. W., and BAGLEY, E. B. 1974. Dispersions or solutions. A mechanism for certain thickening agents. J. Appl. Polym. Sci. 18:2747.

TAYLOR, N. W., and BAGLEY, E. B. 1977. Tailoring closely packed gel—Particle systems for use as thickening agents. J. Appl. Polym. Sci. 21:113.