Yield Stresses in Cooked Wheat Starch Dispersions*

By E. B. Bagley and D. D. Christianson, Peoria**

Wheat starch dispersions of 8 – 15% concentrations were cooked in the temperature range 60° – 75°C for periods up to 75 min. Viscosities of the cooked dispersions were determined in a rotational viscometer at 60°C and 23°C. No yield points were observed in the viscosity behavior at 60°C. At 23°C, viscosity measurements showed yield points in the range 200 – 3,000 dynes/cm² dependent on cook time, cook temperature, concentration and cooling history. Plots of log viscosity versus log shear stress were useful in establishing the existence of yield points where the usual plots of shear rate versus shear stress were ambiguous.

* Lecture presented by D. D. Christianson at the 33rd Starch Convention of the Arbeitsgemeinschaft Getreideforschung at Detmold, April 21 to 23, 1982.

** The 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.

1 Introduction

The gelatinization behavior of starches continues to attract attention both because of the intrinsic scientific interest and because of the significance of the behavior to the starch and food industry. Nevertheless, as recently as 1978 Hizakuri and
Takeda [1] were able to say with confidence that “the reason for the characteristic behavior is not clear”. To elucidate some aspects of the rheological behavior of starch dispersions, Bagley and Christianson [2] reported on the viscosity-shear rate response of wheat starch dispersions. These dispersions, at concentrations from 5 to 25% in water, were cooked for various time in the temperature range 60 – 75°C, and the viscosity-shear rate curves were determined in a Couette viscometer at 60°C.

Initially, the starch particles in a dispersion are rigid and at high enough concentrations show dilatant behavior. As the particles swell and soften they become deformable in the shear field and show the typical non-Newtonian, shear thinning behavior very similar to that of polymer molecules in solution or melt form. This type of response is understandable theoretically since, as Bueche [3] noted, the theories that predict non-Newtonian shear thinning flow for polymer molecules apply equally well to finite deformable particles. These swollen starch granules rotate in the shear field and undergo oscillatory deformation. The response, in terms of the shear rate dependence of viscosity, will depend on the retardation spectrum of the swollen particle.

At long cooking times it was further found that, within experimental error, the viscosity was determined by the volume fraction of the swollen starch granules, independent of the cooking temperature in the range 60 – 75°C. Exactly the same volume fraction dependence was shown by corn starch (Christianson and Bagley, [4] cooked in the range 67 – 80°C).

The viscosity behavior of these dispersions measured at 23°C was in some ways quite different from that observed at 60°C. Although some of the general features of the 60°C behavior were preserved at 23°C [2], there were concentrations and shear rates at which yield points became apparent. The purpose of this communication is to describe these results at 23°C.

2 Materials and Methods

The wheat starch was a commercial sample (obtained from Henkel Corp., Minneapolis, designated Aytex-P) of 12.2% moisture and N < 0.4%. Samples were dispersed in distilled water, giving a pH of 6.5. The concentrations ranged from about 7% to 25% and were calculated on dry basis.

Dispersions of wheat starch in water were cooked in a Corn Industries Viscometer (CIV). For each dispersion, the temperature of the CIV was held constant (namely 60, 65, 70, or 75°C). Samples were normally taken after 15, 30, 45, 60, and 75 min cooking time at each temperature for viscosity determinations. Zero cooking time was arbitrarily taken as the time at which the sample temperature was 2°C below the CIV bath temperature.

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

Apparent viscosities were determined using a Haake Rotovisco viscometer, both at 60°C and at room temperature (23°C), in the apparent shear rate range of 1 – 1000 seconds⁻¹. All data were obtained using the MV Cup (I.D. 4.201 cm) and MV-II bob, of diameter 3.68 cm and length 6.004 cm. No corrections were made for non-Newtonian behavior. Viscosity-shear rate points were determined in order starting at the lowest shear rate. Measurements were normally completed in about 3 min.

Viscosity determinations on a given day were made first at 60°C, with samples of each dispersion being set aside in a glass bottle for later examination at 23°C. After all the 60°C experiments were completed, the viscometer was cooled to 23°C and samples maintained in the glass bottles at room temperature were then measured at 23°C. Normally these samples had been held for 2 – 4 h at room temperature before measurement.

3 Results and Discussion

Figure 1 shows the apparent viscosity in centipoise versus apparent shear rate for a 13% wheat starch dispersion cooked at 60°C for 75 min. At 60°C the flow curve is typical of a shear thinning material almost exactly obeying a power law of slope -0.6. At 23°C the flow curve is slightly concave upward.

Figure 2 shows the equivalent result for the 11% dispersion. At 60°C the curve is shear thinning but at low shear rates is flattening out towards Newtonian behavior, as is normally

---

![Figure 1](image1.png)

**Figure 1.** Apparent viscosities at 60°C and 23°C versus apparent shear rate for a 13% wheat starch dispersion cooked at 70°C for 75 min.

![Figure 2](image2.png)

**Figure 2.** Apparent viscosity at 60°C and 23°C versus apparent shear rate for an 11% starch dispersion cooked at 70°C for 75 min.
observed at low shear rates with many polymeric systems. At 23 °C the results are more unusual. The curve is initially close to power law but at 30 s⁻¹ there appears to be almost a discontinuity in the curve, with the viscosity changing only slightly (from 4,200 to 3,700 cp) with the shear rate doubling from 30 to 60 s⁻¹. In addition, the curves at 11% are more widely separated than at 13%. Clearly the viscosity curves at 60° and 23 °C differ not only quantitatively but qualitatively — that is, both the values of the viscosities and the shapes of the curves can differ.

In discussing Figures 1 and 2 some emphasis was placed on the “apparent” nature of the viscosity and shear rate computed for the rotational Couette viscometer. The problems of computing the true viscosities and true shear rates are discussed in some detail by Van Wazer et al. [5] and by Oka [6] and will be considered further below. At the moment, however, viscosity and shear rate data will be used to compute the shear stresses acting on the dispersions by the simple relation (1):

$$\tau = \eta \dot{\gamma}$$

(1)

where $\dot{\gamma}$ is the apparent shear rate and $\eta$ is the apparent viscosity.

Replotting apparent viscosity at 60 °C versus shear stress in Figure 3 for five concentrations of a dispersion cooked at 70 °C for 75 min gives a series of curves that either are linear (obeying a power law) or are concave downward. The change is, as expected, systematic, and at 11% concentration the viscosity is approaching a Newtonian region as the shearing stress drops. For the 10% dispersion, a Newtonian plateau appears to have been reached at stresses less than 100 dynes/cm².

Figure 3. Apparent viscosities at 60 °C versus shear stress for 10, 11, 12, 13 and 14% starch dispersions cooked at 70 °C for 75 min.

In Figure 4 the apparent viscosity at 23 °C is plotted against shear stress calculated from Eq. (1) for four concentrations cooked at 70 °C for 75 min. These are the same samples as those in Figure 3 except that viscosities for 14% concentration could not be run in our instrument at 23 °C. As can be seen in Figure 4, the three highest concentrations of 11, 12 and 13% give plots which are very steep and concave upwards. The 10% dispersion is concave downwards and is more similar to the curves of Figure 3 than to its companion curves of Figure 4.

Figure 4. Apparent viscosities at 23 °C versus shear stress for the starch dispersions of Figure 3.

The viscosity behavior of the 11, 12 and 13% dispersions of Figure 4 is indicative of the existence of a yield point. The advantages of such double logarithmic plots of viscosity versus shear stress in detecting the presence of a yield stress have been emphasized recently by Mewis [7]. He notes that “For dispersions the low shear viscosity limit often disappears at higher concentrations” and “A yield stress then develops below which there is no macroscopic flow.” In both Figures 3 and 4 it is evident that the viscosity is very sensitive indeed to concentration. It is further noteworthy that a yield point appears at 23 °C, as shown in Figure 4, by a mere change of 1% in concentration, in going from 10 to 11%.

While plots of viscosity versus shear stress as shown in Figure 4 are useful in clearly demonstrating the presence of a yield stress, the normal way of evaluating the yield stress is by plots on a linear scale of the shear stress versus the shear rate. This is shown for four concentrations cooked at 70 °C for 75 min in Figure 5. For 11, 12 and 13% a clear yield point is apparent. The yield point for these three concentrations is not obtainable to better than ±100 dynes/cm². The highest shear rate point shown in Figure 5 is at 58.78 s⁻¹ and for each of these three concentrations lies below the initial straight line as drawn.

Figure 5. Shear stress versus shear rate at 23 °C for four starch concentrations. Yield points are evident at 11, 12 and 13% dispersions but absent in the 10% dispersion. All samples cooked at 70 °C for 75 min.
The lowest concentration curve, the 10% dispersion, clearly is curved and can be assumed to go through the origin as shown in Figure 5. Thus, the 10% dispersion shows no yield point.

It can be argued that if the ordinate of Figure 5 were expanded to examine carefully the shear stress-shear rate behavior between 0 and 5 s\(^{-1}\) that even the lines for the higher concentrations (11, 12, 13%) would curve in to the origin as shown for 10%. Here the plots of Figures 3 and 4 are useful. If the double logarithmic plot of viscosity versus shear stress curves upward (as for 11, 12, 13% dispersions of Fig. 4), then a true yield points exists. If the plots are curved so as to be concave down, as for the 10% plot of Figure 4 and the 10 and 11% curves of Figure 3, then no yield point exists. If the viscosity-shear stress plots obey a power law (12, 13 and 14% dispersions of Fig. 3), the data we have so far obtained suggest that no yield point exists (Fig. 6).

Of course, it has long been known that starch gels cannot form at room temperature. Over 50 years ago Woodruff and Nicoli [8] examined the effect of cooking time, temperature and sucrose concentration on gel strength and noted that maximum gel strength was obtained, for each starch examined, at cooking temperatures of 90\(^\circ\)C or more. Starch gels take time to develop maximum strength, these times being of the order of hours. There may also be effects of shear during cooking. This is indicated in the following experiment. A 13.5% wheat starch dispersion was cooked at 70\(^\circ\)C for 75 min in the CIV. A sample was set aside in a glass bottle for later use at room temperature. The viscosity was then determined as usual at 60\(^\circ\)C on the cooked dispersion. With the cup of the Haake Rotovisco rotating continuously at 3.27 s\(^{-1}\), the viscometer bath temperature was reduced to 50, 40, 30 and 23 \(^\circ\)C, with a flow curve being determined at each temperature. After these experiments were run, the viscosity of the sample initially set aside to cool undisturbed for 2 h was determined. This will be referred to as the rested sample.

Figure 7 shows the results at 60, 50 and 40\(^\circ\)C on a shear stress-shear rate plot. No yield point is seen. In Figure 8 the results for 30, 23\(^\circ\) and for the 23\(^\circ\)C rested sample are shown. Here yield points exist for each sample. For the continuously sheared sample, however, the yield point is only half of that observed for the rested sample. The 30\(^\circ\) sample is uncertain—there may or may not be a yield point. The results, nevertheless, indicate that a gel with a yield stress in these experiments does not occur under continuous shearing until the temperature...
drops to 30° and that the continuously sheared sample at 23° gives a lower yield stress than does the sample rested for a comparable period of time. Further investigation of the kinetics of gel formation, the temperature and the shear history dependence carried out along these experimental lines should provide insight into the mechanism of gel formation in starch dispersions.

Figure 9 shows typical yield stress values at some representative cooking times and cooking temperatures. As would be expected, the higher the cooking temperature the higher the yield stress. The longer the cooking time, the higher the yield stress. The lower the cooking temperature the more effect cooking time has on the yield stress.

3.1 Yield Stresses in Starch Gels

In examining starch dispersions, Evans and Haisman [9] observed yield points at 60°C in contrast to our results where no yield stress was detected at 60°C. Doublier et al. [5] has also recently reported the presence of yield stresses in starch dispersions [10]. The cooking temperature would appear to be the cause of this apparent discrepancy. Evans and Haisman and Doublier cooked their dispersions at temperatures above 90°C whereas our dispersions were prepared in the 60–75°C range. At these lower temperatures less than 5% solubles were exuded, in agreement with Figure 11 of Doublier [10]; at the higher cook temperatures, as much as 60% of the starch can be exuded from the granule as solubles. The presence of such solubles will influence the formation of a structure in the dispersion detectable as a yield value. In addition, as is well known, the swelling of the nonsoluble material will be greater at the higher cook temperatures, and this too will affect the yield stresses observed and the concentration range in which a yield stress occurs.

Lang and Rha [11] examined the yield stresses of dispersions of guar gum and gelatinized corn starch by several methods. The exact temperature and temperature control of their starch dispersions were not described, but measurements were at 25°C. Over a weight percent concentration of 2.5 to 4.3, yield stresses from 10 to 275 dynes/cm² were observed. Evans and Haisman reported yield stresses at 60°C for their corn dispersions ranging from zero at about 3.2% to 125 dynes/cm² at 8% (data from Figure 6 of Reference [7]). The higher temperature of measurement, 60°C, for the Evans and Haisman work thus results in lower yield stresses than observed at 25°C by Lang and Rha, as would be expected. Further, Lang and Rha note that their yield stresses depended on method of measurement and remark that “experimental determination of yield stress must be made relevant to the practical application.” Although we concur that relevance to practice is necessary, nevertheless a more basic approach to the phenomenon of yield stress in dispersions will be needed to fully understand the factors that determine the existence and magnitude of a yield stress. Certainly these structured gels are sensitive to a number of factors. Halmos and Tiu [12] have discussed some of these factors recently and have shown that shear degradability could be quantified in terms of the energy required to destroy the structure of yeast extract. Elliott and Ganz [13] note that, in dynamic measurements of the structure of commercial mayonnaise and salad dressings, strain amplitudes must be kept within the linear viscoelastic limit to establish the properties of essentially undisturbed samples. In our studies, as in Figures 7 and 8, the yield stress of a 13.5% dispersion can range from 900 to 2000 dynes/cm² depending on shear and cooling history; for a lower concentration, a 13% sample with a still different shear and cooling history, a yield point of 2400 dynes/cm² at 23°C was observed. Van Wazer et al. [5] note that the yield value can usually be measured under static conditions. However, it is sometimes difficult to obtain yield points due to experimental difficulties. Thus Collison and Elton [14] found that their 17% starch dispersions were too sticky to permit yield values to be measured by the cone penetration method. They were able to obtain yield points on a 44% gel and found values ranging from approximately 1.000 to 2.000 g/cm² for gel preparation temperatures from 60 to 94°C. These yield values are about 10³ higher than the ones observed here at much lower concentrations. This means that the apparent linearity of yield stress against concentration shown in Figure 9 holds only for a very narrow concentration region. The curves must rise very rapidly at concentrations above 15%. Considering the significance to the food industry of starch used over wide concentration ranges, further investigations of these yield phenomena would appear to be well justified.

Finally, current interest in yield values is giving rise to new methods for determining yield stress. De Kee et al. [15] have, for example, recently reported a method which they have applied to such systems as condensed milk and tomato paste.

3.2 Effect of Yield Stresses on Computed Shear Rates and Viscosities

The shear rates and calculated viscosities reported here are apparent values, calculated assuming Newtonian flow in the viscometer gap. Corrections to the shear rate for non-Newtonian flow can be made following standard procedures outlined by Van Wazer et al. [5] or Oka [6]. The calculation involves the slope of the log shear rate versus log shear stress. For examining the yield points, however, the true shear rate is not necessary. The instrument measures the torque, M, on the rotating cylinder, and the shearing stress is then calculated at any radial position r from the relation (2):

\[ 2\pi hr = M \]

\[ (2) \]

where h is the height of the rotating cylinder and r is any point between this cylinder and the stationary cup. The yield stresses reported here are thus absolute values. From Eq. (2) the stress is highest at the wall of the rotating cylinder and lowest at the stationary wall of the container. If the shearing stress is lower than the yield stress throughout the gap, no flow occurs. If the shear stress is greater throughout the gap than the yield, then flow occurs everywhere in the gap. However, where the yield stress has a value between the shearing stress at the outer wall and that at the inner wall of the viscometer, there is flow only in that portion of the gap in which the shear stress is greater than the yield stress. As Van Wazer et al. [5] put it, “the effective gap size is less than that defined by the viscometer walls”. The effective cup radius for a given stress, \( \tau_w \), at the inner cylinder is \( R_s \). This critical radius, \( R_s \), beyond which flow will not occur in the gap is

\[ R_s = R_k \tau_w / \gamma \]

\[ (3) \]

where \( R_k \) is the radius of the rotating cylinder and \( \gamma \) is the yield stress. The magnitude of this effect can be illustrated with reference to a 13% wheat starch dispersion cooked at 70°C for 75 min with a yield point of 2.340 dynes/cm². The calculated gap size is only 0.4 mm at 3.27 s⁻¹, whereas at 29.37 s⁻¹ flow occurs throughout the whole of the gap (2.6 mm). The general treatment for obtaining true shear rates and true viscosities will not be applied here. These corrections are not
necessary to establish the yield points. The main objective of this work is to illustrate the value of apparent viscosity-shear stress diagrams in establishing the existence and values of the yield points. However, in reporting quantitative viscosity data, it is imperative to correct for changing gap size, where appropriate.

Bibliography


Address of authors: Dr. E. B. Bagley and Mr. D. D. Christianson, Northern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, Peoria, Illinois 61604 (USA) (Received: May 19, 1982)