

Rheological and structural properties of cold-water-swelling and heated cross-linked waxy maize starch dispersions prepared in apple juice and water

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Abstract

The rheological and structural characteristics of dispersions of a cold-water-swelling (CWS) starch and a cross-linked waxy maize (CLWM) starch (3–5% solids concentration) prepared in apple juice and water were studied. At equal starch concentration, the mass fraction of CLWM granules was higher than of CWS starch, and that of either starch prepared in apple juice was higher than in water. The G' and G'' vs. angular frequency profiles of both starches resembled those of dilute cross-linked gels. For both starches, time-dependent flow behavior was observed and the power law consistency coefficient K increased with granule mass fraction in an exponential manner. The first normal coefficient, Ψ_1 , of CWS dispersions exhibited stronger dependence on shear rate than of CLWM, probably due to the CWS granules being more deformable.

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1. Introduction

Often, a starch dispersion (SD) is prepared (heated or hydrated) in the presence of a sugar which could affect the rheological properties of the dispersions; in heated dispersions, the gelatinization temperatures are also affected. Apple juice and other beverages are thickened with starch for consumption by dysphagia patients (Hudson & Daubert, 2002). The proposed mechanisms by which a sugar affects starch gelatinization include: (1) sugar and starch compete for available water and associated changes in free volume (Hoseney, Atwell, & Lineback, 1977; Slade & Levine, 1993); (2) sugar retards gelatinization in a water system by inhibiting the swelling action of starch granules (Bean & Yamazaki, 1978; Wooton & Bamunuarachchi, 1980); and (3) sugar penetrates the starch granule and interacts within the amorphous areas, thus stabilizing this region and increasing

the energy needed to initiate gelatinization (Spies & Hoseney, 1982).

Cold water swelling (CWS) starch can be created by first treating a native starch with alcohol at high temperatures and pressures (Eastman & Moore, 1984) or with an alcohol–alkali mixture (Chen & Jane, 1994a), followed by drying. CWS granules remain intact and swell extensively in cold water; the starch can be used conveniently in dessert formulation (BeMiller & Whistler, 1996; Jane, Seib, Hoseney, & Craig, 1985) and as a controlled drug-release (Chen & Jane, 1995). CWS starches have been produced from a variety of starches: waxy or high-amylose (Eastman, 1987; Eastman & Moore, 1984; Jane & Seib, 1991), banana (Bello-Perez, Romero-Manilla, & Paredes-Lopez, 2000), chickpea (Jackowski, Czuchajowska, & Baik, 2002), and potato (Singh & Singh, 2003). CWS starch, sometimes called pregelatinized starch, is being used in nursing homes to thicken foods for consumption by dysphagia patients without heating them to high temperatures.

It was suggested that the double helical structures in native starch are dissolved during the pregelatinization process (Jane et al., 1985; Jane, Craig, Seib, & Hoseney, 1986a). In turn, V-shaped single helices and semi stable starch structures are formed that contribute to the cold-water

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solubility of CWS starches (Jane, Craig, Seib, & Hosney, 1986b). The stability of a CWS is largely due to entanglement between the amylose and the amylopectin. CWS starch granules are larger than native granules and have an indented appearance (Chen & Jane, 1994a).

Cross-linking of a native starch is intended to add chemical bonds at random locations within granules; the bonds stabilize and strengthen the relatively tender swollen starch granules. For example, cross-linked waxy maize starch pastes are more viscous and heavy bodied, and are less likely to breakdown with extended cooking times, and with increased in acidity or agitation (Langan, 1986).

The volume fraction and the rigidity of the granules play important roles in the rheological behavior of SDs (Bagley & Christianson, 1982; Genovese & Rao, 2003a). However, because granules are compressible, volume fractions of SDs are difficult to measure accurately (Rao, 1999). Therefore, the mass fraction of the starch granules, cQ , is determined, where, c is the concentration (w/w) of dry starch, and Q is the mass of swollen starch granules per unit mass of dry starch.

Amylograph paste viscosity of CWS SD was similar to that of native starch (Jane et al., 1986a). However, viscosities of CWS waxy and high-amylose maize SDs were higher than those of the native starch (Chen & Jane, 1994b). CWS maize SDs exhibited shear-thinning flow behavior (Anastasiades, Thanou, Louis, Stapatoris, & Karapantsios, 2002; Hudson & Daubert, 2002) and slight thixotropy (Anastasiades et al., 2002), and the apparent viscosity increased with increasing starch concentration. Compared to potato CWS SDs, corn CWS SDs showed lower G' and G'' values and higher $\tan \delta$ values (Singh & Singh, 2003).

Both antithixotropic and thixotropic flow behavior has been observed, depending on the magnitude of the shear stress, in cross-linked waxy maize (CLWM) SDs heated in water (Chamberlain, Rao, & Cohen, 1999), and sucrose (Acquarone & Rao, 2003) and fructose (Youn & Rao, 2003) solutions; the former when the shear stress was less than about 150–200 Pa.

The power law model, shown in Eq. (1), was often used to describe the shear rate vs. shear stress data of starch dispersions (Okechukwu & Rao, 1995):

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

where, σ is shear stress (Pa), $\dot{\gamma}$ is shear rate (s^{-1}), K is the consistency coefficient (Pa s^n), and n is the flow behavior index (dimensionless).

Viscoelastic behavior of CLWM SDs has been studied in terms of dynamic rheological properties (e.g. Acquarone & Rao, 2003) and first normal stress difference (Genovese & Rao, 2003b). The latter is responsible for the climbing fluid phenomenon in the steady flow of viscoelastic fluids between coaxial cylinders (Ferry, 1980), known as the 'Weissenberg effect', and is related to the stored elastic

energy. It has been suggested that the deformable interface between the dispersed and continuous phases is responsible for the phenomenon of normal stresses (Vinckier, Minale, Mewis, & 1999). The first normal stress coefficient, Ψ_1 , is obtained from measured first normal stress difference, $\sigma_{11} - \sigma_{22}$

$$\sigma_{11} - \sigma_{22} = -\Psi_1 (\dot{\gamma})^2 \quad (2)$$

where, $\dot{\gamma}$ is the shear rate (Ferry, 1980). Values of Ψ_1 of cross-linked waxy maize dispersions have been shown to decrease with shear rate (Genovese & Rao 2003b; Youn & Rao, 2003).

It appears that there have been limited studies on the effect of sugar on the rheological properties of CWS SDs. The main objectives of this study are to investigate the rheological and structural properties of CWS cross-linked waxy maize and heated CLWM dispersions in apple juice and water.

2. Materials and methods

2.1. Starch samples

CLWM starch (Purity W[®], Batch no. BA-5890) and CWS waxy maize starch (Novation 4600, Batch no. BA-7250) were donated by the National Starch and Chemical Company (Bridgewater, NJ); their moisture contents (AOAC Method 925.09), on a dry basis, were 6.7 and 11.3%, respectively.

2.2. Apple juice

From the refractive index of apple juice (Wegmans, Rochester, NY), measured with a refractometer (ABBE, Leica Microsystems, Inc., Buffalo, NY), its sugar content was estimated to be 12.8%. Mean pH, measured with an Accumet[®] pH Meter (Model 10, Fischer Scientific, Fair Lawn, NJ), was 3.67. Titratable acidity (AOAC Official Method 942.15B) and °Brix/acid ratio of the juice were calculated to be 0.341 and 35.8%, respectively. The viscosity of the apple juice at 20 °C, determined with a capillary viscometer (Cannon S-100-346, Cannon Instrument Co., State College, PA) was 1.4 MPa s. Capillary electrophoresis analysis (fused silica, $l=105$ cm, $L=112.5$ cm, i.d.=50 μm (straight), Hewlett Packard 3D CE, HP, Palo Alto, CA) revealed that the sugars in the apple juice were made up almost entirely of fructose.

2.3. Starch pasting

A modification of the procedure by Okechukwu and Rao (1995) was used to paste the CLWM starch close to isothermal conditions. The weighed dry CLWM starch was suspended in a portion of either apple juice or water inside

a jacketed stainless steel (JSS) vessel at temperature T_y ($< 60^\circ\text{C}$) maintained using a circulating thermal bath (Model DC30, Haake, Paramus, NJ). This suspension was mixed with rest of hot apple juice or water at temperature T_x to obtain the isothermal pasting temperature $T_p = 80^\circ\text{C}$. The temperatures T_x and T_y were calculated using energy balance equations (Okechukwu & Rao, 1995). The hot paste was heated in a rotating round-bottomed flask at 80°C for 30 min and the temperature, monitored by a type T thermocouple, was maintained using a water bath (Rotavapor, Büchi, Switzerland). At the end of the heating time, the round-bottomed flask containing the hot gelatinized dispersion was transferred to a 25°C water bath and cooled to room temperature under rotation.

The CWS SDs were prepared by hydrating the starch in either water or apple juice for 1 h at room temperature ($23 \pm 2^\circ\text{C}$) in a 500 ml Erlenmeyer while being gently mixed with a magnetic stirring bar. The dispersion was then stored overnight in a refrigerator to allow air bubbles to escape.

2.4. Granule size distribution

Granule size distributions of the SDs were determined using a computer-controlled laser diffraction particle size analyzer (Coulter[®] LS 130, Coulter Corporation, Miami, FL) with a small-volume optical module. Starch dispersions were slowly added to the sample vessel until the polarization intensity differential scattering (PIDS) value was between 45 and 50. Results were generated with the Coulter software (Version 2.09) using the Fraunhofer optical model.

2.5. Granule swelling and mass fraction

The mass of swollen starch granules, Q , per unit mass of dry starch in a SD was determined using the method of Leach, McCowen, and Schoch (1959). About 25 mg of the gelatinized SD was weighed and centrifuged (Sorvall[®] RC-5, DuPont Instruments, Wilmington, DE) at $10,000 \times g$ for 5 min to separate the swollen granules. After centrifugation, the swollen granules were weighed immediately to determine their mass fraction; an aliquot of the supernatant was dried in an aluminum pan at 100°C under vacuum for 3 h to determine the solids content. The starch granule mass fraction, cQ , was calculated.

2.6. Dynamic rheological tests

Amplitude sweep experiments were conducted on CLWM SDs using a cone and plate geometry with a solvent trap (6 cm diameter, aluminum, 2° angle, $61\ \mu\text{m}$ minimum gap) and a rheometer (AR1000-N, TA Instruments, New Castle, DE) at 37°C in the 0.5–5.0% strain range to determine the linear viscoelastic region (LVR) of the material at the selected frequencies: 0.6283, 6.283, 62.83 and $125.7\ \text{rad s}^{-1}$, which covered the entire range of

frequency sweeps. Because the CWS granules were larger than heated CLWM granules, rheological tests on CWS SDs were conducted using a parallel plate geometry: 6 cm diameter, aluminum, $1000\ \mu\text{m}$ gap with a solvent trap. Frequency sweep experiments were conducted in the LVR at 37°C , the human body's normal temperature, over the frequency range of $0.628\text{--}125.7\ \text{rad s}^{-1}$. The average frequency sweep data from three samples are presented.

2.7. Flow tests

Shear stress–shear rate data were obtained at 37°C on a SD using the AR1000-N rheometer as it was sheared continuously from a shear rate of $0\text{--}200\ \text{s}^{-1}$ over a period of 15 min (up curve), and then from 200 to $0\ \text{s}^{-1}$ for 15 min (down curve). This process was repeated two more times for each sample. Data from three consecutive shear cycles were used to characterize the flow of the SDs and to estimate parameters of the power law model Eq. (1).

3. Results and discussion

3.1. Granule size distribution (GSD)

The granules of CWS SDs in apple juice (Fig. 1) and water (not shown) exhibited unimodal size distribution. Within the range of starch concentrations studied, starch concentration did not seem to affect the granule size distribution of the CWS dispersions in apple juice. GSDs of CLWM SDs heated in apple juice and water had characteristics similar to those reported in previous studies on them (Acquarone & Rao, 2003; Youn & Rao, 2003) and they are not discussed in detail here. They also had unimodal profiles in both apple juice and water; as expected,

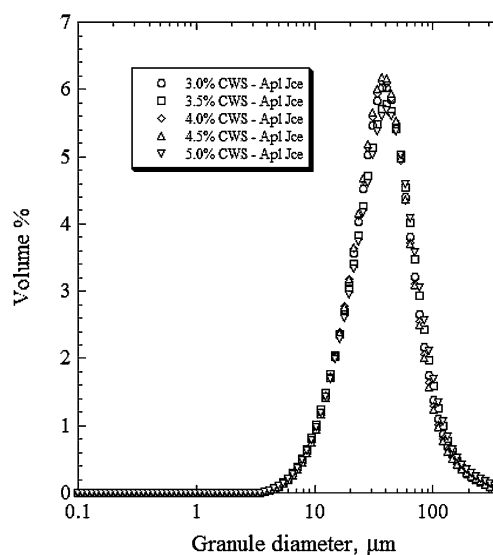


Fig. 1. Granule size distribution of cold-water-soluble starch dispersions prepared in apple juice.

Table 1

Mean granule diameter (μm) of cold-water-swelling and cross-linked waxy maize starch dispersions in apple juice and water

% Starch solids (w/w)	Apple juice	Water	Apple juice	Water
	CWS		Heated CLWM: 80 °C for 30 min	
3.0	48.0 \pm 1.2	52.5 \pm 2.2	41.8 \pm 0.1	37.6 \pm 0.2
3.5	49.0 \pm 1.3	44.5 \pm 0.7	43.3 \pm 0.2	38.1 \pm 0.3
4.0	47.3 \pm 1.1	45.6 \pm 1.0	41.6 \pm 0.1	38.1 \pm 0.2
4.5	47.2 \pm 1.1	46.9 \pm 1.1	40.9 \pm 0.3	38.2 \pm 0.3
5.0	51.2 \pm 1.0	50.1 \pm 2.0	41.6 \pm 0.1	37.7 \pm 0.1

Diameters of ungelatinized CLWM dispersions in apple juice and water were: 17.9 \pm 0.1, 17.7 \pm 1.1, respectively.

gelatinized CLWM granules were larger in diameter than ungelatinized granules. The range of granule sizes of the CWS starch was significantly broader than of gelatinized CLWM: for example, the GSDs of 4.0% dispersions in apple juice of CWS and CLWM ranged over 3–685 and 2–101 μm , respectively. The average diameters of CWS granules in apple juice and water dispersions were about equal in size. The average diameters of CLWM dispersions in apple juice were slightly larger than those in water (Table 1) and probably the result of sugar–starch–water interactions whose exact nature needs to be explored. Calculated values of water binding power of the CLWM dispersions (not shown here) (Meng, 2003) were also higher in apple juice than in water.

3.2. Granule swelling factor and volume fraction

Values of cQ for the CWS and CLWM SDs in apple juice and water were linearly related to starch concentration (Fig. 2), which is to be expected as cQ is in essence the mass fraction of the swollen granules. For the same starch concentration, cQ values of the CLWM dispersions were higher than those of CWS starch; further, for both starches, the cQ values of the dispersions in apple juice were higher than those in water. The higher cQ values in turn contributed to higher values of the rheological parameters of the CLWM

SDs vis-à-vis the CWS SDs, and of the CWS and CLWM SDs in apple juice vis-à-vis the SDs in water.

The CLWM SDs in apple juice had consistently higher cQ values than those in water at all starch concentrations (Fig. 2). However, for the CWS SDs, the difference in the cQ values in apple juice and water decreased from about 10 at 3.0% starch concentration to negligible at 5.0% starch concentration (Fig. 2). These results suggest that the water-absorbing effect was not as pronounced in the CWS as it was in CLWM. The CWS starch was gelatinized prior to being dispersed, so that the network of amylopectin molecules would have been extended beyond their root-mean-square lengths (Ferry, 1980); during the pregelatinization process, structures may also have been lost, thus contributing to less elastic granules. On the other hand, CLWM starch was gelatinized in situ, in which case the networks among the cross-linked amylopectin molecules would have been in their random configuration in the unstrained state (Ferry, 1980).

3.3. Dynamic rheological behavior

Because the 3.0 and 3.5% CWS SDs in apple juice and water were too dilute to exhibit any viscoelastic properties

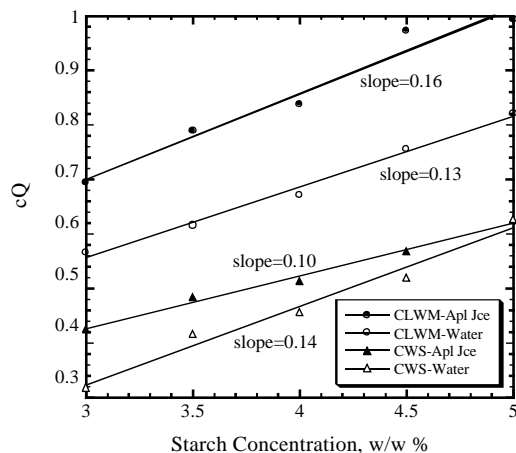


Fig. 2. Values of mass fraction, cQ , of cold-water-soluble and cross-linked-waxy-maize starch dispersions in apple juice as a function of starch concentration.

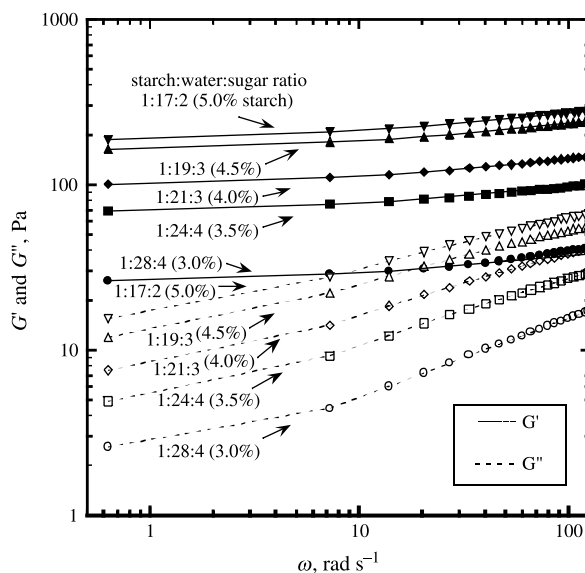


Fig. 3. Double logarithmic plots of G' and G'' against frequency of cross-linked-waxy-maize starch dispersions in apple juice.

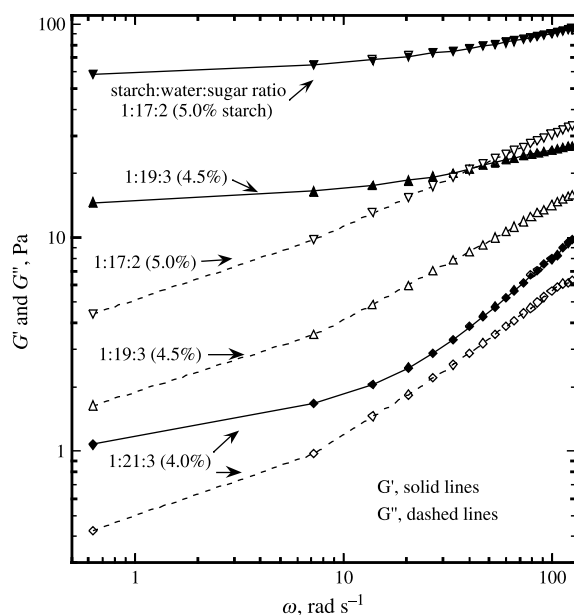


Fig. 4. Double logarithmic plots of G' and G'' against frequency of cold-water-soluble starch dispersions in apple juice.

at the frequencies used, their G' and G'' values are not shown. Double logarithmic plots of G' and G'' against ω of the CWS and CLWM SDs (Figs. 3 and 4) exhibited profiles similar to those of dilute cross-linked gels (Ferry, 1980): G' values were also higher than G'' values for all dispersions; increases in G'' values with ω were higher than of G' . However, values of G' of CLWM dispersions at high values of ω were relatively flat.

Calculated values of starch:water:sugar ratios of the dispersions are presented in Table 2 along with values of G' at 0.628 and 125.7 rad s⁻¹ discussed later. At high starch content (4–5%), CWS dispersions in apple juice (Fig. 4) showed higher G' and G'' values than dispersions in water (Fig. 5). At the same starch:water ratio of 1:19, CWS in apple juice had very similar values of G' and G'' as CWS in water. In contrast, the CLWM–apple juice dispersions had higher G' and G'' values than CLWM–water dispersions at the same starch:water ratio (Figs. 3 and 6).

The effects of starch concentration and continuous medium (apple juice or water) on the CWS and CLWM dispersions were well-reflected in the values of G' at the low (0.628 rad s⁻¹) and high (125.7 rad s⁻¹) values of ω (Table 2). At the low frequency: 0.628 rad s⁻¹, G' may be an estimation of the pseudo-equilibrium modulus of the starch dispersion (Ferry, 1980); when its magnitudes for both CWS and CLWM dispersions were plotted against the corresponding volume fractions: cQ (Fig. 7), they followed a common trend: constant low values at $cQ < 0.5$ and linear increase there after.

Values of $\tan \delta (=G''/G')$ of the SDs reflected the trends in G' and G'' . Here, a few unique features of $\tan \delta$ vs. angular frequency ω are described. For CWS SDs in apple juice with concentrations: 4.0, 4.5, and 5.0% $\tan \delta$ increased with angular frequency ω (Fig. 8); the 4.0% CWS starch dispersion showed a maximum at about 25 rad s⁻¹. The 4.5% CWS starch dispersion in water showed a maximum in $\tan \delta$ at about 30 rad s⁻¹ (not shown); at 4.0%, the maximum was seen at about 6 rad s⁻¹. The maxima are probably due to the dilution effect of water, as an earlier

Table 2

Values of G' and G'' of cold-water-swelling and cross-linked waxy maize starch dispersions in apple juice and water at 0.628 rad s⁻¹ and 125.7 rad s⁻¹

Starch solids (w/w), %	Starch:water:sugar ratio	G' at 0.628 rad s ⁻¹	G' at 125 rad s ⁻¹	G'' at 0.628 rad s ⁻¹	G'' at 125.7 rad s ⁻¹
<i>CWS in apple juice</i>					
3.0	1:28:4	0.0 ± 0.0	2.0 ± 1.7	0.0 ± 0.0	0.4 ± 0.3
3.5	1:24:4	0.0 ± 0.0	3.3 ± 0.8	0.0 ± 0.0	2.0 ± 0.2
4.0	1:21:3	1.1 ± 0.6	9.8 ± 2.6	0.4 ± 0.2	6.3 ± 1.0
4.5	1:19:3	14.7 ± 1.8	27.0 ± 5.9	1.6 ± 0.1	15.9 ± 1.1
5.0	1:17:2	58.2 ± 3.4	94.6 ± 3.5	4.4 ± 0.2	33.5 ± 1.2
<i>CWS in water</i>					
3.0	1:32:0	0.0 ± 0.0	8.5 ± 7.3	0.0 ± 0.0	0.9 ± 0.3
3.5	1:28:0	0.1 ± 0.0	16.1 ± 2.0	0.1 ± 0.0	2.8 ± 0.7
4.0	1:24:0	2.5 ± 1.5	10.7 ± 2.6	0.7 ± 0.2	6.4 ± 1.1
4.5	1:21:0	3.6 ± 1.8	18.7 ± 0.5	0.8 ± 0.2	7.1 ± 1.9
5.0	1:19:0	9.2 ± 2.8	24.6 ± 4.2	2.0 ± 0.6	12.1 ± 2.3
<i>CLWM heated in apple juice at 80 °C for 30 min</i>					
3.0	1:28:4	26.1 ± 0.3	41.1 ± 2.6	2.6 ± 0.0	17.1 ± 0.1
3.5	1:24:4	69.1 ± 0.9	100.3 ± 2.3	4.9 ± 0.1	29.3 ± 0.4
4.0	1:21:3	100.3 ± 1.1	147.7 ± 0.9	7.5 ± 0.0	40.9 ± 0.3
4.5	1:19:3	162.9 ± 3.1	241.9 ± 4.8	11.9 ± 0.2	56.0 ± 0.7
5.0	1:17:2	185.8 ± 1.8	277.4 ± 2.6	15.5 ± 0.1	66.3 ± 0.5
<i>CLWM heated in water at 80 °C for 30 min</i>					
3.0	1:32:0	0.1 ± 0.1	7.5 ± 0.3	0.1 ± 0.0	2.4 ± 0.3
3.5	1:28:0	22.8 ± 1.7	29.8 ± 4.6	1.4 ± 0.1	10.8 ± 0.4
4.0	1:24:0	46.4 ± 0.8	61.3 ± 0.6	3.2 ± 0.0	18.9 ± 0.1
4.5	1:21:0	71.5 ± 2.3	95.3 ± 1.9	4.6 ± 0.0	26.0 ± 0.3
5.0	1:19:0	135.7 ± 2.8	183.8 ± 2.2	7.9 ± 0.3	41.3 ± 0.7

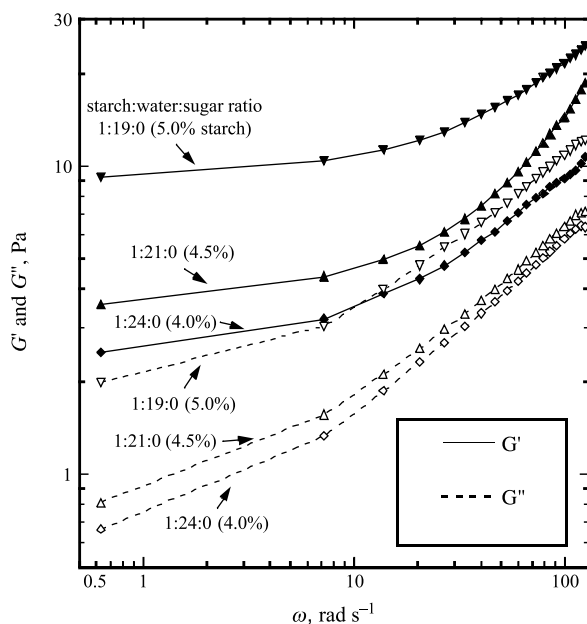


Fig. 5. Double logarithmic plots of G' and G'' against frequency of cold-water-soluble starch dispersions in water.

onset of a maximum $\tan \delta$ value is characteristic of solutions with low polymer concentrations (Ferry, 1980). It is possible that the number of water molecules surrounding each starch granule in 4.0 and 4.5% CWS dispersions may have exceeded a certain threshold under which the elastic components of the system would have been more dominant.

At the same starch concentrations (4.0 and 4.5%), the CLWM-in-apple juice and -water dispersions did not exhibit a maximum in $\tan \delta$ values (not shown) due to

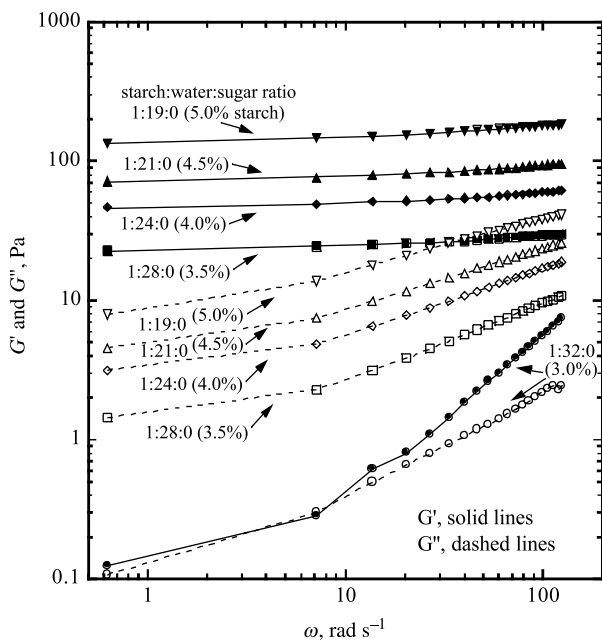


Fig. 6. Double logarithmic plots of G' and G'' against frequency of cross-linked-waxy-maize starch dispersions in water.

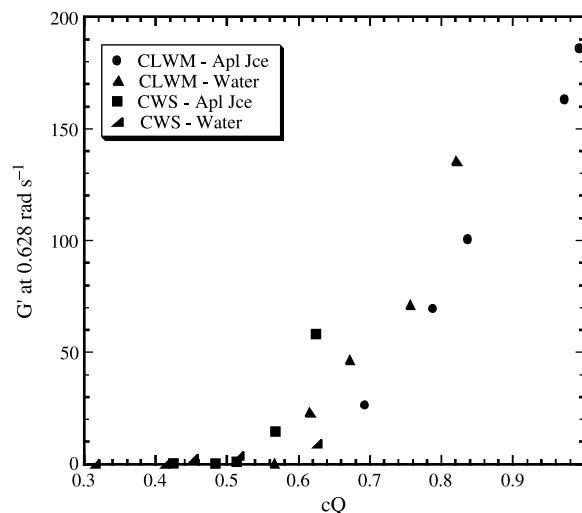


Fig. 7. Values of G' at 0.628 rad s^{-1} of all the starch dispersion plotted against cQ followed a common trend.

their higher elastic nature. Values of $\tan \delta$ of CLWM starch in apple juice and water increased with ω on a double logarithmic plot at all concentrations (not shown). The plots were similar to those of dilute cross-linked gels (Ferry, 1980). Due to plasticization effect of water, the magnitudes of $\tan \delta$ values and the slope of $\tan \delta$ —frequency curves increased with the decreasing starch content.

3.4. Flow behavior

As expected, the shear stress values of all the SDs increased with starch concentration; there was a substantial

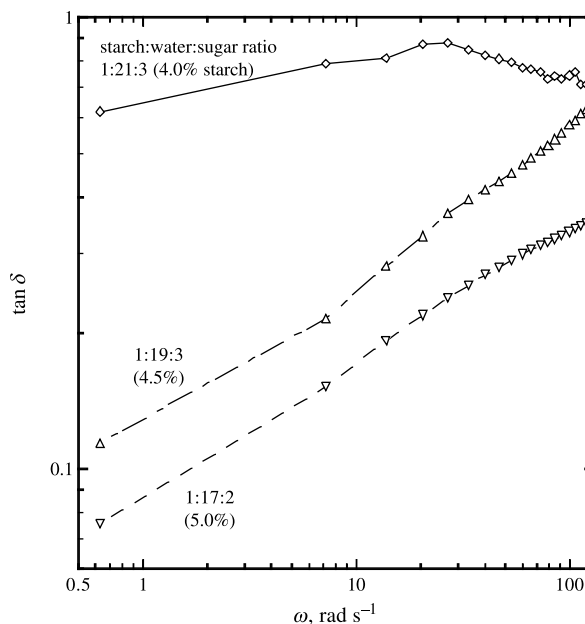


Fig. 8. For cold-water-soluble starch dispersions in apple juice with concentrations: 4.0, 4.5, and 5.0%, the loss tangent ($\tan \delta$) increased with angular frequency, ω .

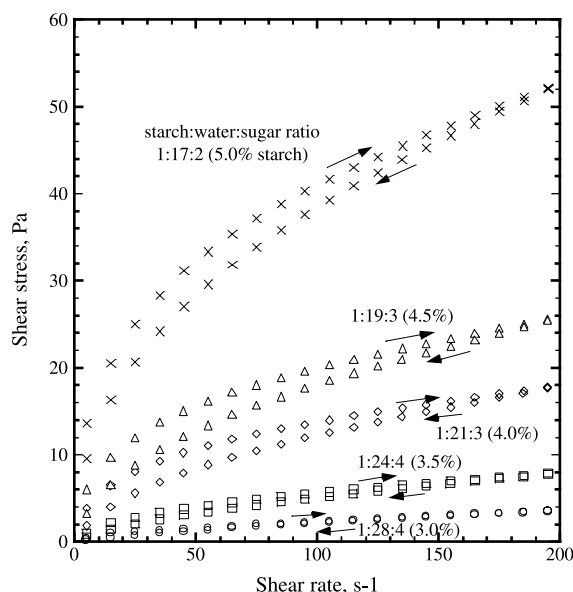


Fig. 9. Flow behavior of cold-water-soluble starch dispersions of different starch concentrations in apple juice. The arrows above the data points indicate whether they were obtained in increasing or decreasing shear rate modes.

increase in values between 4.5 and 5.0%. The dispersions exhibited different time-dependent flow behavior: (1) in the first shear rate vs. shear stress cycle, either a clockwise (thixotropic) or an anticlockwise (antithixotropic) hysteresis loop, and (2) during three consecutive shear cycles, either an increase (antithixotropic) or no change in shear stress. The shear rate vs. shear stress curves in Figs. 9 and 10 shows the clockwise loops in the first shear rate vs. shear stress cycles for CWS SDs in apple juice and in water, respectively.

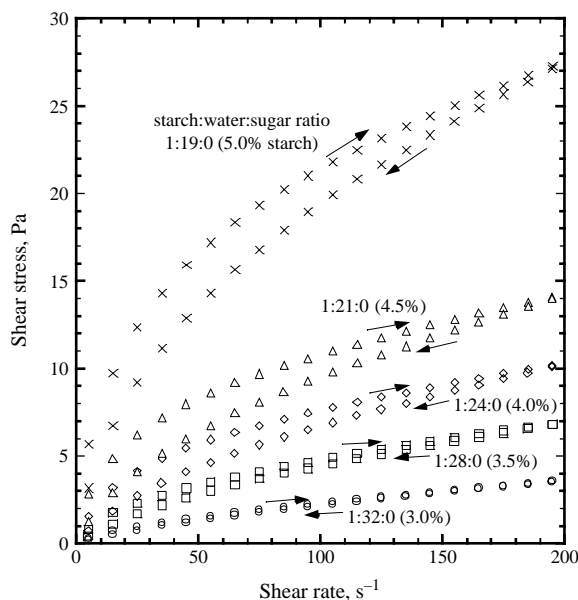


Fig. 10. Flow behavior of cold-water-soluble starch dispersions of different starch concentrations in water. The arrows above the data points indicate whether they were obtained in increasing or decreasing shear rate modes.

All the observations on time-dependent flow behavior are summarized in Table 3.

The time-dependent behavior of 4.0% CWS in water is in agreement with those of Anastasiades et al. (2002) on CWS waxy maize SDs. It appears (Table 3) that in the absence of sugars, a higher concentration of starch solids may have deterred the time-dependent behavior in CWS SDs but not in CLWM SDs. They also suggest that in the presence of sugars, this inhibitory effect was enhanced for both types of starch.

Values of flow behavior index n for CWS dispersions in apple juice and water were similar to those of CLWM dispersions (Table 4); they were less than one indicating that the dispersions were shear-thinning in nature. Shear-thinning behavior was reported for CWS maize starch (Anastasiades et al., 2002; Hudson & Daubert, 2002) and banana starch (Bello-Perez et al., 2000).

When K values of both CWS and CLWM SDs in apple juice and water were plotted against volume fraction cQ (Fig. 11), they all followed a common curve. In agreement with a number of studies on viscosity of dispersions, an exponential relationship ($R^2=0.941$) was seen between K and cQ . The n values of both CWS and CLWM dispersions in apple juice and water decreased with increasing values of cQ (not shown), however, they showed considerable scatter and did not follow a single line.

3.5. First normal stress differences

Fig. 12 on 5% SDs shows the difference between the two types of starches, and the effect of preparation in apple juice and water on Ψ_1 Eq. (2). Values of Ψ_1 of all the SDs in apple juice and water decreased with increasing shear rate. At CWS starch concentrations $<4.5\%$, values of Ψ_1 were quite similar (not shown); they were higher for 4.5 and 5.0% SDs. In contrast, values of Ψ_1 of dispersions of CLWM in apple juice and water showed, in agreement with an earlier study of Genovese and Rao (2003b), clear increase with starch concentration. First normal stress differences have also been observed to increase with the concentrations of solids (glass beads) in silicone oil (Mall-Gleissle, Gleissle, McKinley, & Buggisch, 2002) and of Xanthan gum solutions (Zirnsak, Boger, & Tiraatmadja, 1999).

In addition, Ψ_1 of CWS SDs exhibited slightly stronger dependence of normal stress on shear rate than CLWM, as evidenced by the steeper slopes seen in Fig. 12. These observations indicate that the type of starch, whether CWS or cross-linked waxy maize, had a large influence on the normal stresses of the dispersion. They might indicate that perhaps CWS granules were more deformable than CLWM granules, as reported in an earlier study on tapioca and CLWM SDs (Genovese & Rao, 2003b), possibly due to the pregelatinizing process.

Table 3

Summary of time-dependent flow behavior of cold-water-swelling and heated (80 °C, 30 min) cross-linked waxy maize starch dispersions in apple juice and water

Starch solids, % (w/w)	Starch:water:sugar ratio	First shear cycle	Behavior after three cycles	First shear cycle	Behavior after three cycles
Cold-water-swelling in apple juice					
3.0	1:28:4	Clockwise	Antithixotropic	Anticlockwise	Antithixotropic
3.5	1:24:4	Clockwise	Antithixotropic	Anticlockwise	Thixotropic
4.0	1:21:3	Clockwise	Thixotropic	Anticlockwise	Thixotropic
4.5	1:19:3	Clockwise	–	Clockwise	Thixotropic
5.0	1:17:2	Clockwise	–	Clockwise	Thixotropic
Cold-water-swelling in water					
3.0	1:32:0	Clockwise	Antithixotropic	Anticlockwise	Antithixotropic
3.5	1:28:0	Clockwise	Antithixotropic	Anticlockwise	Antithixotropic
4.0	1:24:0	Clockwise	–	Anticlockwise	Antithixotropic
4.5	1:21:0	Clockwise	–	Anticlockwise	Antithixotropic
5.0	1:19:0	Clockwise	–	Anticlockwise	Antithixotropic

Table 4

Consistency coefficient K and flow behavior index n values of cold-water-swelling and heated (80 °C, 30 min) cross-linked waxy maize starch dispersions in apple juice and water

% Starch solids (w/w)	K , Pa s ^{<i>n</i>}	n , dimensionless	K , Pa s ^{<i>n</i>}	n , dimensionless
Cold-water-swelling in apple juice				
3.0	0.07 ± 0.00	0.74 ± 0.00	0.87 ± 0.01	0.69 ± 0.01
3.5	0.26 ± 0.03	0.65 ± 0.01	3.15 ± 0.07	0.65 ± 0.00
4.0	0.95 ± 0.09	0.56 ± 0.01	5.68 ± 0.06	0.60 ± 0.00
4.5	1.68 ± 0.23	0.52 ± 0.01	12.52 ± 0.30	0.50 ± 0.00
5.0	4.86 ± 0.12	0.45 ± 0.00	15.11 ± 0.54	0.49 ± 0.00
Cold-water-swelling in water				
3.0	0.10 ± 0.01	0.72 ± 0.02	0.61 ± 0.05	0.52 ± 0.01
3.5	0.22 ± 0.05	0.66 ± 0.02	1.86 ± 0.14	0.45 ± 0.01
4.0	0.66 ± 0.21	0.60 ± 0.02	3.29 ± 0.05	0.45 ± 0.00
4.5	0.64 ± 0.03	0.59 ± 0.00	3.65 ± 0.05	0.54 ± 0.01
5.0	1.74 ± 0.04	0.52 ± 0.00	4.69 ± 0.41	0.64 ± 0.01

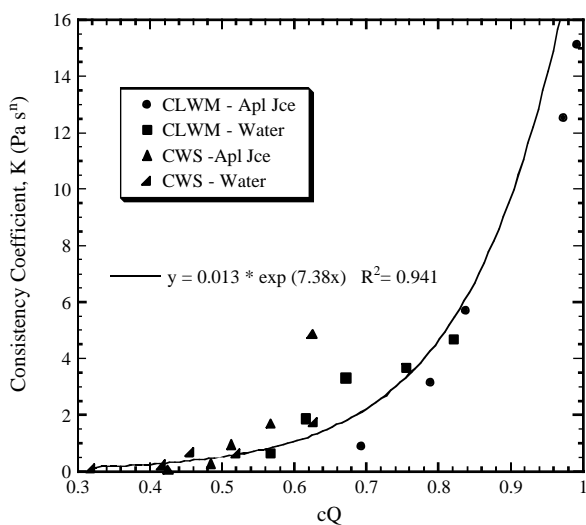


Fig. 11. Values of the power law consistency coefficient of all the starch dispersions followed an exponential relationship with mass fraction, cQ .

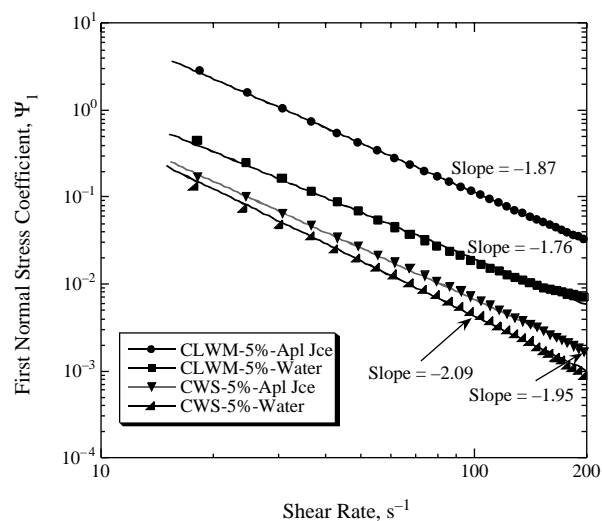


Fig. 12. Values of the first normal stress coefficient of 5% starch dispersions (CLWM: cross-linked-waxy-maize starch; CWS: cold-water-soluble) in apple juice and water.

4. Conclusions

Values of cQ of dispersions in both apple juice and water showed linear dependence on starch concentration. For the same starch concentration, values of cQ of the CLWM SDs were higher than those of CWS starch, and those prepared in apple juice were higher than in water; these factors contributed to the higher values of the rheological parameters of the CLWM dispersions and of those in apple juice. Values of G' and G'' increased with increasing ω for all the SDs in both apple juice and water; G' values were much higher than G'' values and they both increased with increasing starch concentration. Increases in G'' values with ω were greater than G' values. Values of G' at 0.628 rad s^{-1} of all dispersions increased with cQ .

Flow curves of all CWS dispersions exhibited a clockwise hysteresis loop; in contrast, CLWM dispersions in apple juice with starch concentrations less than 4.5% showed an anticlockwise hysteresis loop. While values of the consistency coefficient, K , of CWS SDs were lower than those of CLWM SDs, values of the flow behavior index, n , were similar in magnitudes. The values of K of all the dispersions increased with values of cQ in an exponential manner. Values of n of all the dispersions decreased with increasing cQ ; however, they did not follow a specific trend. It appears that in addition to the pregelatinization process, the presence of sugars affected the swelling ability of CWS and CLWM starch granules which in turn influenced the rheological properties of its dispersions.

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