

Oscillatory Rheometry of Starch-Water Systems: Effect of Starch Concentration and Temperature¹

L. M. HANSEN, R. C. HOSENEY, and J. M. FAUBION²

ABSTRACT

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An oscillatory probe rheometer was used to measure the rheological properties (G^* , G' , and G'') of corn starch-water systems throughout the sol-to-gel transformation. Starch-water suspensions of 5, 7, and 10% (w/w) were heated to endpoint temperatures (EPTs) of 81, 86, and 92°C, and the rheological properties of the pastes and resulting gels were measured. As starch concentration increased, G' increased. For all concentrations analyzed, G' varied depending on EPT. In general, G' was lower for suspensions heated to 81°C than for suspensions heated to 86 or 92°C. The temperature of the sol-to-gel transformation was

determined from the slope of the loss tangent and was dependent on starch concentration and EPT. The higher the starch concentration, the higher the temperature of the sol-to-gel transformation. Regression analysis determined that the amount of amylose and amylopectin leached from the granules, the swelling power of the granules, and the insoluble granules all interact and affect the rheological properties of the resulting gel. High soluble amylose levels and swelling powers increased gel elasticity, whereas high levels of soluble amylopectin were detrimental to gel formation and reduced elasticity.

Starch is a major component of many foods and can be used to manipulate the texture of a system. Starch and water dispersions heated above their gelatinization temperature behave as viscoelastic pastes. Upon cooling, the paste thickens and forms an elastic gel, provided that the starch concentration exceeds 6% (w/w) (Ring 1985). Starch gels are composites of swollen gelatinized granules, containing primarily amylopectin embedded in an amylose gel matrix (Ring and Stainsby 1982, Ring et al 1987).

Several workers (Ring and Stainsby 1982, Eliasson 1986, Ring et al 1987) have suggested that the physical characteristics of starch pastes and gels depend on the concentration of the granules; amount of amylose and amylopectin leached from the granules during heating; shape of the granules; swelling power of the granules; entanglement between the amylose and amylopectin; and granule-granule, amylose-granule, and amylopectin-granule interactions. Studies of amylose and amylopectin indicate that amylose is the predominant gel-forming polymer. However, the amylose and amylopectin solubilized during gelatinization and the remanent granule contribute to the gel's mechanical properties. Ring et al (1987) reported that amylose dominated the short-term (less than 3 hr) development of gel structure in pea starch gels. Orford et al (1987) reported that the initial rate of development of stiffness was correlated with the amount of amylose solubilized during gelatinization. Initial gel stiffness decreased in pea, maize, wheat, and potato starches (in descending order), which correlated with soluble amylose content. Several reports (Miles et al 1985b, Orford et al 1987, Ring et al 1987) have shown that the modulus of starch gels (G') continued to increase for several days. This long-term increase was linked to reversible crystallization involving amylopectin (retrogradation), whereas the initial short-term development was the result of gelation within the amylose matrix. The long-term increase in rigidity was reversible upon heating to 100°C, but the short-term development was irreversible.

Many researchers have measured the viscosities of heated starch dispersions (Mazurs et al 1957, Evans and Haisman 1979, Christianson et al 1984, Eliasson 1986). Most of the instruments used to measure viscosity apply exceedingly large strains and shearing stresses to the system, encouraging shear thinning and nonlinear behavior. Furthermore, many instruments can measure the elastic properties of the paste, but not as it undergoes a sol-to-gel transformation upon cooling. Several researchers have measured the viscoelastic properties of starch gels (Miles et al

1985a,b; Ott and Hester 1965, Orford et al 1987, Ring et al 1987).

Hansen et al (1990) described an oscillatory probe rheometer, an instrument that can measure the rheological properties of interest (i.e., G^* , G' , and G'') of starch pastes and the resulting gels. The advantage of this rheometer is that paste viscosity and gelation can be studied nondestructively at very low strain amplitudes. Neither the paste nor the gel is disrupted by testing. This instrument can measure in fundamental terms the rheological changes that occur during the cooling of starch pastes. The objectives of this study were: 1) to measure the rheological changes occurring in starch dispersions as they undergo sol-to-gel transformation as affected by heating to different endpoint temperatures (EPTs) and various starch concentrations and 2) to investigate how interactions between the amount of amylose and amylopectin leached from the granules during heating, the swelling power of the granules, and the concentration of the insoluble remanent granules affect rheological properties of the gels. The ultimate goal is to relate the molecular structure and interactions to the functional and textural properties of starch systems.

MATERIALS AND METHODS

Ingredients

Native, unmodified corn starch was donated by A. E. Staley Manufacturing Co. (Lot #DF67821, Decatur, IL). The corn starch was defatted by soxhlet extraction with methanol for 24 hr.

Preparation of Starch Suspensions

Defatted corn-starch suspensions were prepared at 5, 7, and 10% (w/w, db) starch concentrations using a procedure detailed previously (Hansen et al 1990). All starch-water dispersions were made to a total weight of 425 g. Suspensions were heated for 40 min in a water bath to an EPT of 81, 86, or 92°C. EPT was controlled by the temperature of the water in the water bath. After heating, approximately 320 ml of the hot starch suspension was used for rheological measurements; 50-75 ml was transferred to a 250-ml plastic centrifuge bottle for determination of swelling power and solubles.

Rheological Measurements

Complex modulus (G^*), storage modulus (G'), and loss modulus (G'') were determined using an oscillating rheometer (model 2110, Nametre Co., Metuchen, NJ) according to a procedure detailed previously (Hansen et al 1990). At least three replications were performed for each treatment.

Swelling Power and Percent Solubles

Swelling power was determined using a modification of the method of Leach et al (1959). The heated starch suspension (50-75 ml) was diluted with 100 ml of distilled water and placed in a 250-ml plastic centrifuge bottle, shaken 50 times, and allowed

¹ Contribution No. 90-303J. Kansas Agricultural Experiment Station, Manhattan, KS.

² Research associate, professor, and associate professor, respectively. Department of Grain Science and Industry, Kansas State University, Manhattan, KS 66506-2201.

to sit for about 2 hr before centrifuging at $2,000 \times g$ for 20 min. The supernatant that contained the solubles leached during heating was lyophilized and weighed. The precipitate was weighed, and swelling power was calculated by equation 1, as follows:

$$\text{swelling power} = \frac{\text{precipitate (wet weight)}}{\text{starch (db) - solubles (db) in suspension}} \quad (1)$$

The weight of the starch in the suspension (db) was calculated based on the percent of starch used to make the dispersion.

Percent Amylose and Amylopectin

The percent amylose in the lyophilized solubles was determined using the iodimetric method of Schoch (1964). Percent amylopectin was calculated as 100 minus percent amylose. These values then were used to calculate the amount (in grams) of amylose and amylopectin leached from the granules at each concentration and EPT.

Statistical Procedures

All statistical analyses were performed using CoHort Software, Berkeley, CA (1988).

RESULTS AND DISCUSSION

Complex Viscosity (G^*)

The sol-to-gel transformation was monitored using the oscillating probe rheometer. The data for G^* , G' , G'' , and G''/G' for all the starch concentrations (5, 7, and 10%) and EPTs (81, 86, and 92°C) are given in Table I. The G^* values for 7% starch dispersions heated to different EPTs and slowly cooled ($\sim 4^\circ\text{C}/\text{hr}$) to 20°C are illustrated in Figure 1. Similarly shaped curves that differed in the magnitude of G^* were obtained for the 5 and 10% dispersions. The 5% dispersion heated to 81°C

did not form a gel upon cooling. With all concentrations, G^* increased as the temperature decreased. Higher G^* values were obtained when the starch was heated to 86 or 92°C than when heated to 81°C. At all concentrations, few differences in G^* were found between the samples heated to 86°C and those heated to 92°C. G^* increased as concentration increased; however, it was not a linear function of concentration.

Storage Modulus (G') and Loss Modulus (G'')

Changes in G' as a function of temperature and EPT for a 7% starch-water dispersion are shown in Figure 2. Similarly shaped curves were obtained for 5 and 10% starch-water dispersions. G' increased as the sample cooled and became more gel-like. Over the same temperature range, G'' also increased (data not shown). The large change in G' indicated a large increase in the elastic properties of the suspension. Little difference was found between the 7% samples heated to 86 or 92°C; however, the 7% sample heated to 81°C had significantly lower G' values below approximately 35°C. The 5% sample heated to 92°C had higher G' values than did the 5% samples heated to 86°C. The 10% suspensions had similar G' values above 30°C, but below 30°C, significant differences were found between samples heated to different EPTs. G' was greatest for the sample heated to 86°C.

The initial G' values obtained between 60 and 70°C for the 10% starch pastes were in the same range as those reported by Eliasson (1986) for 10% maize starch systems. Orford et al (1987) reported G' values of 5,000–6,000 N/m^2 for 10% starch gels at 20°C, very similar to our results of 6,000–7,000 N/m^2 for a 10% corn-starch gel at 20°C.

G' increased as starch concentration increased (Table I). G' also increased as EPT was increased from 81 to 86°C, with the changes between 86 and 92°C being more variable. These results indicate that the storage modulus depends not only on the concentration of the starch-water dispersion but also on the temperature to which the gel is heated.

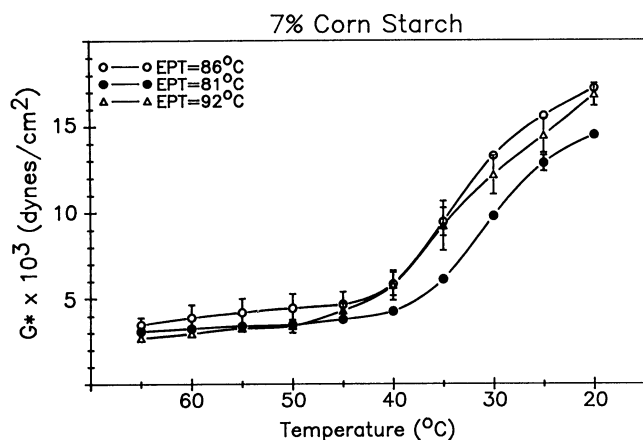


Fig. 1. Complex modulus (G^*) of 7% corn-starch dispersions as a function of decreasing temperature. Dispersions were heated to EPTs of 81, 86, or 92°C before cooling.

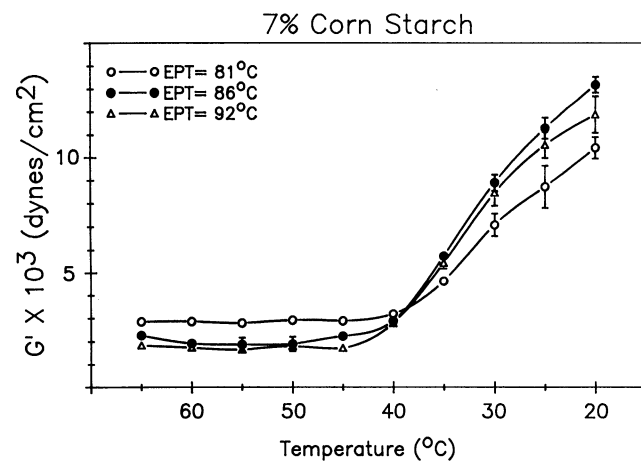


Fig. 2. Shear storage modulus (G') of 7% corn-starch dispersions as a function of decreasing temperature. Dispersions were heated to EPTs of 81, 86, or 92°C before cooling.

TABLE I
Rheological Property Values^a Measured at 20°C for Starch-Water Dispersions After Heating to Endpoint Temperature (EPT)

Concentration (%)	EPT (°C)	G^* (dynes/cm ²)	G' (dynes/cm ²)	G'' (dynes/cm ²)	G''/G'
5	86	5,734 ± 334	2,828 ± 317	4,974 ± 381	1.784 ± 0.283
5	92	6,500 ± 223	3,858 ± 164	5,219 ± 392	1.359 ± 0.159
7	81	14,498 ± 104	10,437 ± 469	10,031 ± 639	0.966 ± 0.105
7	86	17,204 ± 237	13,180 ± 340	11,034 ± 676	0.839 ± 0.072
7	92	16,850 ± 661	11,891 ± 796	11,917 ± 559	1.007 ± 0.088
10	81	67,534 ± 1,865	53,703 ± 891	40,937 ± 1,915	0.762 ± 0.023
10	86	72,794 ± 5,648	57,104 ± 3,584	44,976 ± 5,852	0.787 ± 0.088

^aValues are the mean and SD of three runs.

Loss Tangent (G''/G')

The ratio of G'' to G' (loss tangent or tangent) compares the energy lost with the energy stored during each oscillation of the probe (Fitzgerald et al 1988). As the sample changes from a sol to a gel, the energy stored increases, while the energy lost decreases. Consequently, the tangent decreases as the sample cools and becomes more gel-like.

The tangents for the 7 and 10% starch-water dispersions heated to various EPTs are shown in Figures 3 and 4, respectively. The loss tangent for the 7% starch systems varied as a function of EPT until the sample cooled to 30°C. Once the samples cooled to 30°C, the tangents for differing EPTs were similar. Throughout cooling, the tangent of 10% starch systems heated to 92°C EPT had higher values than the samples of equivalent starch content heated to EPTs of 86 and 81°C.

In solution, amylose molecules have an inherent tendency to undergo conformational ordering and subsequent alignment or aggregation (Dea 1982). Eventually, these aggregations or cross-links forms a continuous network throughout the system, resulting in a sol-to-gel transformation. At this point, a sharp increase occurs in the elastic properties of the system. We suggest that the gel point, or the temperature at which the suspension changes from a sol to a gel, occurs at the point where G' begins to change rapidly. This temperature can be extrapolated from the curves.

As starch concentration increased, so did the temperature of gel formation. For example, the gel temperatures for the 5, 7, and 10% suspensions heated to an EPT of 86°C were approximately 28, 40, and 55°C, respectively. At 5 and 7% starch concentration, gel temperature increased with higher EPT. At 10% starch, EPT appeared not to affect the temperature of gel formation.

Starch concentration alone does not explain rheological differences between samples, because we found differences in G^* , G' ,

G'' , and the tangent within each concentration, depending on EPT. Possibly, the amount of amylose and amylopectin leached from the granules during heating, the swelling power of the granules, and the concentration of insoluble remanent granules all interact and affect the rheological properties of the starch systems.

Determinations of Swelling Power, Amylose, and Amylopectin

The swelling power and concentrations of amylose, amylopectin, and insoluble starch (remanent granules) were determined at each starch concentration and EPT (Table II). Values were obtained at 20°C, the temperature at which all samples were gels. As starch concentration increased, swelling power decreased. As EPT increased, the amount of amylopectin leached from the granules increased. Using those data, regression equations 2 and 3 were calculated, setting G^* at 20°C and G' at 20°C as the dependent variable, respectively.

$$G^* \text{ (at } 20^\circ\text{C)} = -104,420 + 2,059.8 (SP) + 2,297.7 (A) - 2,860.6 (AP) + 3,749.1 (IS) \quad (2)$$

$$G' \text{ (at } 20^\circ\text{C)} = -83,859 + 1,544.9 (SP) + 2,248.6 (A) - 2,496.4 (AP) + 2,923.65 (IS) \quad (3)$$

where SP = swelling power of heated starch granules (%), A = amylose content leached from the granules (g/425 g of dispersion), AP = amylopectin concentration leached from the granules (g/425 g of dispersion), and IS = concentration of insoluble starch (g/425 g of dispersion). Both equations have R^2 values of 0.991.

Using equation 2, a plot of G^* was developed as a function of amylose and amylopectin content for a 7% gel with swelling

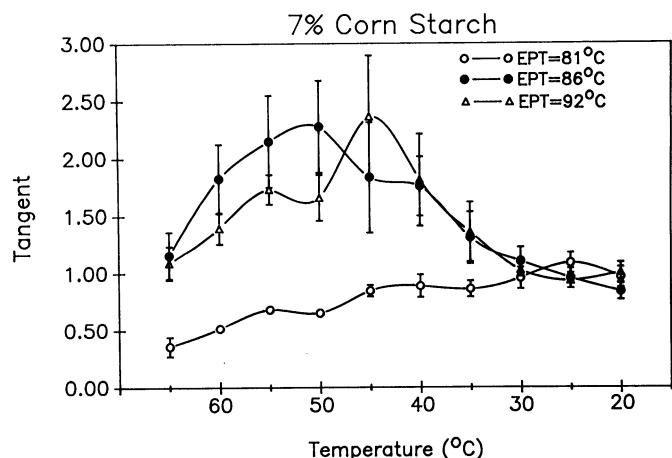


Fig. 3. Loss tangent (G''/G') of 7% corn-starch dispersions as a function of decreasing temperature. Dispersions were heated to EPTs of 81, 86, or 92°C before cooling.

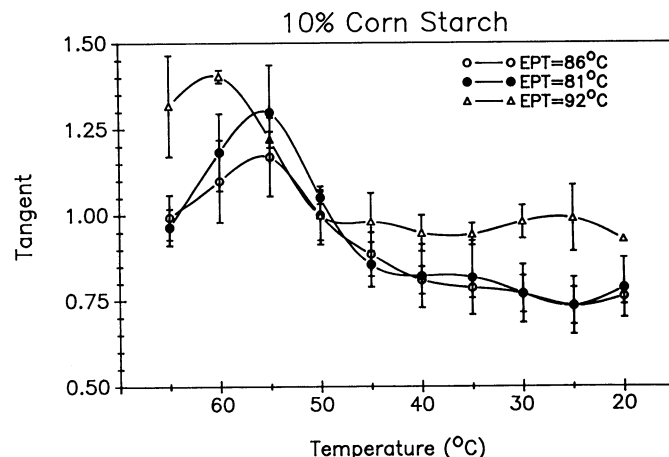


Fig. 4. Loss tangent (G''/G') of 10% corn-starch dispersions as a function of decreasing temperature. Dispersions were heated to EPTs of 81, 86, or 92°C before cooling.

TABLE II
Amylose and Amylopectin Contents, Insoluble Granules, and Swelling Power of Starch-Water Dispersions^a

Concentration (%)	EPT ^b (°C)	Soluble Amylose ^c	Soluble Amylopectin ^c	Insolubles ^c	Swelling Power (%)
5	92	4.97 ± 0.99	2.94 ± 0.25	13.26 ± 1.48	27.54 ± 2.19
5	86	3.64 ± 0.08	0.53 ± 0.16	17.07 ± 0.14	17.45 ± 0.64
7	92	4.63 ± 0.31	1.94 ± 0.37	20.69 ± 0.67	20.00 ± 0.74
7	86	4.05 ± 0.22	0.90 ± 0.20	22.32 ± 0.36	15.02 ± 0.09
7	81	4.27 ± 0.17	0.34 ± 0.09	22.66 ± 0.26	13.35 ± 0.49
10	92	6.52 ± 1.05	1.53 ± 0.37	34.44 ± 1.42	16.45 ± 2.18
10	86	5.58 ± 0.82	0.84 ± 0.17	36.37 ± 0.66	14.35 ± 0.36
10	81	5.07 ± 0.08	0.74 ± 0.10	36.69 ± 0.05	13.01 ± 0.19

^aAll starch-water dispersions (w/w) were made to a total weight of 424 g.

^bEndpoint temperature.

^cGrams per grams of starch-water dispersion. Values are the mean of three runs.

power held constant at 15 and insoluble starch held constant at 21.76 g (Fig. 5). The values for swelling power and insoluble starch were means of the data obtained from 7% starch-water dispersions. The plot shows that for a given amylopectin content,

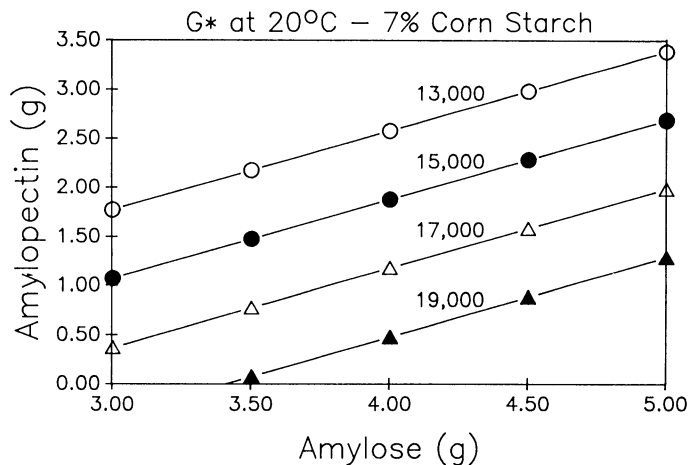


Fig. 5. Complex modulus values (G^*) for 7% starch gels at 20°C calculated using equation 2 (see text). Values for G^* are dynes/cm². Soluble amylose and amylopectin levels were varied. Constant values (means for 7% starch gels) for swelling power (15) and insoluble granules (21.76 g) were used.

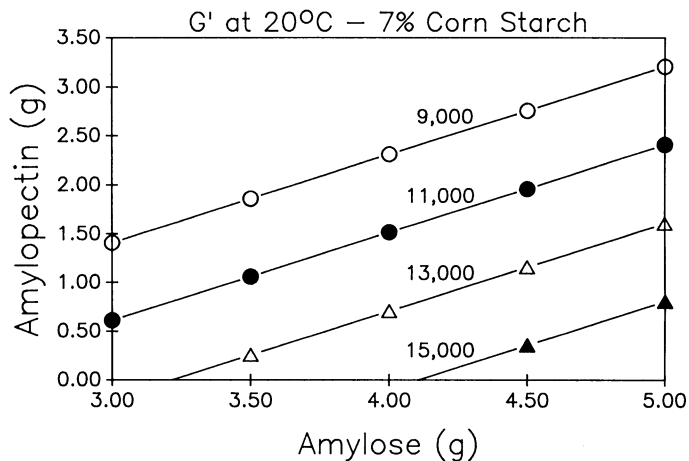


Fig. 6. Shear storage modulus (G') for 7% starch gels at 20°C calculated using equation 3 (see text). Values for G' are dynes/cm². Soluble amylose and amylopectin levels were varied. Constant values (means for 7% starch gels) for swelling power (15) and insoluble granules (21.76 g) were used.

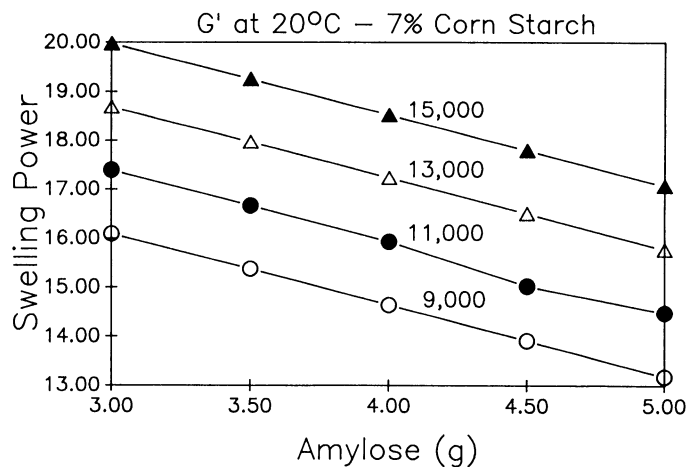


Fig. 7. Shear storage modulus (G') for 7% starch gels at 20°C calculated using equation 3 (see text). Values for G' are dynes/cm². Soluble amylose and swelling power were varied. Constant values (means for 7% starch gels) for amylopectin (1.15 g) and insoluble granules (21.76 g) were used.

G^* increases as amylose content increases, and at any amylose value, G^* decreases as amylopectin is increased. Figure 6 shows a plot of G' as a function of amylose and amylopectin concentration, developed from equation 3. Again, swelling power and insoluble starch were held constant at 15 and 21.76 g, respectively. As was true for G^* , G' increased as amylose increased for any given amylopectin content and decreased with increased amylopectin at any given amylose concentration. Therefore, amylopectin has detrimental effects on gel formation and rigidity.

These data are consistent with the findings of Miles et al (1985a) and Ring et al (1987). In a pure amylose system, a minimum level of amylose is required for gel formation. Below this level, amylose will precipitate and not form a gel (Miles et al 1985a). Amylopectin alone will not form a gel, except at very high concentrations or low temperatures (Ring et al 1987). However, the minimum level of amylose required for gel formation in a system of amylose-amylopectin insoluble granules has not been established.

Plots showing the relationship between swelling power and amylose content were developed with amylopectin concentration held constant at 1.15 g/425 g of starch-water dispersion and insoluble granules held constant at 21.76 g (Fig. 7). The value used for amylopectin content was the average found leached from the granules when 7% starch concentrations made to total weights of 425 g were heated to different EPTs. Fig. 7 shows that at any constant amylose content, G' increased as swelling power increased. Also, decreases in swelling power could be compensated for by increases in amylose content to produce gels with comparable G' values. Similar results for G^* and G' were obtained for the 5% concentrations (data not shown). At the 10% concentration, differences in swelling power caused only small variations in G^* and G' .

In general, over the period investigated, high levels of amylopectin tended to be detrimental to gel strength, whereas high levels of amylose and swelling power were beneficial and produced more rigid gels. It may be that amylopectin interferes with the interactions between amylose molecules. These results agree with those of Orford et al (1987), that the short-term development of gel stiffness and strength is related to the amount of amylose solubilized during gelatinization.

CONCLUSIONS

The sol-to-gel transformation during cooling of a starch paste can be measured with an oscillatory rheometer. The temperature at which the starch sol becomes a gel depends on the starch concentration in the dispersion, and at a specific concentration (i.e., 7%), the gel temperature can be manipulated by heating to different EPTs. G^* and G' varied as a function of concentration and EPT. Regression analysis demonstrated that the amount of amylose and amylopectin leached from the granules during heating, the concentration of the insoluble granules, and the swelling power all interact and affect the rheological properties of the gels. In general, higher swelling power and high concentrations of amylose produce more rigid and more elastic gels, whereas high levels of amylopectin interfere and hinder gel development.

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