

Granule size and rheological behavior of heated tapioca starch dispersions

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Abstract

Rheological behavior of starch dispersions is strongly influenced by the granules. From granule size data of 2.6% tapioca starch dispersions (STDs) isothermally heated in the range 61°C–74°C obtained by laser diffraction, the maximum average granule size was found to be $3.7 \times$ the raw starch granule mean diameter. Compared to corn and cowpea starches, heated tapioca starch granules had a higher initial maximum diameter that was less dependent on the heating temperature, and the ratio of the heated to unheated starch granule diameter ratio contributed to a higher increase of notional volume fractions (cQ) of the tapioca STDs. Shear-thickening flow behavior was observed in STDs heated at 61°C for 1, 5 and 15 min, and shear-thinning in all other dispersions. The Casson and Quemada models described well the apparent viscosity versus shear rate data of the STDs at different notional volume fractions. The power law consistency index increased exponentially with granule size reflecting increase in dispersion viscosity. The relative viscosity vs cQ data of the STDs followed Quemada's structural model. A modified Cox–Merz rule described the relationship between complex viscosity and apparent viscosity of a 4% dispersion. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Granule size; Rheological behaviour; Tapioca starch dispersions

1. Introduction

In excess water content, starch granules begin to swell and imbibe water when energy is applied to break some of the intermolecular hydrogen bonds in amorphous regions. After a critical temperature is reached, the water molecules disrupt hydrogen bonding and penetrate the granules, and the starch granules swell. Heating of starch dispersions (STDs) also results in loss of radial orientation of the micelles and birefringence. Further heating of the starch suspension results in more loosening of the micelle's network, enhanced water absorption, and enlarged granule size.

In corn and cowpea (Rao et al., 1997), and cross-linked waxy maize (Chamberlain, 1996) STDs, as expected, increase in the average starch granule size resulted in increase in the notional volume fraction, cQ , where c is the concentration of starch (g dry starch per g dispersion) and Q is the swelling power of the starch granules (g swollen starch per g dry starch) (Christianson and Bagley, 1983), as well as in the power law (Eq. 1) consistency index of the STDs.

$$\sigma = K \dot{\gamma}^n \quad (1)$$

where σ is the shear stress, $\dot{\gamma}$ is the shear rate, n is the flow behavior index (dimensionless), and K is the consistency index (Pa s^n). In addition, the yield stress of gelatinized STDs, determined using the Casson model (Eq. 2), increased with cQ (Christianson and Bagley, 1984; Rao et al., 1997).

$$(\sigma)^{0.5} = (\sigma_{0c})^{0.5} + (\eta_{\infty} \dot{\gamma})^{0.5} \quad (2)$$

Usually, σ_{0c} and η_{∞} are calculated from the intercept (K_{0c}) and slope (K_c) of a $\dot{\gamma}^{0.5}$ versus $\sigma^{0.5}$ plot, respectively.

Quemada et al. (1985) proposed a rheological model (Eq. 3) for dispersed systems based on the zero-shear, η_0 , and infinite-shear, η_{∞} , viscosities, and a structural parameter, λ , dependent on the-shear rate (Eq. 4):

$$\eta = \frac{\eta_{\infty}}{\left\{ 1 - \left[1 - \left(\frac{\eta_{\infty}}{\eta_0} \right)^{0.5} \right] \lambda \right\}^2} \quad (3)$$

$$\lambda = \frac{1}{[1 + (t_c \dot{\gamma})^{0.5}]} \quad (4)$$

The time constant t_c is related to the rate of aggregation of particles due to Brownian motion. For highly concentrated dispersed systems, η_{∞} will be much lower than η_0 , so that $(\eta_{\infty}/\eta_0) \ll 1$ and the dispersion may have a yield stress, and Eq. (3) reduces to the Casson model (Eq. 2) (Tiu et al., 1990)

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with the Casson yield stress, $\sigma_{0c} = (\eta_{\infty}/t_c)$. The generalized Casson model, written in terms of either the shear stress (Eq. 5) or the apparent viscosity (η_a) (Eq. 6), was used to examine rheological behavior of cocoa dispersions ranging from only shear-thinning to shear-thinning plus yield stress (Fang et al., 1996).

$$(\sigma)^m = (\sigma_{0c})^m + (\eta_{\infty}\dot{\gamma})^m \quad (5)$$

$$(\eta_a)^m = (\sigma_{0c}/\dot{\gamma})^m + (\eta_{\infty})^m \quad (6)$$

The Cox–Merz (Cox and Merz, 1958) rule (Eq. 7) relating dynamic viscosity (η^*) and η_a was found to be applicable to homogeneous dispersions, but not to heterogeneous dispersions (Mills and Kokini, 1984; da Silva et al., 1993); for the latter, a modified Cox–Merz rule (Eq. 8) has been used.

$$\eta^*(\omega) = \eta(\dot{\gamma})|_{\omega=\dot{\gamma}} \quad (7)$$

$$\eta^*(\omega) = C[\eta_a(\dot{\gamma})]^\alpha|_{\omega=\dot{\gamma}} \quad (8)$$

where C and α are constants to be determined.

Two objectives of this study were to investigate the influence of granule size on the values of cQ , and on the rheological properties of gelatinized 2.6 w/w% tapioca STDs and tapioca STDs with concentrations from 1.3 to 2.3 w/w% in terms of the Casson–Quemada and power law models. A third objective was to study the relationship between η^* and η_a of tapioca starch dispersions, including applicability of the Cox–Merz rule. Lastly, when possible, data on granule size and rheological behavior on tapioca STDs were compared with those on other starches.

2. Experimental

2.1. Starch

The tapioca starch used (Batch No. CEB8015, National Starch and Chemical Co.) had 11% moisture, calculated from 11 replicates (5 g sample dried to a constant weight at 105°C), and 27.5% (dry weight basis) amylose, determined using a rapid colorimetric method (Williams et al., 1970).

2.2. Differential scanning calorimetry (DSC)

DSC (Model 2910, TA Instruments) was used to determine the gelatinization temperature range of 10% and 20% tapioca STDs. After hydration for 2 h at room temperature, approximately 10 mg of well-stirred STD was sealed in a DSC hermetic aluminum pan. The samples were heated from 40 to 100°C at a heating rate of 5°C min⁻¹ with a sealed empty pan as the reference. The concentration of starch sample in the DSC pan was determined by puncturing the pan's lid and drying the contents in a 100°C oven to a constant weight.

2.3. Starch pasting procedure

To obtain isothermal conditions rapidly, the procedure of Okechukwu and Rao (1995) was used to prepare the STDs. The pasting temperatures (T_p) used were: 61°C, 67°C, 70°C, and 74°C. The temperature of the unheated dispersion T_s (<60°C) was measured and T_w was calculated as:

$$40T_s + 310T_w = 350T_p \quad (9)$$

Isothermal conditions were maintained by means of a circulating water bath (Fisher Isotemp Circulator) and a copper–constantan thermocouple was used to monitor the temperature. The dispersion was mildly agitated using a magnetic spin bar (5.5 × 1.3 cm) at a low fixed stirring rate that was just enough to keep the starch granules suspended. About 50 ml of gelatinized starch were withdrawn into test tubes at various times that were immediately immersed in an ice bath to quickly cool the dispersion to room temperature in about 1 min when aliquots were taken for granule size scan and rheometry.

2.4. Flow characteristics

Steady shear data on the STDs were determined using a Carri-Med CSL² 100 rheometer (TA Instruments) with a cone (acrylic, 2°, 6 cm diameter) and plate geometry. Each sample was sheared at 20°C from 0.01 Pa shear stress to a maximum shear stress that depended on sample consistency and back to 0.01 Pa. The shearing time was 5 min each for the ascending and descending shear cycles. Only the descending shear data were analyzed for the flow behavior.

2.5. Complex viscosity (η^*) and apparent viscosity (η_a) of 4% dispersion

Dynamic rheological parameters of 2.6% dispersions were too low to be considered reliable over a wide range of oscillatory frequencies. Therefore, η^* and η_a data were obtained at 20°C on 4% STDs that were heated at 70°C for 5 and 30 min using the cone and plate geometry described above. Torque sweep tests were performed first from 0.6 to 40 Pa at 31.4 rad s⁻¹ to determine the linear viscoelastic range. Frequency sweep tests were conducted at 3% strain and 0.1–30 Hz (188.5 rad s⁻¹); the steady shear experiments were conducted over a similar shear rate range (0.6–180 s⁻¹); a shearing time of 5 min was used in the steady shear experiments.

2.6. Granule size

The granule size distribution of the gelatinized starch dispersions was determined using a laser diffraction particle size analyzer (Coulter LS 130, Coulter Corporation) as described earlier (Okechukwu and Rao, 1995).

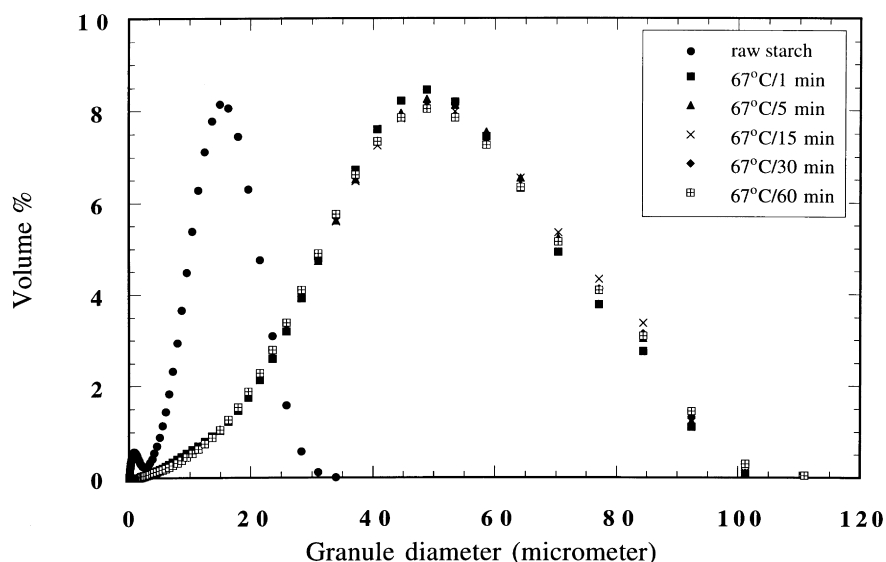


Fig. 1. Granule size distribution of 2.6% tapioca starch dispersions heated at 67°C and of raw tapioca starch granules.

2.7. Notional volume fraction of starch granules

The notional volume fraction of the gelatinized starch granules, cQ , was determined as described earlier (Okechukwu and Rao, 1995). The total soluble solids was determined by drying the supernatant to a constant weight in a 105°C hot air oven.

2.8. Supernatant viscosity

A glass capillary viscometer (size no. 100, Cannon Instrument Co.) was used to obtain the supernatant viscosity at 20°C. The viscometer was first calibrated using cooled boiled distilled water.

3. Results and discussion

3.1. Gelatinization temperature range with DSC

DSC thermograms (not shown here) of 10% and 20% tapioca STDs heated from 40°C to 100°C at 5°C min⁻¹ revealed a single endotherm with the onset, peak, and concluding gelatinization temperatures: 60°, 67°, and 75°C, respectively. In agreement with previous studies (Leach, 1965; Balagopalan et al., 1988; Roos, 1995), gelatinization of tapioca STDs occurred over a 15°C range. The gelatinization temperature range determined with DSC was useful in the selection of heating temperatures of the STDs.

3.2. Starch granule size distribution

The granule size distribution curve of raw hydrated starch (Fig. 1) was left-skewed and platykurtic with the size range of 0.1–34 μm. A slight shoulder at the low end of the size distribution curve represents small granules or granule fragments that may have been generated during the starch

production process. The volume average diameter of the raw hydrated starch granules was 12.9 μm with a standard deviation of 6.8 μm. Upon heating at a specific temperature, the size distribution curves shifted to a wider range of about 0.4–100 μm with increasing mean granule sizes that depended on heating times, and they were right skewed and platykurtic. Fig. 1 also contains granule size distribution data of dispersions heated at 67°C. Similarly shaped distributions were observed for the 2.6% tapioca starch dispersion heated at the other temperatures. The maximum average granule size of around 48 μm (S.D. ≈ 22 μm) was found in the starch dispersion heated at 70°C for 5 min.

Heating the tapioca STDs at 75°C and 80°C resulted in a decrease in the average granule diameters; in tapioca STDs heated at 75°C for 5 min and 80°C for 5 min, they were 43.6 and 40.5 μm, respectively. Sustained heating at the lower temperatures also reduced the average granule diameter. For example, STDs held at 61°C for 240, 300, and 540 min had average granule diameters of 43.5, 42.6 and 41.0 μm, respectively. This trend was also observed when the starch dispersion was heated at 67°, 70°, and 74°C. The reduction in starch granule size was accompanied by an increase in the amount of total soluble solids in the continuous phase from 0.8% in a dispersion heated at 67°C for 60 min to 0.9% at 67°C for 180 min, and 1.4% at 75°C for 5 min.

In tapioca STDs with intact granules, the maximum mean diameter (D_{eT}) increased with increasing gelatinization temperature (T):

$$D_{eT} = A \exp(A'T) \quad (10)$$

where $A = 22.5 \mu\text{m}$, $A'' = 0.011^\circ\text{C}^{-1}$, and $R^2 = 0.968$ over the temperature range 61–74°C. For corn starch (Okechukwu and Rao, 1995) the corresponding values were: $A = 8.1 \mu\text{m}$, $A'' = 0.019^\circ\text{C}^{-1}$, and $R^2 = 0.97$ ($T = 70$ – 90°C) and for cowpea starch (Okechukwu and Rao, 1996) $A = 18.1 \mu\text{m}$, $A' = 0.016^\circ\text{C}^{-1}$, and $R^2 = 0.968$ ($T =$

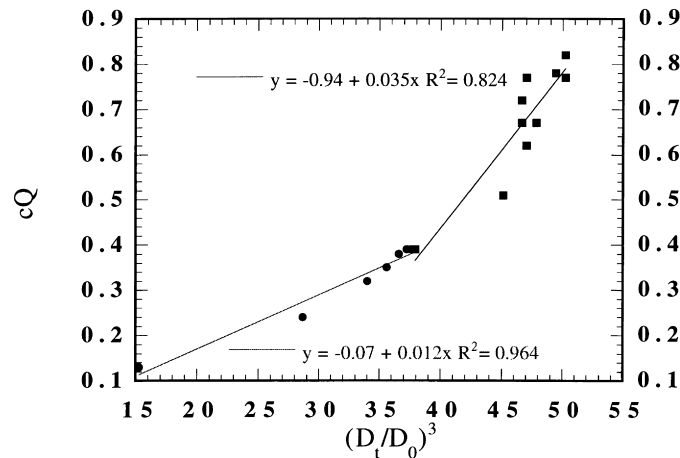


Fig. 2. Variation of notional volume fraction (cQ) of swollen starch as a function of the cube of the starch granule diameter ratio: $(D_t/D_0)^3$ for 2.6% tapioca starch dispersions.

70–86°C). The highest A value and the lowest A' value indicate that, compared to corn and cowpea starches, tapioca starch granules had a higher initial D_{eT} and that D_{eT} was less dependent on heating temperature.

3.3. Notional volume fraction (cq)–granule size relationship

Linear relationships were found between cQ and $(D_t/D_0)^3$ over a wide range of the latter for heated STDs of corn and cowpea (Rao et al., 1997), and cross-linked waxy maize starches (Chamberlain, 1996). For the tapioca STDs two linear relationships provided a better fit of the data: one for values of $(D_t/D_0)^3$ from about 15 to 40 and the other from 40 to about 50 (Fig. 2):

$$cQ = -0.07 + 0.012(D_t/D_0)^3 \quad (11)$$

$$cQ = -1.4 + 0.044(D_t/D_0)^3 \quad (12)$$

In determination of Q , centrifuging and siphoning off the top layer of supernatant fluid are not precise procedures that contributed to the spread of the cQ data in Fig. 2. For tapioca starch dispersions, a large increase in cQ at high values of $(D_t/D_0)^3$ is noteworthy. In both equations, the small physically meaningless negative intercepts obtained were due to errors in extrapolation of the data. While linear relationships were used between cQ and $(D_t/D_0)^3$ to allow for comparison with corn and cowpea starch dispersions, a single exponential equation described well the tapioca starch dispersion data:

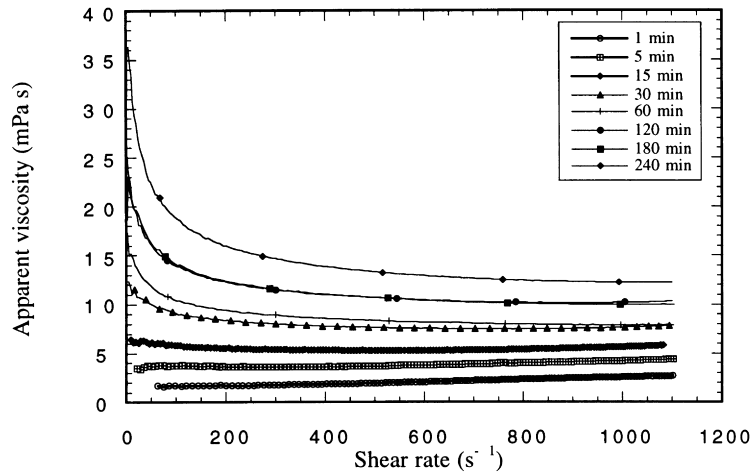
$$cQ = 0.0535 \exp[0.0535(D_t/D_0)^3], \quad R^2 = 0.962 \quad (13)$$

The maximum mass fraction of gelatinized 2.6% tapioca starch dispersion was 0.82, which corresponded to a value of (D_t/D_0) of around 3.7. For the purpose of comparison, the values of intercept, slope, and R^2 for other heated STDs in Eq. (11) were: 0.16, 0.011, and 0.86 for 2.6% unmodified corn starch (Okechukwu and

Rao, 1995), 0.09, 0.013, and 0.84 for 2.6% cowpea starch (Okechukwu and Rao, 1996), and 0.23, 0.0015, 0.98 for 2.6% cross-linked waxy maize starch (Chamberlain, 1996), respectively. Because tapioca starch had a higher value of slope, especially at high $(D_t/D_0)^3$ values, the starch granule diameter ratio contributed to a higher increase of cQ of tapioca STDs.

3.4. Flow behavior

Shear-thickening behavior was observed in STDs gelatinized at 61°C up to 15 min (Fig. 3). Starch–water systems exhibit shear-thickening behavior when the starch granules are rigid enough to resist shear and the concentrations are high enough for particle crowding to occur (Christianson and Bagley, 1983). Shear-thickening behavior was observed in heated STDs of wheat (Bagley and Christianson, 1982), native and cross-linked waxy maize (Dail and Steffe, 1990a, 1990b), corn (Okechukwu and Rao, 1995), cowpea (Okechukwu and Rao, 1996), and cross-linked waxy maize (Chamberlain, 1996). In the lower part of Fig. 3, it can be seen that the shear-thickening behavior of the dispersions heated at 5 and 15 min was preceded by shearthinning behavior. The critical shear rate ($\dot{\gamma}_c$) at which the transition from shear-thinning to shear-thickening flow behavior occurred was about 300 s^{-1} for the dispersion heated for 5 min and about 500 s^{-1} for that heated for 15 min. Because of the low magnitude of viscosity of the dispersion heated for 1 min, the magnitude of $\dot{\gamma}_c$ could not be established. Nevertheless, the transition from shear-thinning to shear-thickening flow behavior occurred at high shear rates. Values of $\dot{\gamma}_c$ for a 2.6% cowpea starch dispersion heated at 67°C for 0.5–90 min were also high, in the range 337 – 372 s^{-1} (Okechukwu and Rao, 1996). With increase in heating temperature and time, the starch granules softened and became more deformable to shear forces resulting in shear-thinning behavior.



Apparent viscosity versus shear rate of 2.6% tapioca starch dispersions heated at 61°C

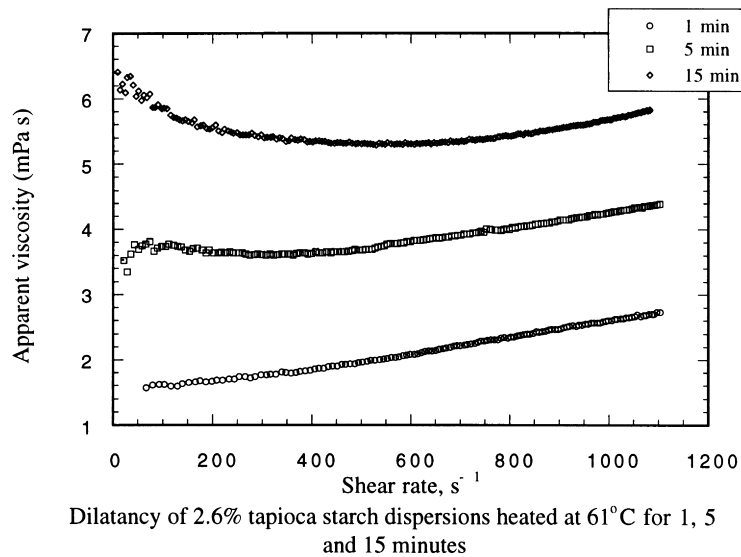


Fig. 3. Apparent viscosity versus shear rate behavior of 2.6% tapioca starch dispersions gelatinized at 61°C.

3.5. Casson–Quernada models for shear-thinning dispersions

For the shear-thinning dispersions that also exhibited yield stress, the generalized Casson model (Eq. 6) with the exponent $m = 0.25$ described better the η_a vs $\dot{\gamma}$ data than the traditional exponent $m = 0.5$. Values of $m = 0.10$ – 0.50 were tested and the exponent $m = 0.25$ provided best fits to rheological data on most of the studied dispersions. The difference between predicted values with $m = 0.25$ and $m = 0.50$ can be seen in Fig. 4 that contains η_a versus $\dot{\gamma}$ data on two dispersions and the predicted η_a values with $m = 0.25$ and $m = 0.5$. In general, the yield stress values obtained using $m = 0.25$ from nonlinear regression were lower than

those using $m = 0.5$ from linear regression analysis of $\dot{\gamma}^{0.5}$ vs $\sigma^{0.5}$ data (Table 1). The estimated values of σ_{0c} and η_{∞} increased with dispersion heating temperature and time.

Increase in the volume fraction of solids in a starch dispersion can be achieved by either increasing the concentration of the solids or through volume expansion of the solids. η_a vs $\dot{\gamma}$ data of dispersions with starch concentrations 1.3%, 1.6%, 2.0%, and 2.3% that were heated at 74°C for 1 min are shown in Fig. 5. While the data of the 1.3% and the 1.6% dispersions exhibited no yield value, the other dispersions clearly exhibited yield stresses. The progression from only shear-thinning rheological behavior to shear-thinning plus yield stress behavior as the starch concentration, hence cQ of granules, was increased is noteworthy. In Fig.

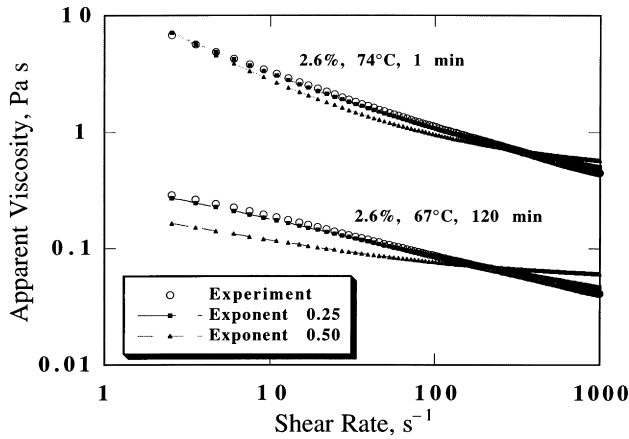


Fig. 4. Apparent viscosity (η_a) versus shear rate ($\dot{\gamma}$) data on two dispersions and the Casson model predicted η_a values with $m = 0.25$ and $m = 0.5$. Values predicted by the Casson model with exponent of $m = 0.25$ were closer to the experimental data.

5, the Quemada model (Eq. 3) described well the η_a versus $\dot{\gamma}$ data of the 1.30% dispersion ($\eta_0 = 0.346$ Pa s, $\eta_\infty = 0.070$ Pa s, and $t_c = 0.021$ s; $R^2 = 0.97$) and of the 1.6% dispersion ($\eta_0 = 2.161$ Pa s, $\eta_\infty = 0.115$ Pa s, and $t_c = 0.014$ s; $R^2 = 1.00$), while the generalized Casson model (Eq. 6) with $m = 0.25$ described well the data of the 2.0% dispersion ($\sigma_{0c} = 0.610$ Pa, $\eta_\infty = 0.100$ Pa s; $R^2 = 1.00$) and of the 2.3% dispersion ($\sigma_{0c} = 1.370$ Pa, $\eta_\infty = 0.125$ Pa s; $R^2 = 1.00$).

3.6. Power law model

Because of the relatively low magnitudes of yield stresses, the flow behavior of the dispersions was also described by the simple power law model (Eq. 1); an additional reason for using the power law model was to compare the power law parameters of the tapioca starch STDs with those of corn, cowpea, and cross-linked waxy maize starches (Rao et al., 1997; Chamberlain, 1996). The consistency index (K) and flow behavior index (n) were calculated using a power fit function (Kaleidagraph) in the shear rate range of 200–1100 s^{-1} . With increase in the gelatinization temperature

and time, K increased while n decreased indicating increase in shear-thinning behavior.

The dispersed phase characteristics (starch concentration, granule size and size distribution, granule shape, swelling pattern of the starch, and granule rigidity) affect the rheological behavior of a STD (Eliasson, 1986). Fig. 6 shows the relationship between the granule diameter ratio (D_t/D_0) and the consistency index (K) of gelatinized 2.6% tapioca STDs, that can be expressed by the equation:

$$K = K_0 \exp \left[\epsilon \left(\frac{D_t}{D_0} \right) \right] \quad (14)$$

where K_0 and ϵ are empirical constants. K increased gradually at the beginning and rapidly as the granule diameter ratio approached its maximum value. At $(D_t/D_0) = 3.4$, values of K started to increase rapidly. The estimated values of K_0 , ϵ , and R^2 for the 2.6% tapioca STDs were 6.14×10^{-10} (mPa sⁿ), 7.40, and 0.90, respectively; the corresponding values for 2.6% corn starch were: $K_0 = 2.07 \times 10^{-5}$ (mPa sⁿ), $\epsilon = 3.69$, and $R^2 = 0.99$ (Okechukwu and Rao, 1995), for 2.6% cowpea starch were: $K_0 = 2.40 \times 10^{-5}$ (mPa sⁿ), $\epsilon = 4.84$, and $R^2 = 0.96$ (Okechukwu and Rao, 1996), and 2.6% cross-linked waxy maize starch were: $K_0 = 2.13 \times 10^{-7}$ (mPa sⁿ), $\epsilon = 3.36$, and $R^2 = 0.92$ (Chamberlain, 1996). The higher value of ϵ for tapioca starch indicates that, compared to corn, cowpea and cross-linked waxy maize starches, the starch granule diameter ratio had the highest influence on the consistency index (K) of the tapioca starch dispersions.

3.7. Notional volume fraction vs relative viscosity

The relative viscosity of the gelatinized 2.6% tapioca STDs was calculated using Eq. (14):

$$\eta_r = \frac{\eta_\infty}{\eta_s} \quad (15)$$

where η_r is the relative viscosity, η_∞ is the Casson viscosity (mPa s) (Table 1), and η_s is the viscosity (mPa s) of the supernatant determined at 20°C. The η_r values of tapioca STDs strongly depended on their volume fraction and there was considerable scatter in the values as a result of

Table 1

Notional volume fraction (cQ), Casson yield stress [σ_{0c} (Pa) $m = 0.25$ and $m = 0.50$] and infinite shear viscosity [η_∞ (mPa s)], viscosity of supernatant [η_s (mPa s)], and relative viscosity (η_r) of tapioca starch dispersions.

Dispersion ^a	cQ	σ_{0c} , $m = 0.25$	η_∞ , $m = 0.25$	σ_{0c} , $m = 0.50$	η_s	η_r
61°C, 240 min	0.39	0.002	7.2	0.11	1.53	4.7
67°C, 5 min	0.62	0.120	12.1	1.13	2.02	6.0
67°C, 15 min	0.67	0.071	27.0	1.48	2.48	10.9
67°C, 30 min	0.72	0.181	13.9	1.64	2.60	5.3
67°C, 60 min	0.77	0.188	14.3	1.78	2.76	5.2
70°C, 5 min	0.77	0.078	30.1	1.96	1.97	15.3
70°C, 15 min	0.82	0.098	32.1	2.10	2.82	11.4
74°C, 1 min	0.78	2.77	139.45	2.25	2.85	48.9

^aHeating temperature and time.

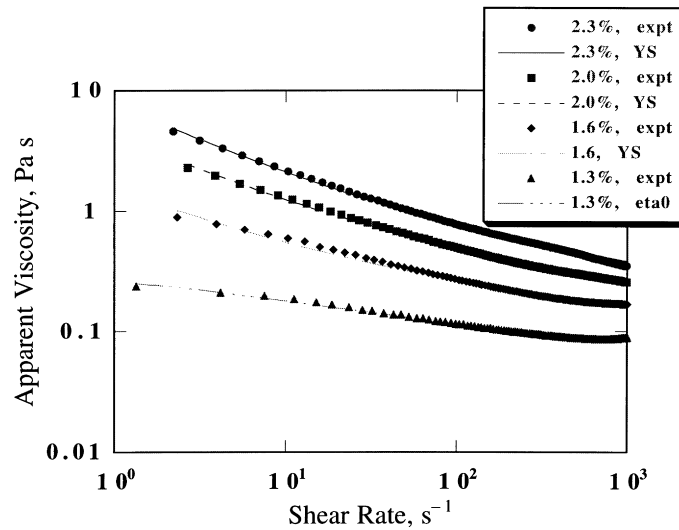


Fig. 5. Apparent viscosity (η_a) versus shear rate ($\dot{\gamma}$) data of dispersions with starch concentrations 1.3%, 1.6%, 2.0%, and 2.3% that were heated at 74°C for 1 min. The rheological behavior progressed from shear-thinning to shear-thinning plus yield stress as the starch concentration, hence the notional volume fraction of granules, was increased.

uncertainties in estimating η_∞ and cQ values (Fig. 7). The line in Fig. 7 represents values predicted by the model (Eq. 16) of Quemada et al. (1985) with the structural parameter $k = 1.80$:

$$\eta_r = [1 - 0.5k(cQ)]^{-2} \tag{16}$$

Quemada et al. (1985) reported values of k in the range 2.50–3.82 for dispersions of rigid solids, and 1.70–1.85 for red blood suspensions. Because heated starch granules are deformable, the value $k = 1.80$ of red blood cells was selected for estimating the η_r values of tapioca STDs. Given that the Krieger–Dougherty model’s predictions were substantially different than experimental η_r values of STDs (Ellis et al., 1989;

Noel et al., 1993; Tattiyakul, 1997), the reasonable applicability of Eq. (15) (Quemada et al., 1985) to tapioca STDs is noteworthy. However, the model of Quemada et al. (1985) is a phenomenological model with a structural parameter, while that of Krieger–Dougherty is based on the intrinsic viscosity of a rigid sphere.

3.8. Dynamic rheological data and relationship between η^* and η_a of 4% dispersion

Fig. 8 is a log–log plot of η^* and η_a of a 4% dispersion heated at 70°C for 30 min against shear rate ($\dot{\gamma}$) and dynamic frequency [ω (rad s⁻¹)], respectively, that were described by eqns (17), (18), respectively.

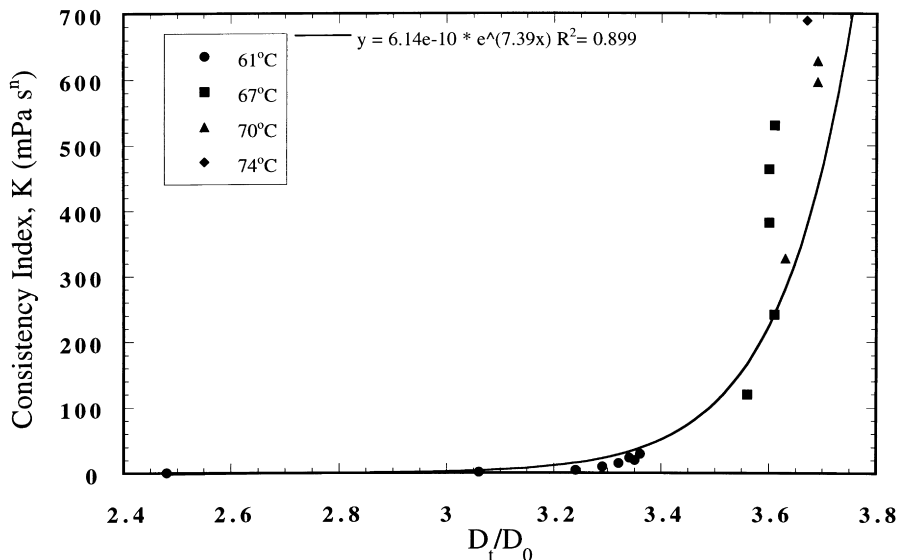


Fig. 6. The effect of starch granule size (D_t/D_0) on the consistency index (K) of gelatinized 2.6% tapioca starch.

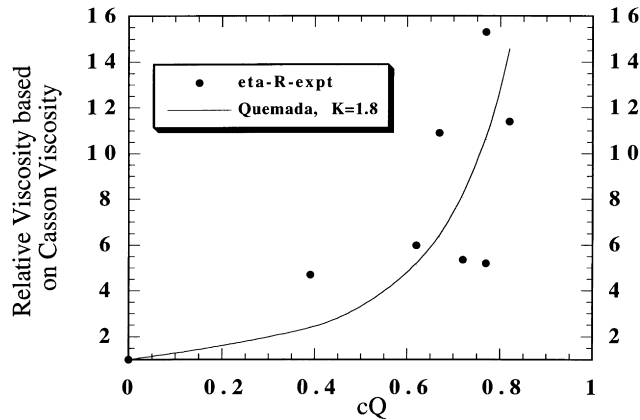


Fig. 7. Relative viscosity versus notional volume fraction of tapioca starch dispersions; the line represents values predicted by the model of Quemada et al. (1985) with $k = 1.80$.

$$\eta^* = 18.32\omega^{-0.74} \quad R^2 = 1.00 \quad (17)$$

$$\eta_a = 8.36\dot{\gamma}^{-0.73} \quad R^2 = 1.00 \quad (18)$$

The modified Cox–Merz rule (Eq. 8) parameters C and α were found to be 2.24 and 1.04, respectively, so that the relationship between η^* and η_a was:

$$\eta^*(\omega) = 2.24[\eta_a(\dot{\gamma})]^{1.04}|_{\omega=\dot{\gamma}} \quad R^2 = 1.00 \quad (19)$$

This relationship is useful for calculation of apparent viscosity data from complex viscosity data or vice versa.

For the 4% dispersion heated at 70°C for 5 min, values of η_a decreased with $\dot{\gamma}$, but those of η^* increased with ω after an initial decrease (Fig. 9) in a manner similar to the shear-thinning to shear-thickening transition behavior of the 2.6% tapioca starch dispersion heated at 61°C for 5 and 10 min; the critical frequency (ω_c) at which the shear-thinning to

shear-thickening transition occurred was about 100 rad s^{-1} . In comparison to $\dot{\gamma}_c$ values ($300\text{--}500 \text{ s}^{-1}$) for shear-thinning to shear-thickening flow behavior of 2.6% cowpea starch dispersions (Okechukwu and Rao, 1996), the value of ω_c is much lower. It is possible that for the η_a versus $\dot{\gamma}$ data of the 4% tapioca STD heated at 70°C for 5 min, the shear-thinning to shear-thickening transition occurred at a high shear rate. However, because the objective was to examine applicability of the Cox–Merz relationship, values of $\dot{\gamma}$ higher than 180 s^{-1} were not used.

Because $\eta^* = (G^*/\omega)$ and $G^* = \sqrt{(G')^2 + (G'')^2}$, further examination of G' and G'' of the two dispersions (Fig. 10) revealed that whereas both G' and G'' of the 70°C for 30 min dispersion and G' of the 70°C for 5 min dispersion increased gradually with ω in a convex up manner, G' of the 70°C for 5 min dispersion increased dramatically with ω in a convex down manner. The above described dynamic rheological behavior of both dispersions was reproduced in several replicate rheological measurements, so that it appears that the shear-thickening behavior of η^* of the 70°C for 5 min dispersion was the result of dramatic increase in elastic behavior of the dispersion at the small strain ($\gamma = 3\%$) values used. At the shear rates ($d\gamma/dt$) used to obtain η_a data on the same 70°C for 5 min 4% dispersion, shear-thickening was not observed probably because shear-thinning to shear-thickening transition occurred at higher shear rates than used; Okechukwu and Rao (1996) observed that such transition occurred in cowpea starch dispersions at about 340 s^{-1} . Given that heated starch dispersions were found to exhibit shear-thinning and shear-thickening (Bagley and Christianson, 1982; Okechukwu and Rao, 1995, 1996), as well as time-dependent shear-thickening (Dintzis and Bagley, 1995; Chamberlain, 1996; da Silva et al., 1997) flow behavior, perhaps it should not be surprising that shear-thickening should be seen in η^* versus ω data.

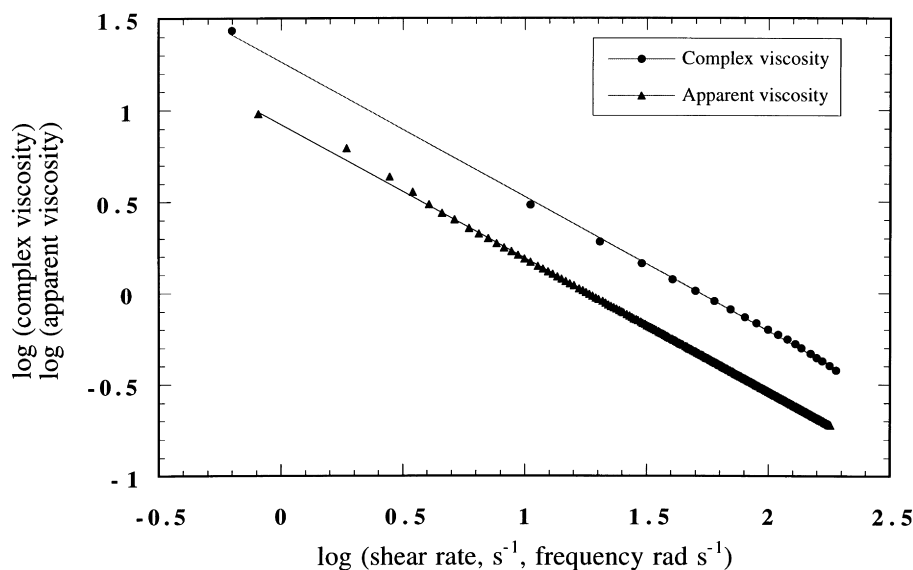


Fig. 8. Plot of complex viscosity (η^*) and apparent viscosity (η_a) of 4% tapioca starch dispersion heated at 70°C for 30 min against shear rate and dynamic frequency, respectively. A modified Cox–Merz rule described the relationship between η^* and η_a .

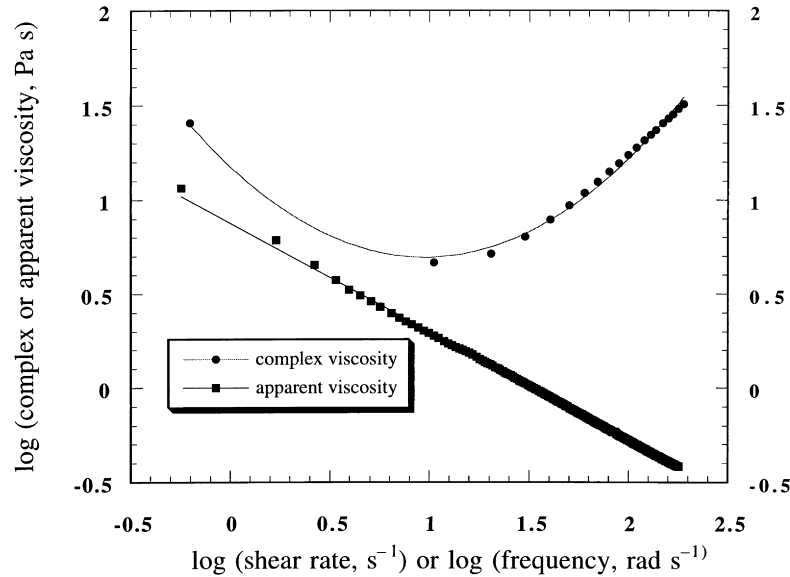


Fig. 9. Plot of complex viscosity (η^*) and apparent viscosity (η_a) of 4% tapioca starch dispersion heated at 70°C for 5 min against shear rate and dynamic frequency, respectively. The η^* data showed shear-thickening behavior.

4. Conclusions

Swelling of tapioca STDs was temperature and time dependent. Heating the starch dispersion at elevated temperatures and/or prolonged times resulted in granule rupture and leaching of the granule contents. The heated 2.6% tapioca STDs showed shear-thickening flow behavior in the early stages of gelatinization and shear-thinning behavior at higher heating temperatures or prolonged times. The Casson model with exponent 0.25 and the Quemada model described well the flow behavior of heated tapioca STDs with or without yield stresses, respectively. The power law consistency index (K) was found to increase exponentially with increasing mean granule size. A modified Cox–Merz model described the relationship between apparent and complex viscosities of a 4% dispersion heated at 70°C for 30 min. However, η^* vs ω data of a 4% dispersion heated at 70°C for 5 min, exhibited shear-thickening that was mainly due to a large increase in the dispersion’s storage modulus.

Nomenclature

A, A'	constants in Eq. (10)
c	starch concentration (w/w)
c	constant in Eq. (8)
cQ	starch granule mass fraction
D_t	starch granule diameter at any time (m)
D_0	mean diameter of ungelatinized granules (m)
D_{eT}	maximum mean diameter (m)
G'	storage modulus (Pa)
G''	loss modulus (Pa)
G^*	complex modulus $G^* = \sqrt{(G')^2 + (G'')^2}$ (Pa)

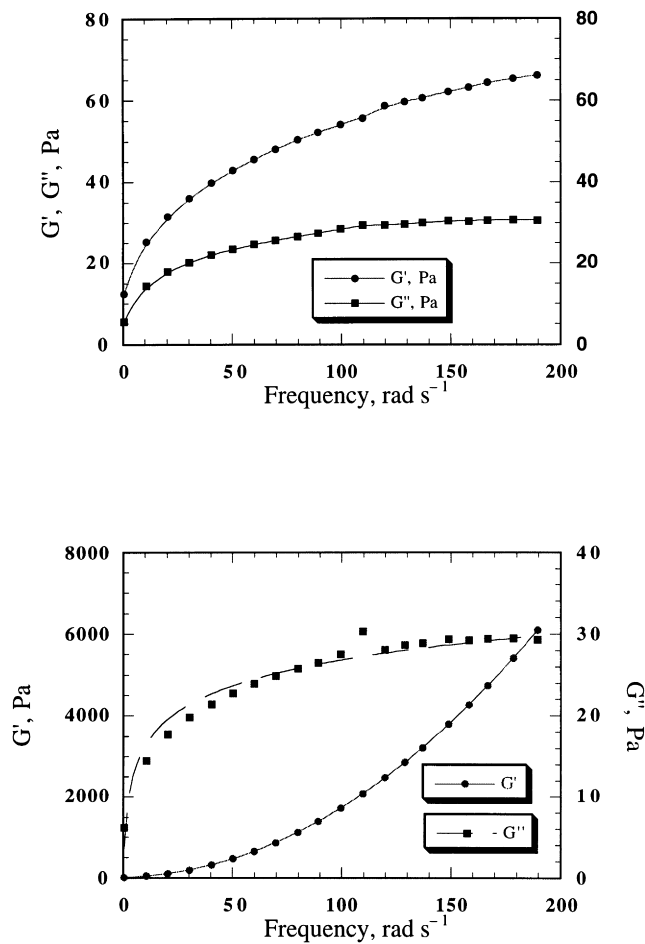


Fig. 10. Plot of G' and G'' versus dynamic frequency of 4% tapioca starch dispersions heated at 70°C for 30 min (top) and at 70°C for 5 min (bottom).

k	structural parameter in Eq. (15) (dimensionless)
K	consistency index (Pa s^n)
K_c	slope of a $\dot{\gamma}^{0.5}$ vs $\sigma^{0.5}$ plot
K_0	constant in Eq. (13) (Pa s^n)
K_{0c}	intercept of a $\dot{\gamma}^{0.5}$ vs $\sigma^{0.5}$ plot
n	flow behavior index (dimensionless)
Q	mass of heated starch granules per unit weight of dry starch
STD	starch dispersion
t_c	time constant in Eq. (4) (s)
T	temperature ($^{\circ}\text{C}$)

Greek letters

α	constant in Eq. (8)
γ	strain (dimensionless)
$\dot{\gamma}$	shear rate (s^{-1})
$\dot{\gamma}_c$	critical shear rate at which shear-thickening begins (s^{-1})
ϵ	empirical constant in Eq. (13) (dimensionless)
λ	structural parameter (dimensionless)
η_a	apparent viscosity (Pa s)
η_{Ca}	Casson viscosity (Pa s)
η_0	zero shear viscosity (Pa s)
η_r	relative viscosity (dimensionless)
η_s	viscosity of continuous phase (Pa s)
$\eta_{\infty} = (K_c)^2$	infinite shear viscosity (Pa s)
η^*	complex viscosity (Pa s)
σ	shear stress (Pa)
$\sigma_{0c} = (K_{0c})^2$	Casson yield stress (Pa)
ϕ	volume fraction, $\phi = cQ$
ϕ_m	maximum volume fraction
ω	dynamic frequency (rad s^{-1})
ω_c	critical frequency at which shear-thickening begins (rad s^{-1})

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