Effects of Sucrose on the Rheological Behavior of Wheat Starch Pastes

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Synopsis

The rheological properties of starch–water–sucrose pastes have been determined under steady and oscillatory shear conditions. The results show that the effect of sucrose at concentrations of less than about 20% w/w is to increase the apparent viscosity, yield stress, dynamic viscosity, and dynamic rigidity. At higher sucrose concentrations the yield stress and dynamic rigidity tend to zero while values of the dynamic viscosity and apparent viscosity are reduced compared with controls. Sucrose causes the dispersed gel particles in pastes to change volume, and it is suggested that this is one of the factors responsible for the observed effects of sucrose on rheological behavior.

INTRODUCTION

Starch pastes consist of colloidal gel particles dispersed in a continuous phase. Thus they are types of microgel systems.[1] The gel particles are swollen starch granule fragments in which polyglucan molecules are linked together by crystalline junctions. These junctions form in the cooling stage of paste manufacture. The continuous phase is an aqueous solution containing low concentrations of polysaccharide molecules that have leached out of the swollen granules.[2]

Starch pastes are viscoelastic fluids with rheological properties that can be exploited in industry.[3–5] In the steady shear range 10–4000 s^{-1}, pastes behave as shear thinning liquids. At low shear rates a yield stress is apparent. Under oscillatory shear conditions the dynamic viscosity decreases slightly with frequency in the range 0.002–1.0 Hz while the dynamic rigidity increases. No major relaxation processes occur in this range. The viscoelastic properties exhibited by pastes are the type shown by weak gels and by concentrated polymer solutions. Recent work has shown that the rheological behavior of pastes can be related to their swelling volumes.[3–5] The swelling volume is the volume which gel particles occupy when closed packed provided excess solvent is present. In some cases behavior also depends on the size distributions of the granules in the starch samples used to form pastes.[4,5] This is apparent from the laws governing paste properties:

$$\eta_{\dot\gamma} = \eta_0[(C - C_s)S]^{K_1} \tag{1}$$

$$\tau = \tau_0[(C - C_s)S]^{K_2}[P]^{N_2} \tag{2}$$

$$G' = G'_0[(C - C_s)]^{K_3}[P]^{N_3} \tag{3}$$

$$\eta' = \eta'_0[(C - C_s)S]^{K_4}[P]^{N_4} \tag{4}$$

where $\eta_{\dot\gamma}$ is the apparent viscosity at shear rate $\dot\gamma$, τ is the yield stress, G' is the dynamic rigidity at given frequency and η' is the dynamic viscosity at given

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frequency. η_0, τ_0, G'_0, η'_0, K_1, K_2, K_3, K_4, N_2, N_3 and N_4 are constants. N_4 has a negative value. C is the concentration of starch (g/mL), C_s is the concentration at which starch particles are just close-packed throughout the volume of the paste. S is the swelling volume (mL/g); this gives C_s. P is the number fraction of large granules (hydrated diameter greater than 12 μm) in the starch sample from which the paste is formed. This relates to the size distribution of gel particles in pastes. The equations apply when $C \geq 1.1C_s$.

The flow properties of starch–water pastes may be altered by the presence of other components. One example of this that is of considerable commercial significance is the effect of sugars such as sucrose. According to measurements made using empirical testing devices, if the concentration of sucrose is greater than about 35% w/w, there is a marked reduction in paste viscosity.[6–8] The effect of lower concentrations of sucrose is less certain. Increases in viscosity have been reported,[7,8] though other work suggests pastes are not affected. Sugars would be expected to alter the swelling of starch granules and so paste behavior. Earlier work suggests that sucrose causes a reduction in swelling[6]; however, more recent data indicates that an increase may occur.[7] All investigations show that sugars increase the temperature required to form viscous pastes.

The present paper describes an investigation of effects of sucrose on the rheological behavior of wheat starch pastes measured under defined shear conditions. Changes in paste structure that could account for the effects so determined are also reported. Wheat starch was used in the investigation as this variety is of most economic interest in Australasia.

EXPERIMENTAL

Starch was extracted from wheat (c.v. Gamenya) according to the method of Meredith et al.,[9] air-dried at ambient temperature to a moisture content of about 10%, and stored at 5°C. Two batches of wheat were used; similar results were obtained from both.

Pastes were prepared by heating a dispersion of starch granules in sucrose solution at 95°C for 1 h using the procedure specified elsewhere.[4,5] A small amount of evaporation occurred during this heat treatment; hence the concentration of pastes was adjusted to required levels before cooling. Pastes were equilibrated at 30°C for 0.5 h before measurements were made.

Steady shear measurements were made with a Ferranti-Shirley cone and plate viscometer. The cone angle was 1.5° and the cone diameter 7.0 cm. The rate of shear was varied from 0.4–4000 s^{-1}. Further information about the method used has been given elsewhere.[5]

The dynamic viscosity and rigidity of pastes were measured with a top-drive co-axial viscometer. The instrument operated over a frequency range of 0.002–1.0 Hz. Measurements were made using a shear amplitude of less than 0.05 rad as pastes exhibit linear viscoelastic behavior in this range. Full details of the experimental procedure used have been described previously.[4]

Swelling volumes were determined by the standard centrifugation method except that a correction for compression of the bed of sedimented particles was made.[4]

All measurements were made at 30°C.

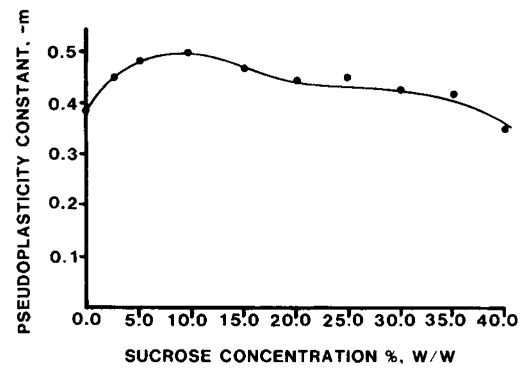

Fig. 1. The relationship between the pseudoplasticity constant and sucrose concentration in a paste containing 4% w/w starch.

RESULTS

Steady Shear Conditions

At high shear rates 10–4000 s^{-1} starch–water–sucrose pastes behave as shear thinning liquids when the sucrose concentration is in the range of 0–40% w/w. The pastes obey the following law:

$$\eta_{app} = K\dot{\gamma}^m$$

where η_{app} is the apparent viscosity and K and m are constants. The value of the pseudoplasticity constant m as a function of sucrose concentration is shown for a typical case in Figure 1. The value of m would be expected to tend to zero at high concentrations of sugar since starch swelling is inhibited and the behavior of the dilute starch suspension tends towards that of the disperse phase, namely a Newtonian sugar solution.

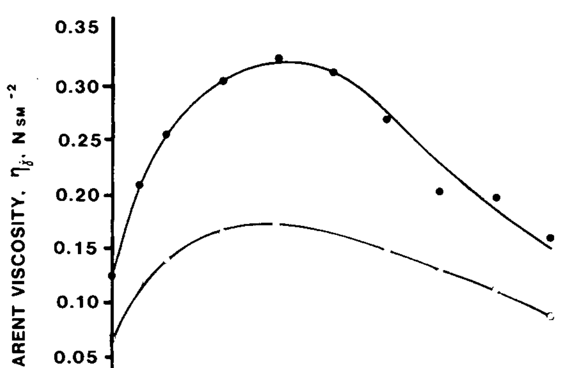

Fig. 2. The apparent viscosity of pastes measured at a shear rate of 120 s^{-1} against sucrose concentration for pastes containing 3.5% w/w (O) and 4.0% w/w (●) starch.

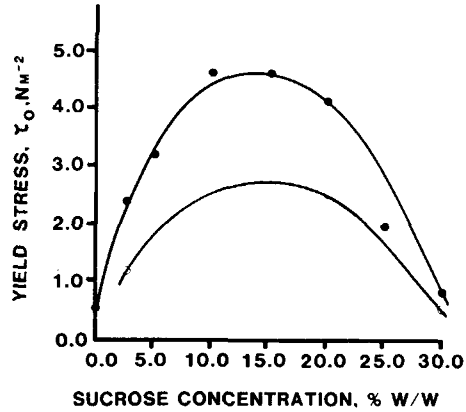

Fig. 3. Yield stress as a function of sucrose concentration for pastes containing 3.5% w/w (O) and 4.0% w/w (●) starch.

The effect of sucrose on the steady shear behavior can also be demonstrated by plotting the apparent viscosity at a given shear rate as a function of sugar concentration; typical results are given in Figure 2. At 40% w/w sucrose the apparent viscosity still has a sufficiently high value for pastes to be used in industry as thickening agents.

At low shear rates a yield stress is evident when the sucrose content of pastes is less than about 25% w/w. Hence in this range pastes containing sucrose behave as soft solids. Above a concentration of 25% w/w the yield stress is either non-existent or too small to be detected given the sensitivity of the test instrument used. Representative results are shown in Figure 3.

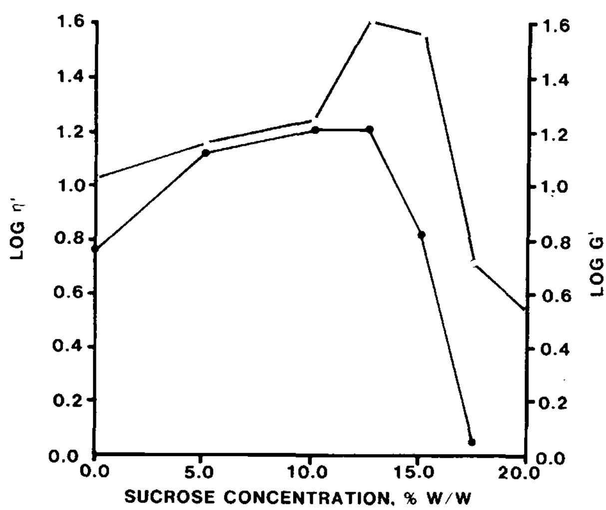

Fig. 4. Dynamic rigidity (●) and dynamic viscosity (O), measured at an angular frequency of 0.016 Hz, as a function of sucrose concentration for pastes containing 3.0% w/w starch.

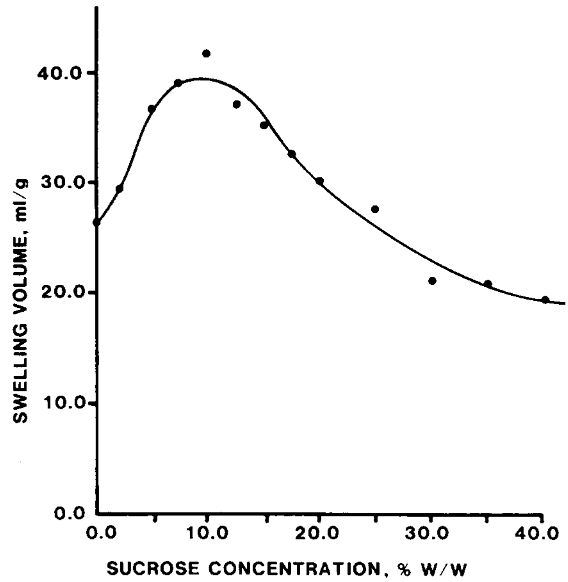

Fig. 5. Swelling volume as a function of sucrose concentration.

Oscillatory Shear Conditions

In the frequency range studied (0.002–1.0 Hz), when the sucrose concentration varies from 0% to about 20% w/w, starch–water–sucrose pastes show the type of viscoelastic behavior given in the absence of sugar. Typical results demonstrating the variation of the dynamic rigidity and dynamic viscosity with sucrose concentration are given in Figure 4. Once the sucrose concentration exceeds about 20% w/w, the dynamic viscosity has a comparatively small value while the dynamic rigidity tends to zero.

Swelling Volumes

The influence of sucrose on the swelling volume of starch is shown in Figure 5. The presence of sugars has been reported to decrease the extent of granule disintegration and implosion that takes place during paste formation,[6] and this could account for the increase in swelling volume that occurs when the sucrose percentage is below about 25% w/w. Fragments from granules that disintegrate would be expected to make relatively little contribution to total bed volume as they tend to fill voids between large granules. At higher concentrations of sugar, osmotic-type effects may dominate, and the swelling of particles may be reduced. Insufficient theory concerning the swelling of polymer–diluent–solute systems is available to make a more rigorous interpretation of these results.

DISCUSSION

For any given sucrose concentration and starch batch, the swelling volume and the number fraction of large granules are constant. Hence provided the

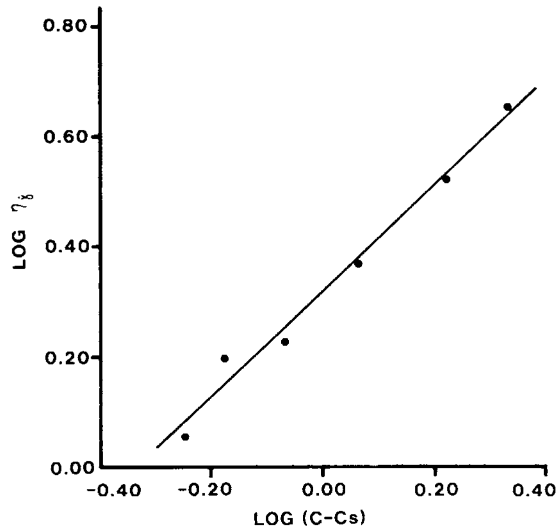

Fig. 6. Plot of log apparent viscosity at a shear rate of 120 s^{-1} vs. log $(C - C_s)$ for pastes containing 10% w/w sucrose.

sugar concentration is less than about 20% w/w, the behavior of pastes would be expected to conform to eqs. (1)–(4). Check measurements were made to confirm that this is the case; typical results are shown in Figure 6.

If the sole effect of sucrose on pastes is to alter swelling volumes and hence rheological behavior, then eqs. (1)–(4) should allow such effects to be predicted. The typical results in Table I show that, although the overall trend in the variation of rheological properties with sucrose is predicted correctly, the agreement between the calculated and measured results is poor. Part of this disagreement may be due to the fact that sucrose may alter the size distribution of particles in pastes. If this occurs then according to eqs. (1)–(4) this would alter the value of the yield stress and the viscoelastic parameters. It is not possible to measure the size distribution of granules directly in pastes[10] and so test this hypothesis. However, sugars also change the viscosity of many aqueous polysaccharide solutions by decreasing the dielectric constant of the solvent, by dehydration action, and by hydrogen bond formation.[11,12] These factors are likely to alter the rheological behavior of the individual gel particles in pastes and so the properties of the bulk system.

The results of the present study and previous work[4,5] provide a basis for understanding some of the apparent discrepancies in the conclusions reached from investigations of starch–water–sugar systems using empirical test devices. In the first instance, the rheological properties of pastes are a function of the time–temperature treatment and shear received during their preparation.[4,5] This is because these factors influence swelling volumes. With measurements made using empirical test devices, the thermal treatment and shear to which samples are subjected are not known and are likely to differ from one design of instrument to another. Hence results would be expected to be a function of the empirical measurement system used. Secondly, the temperature to which the paste is subjected is significant in that at high sugar concentrations the crystal-

TABLE I
Predicted and Measured Values of Dynamic Viscosity, Dynamic Rigidity, Apparent Viscosity, and Yield Stress as a Function of Sucrose Concentration for Pastes Containing 3.5% w/w Starch

Sucrose concn (% w/w)	Dynamic viscosity ($N \cdot s \cdot m^{-2}$) at 0.016 Hz		Dynamic rigidity ($N \cdot m^{-2}$) at 0.016 Hz		Apparent viscosity ($N \cdot s \cdot m^{-2}$) at $\dot{\gamma} = 120\ s^{-1}$		Yield stress ($N \cdot m^{-2}$)	
	Predicted	Measured	Predicted	Measured	Predicted	Measured	Predicted	Measured
0.0	1.25	1.25	0.51	0.51	0.064	0.064	—	—
2.5	1.58	2.04	1.25	0.89	0.074	0.118	—	1.20
5.0	9.12	2.50	3.31	1.64	0.209	0.141	0.87	2.25
7.5	19.95	3.15	4.07	2.20	0.269	0.154	1.51	2.35
10.0	31.62	3.80	4.79	2.85	0.324	0.166	1.99	2.45
12.5	10.47	3.58	3.16	3.35	0.200	0.170	0.79	2.58
15.0	7.08	3.00	2.88	4.10	0.182	0.173	0.63	2.60
17.5	3.98	3.70	2.29	5.00	0.126	0.168	0.30	2.58
20.0	2.13	4.00	1.38	5.80	0.092	0.159	—	2.50
22.5	1.99	2.40	1.20	0.39	0.085	0.151	—	2.06
25.0	1.78	2.00	1.14	0.32	0.083	0.149	—	1.40
30.0	—	—	—	—	—	0.130	—	0.52
35.0	—	—	—	—	—	0.114	—	—
40.0	—	—	—	—	—	0.091	—	—

line–amorphous transition[13] required for paste formation takes place only when the temperature is elevated by about 30° compared with controls.[14] Some of the temperature treatments used in empirical test regimes do not allow pastes to form completely. Finally, results depend markedly on the concentration of sugar employed since viscosity at first increases, reaches a maximum, and then decreases as sugar concentration increases.

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