

POWER-LAW RHEOLOGY OF ALKALINE STARCH PASTES¹

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ABSTRACT

Starch pastes containing from 5 to 10% starch and various amounts of sodium hydroxide (alkali) were prepared by different cooking procedures. The viscosities of the pastes were measured at temperatures up to 71°C. in the amylograph and at various speeds by the Brookfield viscometer. The data followed the power law fairly well, and the parameters of this model were calculated for selected starch pastes with and without alkali. The proportionality constant was related to the yield stress, which was not negligible. The pseudoplasticity constant was nearly independent of conditions and equal to about 0.7.

During the preparation of 10% starch pastes for use in making starch xanthate solutions (1) difficulties were encountered, particularly in continuous cooling of the paste before the carbon disulfide was introduced. As is well known, starch pastes exhibit almost all possible rheological properties (2). Thus, no rheological model describes them completely, and problem-solving becomes an extremely difficult task. Pending future discoveries that will illuminate the situation better, heat-transfer and steady-state flow problems have been solved by means of what is known as the power-law parameters (3).

The Newtonian equation relating rate of shear to shear stress may

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be modified to account for a wide variety of rheological systems to give the power-law equation:

$$\tau = b \left(\frac{d\gamma}{d\Theta} \right)^s + c$$

where τ is shear stress, $d\gamma/d\Theta$ is the rate of shear, b the proportionality constant, s the pseudoplasticity constant, and c the yield stress that occurs with solids of the Bingham type. With a Newtonian fluid, s is unity and c is zero, so that b becomes the viscosity, η , the constant ratio between shear stress and rate of shear.

For any rotational viscometer, there exists a relation between the torque observed at the sensing member and the speed of rotation, which may be derived from the physical arrangement and the fundamental power law. For a Brookfield viscometer, the general equation is (3):

$$2\pi N b^{1/s} = \left(\frac{R_\tau}{R_1} \right) \left[\frac{A}{2\pi R^2 L} - c \right]^{1/s} \left[-\frac{1}{R} \right] dR$$

where N is speed in r.p.s.;

R , distance from center of rotation to a streamline, cm.;

R_1 , spindle radius, cm.;

R_2 , boundary of flow streamlines, cm.;

A , torque, dyne cm.;

L , immersed spindle length, cm.;

and b , s , and c are the power-law parameters as before.

The way this equation is solved is, first, to determine the yield stress. To do this, the square root of the torque is plotted against the square root of the speed and the line is extrapolated to zero speed. The yield stress is calculated from the no-speed torque. The pseudoplasticity constant comes next. The logarithm of the parenthetical expression (but using R_1) is plotted against the logarithm of the speed. The slope of the line is $1/s$. The proportionality constant must then be found by a mechanical integration of the right-hand side of this equation.

Calculations are easier if the traditional notion of viscosity is abandoned (3,4), although "apparent" viscosities can be calculated from b and s and used successfully (5).

Since no information was found in the literature on power-law constants for starch pastes or on the effect of important variables on these parameters, a series of experiments on cooking and viscosity relationships was undertaken to aid in designing a cooker-cooler. Though far from complete or rigorous, the results reported here demonstrate the

degree to which power-law rheology can be used in starch technology.

Materials and Methods

The starch used was pearl-grade commercial corn starch. Alkali was added as a 40% solution made from CP-grade pellets of sodium hydroxide.

The pastes were cooked in several ways, which had some influence on their properties. The cooking methods are given with the properties under "Results." The viscosity measurements were made with a Brookfield Syncho-lectric Viscometer, Model LVT-4, equipped with a No. 4 spindle. Readings of percent of full scale were made at various spindle speeds and at various times in the paste's history. The Brookfield readings were converted to torque in dyne centimeters by multiplying them by 6.737, the factor supplied by the manufacturer.

Results and Discussion

Amylograph Cooking. Pastes were cooked in a VISCO/amylo/GRAPH (C. W. Brabender Instruments Inc.; Type VAV 1) for 15 min. at 92°C. after they were heated to that temperature at the 1.5°C.-per-min. increase for which this machine is programmed. The viscosity data were converted to torque by multiplying the B.U. readings by 0.001 times the nominal spring torque for the cartridge used. This is because there are 1,000 B.U. for full-scale torque, and both the 700- and 2,000-cmg. springs were used. The effects of starch concentration, alkali concentration, and temperature were studied. In general, the amylograph provided unnecessarily severe cooking conditions for the pastes containing alkali, and they were slightly off-color.

Figure 1 illustrates the reduction in apparent viscosity produced

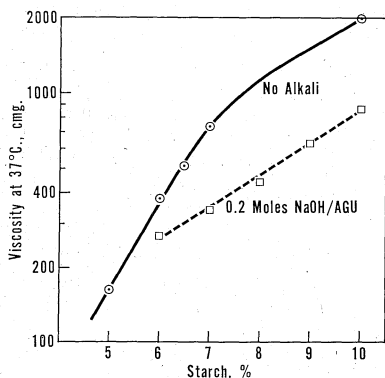


Fig. 1. Viscosity of amylograph-cooked pastes. Brabender units \times cartridge spring constant $\times 10^{-3}$ at 75 r.p.m. and 37°C. after 17 min. of cooking at 90°C.

by introducing alkali. The expected nearly logarithmic response of starch serves as a reference.

Batch Cooking. Several batches were prepared by sparging steam into a pot containing the starch slurry, which was agitated vigorously. When the temperature reached 99°C., the steam was turned off and the paste was allowed to cool to 38°C. This cooking required 5–8 min., and the cooling, in a cold-water bath with periodic stirring of the cooling paste, required about 1.5 hr. A 500-g. sample was then poured into the amylograph for measurement of the viscosity. The comparison between cooking methods based on the amylograph values is given in Fig. 2,

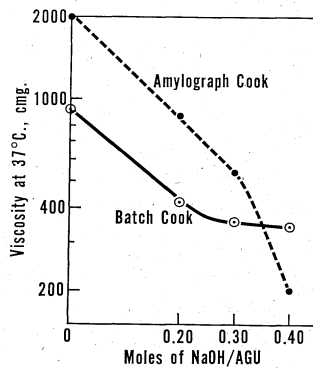


Fig. 2. Amylograph viscosities of 10% starch pastes decrease rapidly with alkali and depend to some extent on the method of cooking.

along with the effect of alkali. With high amounts of alkali, the batch-cooked pastes were also off-color. The problem of paste reproducibility is an important consideration when rheological data are interpreted. Microscopic examination of the batch-cooked pastes showed that the granules had been ruptured to a greater extent than in the amylograph at the same cooking temperature.

Power-Law Results. The Brookfield viscometer more nearly measures the laminar resistance associated with classic concepts of viscosity. Therefore, data from it were analyzed according to Charm (3), concentrated primarily on the starch pastes prepared in the amylograph without alkali and with 0.2 moles of alkali per anhydroglucose unit (AGU) (equivalent to 0.5 g. NaOH/100 g. mixture for a 10% starch slurry or 0.3 g. NaOH/100 g. for 6% starch). The stoichiometric constancy was maintained as a matter of convenience, although the viscosity obtained also depends on starch and alkali concentration. A number of relationships were observed.

Figure 3 demonstrates how the proportionality constant b from the

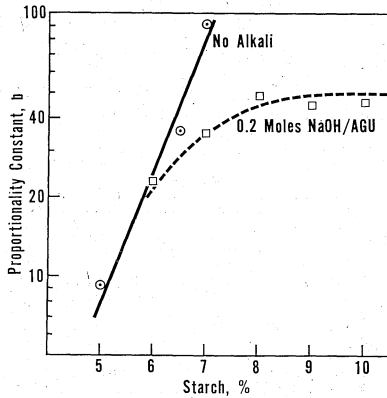


Fig. 3. The proportionality constant or adjusted torque at unit shear rate differs in behavior from the amylograph viscosity. Measurements were at 37°C.

Brookfield data depends on alkali and starch concentration. This plot is the same type as that made from the amylograph values in Fig. 1. The proportionality constant is in reality the stress at unit shear rate corrected for stress at zero flow. Although the amylograph purports to measure a "viscosity," the proportionality constant is more nearly a "true" viscosity. Within a specific type of paste, the yield stress, c , relates to the proportionality constant, b , as shown in Fig. 4. The exist-

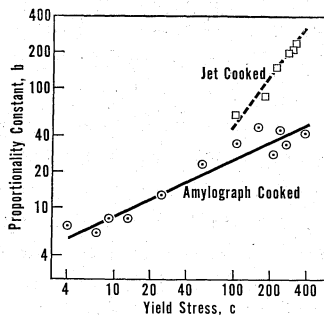


Fig. 4. The proportionality constant and yield stress show a good empirical relationship over a variety of conditions. These data are for pastes containing 0.2 mole alkali per AGU.

ence of this relation suggests that the yield stress is not due to Bingham characteristics, but is due to a strong elastic component as reported by Collison and Elton (2). A simple yield value probably does not exist. Since data in Fig. 4 cover a range of temperatures and starch concentrations, the relationship seems more than fortuitous, and may be explainable in terms of the yield-value artifact.

The proportionality constant b and, because of the relationship just described, the yield stress c both decrease with increasing temperature. A plot of $\log b$ vs. $1/T$, where T is the absolute temperature ($^{\circ}\text{K}.$), is usually employed to demonstrate this dependency (6), and Fig. 5 illus-

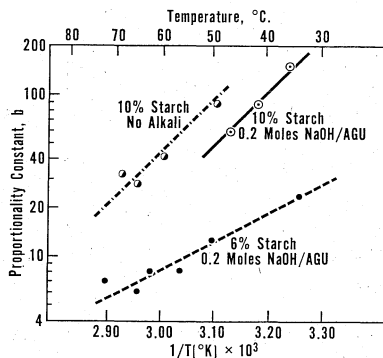


Fig. 5. The proportionality constant decreases with increasing temperature.

trates the changes that occur. When the data from which the parameters were calculated are inspected closely, some differences in the pseudoplasticity constant s and therefore in the estimated proportionality constant b are noted; but considering the tendency of the pastes to enter into difficultly reversible gel states, particularly with no alkali and at the higher concentrations, the relation shown in Fig. 5 is a fair estimate of the properties of a flowing paste.

To summarize, starch pastes, at least in the region where the gel-state properties do not predominate, follow power-law rheology fairly well. Nonalkaline starch pastes containing less than 7% starch follow the model at room temperatures, and pastes containing as high as 10% starch behave well at temperatures in the region of $60^{\circ}\text{C}.$ Alkaline starch pastes show a diminished tendency to gel, so that power-law parameters apply to pastes containing up to 10% starch at all temperatures. There is a significant yield stress, c , which is correlated with the proportionality constant, b . The pseudoplasticity constant, s , is independent of concentration of either starch or alkali and essentially, also of temperature. It has an average value of about 0.7. The range of values estimated from the data is 0.55 to 0.80, which includes pastes that are nearly completely gelled. Apparently, the power law can be useful in characterizing a paste and could be useful in characterizing the mixtures which constitute the transitional compositions between pastes and fully rigid gels.

Continuous Cooking. Pastes of starch can be made continuously by

commixing a starch slurry and steam in a flow-through system. As in batch cooking, the degree of cook depends primarily on the temperature and holding time. In continuous steam-jet cooking, higher temperatures are usually substituted for longer times or high-shear agitation. Cooking even a 10% starch paste in a jet cooker, followed by a pipe mixer providing 3 min. retention time, posed no severe problems. The only precaution necessary was to provide sufficient steam pressure to the jet so that the back-pressure of the paste flowing through the mixer did not reduce the steam flow rate. When more concentrated solutions were cooked, however, the steam pressure required was quite high.

The greatest problems arose while the cooked paste was cooling to room temperature. Because of the high viscosity, low heat-exchange rates were encountered. When attempts were made to increase the exchange area simply by increasing the number of tubes connected in parallel in a conventional exchanger, some of the tubes plugged with gelled material. When the area was extended by lengthening a single tube, the pressure required was high. Consequently, there was incentive for examining the rheology of the pastes to attempt to quantify the requirements for the cooler.

Preliminary calculations by the method of Charm (3) were made for pressure drop in $\frac{3}{8}$ -in.-i.d. tubing, assuming the rheological properties were those of the exit temperature during cooling. Results indicated a pressure drop of 3 lb./sq. in./ft. of pipe. In actual tests, the pressure drop was nearer 60 lb. for a 10-ft. length. The paste was cooled from 82° to 66°C. at a rate of 2 lb./min. of paste. The power-law information has thus enabled the calculation of system behavior within an order of magnitude.

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