

Rheological Characteristics of Wheat Starch Pastes Measured under Steady Shear Conditions

R. B. K. WONG and J. LELIEVRE, *Food Technology Department, Massey University, Palmerston North, New Zealand*

Synopsis

Wheat starch pastes consist basically of swollen gel particles of various sizes which are dispersed in a continuous phase containing dissolved polysaccharides. The rheological properties of such pastes have been measured in the steady shear mode. At high shear rates the pastes behave as shear thinning liquids, while at low shear rates they exhibit a yield stress. The rheological properties vary with wheat starch variety and paste preparation conditions; this variation is of considerable economic importance to the starch industry. The present investigation shows that the flow behavior of pastes depends largely on two factors, namely, the volume which the starch gel particles would occupy when close packed if excess solvent were present, and the size distribution of the particles. Starch variety and paste preparation conditions influence these two factors and hence steady shear properties.

INTRODUCTION

Some starches form pastes which have rheological characteristics that can be utilized in industry.¹ Such pastes are formed by heating an aqueous suspension of starch granules above the gelatinization temperature²; this process has been described in detail elsewhere.¹ The starch used can be extracted from various plant species; in Australasia wheat is generally used as a source. However, starches from some wheat cultivars do not form pastes with the desired rheological properties.³ The behavior of pastes also depends on the conditions used during their preparation.¹ An explanation of the above differences in paste properties would be of interest to the starch industry.

Starch pastes consist of a range of components including the polysaccharides amylose and amylopectin in solution, complexes between lipids and amylose, crystallized amylose, and remnants of swollen granules of varying sizes.¹ The swollen granules are dispersed through the paste and are, in effect, viscoelastic gel particles.⁴ An abrupt change in rheological behavior is found at about the concentration at which these particles are packed throughout the total volume of the system.^{5,6} A recent definitive study has shown that under conditions of both oscillatory and simple shear, the rheological properties of some pastes can be attributed to interactions between swollen starch granules and to the viscoelasticity and compressibility of the granules themselves.⁵ However, this study did not investigate wheat starch pastes where results might be expected to differ, as a range of granule sizes is present. The rheological properties of some microgels, that is, systems containing discrete particles of gel dispersed in a solvent, are known to depend on their particle size distributions.⁷ Previous work from this laboratory has demonstrated that differences in the dynamic rigidities and viscosities of wheat starch pastes may be attributed to differences in the size distributions and the volume fractions of swollen granules they contain.⁶ The

present study describes the measurement of the rheological properties of wheat starch pastes under steady shear conditions. The information so obtained was used to find general empirical equations that describe the behavior of pastes formed from different wheat starches under a variety of conditions. Other investigators have already established general rules that govern the behavior of some microgel dispersions.^{8,9}

EXPERIMENTAL

Starch was extracted according to the method of Meredith et al.¹⁰ from five different wheat varieties, air dried at ambient temperature to a moisture content of about 10%, and stored at 5°C.¹¹ The numbers and size distributions of starch particles were determined using a Coulter Counter model B. Small and large granules were defined as particles with hydrated diameters lower and higher than 12 μm respectively in the bimodal size distribution so obtained.

The standard method of making pastes was by heating an aqueous suspension of starch granules at 95.0°C for 1 h using the procedure specified elsewhere.⁶ In experiments in which paste preparation conditions were varied, temperatures ranging from 85.0 to 95.0°C and times ranging from 5 to 60 min were employed. These conditions are in accord with those used in industry to form pastes.¹ Volumes of gelatinized granules were determined using swelling capacity measurements as described previously.⁶

Measurements of the behavior of pastes during steady shear were made using 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 to 4000 s^{-1} ; mea-

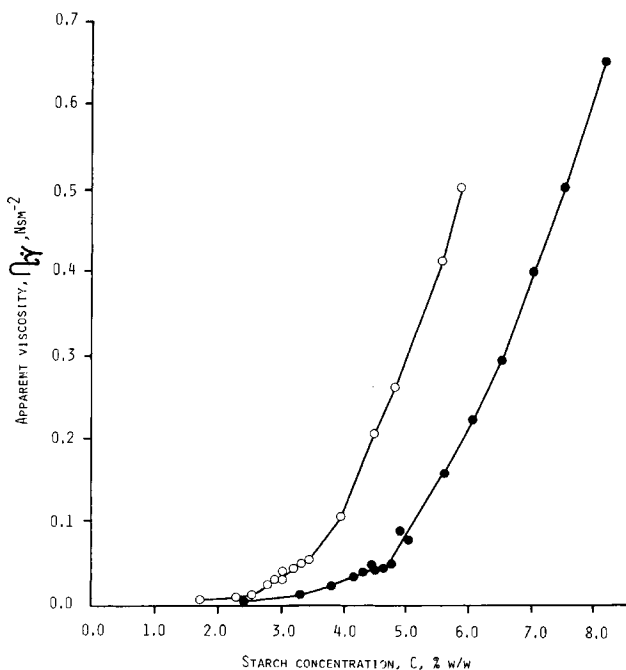


Fig. 1. Apparent viscosity of pastes measured at a shear rate of 120 s^{-1} vs. starch concentration for wheat starches Raven (O) and Karamu (●).

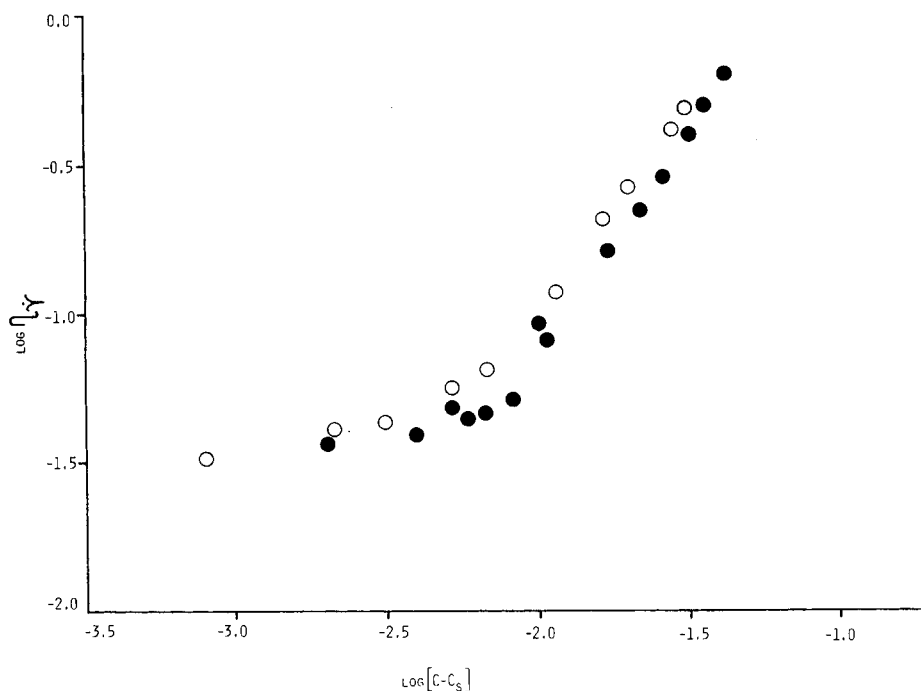


Fig. 2. Plot of log of apparent viscosity measurement at a shear rate of 120 s^{-1} vs. $\log[C - C_s]$ for wheat starches Raven (○) and Karamu (●).

measurements were made at the lowest shear rate first. Values obtained at the high end of this shear range tended to drift down with time, hence results were taken as quickly as the instrument response permitted. All measurements were made at 30°C .

RESULTS AND DISCUSSION

Under steady shear conditions, the behavior of pastes formed from wheat starch was found to be similar to that reported for starches from other plant species.^{4,5} Thus, at high shear rates ($10\text{--}4000 \text{ s}^{-1}$), wheat starch pastes are shear-thinning fluids that obey the law

$$\eta_{\text{app}} = K \dot{\gamma}^m \quad (1)$$

where η_{app} is the apparent viscosity, $\dot{\gamma}$ is the shear rate, and K and m are constants. K and m are a function of the concentration and variety of starch and of the temperature treatment used during paste preparation.

Figure 1 demonstrates the variation of apparent viscosity at a given shear rate with starch concentration C . The same trend was obtained at other shear rates and with other starch varieties and paste preparation conditions. The results show that there is an abrupt change in apparent viscosity at about the concentration C_s at which starch particles are just close packed throughout the paste volume; C_s has a value of 2.82% for Raven and 3.92% for Karamu. When the starch concentration is less than about $0.7C_s$, a stage is reached where apparent viscosities are too low for the pastes to be used in industry as thickening agents.

TABLE I
 Representative Data Giving Apparent Viscosities at Specified Shear Rates, Yield Stresses, and Other Characteristics of Pastes from Different Wheat Starches Formed under a Range of Conditions

Starch variety used to prepare starch	Starch concentration, g/mL	Swelling capacity, mL/g	Number fraction of large granules	Temperature/time treatment, °C/h	Apparent viscosity, Nsm^{-2}			Yield stress, τ_0 Nm^{-2}
					$\dot{\gamma} = 20 \text{ s}^{-1}$	$\dot{\gamma} = 120 \text{ s}^{-1}$	$\dot{\gamma} = 1200 \text{ s}^{-1}$	
Karamu	0.0427	25.50	0.075	95.0/1.0	0.07	0.05	0.03	—
	0.0471	25.50	0.075	95.0/1.0	0.17	0.09	0.04	1.2
	0.0535	25.50	0.075	95.0/1.0	0.31	0.17	0.06	2.0
	0.0575	25.50	0.075	95.0/1.0	0.46	0.21	0.08	3.0
	0.0615	25.50	0.075	95.0/1.0	0.60	0.26	0.10	4.2
	0.0661	25.50	0.075	95.0/1.0	0.73	0.31	0.11	5.6
	0.0704	25.50	0.075	95.0/1.0	1.20	0.36	0.15	6.5
	0.0760	25.50	0.075	95.0/1.0	1.30	0.42	0.18	—
	0.0487	26.25	0.095	95.0/1.0	0.22	0.13	0.06	1.1
	0.0517	26.25	0.095	95.0/1.0	0.37	0.17	0.07	2.0
Aotea	0.0574	26.25	0.095	95.0/1.0	0.61	0.27	0.09	3.5
	0.0598	26.25	0.095	95.0/1.0	0.83	0.34	0.12	5.4
	0.0649	26.25	0.095	95.0/1.0	1.05	0.50	0.16	7.0
	0.0309	35.50	0.150	95.0/1.0	0.05	0.04	0.02	—
Raven	0.0324	35.50	0.150	95.0/1.0	0.05	0.05	0.02	—
	0.0340	35.50	0.150	95.0/1.0	0.07	0.06	0.03	—

	0.0384	35.50	0.150	95.0/1.0	0.20	0.12	0.05	—
	0.0433	35.50	0.150	95.0/1.0	0.44	0.21	0.08	0.9
	0.0464	35.50	0.150	95.0/1.0	0.57	0.26	0.10	2.0
	0.0531	35.50	0.150	95.0/1.0	0.82	0.41	0.13	3.6
	0.0558	35.50	0.150	95.0/1.0	1.13	0.55	0.20	6.4
	0.0525	28.02	0.102	95.0/1.0	0.85	0.35	0.11	4.8
	0.0584	28.02	0.102	95.0/1.0	1.11	0.48	0.13	6.5
	0.0607	28.02	0.102	95.0/1.0	1.40	0.55	0.16	8.2
	0.0571	24.00	0.102	92.5/1.0	0.55	0.25	0.10	1.9
	0.0480	24.00	0.102	92.5/1.0	0.21	0.11	0.05	2.6
	0.0610	24.00	0.102	92.5/1.0	1.04	0.46	0.16	3.0
	0.0571	19.30	0.102	90.0/1.0	0.38	0.16	0.07	0.5
	0.0610	16.40	0.102	87.5/1.0	0.44	0.23	0.08	—
	0.0526	29.00	0.105	95.0/1.0	0.57	0.27	0.08	2.8
	0.0569	29.00	0.105	95.0/1.0	0.99	0.43	0.12	4.0
	0.0623	29.00	0.105	95.0/1.0	1.50	0.56	0.12	5.3
	0.0480	28.30	0.105	95.0/0.75	0.38	0.24	0.08	1.8
	0.0480	27.10	0.105	95.0/0.5	0.35	0.20	0.07	1.6
	0.0550	28.30	0.105	95.0/0.75	0.86	0.41	0.12	3.2
	0.0550	27.10	0.105	95.0/0.5	0.82	0.41	0.11	3.0
	0.0550	25.60	0.105	95.0/0.33	0.64	0.31	0.08	2.0
	0.0550	24.20	0.105	95.0/0.25	0.59	0.26	0.05	1.3

Gamut

Hilgendorf

TABLE II
Values of Regression Coefficients and Correlation Coefficients for Fits of Eq. (3) at Specified Shear Rates

	$\dot{\gamma} = 20 \text{ s}^{-1}$	$\dot{\gamma} = 120 \text{ s}^{-1}$	$\dot{\gamma} = 1200 \text{ s}^{-1}$
$\log \eta_0$	0.03	-0.313	-0.885
K_1	1.33 ± 0.06	1.18 ± 0.06	0.80 ± 0.06
Correlation coefficient	0.95	0.95	0.94

Previous work suggests that the results in Figure 1 may be explained by an equation of the form

$$\eta_{\dot{\gamma}} = \eta_0(C - C_s)^{K_1} \quad (2)$$

where $\eta_{\dot{\gamma}}$ is the apparent viscosity at a given shear rate and η_0 and K_1 are constants at any given shear rate whose magnitudes depend on starch variety and paste preparation conditions.^{5,6} Figure 2 shows results conform to this expression where $C \geq 1.1C_s$ or $\log(C - C_s) \geq -2.5$ and -2.4 for Karamu and Raven, respectively. The discontinuity in the results when $C = 1.1C_s$ may reflect the fact that below this concentration paste structure changes and more porous arrangements of packed starch particles can exist, perhaps as a result of the system dilating.¹²

Although eq. (2) accounts for the variation in the apparent viscosity of any given paste with starch concentration, the parameters K_1 and η_0 depend on starch variety and sample preparation conditions. This equation was therefore modified in an attempt to establish a more general relationship. A number of investigators have suggested methods of unifying rheological data obtained from systems consisting of dispersed gel particles.^{8,9,13} These methods relate rheological measurements to the volume that the bed of close-packed gel particles would occupy if excess solvent were present. In the current study, this is determined by the swelling capacity of the starch and therefore depends on sample variety and paste preparation conditions.⁶ In some cases, it is also necessary to make reference to the size distribution of particles to unify results.⁶ With the present viscosity data, a general relationship was found without including a term for the particle size distribution:

$$\eta_{\dot{\gamma}} = \eta_0[(C - C_s)S]^{K_1} \quad C \geq 1.1C_s \quad (3)$$

where S is the swelling capacity of the starch. This equation also gives C_s , which is now in units of g/ml; η_0 and K_1 are constants at any given shear rate. The fits of the logarithmic form of eq. (3) at given shear rates to the experimental data, which are shown in part in Table 1, are given in Table II. A term for the particle size distribution was not included in eq. (3), as this increased correlation coefficients by only about 0.02.

Taylor and Bagley suggest a different method of unifying data such as that shown in Figure 1, namely, by relating viscosity values to the viscosity at the point at which the dispersed particles are just close packed throughout the entire system.⁸ In the present context, this leads to an equation of the form

$$\frac{\eta_{\dot{\gamma}}}{\eta_{cs}} = K_2 \left(\frac{C}{C_s} \right)^M \quad (4)$$

where η_{cs} is the apparent viscosity at a shear rate $\dot{\gamma}$ and concentration C_s , and

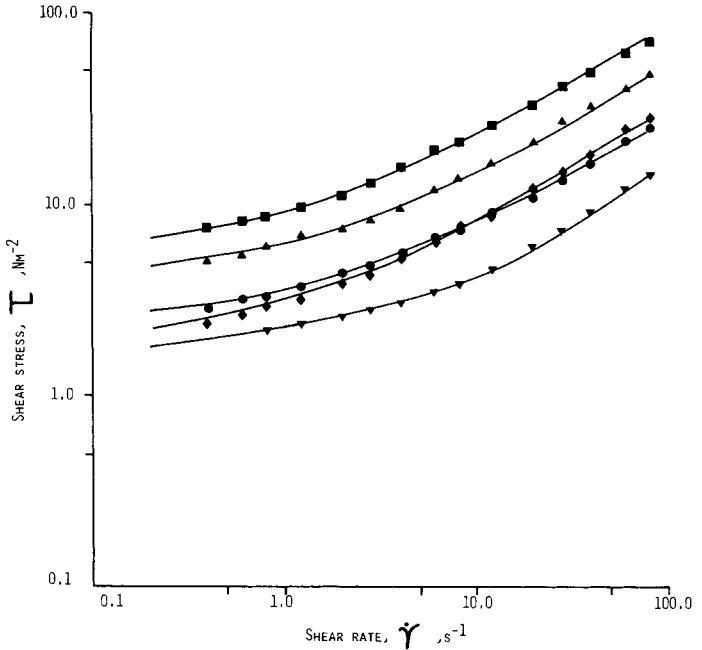


Fig. 3. Plots of log of shear stress as function of log of shear rate for various pastes: (■) 6.14% w/w Gamut; (●) 5.50% w/w Hilgendorf; (▼) 6.04% w/w Karamu; (▲) 7.1% w/w Gamut; (◆) 6.49% w/w Karamu.

K_2 and M are constants. The fit of the logarithmic form of this expression to the results, which are presented in part in Table I, gives a correlation coefficient of 0.99; similar values of the correlation coefficient were obtained at other shear rates. Although eq. (4) unifies paste viscosity data more successfully than eq. (3), the relationship is less general, as it requires knowledge of η_{cs} for each starch variety and set of paste preparation conditions.

At low shear rates ($0.4\text{--}10\text{ s}^{-1}$), a yield stress is evident (see the typical results in Fig. 3), and pastes conform to the equation

$$\tau = \tau_0 + K_3 \dot{\gamma}^n \quad (5)$$

where τ is the shear stress and τ_0 is the yield stress. The values of τ_0 , K_3 , and n depend on the concentration and variety of starch and on paste preparation conditions. A general expression for the yield stress was found which is analogous to that established previously for the dynamic mechanical behavior of wheat starches⁶:

$$\tau_0 = \tau_c [(C - C_s)(S)]^{K_4} [P]^N \quad (6)$$

where τ_c , K_4 , and N are constants and P is the number fraction of large granules in the starch. Since the sensitivity of the viscometer used was such that C must be greater than $1.1C_s$ to detect a yield stress, it is not clear whether this equation applies when the starch concentration is decreased below this limit. Statistical analysis of the application of the logarithmic form of eq. (6) to the experimental data, which is shown in part in Table I, was found to give a correlation coefficient of 0.93, the values of $\log \tau_c$, K_4 , and N being -0.05 , 1.33 , and -0.794 , respectively. Without the term for the number fraction of large granules, the correlation

coefficient is reduced to 0.64. The inverse relationship between yield stress and the number fraction of large granules is consistent with the work of Erdi et al. on polymeric microcrystal gels.⁷

The results of the present study show that under steady shear conditions, the properties of wheat starch pastes can be related to two parameters, namely, the volume the gel particles would occupy when close packed if excess solvent were present, and the size distribution of the particles. Hence, in this respect the behavior of wheat starch pastes is similar to that of other dispersed gel systems. The values of the apparent viscosity and yield stress depend on the source of starch, since this affects particle swelling volumes and size distributions. Paste preparation conditions influence rheological properties since they alter the volume occupied by gelatinized granules. The lack of theory dealing with viscoelastic particles in suspensions,¹⁴ combined with the fact that starch pastes have complicated structures, precludes a more fundamental interpretation of these results.

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