

# Role of Starch Granule Characteristics (volume fraction, rigidity, and fractal dimension) on Rheology of Starch Dispersions With and Without Amylose

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## ABSTRACT

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The link between rheological behavior and morphological-structural characteristics of gelatinized starch granules has been studied in two starch dispersions (SDs): a cross-linked waxy maize (CLWM), and tapioca starch, a tuber starch with 19.3 % amylose. Based on the power law relationship between the elastic modulus and volume fraction of the granules predicted by scaling theory, fractal dimension values were obtained for CLWM starch  $D = 2.81$ , and tapioca starch  $D = 2.79$ ,

suggesting that both starch granules have highly convoluted surfaces. However, the preexponential coefficient ( $G'_{\infty=1}$ ) for CLWM SDs was an order of magnitude greater than that for tapioca SDs, in the same range of volume fractions. The  $G'_{\infty=1}$  was mainly dependent on the granule rigidity, and the amylose content in the continuous phase played only a minor role in the rheological behavior.

Starch occurs naturally as semicrystalline granules that are mainly composed of a mixture of two polysaccharides: amylose and amylopectin. Starch granules swell only slightly in cold water. But when this starch-water mixture is heated above a certain temperature, called the gelatinization temperature or gelling point, the granules lose their crystallinity, which allows them to absorb large amounts of water, swelling to several times their initial size, and leaching out amylose to some extent. Upon cooling, a gel composed of swollen starch granules in an amylose matrix is formed (Evans and Haisman 1979; Eliasson 1986; Kalichevsky and Ring 1987; BeMiller and Whistler 1996; Carnali and Zhou 1996; Hosney 1998; Rao 1999). The rheological behavior of such a material will depend on characteristics of the dispersed and the continuous phases, and on the interactions between them (Eliasson 1986; Carnali and Zhou 1996).

Besides the viscoelasticity of the continuous phase, the rheology of starch dispersions (SDs) depends on concentration of the granules, size and size distribution, shape and deformability, as well as interactions between the granules (Evans and Haisman 1979; Wong and Lelievre 1981; Eliasson 1986). In corn, cowpea (Rao et al 1997), and tapioca (Rao and Tattiyakul 1999) SDs, the consistency index, defined as the shear stress at a shear rate of 1.0/sec, increased with granule mean diameter, while the standard deviation of the granule size distribution affected the transition from shear thickening in the early stages of gelatinization to shear thinning in the latter stages. The time dependent shear thickening (antithixotropic) behavior observed in cross-linked waxy maize SDs has been attributed to shear-induced cluster formation of granules (Chamberlain 1996).

Special attention should be paid to the SDs pasting procedure because it determines the extent of granule swelling and integrity (Doublier et al 1987). Overheating much above the gelatinization temperature for long time or high shearing conditions results in disintegration of the granules, leading to decrease in their volume fraction and exuding their contents, especially amylose, into the continuous phase (Rao 1999).

The influence of the dispersed phase on the rheology of SDs can be described mainly by the volume fraction and rigidity of the granules (Evans and Haisman 1979; Bagley and Christianson 1982; Eliasson 1986; Doublier et al 1987; Steeneken 1989; Rolee and Le Meste 1997). In this work, rigidity is used in connection

with a starch granule and elasticity with SDs. Eliasson (1986) and Evans and Haisman (1979) claimed that the surface roughness of the granules also could play an important role, but it has never been quantitatively determined.

Recently, the fractal dimension concept has been a useful tool for measuring the surface roughness of synthetic and natural particulate materials. In food systems, it has been successfully applied to coffee particles (Peleg and Normand 1985), fat crystal networks (Marangoni and Rousseau 1996; Narine and Marangoni 1999a,b), and starches (Nagai and Yano 1990; Hanselmann et al 1996; Suzuki et al 1997; Calzetta et al 1999).

The fractal concept was first proposed by Mandelbrot in 1983, who introduced dimensions “between” the conventional Euclidean dimensions of 1, 2, and 3 to describe structures that are not Euclidean lines, surfaces or solids. Fractal dimension indicates the degree to which an image or object outline deviates from smoothness and regularity. For example, a fractal dimension from 1 to 2 describes the area-filling capacity of a convoluted line and a fractal dimension from 2 to 3 describes the volume filling capacity of a highly rugged surface (Barret and Peleg 1995). According to this definition, smooth surfaces are associated with a value of surface fractal dimension  $D = 2.0$ , while extremely convoluted surfaces have values approaching 3.0 (Nagai and Yano 1990; Barret and Peleg 1995; Calzetta et al 1999). A characteristic of fractal objects is “self-similarity”, the attribute of having the same appearance at all magnifications. However, real materials or “natural fractals” are self-similar only over a limited range of scales (Barret and Peleg 1995; Marangoni and Rousseau 1996).

The fractal dimension can be estimated by several techniques, including structured walk (Richardson’s plot), bulk density-particle diameter relation, sorption behavior of gases, pore size distribution, and viscoelastic behavior. According to Rahman (1997), the fractal dimension obtained by each method has its own physical meaning.

Shih et al (1990) developed a scaling relationship to explain the elastic properties of colloidal gels by considering the structure of a gel network to be a collection of close-packed fractal flocs of colloidal particles. Marangoni (2000) credited other groups for developing this theory which predicts a power-law dependence of the shear elastic modulus on the volume fraction of network mass. Furthermore, the power exponent was related to the mechanism of particle aggregation. Shih et al (1990) also defined two separate rheological regimes, depending on the strength of the interfloc links relative to that of the flocs themselves: 1) The strong-link regime is observed at low particle concentrations, allowing the flocs to grow to be very large, so that they can be considered weak springs. Therefore, the links between flocs have a higher elastic

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constant than the flocs themselves. (2) The weak-link regime is observed at high particle concentrations, where the small flocs are stronger springs, and the links between flocs have a lower elastic constant than the flocs themselves.

In this study, we selected two starches that were substantially different from each other: a cross-linked waxy maize (CLWM) and tapioca, a tuber starch with 19.3% amylose. The volume fraction occupied by starch granules ( $\phi$ ) depends on 1) starch concentration, and 2) the extent to which the granules have swelled. In excess water,  $\phi$  can be calculated as the granule mass fraction:

$$\phi = cQ \quad (1)$$

where  $c$  is the dry starch concentration (w/w), and  $Q$  is the swelling ratio or mass of hydrated starch granules per unit weight of dry starch (Bagley and Christianson 1982; Rao 1999). Although this is a weight ratio, it can also be considered a volume ratio because the density of the highly swollen granules after gelatinization is so close to that of the surrounding matrix (Carnali and Zhou 1996). The volume fraction of granules can be determined using the Blue Dextran exclusion method. This method is based on the observation that Blue Dextran dye (a big molecule, MW  $2 \times 10^6$ ) will dissolve in interstitial water but not in the intragranular water, because it cannot penetrate swollen granules (Evans and Haisman 1979; Tester and Morrison 1990).

According to Shih et al (1990) the scaling theory should be applicable to gels that are well above the gelation threshold. Based on preliminary experiments, in the SDs studied here this limit was found for starch granule volume fractions greater than  $\approx 0.5$  for CLWM starch and  $\approx 0.6$  for tapioca starch. At these high concentrations, we can assume that the studied SDs were in the weak-link regime (Marangoni and Rousseau 1996; Narine and Marangoni 1999a), where the elastic modulus ( $G'$ ) is related to the particle volume fraction ( $\phi$ ) by the following relationship:

$$G' \approx \phi^{(d-2)/d-D} \quad (2)$$

where  $d$  is the Euclidean dimension of the network, usually 3, as in the present case. For fat crystal networks, Narine and Marangoni (1999b) introduced a proportionality constant  $\gamma$ , pointing out that it is dependent on the size of the primary particles and on the interactions between them, although its exact dependence on network properties has not been formulated. Physically,  $\gamma$  is equivalent to the elastic modulus when  $\phi = 1$ . For SDs, it means the point where the close packed granules have absorbed all the water available and are still fully swollen (if the concentration of granules is higher, they will take in all the water,

but each granule will be only partially swollen). Therefore, Equation 2 can be rewritten as:

$$G' = G'_{\phi=1} \phi^{1/(3-D)} \quad (3)$$

It appears that the scaling theory of Shih et al (1990) has not been applied to gelatinized SDs. Therefore, the primary aim of this work was to quantitatively characterize the starch granule's surface morphology (by means of  $D$ ) and its influence on the rheology of SDs. The second objective was to determine the influence of the dispersed (granules) and the continuous (amylose) phases on  $G'_{\phi=1}$ . With this purpose, small-amplitude oscillatory (dynamic) and continuous shear rheological measurements were performed on two different gelatinized SDs, CLWM and tapioca, at different concentrations. The last objective was to determine whether the antithixotropic flow behavior of CLWM SDs is primarily due to the dispersed starch granules and whether it is influenced by dissolved amylose in the continuous phase.

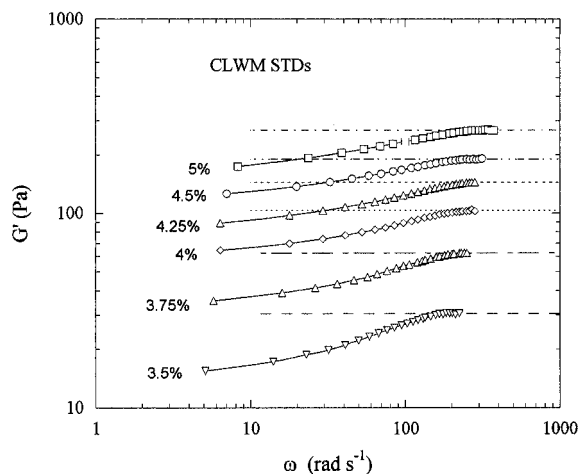
## MATERIALS AND METHODS

### Sample Preparation

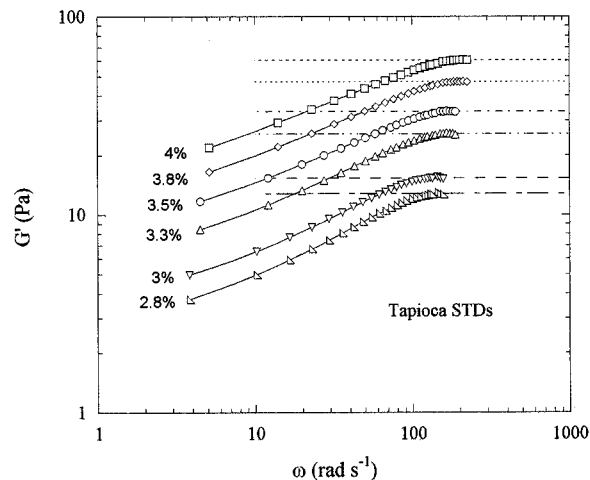
Gelatinized CLWM SDs (Purity W, National Starch and Chemical Company, Bridgewater, NJ) with starch concentrations 3.5, 3.75, 4, 4.25, 4.5, and 5% (w/w) were prepared by heating in distilled water at 80°C. Tapioca SDs (National Starch and Chemical Company, Bridgewater, NJ) with starch concentrations 2.8, 3, 3.3, 3.5, 3.8, and 4% (w/w) were prepared by heating in distilled water at 70°C. Both starches were pasted by heating their dispersions for 10 min in a rotating round-bottom flask submerged in a thermostatic bath (Rotavapor, Büchi 011, Switzerland). By using only the rotating motion of the flask, we minimized rupture of the swollen starch granules.

It should be noted that CLWM is a high-amylopectin (almost free of amylose) modified corn starch, while tapioca is a tuber starch with an amylose content of 19.3% (dry weight basis), as previously determined by Tattiyakul (1997).

To achieve an almost isothermal pasting of the samples, the procedure proposed by Okechukwu and Rao (1995) was followed. A concentrated suspension of starch in water was allowed to hydrate for 1 hr under gentle stirring at room temperature. Then the suspension was taken to a chosen temperature below the gelling point, such that when mixed with hot water, the final mixture instantaneously attained the desired pasting temperature. Finally, the paste was quickly transferred to the round flask and submerged into the thermostatic bath. The required temperatures and masses of the starch-water suspensions and hot water were



**Fig. 1.** Storage modulus ( $G'$ ) of cross-linked waxy maize (CLWM) starch dispersions at different concentrations (% w/w) as a function of angular frequency ( $\omega$ ). Dashed lines represent the plateau value.



**Fig. 2.** Storage modulus ( $G'$ ) of tapioca starch dispersions at different concentrations (% w/w) as a function of angular frequency ( $\omega$ ). Dashed lines represent the plateau value.

calculated from energy balances. After pasting, the SDs were quickly cooled in a water-ice bath until they reached room temperature. The gelatinization temperature or gelling point of CLWM and Tapioca SDs has been previously determined by Chamberlain (1996) and Tattiyakul (1997), respectively.

### Dynamic and Continuous Shear Rheological Tests

All rheological measurements were performed with a stress-controlled rheometer (AR-1000N, TA Instruments, New Castle, DE), using a cone and plate geometry (6 cm diameter acrylic cone, 2°, 69 μm minimum gap). The cone-plate geometry has the advantage of uniform shear rate in the gap. In the cone used, the gap varied between 69 μm at the center to more than 1,000 μm at the edges, so most of the geometry gap was more than 10 times greater than the starch granules. In addition, the granules were not physically isolated from the continuous medium with clear boundaries but intimately bound to the continuous medium, so that the studied samples could be characterized as gels. For these reasons, it is believed that the granule size did not affect the rheological measurements using the cone-plate geometry. All measurements were done at 20°C, in triplicate, and averaged for further analysis. Because the samples were exposed to relatively low temperature and short time (≤20 min) conditions, drying was considered insignificant.

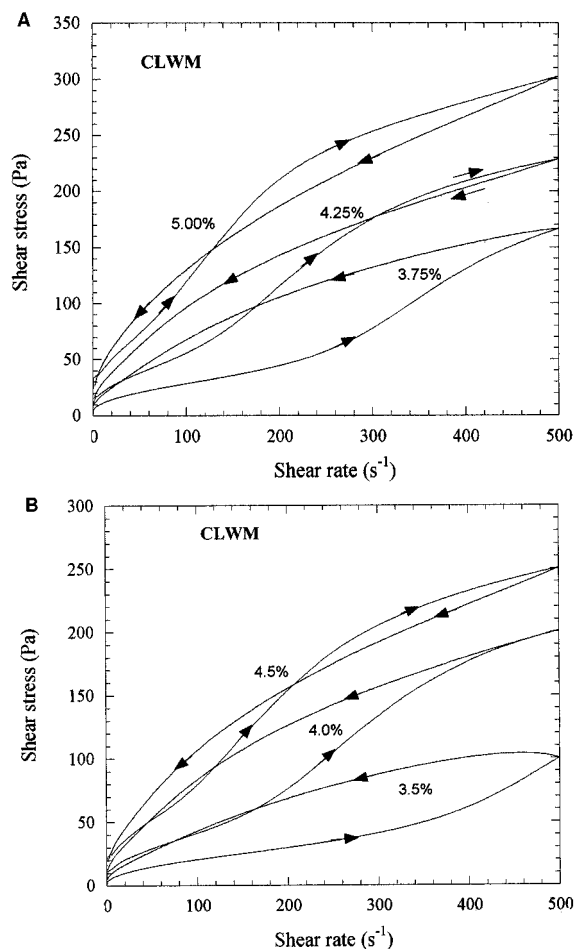
Dynamic rheological experiments were performed in two steps. First, a strain amplitude ramp (at two different frequencies: 6.28 and 12.56 rad/sec) determined the linear viscoelastic range (LVR), which was within 3% strain for all the samples. Next, frequency sweep tests were carried out in the LVR, with an initial frequency

of 0.63 rad/sec. The final frequency was the point where the elastic modulus reached its maximum plateau value, which was taken when five consecutive points showed a standard deviation ≤1%. This frequency value depended on the starch variety and concentration. Flow tests were performed by applying a continuous-ramp shear rate in the range 0.1–500/sec to the gelatinized SDs. The shearing time was 10 min for both the ascending and descending shear cycles.

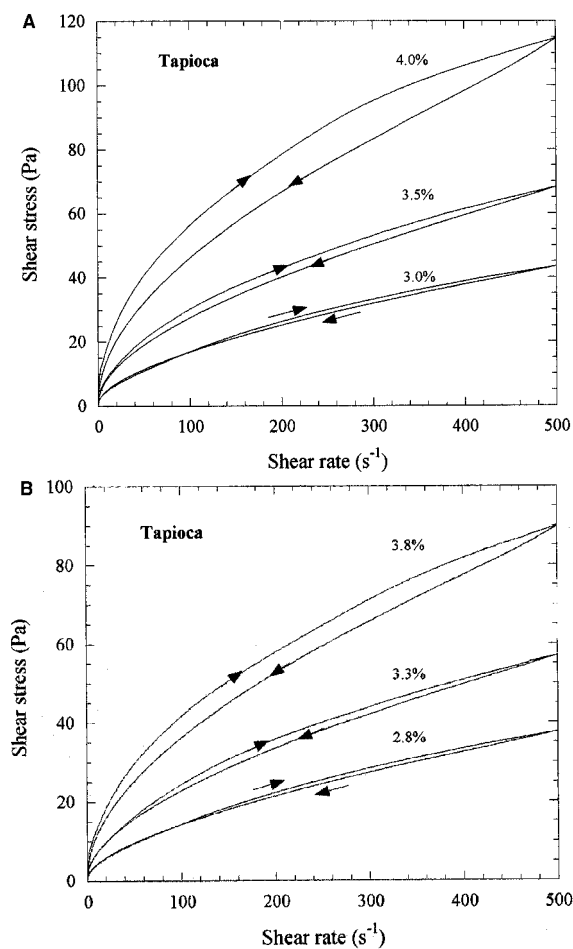
### Granule Swelling Factor and Volume Fraction

The swelling factor  $Q$  was determined by the Blue Dextran exclusion method (Ellis et al 1989). A known weight of the gelatinized starch sample and a 0.07% solution of Blue Dextran (Sigma Chemical Co., St. Louis, MO) were mixed inside 50-mL screw-cap tubes by gently inverting the closed tubes several times (Tester and Morrison 1990) and centrifuging at 10,000 ×  $g$  for 5 min in a 5°C refrigerated centrifuge (RC-5 Superspeed, Sorvall, Dupont Inst.) to precipitate the granules. The supernatant was removed and its absorbance at 620 nm was measured in a Spectrophotometer (Lightwave, Brand Tech, Scientific Inc.). Previously, a standard calibration curve was prepared with Blue Dextran solutions at seven different concentrations ( $c_{bd}$ ) ranging from 0.01 to 0.07% ( $c_{bd} = 0.1118 \times \text{Abs}_{620 \text{ nm}} - 9.444 \times 10^{-4}$ ,  $R^2 = 0.999$ ). All measurements were done in triplicate.

The swelling ratio was calculated as  $Q = (w_b + w_d)/w_d$ , where  $w_d$  is the weight of dry granules and  $w_b$  is the weight of water absorbed by the granules, calculated as  $w_b = w_t - w_{bd} \times 0.07/c_{bd}$ , where  $w_t$  is the total weight of water (water in starch dispersion + water in Blue Dextran solution),  $w_{bd}$  is the weight of the 0.07%



**Fig. 3.** Flow behavior, ascending and descending curves, of cross-linked waxy maize (CLWM) starch dispersions at (A) 3.75, 4.25, and 5% (w/w), and (B) 3.5, 4 and 4.75% (w/w).



**Fig. 4.** Flow behavior, ascending and descending curves, of tapioca starch dispersions at (A) 3, 3.5 and 4% (w/w) and (B) 2.8, 3.3, and 3.8% (w/w).

Blue Dextran solution and  $c_{bd}$  is the % concentration of Blue Dextran in the supernatant. The term,  $w_{bd} \times 0.07/c_{bd}$ , accounts for the interstitial water between the granules.

### Granule Size Distribution

An automated laser diffraction particle size analyzer (LS130, Coulter Corporation, Hiialeah, FL) was used to determine the granule size distribution of the raw (ungelatinized) CLWM and tapioca starches. Previously, the samples were hydrated during 2 hr under gentle agitation at room temperature. Three samples were prepared for each starch, and each sample was measured in triplicate.

### Interchange of the Continuous Phase

To determine the relative role of the continuous and dispersed phases on the flow behavior, experiments were conducted in which the continuous phase was interchanged. Two SDs with similar volume fraction of granules ( $\phi \approx 0.64$ ): 4.25%, w/w, CLWM, and 3.0%, w/w, tapioca were weighed and centrifuged at  $10,000 \times g$  for 5 min, the supernatants were removed and poured in vials, and the sediments weighed. The supernatant of the CLWM sample (mainly water) was added to the tapioca sediment, in the same weight proportion as it was present in the original sample of the tapioca SDs, and gently agitated in a rotating round-bottom flask (Rotavapor, Büchi 011, Switzerland) for 1 hr, until both phases were well mixed. The same procedure was used to mix the supernatant of tapioca, essentially a solution of amylose in water, with the CLWM sediment. Rheological experiments were performed on these samples under the same conditions used for tapioca 3% and CLWM 4.25% SDs.

## RESULTS AND DISCUSSION

### Plateau Values of Storage Modulus

Plots of elastic modulus ( $G'$ ) of SDs at different concentrations, as a function of angular frequency ( $\omega$ ), are shown for CLWM

(Fig. 1) and tapioca (Fig. 2). The dashed line asymptote to each curve is the average of the last five experimental points, and was taken as the plateau equilibrium value,  $G'_{\infty=1}$  (Shih et al, 1990). In all cases, the loss modulus ( $G''$ ) curves (not shown) were below the  $G'$  curves in the range of frequencies studied. According to the definition of Clark and Ross-Murphy (1987), the mechanical spectra of both CLWM and Tapioca SDs may be associated with an intermediate behavior between a weak gel and an elastic or strong gel, as also described by Yoshimura et al (1998) for corn SDs (2.10–3.50 wt%).

### Flow Behavior of SDs

Flow curves of CLWM (Fig. 3A and B) showed overall shear thinning behavior combined with antithixotropy (at low shear rates) and thixotropy (at high shear rates) at concentrations of 4–5%, as previously reported by Tattiyakul and Rao (2000), while concentrations of 3.5 and 3.75% only showed shear thinning antithixotropic behavior. Figure 4A and B show the shear thinning and thixotropic behavior for tapioca SDs at all concentrations except for 2.8 and 3.0%, where a slight antithixotropy can be observed at shear rates lower than  $\approx 100/\text{sec}$ . For the 2.6% tapioca SDs pasted in similar conditions, Tattiyakul (1997) found superimposition of the ascending and descending curves at low shear rates, pointing out that the original internal structure of the samples was recoverable.

### Starch Granule Size of SDs

Results of particle size analysis of ungelatinized SDs showed granule sizes of 0.1–40  $\mu\text{m}$  for CLWM, with a volume average diameter of  $15.2 \pm 0.1 \mu\text{m}$ ; granules sizes of 0.1–34  $\mu\text{m}$  for tapioca, with a volume average diameter of  $12.8 \pm 0.2 \mu\text{m}$ . Similar granule size distribution curves were obtained in previous works (Rao et al 1997; Rao and Tattiyakul 1999).

### Swelling and Volume Fraction of Granules

The volume fraction ( $\phi$ ) occupied by the swollen granules for each cultivar and concentration was calculated using Equation (1). The swelling ratio ( $Q$ ) values obtained are shown in Table I, which shows that the  $Q$  values did not depend on the starch concentration in the range of values studied. However, because the raw granules of both starches were about the same size, the higher  $Q$  values for tapioca clearly suggest that its granules grew bigger than those of the CLWM during gelatinization. This is reasonable because tapioca has been classified as a type A high swelling starch, while CLWM is a type C restricted swelling starch (Tattiyakul and Rao 2000). Quantitatively, Rao et al (1997) found that after heating CLWM during 10 min at  $80^\circ\text{C}$ , the granule average diameter increased  $\approx 2.4$  times (from 16.3 to 38.8  $\mu\text{m}$ ),

TABLE I  
Swelling Ratio Values ( $Q$ ) for Cross-Linked Waxy Maize (CLWM) and Tapioca Starch Dispersions at Different Concentrations ( $c$ ), Calculated with Blue Dextran Exclusion Method<sup>a</sup>

CLWM 80°C at 10 min		Tapioca 70°C at 10 min	
$c$ %	$Q$	$c$ %	$Q$
3.50	$13.85 \pm 0.08$	2.8	$21.56 \pm 0.08$
3.75	$13.81 \pm 0.25$	3.0	$21.34 \pm 0.98$
4.00	$14.69 \pm 0.23$	3.3	$20.10 \pm 0.21$
4.25	$15.02 \pm 0.39$	3.5	$20.22 \pm 0.36$
4.50	$14.20 \pm 0.10$	3.8	$20.60 \pm 0.20$
5.00	$14.50 \pm 0.16$	4.0	$20.95 \pm 0.43$

<sup>a</sup> Pasting conditions are shown for each starch.

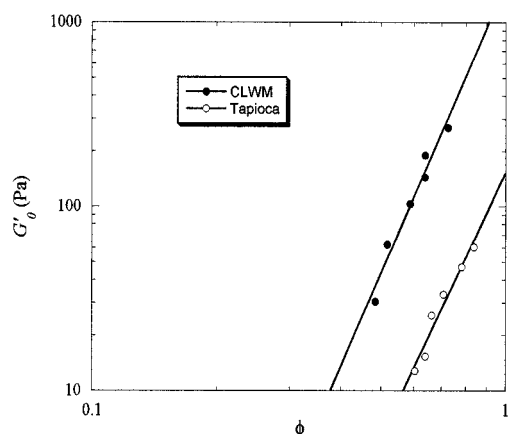


Fig. 5. Plateau values of storage modulus ( $G'_0$ ) as a function of granule volume fraction ( $\phi$ ) of cross-linked waxy maize (CLWM) and tapioca starch dispersions. Lines are values predicted by Eq. 3.

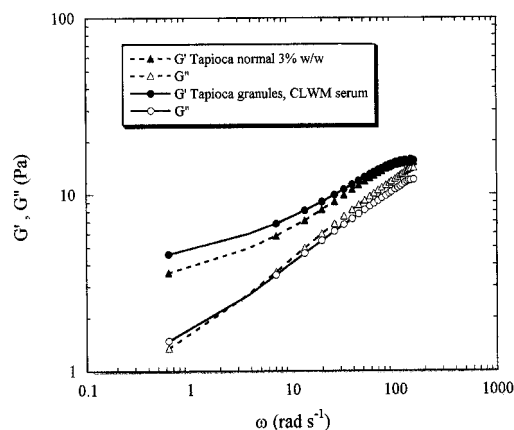
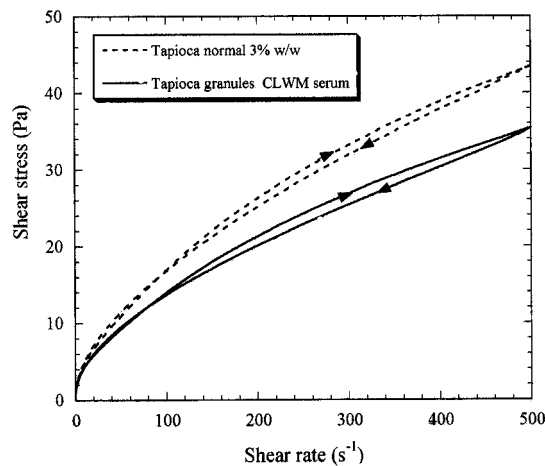


Fig. 6. Storage ( $G'$ ) and loss ( $G''$ ) moduli versus angular frequency ( $\omega$ ) of tapioca granules mixed with the cross-linked waxy maize (CLWM) continuous phase, compared with original tapioca (3%, w/w).



**Fig. 7.** Flow behavior ascending and descending curves of tapioca granules mixed with the cross-linked waxy maize (CLWM) continuous phase, compared to the original tapioca (3%, w/w).

while Rao and Tattiyakul (1999) observed that after heating tapioca at 70°C for either 5 or 15 min, the granule average diameter increased  $\approx 3.7$  times in both cases (from 12.9 to 47.7–47.8  $\mu\text{m}$ , respectively).

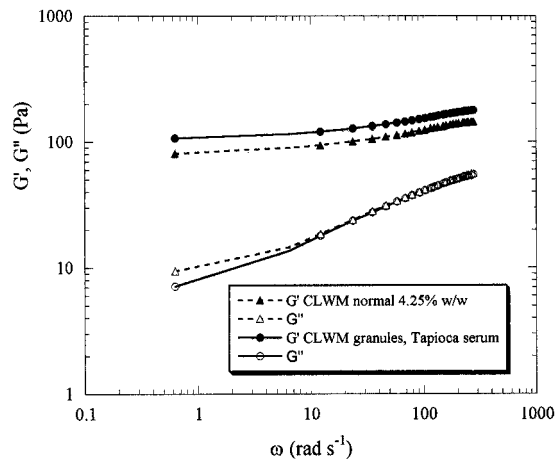
### Scaling Analysis

The equilibrium  $G'_0$  values obtained for CLWM and tapioca were plotted against  $\phi$  (Fig. 5). The double logarithmic plot resulted in reasonably straight lines ( $R^2 \geq 0.95$ ) for both starches, fulfilling the power law relationship inferred by Equation (3). Similar behavior was noted by Wong and Lelievre (1981) with wheat starch pastes.

The fractal dimensions of the two starch granules were calculated from the slope of the curves to be:  $D = 2.81$  for CLWM and  $D = 2.79$  for tapioca, respectively. According to the fractal theory, it means that both starches have granules with highly convoluted surfaces. Also, there is no significant difference in this aspect between starches.

The fractal dimensions obtained in this work are in good agreement with the value  $D = 2.77$  found by Calzetta et al (1999) for amaranth starch using the gas adsorption method. Hanselmann et al (1996) found lower values ( $D \approx 2.4$ ) for corn and potato starch using a light-scattering technique, but these starches were pasted at extremely rigorous conditions (160–175°C, 20–60 min) which may have resulted in rupture of the granules. Nagai and Yano (1990) found similar values ( $D = 2.2$ – $2.4$ ) for potato starch using the gas adsorption method. Applying small-angle X-ray scattering technique for corn and potato starch at high concentrations ( $c > 50\%$ , w/w), Suzuki et al (1997) suggest that both starches have smooth fractal surfaces ( $D \approx 2.0$ ) both in raw (24°C) and gelatinized (95°C) states. Finally, it should be noted that the highly convoluted surface of swollen CLWM granules has been previously observed by Chamberlain (1996) in SEM images.

On the other hand, the preexponential constant for CLWM,  $G'_{\phi=1} = 1,614$  Pa, was an order of magnitude greater than that for tapioca,  $G'_{\phi=1} = 152.6$  Pa. Starch gels can be considered to be composite materials, consisting of a continuous amorphous network (often made up of an aqueous solution of amylose) filled and reinforced by the swollen granules, whose contribution to the paste and gel rheology depends on (besides  $\phi$ ) their compressibility or deformability (Keetels 1995; Carnali and Zhou 1996; Rolee and Le Meste 1997). But, according to this model, the rheology of SDs should also be a linear function of that of the continuous phase (Carnali and Zhou 1996). Therefore, the different amylose content of both SDs could have some effect on the storage modulus. However, several authors (Evans and Haisman 1979; Eliasson 1986; Keetels 1995) have observed that the amylose content in the continuous phase plays only a minor role in the rheology of the SDs.



**Fig. 8.** Storage ( $G'$ ) and loss ( $G''$ ) moduli versus angular frequency ( $\omega$ ) of cross-linked waxy maize (CLWM) granules mixed with the tapioca continuous phase, compared with original CLWM (4.25%, w/w).

### Influence of Dispersed and Continuous Phases

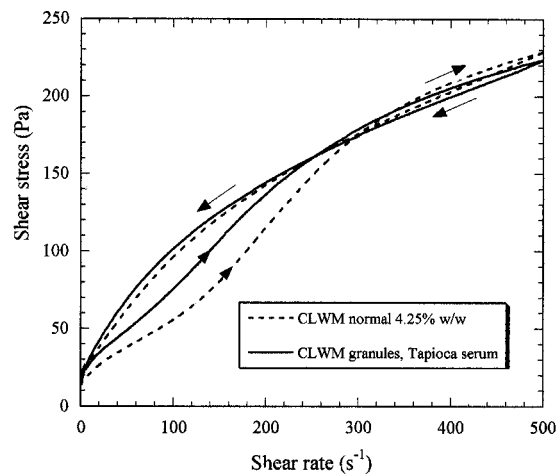
To determine the influence of the dispersed and continuous phases on  $G'_{\phi=1}$ , additional experiments were performed in which the continuous phases of the SDs were interchanged. The CLWM sediment represented  $\approx 80\%$ , w/w, of the sample, and the tapioca sediment represented  $\approx 78\%$ , w/w. The 2% lower weight of sediment in tapioca could be attributed to the siphoning of some granules during the separation process because the sediment-supernatant interphase in tapioca was more diffuse than in CLWM, probably because the highly swollen tapioca granules had a density more similar to the continuous phase and tended to resuspend easier than the CLWM granules. The difference between the weight fraction of the sediment (0.78–0.80) and  $\phi$  ( $\approx 0.64$ ) is probably due to the interstitial aqueous solution between the granules that could not be removed in the centrifugation process.

The dynamic and continuous shear rheological behaviors of the SDs made up of tapioca granules in CLWM continuous phase are compared with those of the original tapioca (3%, w/w) in Figs. 6 and 7, respectively. The absence of amylose from the continuous phase did not have a noticeable effect on the storage ( $G'$ ) and loss ( $G''$ ) moduli, but resulted in a significant decrease in the viscosity. However, the slight antithixotropic behavior at low shear rates was again observed, suggesting that this phenomenon is governed by the granules.

The dynamic and continuous shear rheological behaviors of the SDs made up of CLWM granules in tapioca continuous phase and the original CLWM (4.25%) are compared in Figs. 8 and 9, respectively. The addition of amylose to the continuous phase produced a moderate increase in  $G'$ , but  $G''$  remained almost the same. The flow curves were also very similar, exhibiting the combined antithixotropic and thixotropic behavior, although the anticlockwise hysteresis loop at low shear rates was smaller due to a slight increase of the viscosity in the ascending curve.

In general, the presence of amylose in the continuous phase may increase the viscosity of SDs, but it does not affect either the antithixotropic or the thixotropic behavior; these seem to depend on the characteristics of the dispersed phase. The loss modulus does not change noticeably in the presence of amylose, and the effect on the storage modulus, if any, is a moderate increase. Therefore, the higher elasticity of the CLWM SDs, with lower amylose content than tapioca, may be attributed exclusively to the structural properties of the granules.

Unswollen or underswollen granules are less deformable than fully swollen granules (Bagley and Christianson 1982; Doublier et al 1987), and more highly swollen (and presumably softer) granules reduce starch paste elasticity (Eliasson 1986). Therefore, it is evident that the smaller CLWM granules are also harder than the highly swollen tapioca granules, thus providing a higher elasticity to



**Fig. 9.** Flow behavior ascending and descending curves of cross-linked waxy maize (CLWM) granules mixed with the tapioca continuous phase, compared with original CLWM (4.25%, w/w).

the gel network in the same range of volume fractions. Besides its size, this higher strength and rigidity of the CLWM granules can also be attributed to the higher degree of amylopectin cross-linking (Steeneken 1989; Role and Le Meste 1997; Rao 1999). Cross-links provide structural stability to the granules and retain their integrity under high temperature and high shear conditions (Chamberlain 1996).

## CONCLUSIONS

Starch gels can be considered to be granule-reinforced continuous networks. The elasticity of this network increases with the volume fraction of the granules according to a power-law relationship. According to the scaling theory, the exponential factor depends on the granule's surface morphology, which can be quantitatively characterized by the fractal dimensions  $D = 2.81$  and  $D = 2.79$ , respectively, for gelatinized CLWM and tapioca SDs. For a specific value of volume fraction, elasticity of SDs increases with hardness of the granules, characterized by the pre-exponential coefficient  $G'_{\infty-1}$ . It seems that the amylose content in the continuous phase plays only a minor role in the rheology of gelatinized SDs.

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