

Rheological and Thermal Properties of Aged Starch Pastes from Three Waxy Maize Genotypes

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ABSTRACT

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The rheological and thermal properties of aged starch gels (15:85 starch-water) from three waxy maize genotypes (*wx*, *wx sh1*, and *du wx*) during storage (4°C for up to 25 days) were studied. After storage, changes of storage modulus (G') and phase angle (δ) of the gels as a function of temperature were measured using oscillatory rheometry. For the *du wx* samples, G' at 25°C increased rapidly during the first four days of storage at 4°C, compared to the gradual increases over the 25-day storage period for the *wx* and *wx sh1* samples. A peak in G' at 45°C was observed during heating for the *du wx* samples after 10 days of storage and for the *wx* sample stored for 25 days. The G' peak may have been due to syneresis in the gels. Retrogradation of amylopectin of the aged

starch samples was examined using differential scanning calorimetry. The *du wx* starch had greater retrogradation enthalpies than the other two samples (which showed similar retrogradation behavior) throughout the storage. The retrogradation enthalpy of the *du wx* samples increased rapidly during the first seven days, followed by a slower increase through the rest of storage. For the *wx* and *wx sh1* samples, no endotherm was observed during the first four days of storage, after which the enthalpy increased steadily as a function of storage time. Addition of sucrose delayed the formation of gel networks for all three starches. The greater tendency for gelling and retrogradation of the *du wx* starch might be attributed to the greater proportion of DP20–30 chains of the amylopectin.

Starch gels have been considered as composites containing gelatinized granules embedded in an amylose matrix (Bohlin et al 1986, Eliasson 1986, Miles et al 1985). Therefore rheological properties of starch gels are determined by both the dispersed swollen granules and the continuous phase. The short-term development of gel structure and crystallinity in starch gels has been found to be dominated by irreversible ($T < 100^\circ\text{C}$) gelation and crystallization within an amylose matrix. The long-term increase in the moduli of starch gels has been linked to a reversible crystallization, involving amylopectin, within the granules (Miles et al 1985, Biliaderis and Zawistowski 1990). Miles et al (1985) suggested that the amylopectin crystallization resulted in an increase in the rigidity of the granules and thus enhanced their reinforcement of the amylose matrix. For waxy maize starches, the development of gel modulus should be largely controlled by the rate of amylopectin recrystallization (Ring et al 1987), which is closely related to the structure of amylopectin molecules (Kalichevsky et al 1990, Yuan et al 1993).

Doublier et al (1987) suggested that the overall viscosity of starch pastes is primarily governed by a combination of the volume fraction of the dispersed phase and the concentration and composition of the continuous phase. At a high concentration ($\approx 10\%$ solids), deformability of swollen particles seems to play a prevailing role. Steeneken (1989) reported that pastes of low-swelling starches had a lower viscosity than pastes of high-swelling starches at low concentration. However, at high concentration, this situation was reversed. It was proposed that in the dilute regime (when the volume of swollen granules is less than the total volume), the viscosity is governed by the volume fraction of swollen granules, whereas in the concentrated regime, it is governed by particle rigidity (Steeneken 1989).

Oscillatory rheometry is frequently used to monitor the development of starch gelation by measuring shear moduli (G' or G'') of starch pastes (Eliasson 1986, Biliaderis and Zawistowski 1990, Hansen et al 1991, Svegmarm and Hermansson 1991, Eliasson and Kim 1992, Kim and Eliasson 1993, Kim et al 1993, Svegmarm et al 1993). Differential scanning calorimetry (DSC) analysis has been used to correlate the rheological measurements and to identify the contribution of amylopectin retrogradation to the increase in storage modulus (Biliaderis and Zawistowski 1990, Kalichevsky

et al 1990). Kalichevsky et al (1990) studied amylopectins isolated from various starches and found that there was no simple relationship between retrogradation enthalpy and shear modulus, and no obvious correlation between shear modulus and amylopectin chain profile. Those authors suggested that the overall molecular structure (e.g., heterogeneity of branching of different amylopectins) may be important. However Shi and Seib (1992) reported that a decrease in the mole fraction of amylopectin chains between DP14 and 24 decreased the retrogradation tendency of waxy-type starches.

The objective of the present work was to study the rheological properties of aging starch gels from various waxy maize genotypes using small-strain oscillatory rheometry as a function of temperature. The thermal properties of the gels were measured by DSC to better understand the contribution of amylopectin recrystallization to gel structure formation and loss of gel structure on heating. Chain-length distribution of amylopectin was determined using high-performance size-exclusion chromatography (HPSEC) following isoamylase debranching to relate the molecular structure to thermal and rheological properties.

MATERIALS AND METHODS

Starch Materials

Three waxy-type maize starches (*wx*, *wx sh1*, and *du wx*) were obtained from the same commercial source (American Maize Products Co., Hammond, IN, now Cerestar USA, Inc.).

Sample Preparation

Starch slurries with or without sucrose (see Table I for composition) were prepared by mixing in 1-L canning jars. The lids were screwed tight and the slurries were gelatinized in a 95°C waterbath shaker. To prevent the starch granules from settling during heating, the samples were shaken in the waterbath for ≈ 15 min or until the slurries thickened. After heating for 1 hr, the samples

TABLE I
Composition of Starch Slurries for Rheological Properties Determination^a

Component	Without Sucrose		With Sucrose	
	wt (g)	%	wt (g)	%
Starch (dwb)	45	15	45	12.5
Water	255	85	255	70.8
Sucrose	0	0	60	16.7

^a 15:85 Starch-water.

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were removed from the waterbath and cooled at room temperature for 1 hr. A portion of starch paste was then removed from the jar and placed between two plexiglass plates ($9 \times 9 \times 0.3$ cm) with

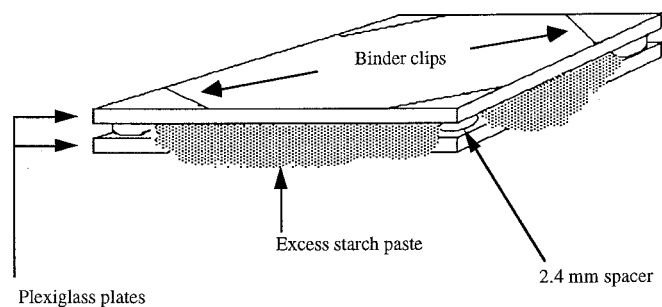


Fig. 1. Sample preparation for dynamic rheological tests.

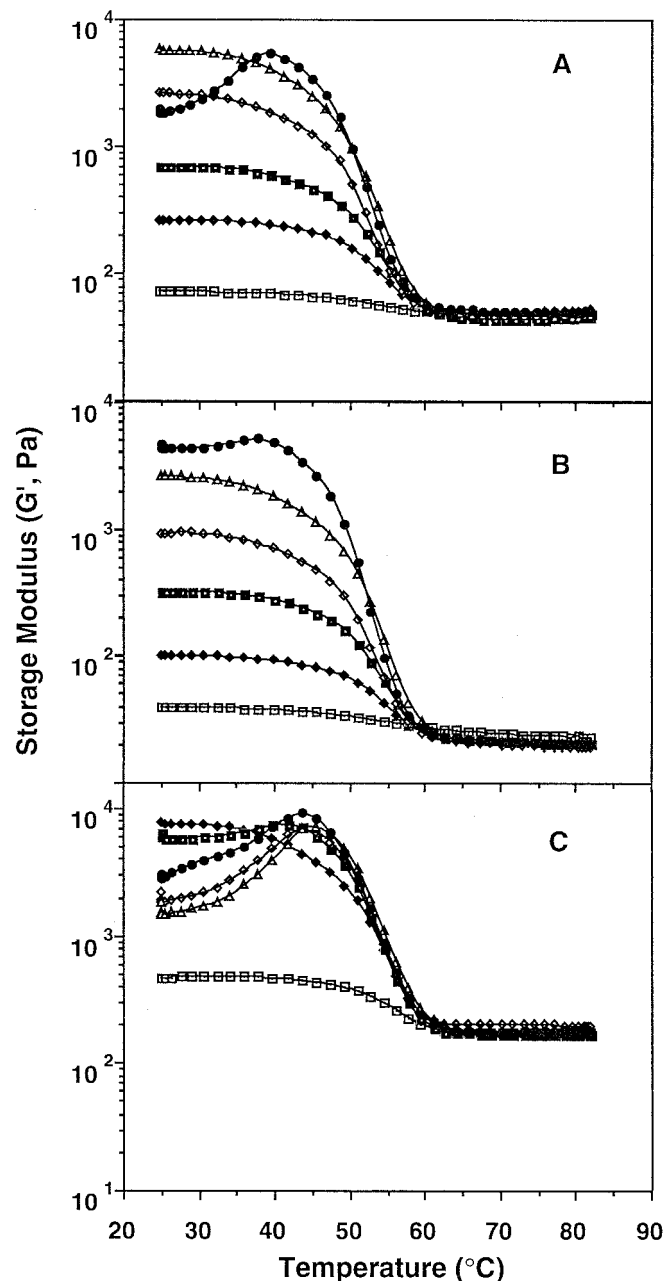


Fig. 2. Representative plots of changes in storage modulus (G') during heating of starch pastes (15:85 starch-water) for maize genotypes *wx* (A), *wx sh1* (B), and *du wx* (C) stored at 4°C for 1 (\square), 4 (\blacklozenge), 7 (\blacksquare), 10 (\diamond), 15 (\triangle) and 25 (\bullet) days.

four sealed stainless steel DSC pans as spacers (Fig. 1). The starch paste was then shaped between the plates by clamping the corners with binder clips. Excess starch paste was used so that some portion of the paste was expressed out of the plates. The sample was then wrapped with two layers of polyethylene food wrap before storage at 4°C . Eight specimens were prepared for each starch sample.

Rheological Measurements

Rheological properties of the starch gels were measured using a rheometer (RFS II, Rheometrics, Inc., Piscataway, NJ) with parallel plate (5-cm dia) geometry.

A separate specimen was removed from the 4°C refrigerator after 1, 4, 7, 10, 15, and 25 days of storage. The plexiglass plates were carefully separated so that the starch gel stayed intact on one plate. A 6-cm diameter disk was cut from the center of the gel. The disk was then transferred to the sample stage of the rheometer. The sample was then trimmed to the size of the parallel plate. A thin film of vacuum pump oil (19 cv, Capital Vacuum, Chantilly, VA) was applied to the edge of the sample to prevent evaporation during heating. The temperature of the stage was controlled (Environmental Control Circulator, Rheometrics, Inc., Piscataway, NJ). For each analysis, the temperature of the sample was increased from 25 to 82°C at a rate of $5^\circ\text{C}/\text{min}$. Storage modulus (G') and phase angle (δ) of the gel at 2% strain and 10 rad/sec oscillating frequency were measured every 20 sec during heating. Three separate analyses were performed for each sample. Results of the three analyses were in good agreement and only one analysis is presented.

DSC Analysis

Retrogradation behaviors of the three starches as a function of storage time at 4°C were studied using a differential scanning calorimeter (DSC-7, Perkin-Elmer, Norwalk, CT).

Starch powder sample (≈ 5.0 mg, dry basis) was placed in a preweighed stainless steel DSC pan (Perkin-Elmer) and the precise weight (± 0.01 mg) determined using an autobalance (AD2B, Perkin-Elmer). The calculated amounts of deionized water or sucrose solution were then added to adjust the composition to those shown in Table I. The pan containing the starch slurry was hermetically sealed, and the starch was then gelatinized by heating in a 95°C convection oven for 30 min. The gelatinized starch samples were then stored at 4°C for up to 25 days. After each storage period, the sample was heated in the DSC from 10 to 100°C . The extent of amylopectin retrogradation was determined by the enthalpy of the peak near 55 – 60°C . Temperature and enthalpy of the instrument were calibrated using an indium standard.

Amylopectin Structure Analysis

Chain length distribution of amylopectin was examined by size-exclusion chromatography following isoamylase-debranching as described by Yuan et al (1993). The chromatograms were divided into three fractions using two demarcations (the same demarcations were used for all three starches) as determined based on the minimum and the apparent inflection point observed in the chromatogram of the *wx* starch.

RESULTS

Dynamic Rheological Properties

The G' of the gels from the three starches as a function of temperature are shown in Fig. 2. For the *wx* starch, the initial G' at 25°C increased with storage time through 15 days. At day 25, the initial G' was lower than that at day 15. The G' of the 25-day sample increased with heating and peaked at $\approx 40^\circ\text{C}$. All *wx* samples except that at day 1 showed a sharp drop in G' from 45 to 60°C , indicating a breakdown in gel structure with increasing temperature. For *wx sh1* starch, the initial G' increased from ≈ 40 Pa at day 1 to $\approx 45,000$ Pa at day 25. At day 25, the G' showed an

indication of peaking $\approx 38^\circ\text{C}$. Except at day 25, initial G' of all *wx sh1* samples were lower than the similarly aged *wx* samples. The *du wx* starch showed a relatively high initial G' of 450 Pa on day 1, indicating more rapid gel network formation as compared to the *wx* and *wx sh1* starches. Initial G' of the *du wx* starch increased to $\approx 7,800$ Pa on day 4. Tests for the *du wx* starch gels at day 7 and later showed a peak in $G' \approx 45^\circ\text{C}$ during heating.

Phase angle (δ) is also related to the structural properties of a viscoelastic material. The lower the value of δ , the more elastic is the structure. Figure 3 shows the changes in δ during heating of the starch gels after each storage period. The *wx* and *wx sh1* starch gels exhibited a similar pattern in that initial values of δ decreased with increasing storage time up to 15 days. On day 25, initial values of δ were higher than those at day 1; upon heating, the δ dropped sharply between 30 and 40°C and reached a minimum between 40 and 50°C . For the *du wx* genotype starch, the initial δ values were much lower than the other two samples at day 1, indicating a more elastic gel. After day 4, the *du wx* samples started to show a minimum in $\delta \approx 52^\circ\text{C}$, which was not observed in the *wx* and *wx sh1* samples until day 25. For all three samples, the occurrence of a minimum $\delta \approx 50^\circ\text{C}$ corresponded to the appearance of a G' peak.

The changes of G' and δ of the starch gels in the presence of sucrose are shown in Figs. 4 and 5, respectively. For *wx* and *wx sh1* samples, the initial values of G' were higher at day 1 than

their respective non-sucrose-containing counterparts. However the initial G' values were lower than the non-sucrose-containing samples at each of the subsequent storage periods. Neither the G' peak nor the δ minimum was observed for the *wx* and *wx sh1* samples in the presence of sucrose. For *du wx* samples, the addition of sucrose did not completely eliminate the appearance of the G' peaks and δ minima.

DSC Analysis

All observed retrogradation endotherms had a peak temperature between 55 and 60°C , typical for the melting of retrograded amylopectin (Ring et al 1987). Enthalpies of the retrogradation endotherms are summarized in Table II. The retrogradation enthalpy as a function of storage time is shown in Fig. 6. For the *wx* and *wx sh1* samples, no retrogradation was observed by DSC after four days of storage. The two starches then showed a similar increase in enthalpy from day 7 to day 25. Although the enthalpy of the *wx* starch was

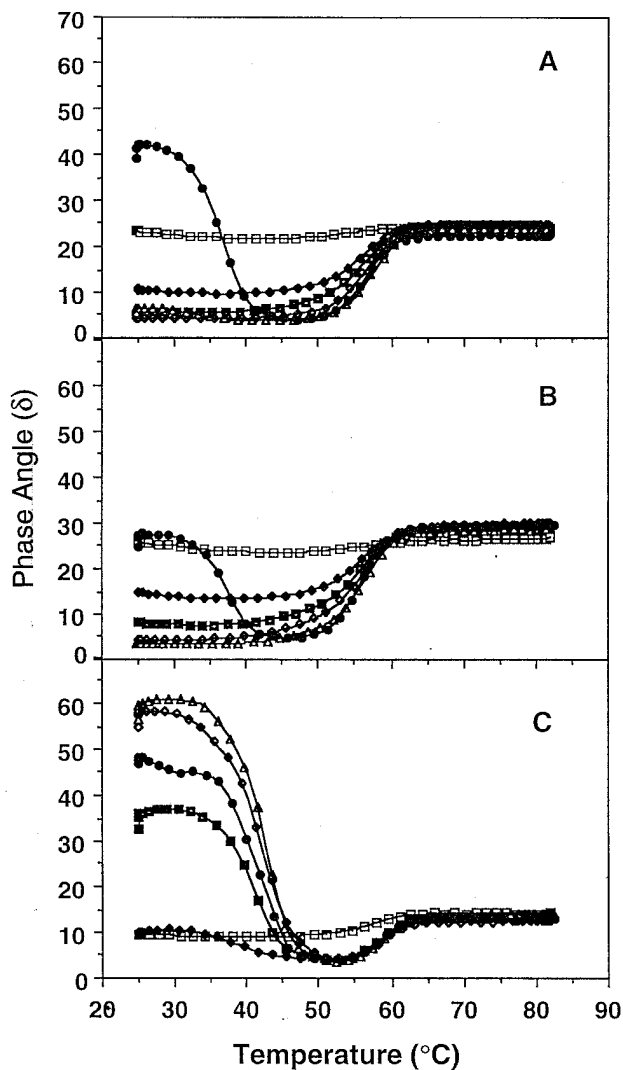


Fig. 3. Representative plots of changes in phase angle (δ) during heating of starch pastes (15:85 starch-water) for maize genotypes *wx* (A), *wx sh1* (B), and *du wx* (C) stored at 4°C for 1 (\square), 4 (\blacklozenge), 7 (\blacksquare), 10 (\diamond), 15 (\triangle), and 25 (\bullet) days.

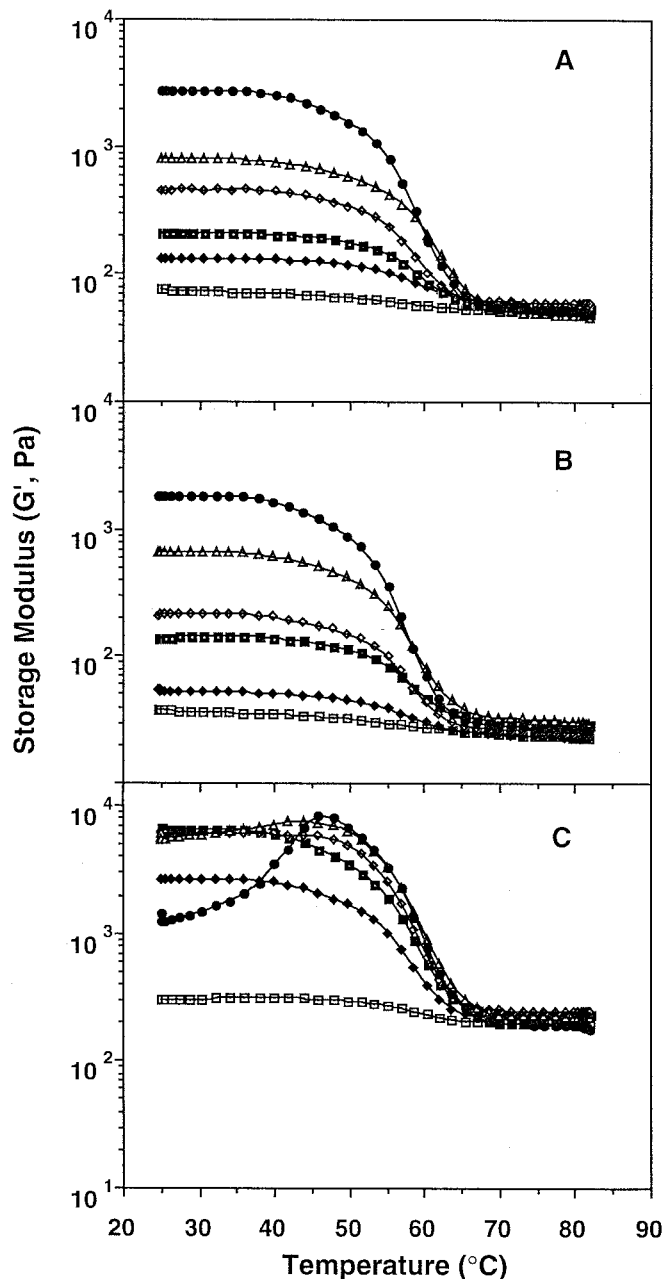


Fig. 4. Representative plots of changes in storage modulus (G') during heating of starch pastes (15:85 starch-water) containing 16.7% sucrose for maize genotypes *wx* (A), *wx sh1* (B), and *du wx* (C) stored at 4°C for 1 (\square), 4 (\blacklozenge), 7 (\blacksquare), 10 (\diamond), 15 (\triangle) and 25 (\bullet) days.

higher than the *wx sh1* starch at days 7 and 10, no significant difference was found between the two samples at days 15 and 25. The *du wx* sample showed a small endotherm (2.8 J/g) after one day at 4°C. The enthalpy then increased rapidly to 9.2 J/g on day 7, followed by a slower rate of increase from day 10 (9.3 J/g) to day 25 (11.5 J/g). The enthalpies of the *du wx* sample were significantly higher than the other two starches at all storage periods.

The enthalpies of the aged starch gels containing sucrose are plotted versus storage time in Fig. 7, which shows trends similar to those in Fig. 6 for the starches without sucrose. In general, the added sucrose decreased the enthalpies of the endotherms when compared to the non-sucrose-containing samples. However the effect of sucrose was only evident after days 10 and 15 for the *wx sh1* and *wx* starches respectively.

Chain Length Distribution of Amylopectin

Figure 8 shows representative HPSEC chromatograms for the isoamylase-debranched starches from the three *wx*-containing maize genotypes. The chain length distribution parameters for the chromatograms are listed in Table III. The high molecular weight peak ($DP \approx 320$) of the debranched *du wx* starch, accounting for $\approx 3\%$ of total area, was not included in the calculations for the chain length distribution of the amylopectin because it was assumed to come from amylose. Considering fractions I-III as a whole, the

number-average degree of polymerization (DP_n) was 15 for all three samples. The weight-average degree of polymerization (DP_w) was 22 for the *wx* and *wx sh1* and 20 for the *du wx*. For the *wx* and *wx sh1* samples, the chain length distributions in the three fractions were virtually the same. The *du wx* starch appeared to have a greater proportion of fraction II but a smaller amount of fraction I than the other two samples.

DISCUSSION

The rheological measurements (Figs. 2 and 3) showed that *du wx* starch formed a gel network within one day of storage at 4°C, as evidenced by the decrease in G' at $\approx 50\text{--}60^\circ\text{C}$ upon heating. A maximum initial G' was reached after four days. On the other hand, *wx* and *wx sh1* starches developed the gel network steadily and rather slowly over the 25-day period. The rheological properties of the 15% (w/w) *wx* and *wx sh1* starch pastes after one day are consistent with the report that gelation of waxy maize starch within 24 hr only occurred when the concentration was $>20\%$ (Biliaderis and Zawistowski 1990).

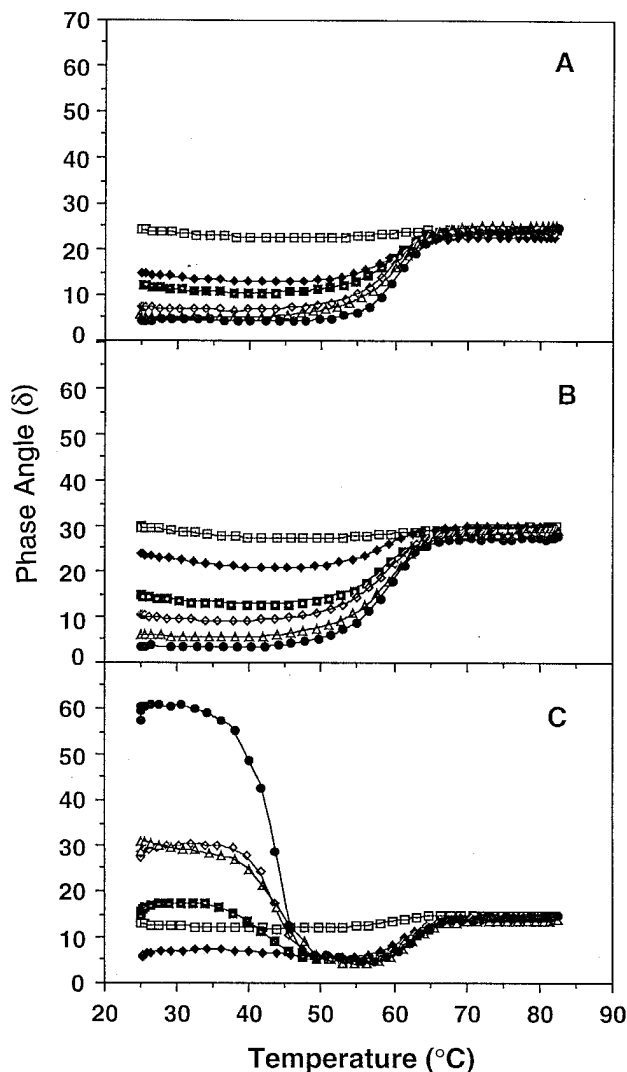


Fig. 5. Representative plots of changes in phase angle (δ) during heating of starch pastes (15:85 starch-water) containing 16.7% sucrose for maize genotypes *wx* (A), *wx sh1* (B), and *du wx* (C) stored at 4°C for 1 (□), 4 (◆), 7 (■), 10 (◇), 15 (Δ) and 25 (●) days.

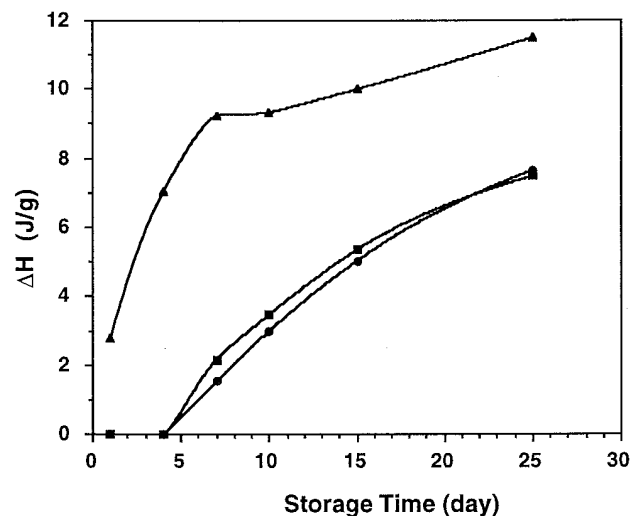


Fig. 6. Retrogradation enthalpy (ΔH , J/g) of maize genotypes *wx* (■), *wx sh1* (●) and *du wx* (▲) for aged starch gels (15:85 starch-water) as a function of storage time. Each point is a mean of three measurements.

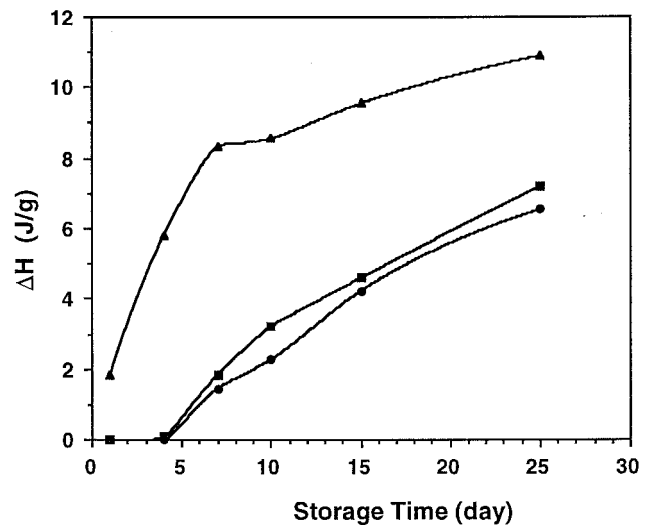


Fig. 7. Retrogradation enthalpy (ΔH , J/g) of maize genotypes *wx* (■), *wx sh1* (●) and *du wx* (▲) for aged starch gels (15:85 starch-water) containing 16.7% sucrose as a function of storage time. Each point is a mean of three measurements.

At 15:85 starch-water ratio, the starch pastes used in the present study were in a concentrated regime as the swelling of the starches was limited. This system, however, is different from the concentrated regime described by Steeneken (1989) where rheology is dominated by the rigidity of the presumably intact swollen granules. Light microscopy (data not shown) showed all three pastes of the present study were composed of solubilized amylopectin with some fragments of swollen granules. The change in rheological properties of these pastes upon storage should be largely governed by the retrogradation of the continuous phase, that is, solubilized amylopectin.

Shi and Seib (1992) reported that a decrease in the mole fraction of amylopectin chains between DP14 and 24 decreased the retrogradation tendency of waxy-type starches. In the present study, the *du wx* starch seemed to have a more prominent shoulder in fraction II than the other two starches. There appeared to be a tendency that the *du wx* starch had a greater proportion of fraction II (DP20–30) than the other two starches. A greater proportion of this fraction in *du wx* starch could explain the more rapid increases in G' and ΔH during storage. The rapid gelling behavior of the *du wx* starch is also consistent with the hypothesis (R. Hauber, *personal communication*, 1995) that the commercial *du wx* starch has more long exterior chains (DP>12) than the *wx* and *wx sh1* starches. Yuan et al (1993) reported that *du wx* starches from maize inbred lines had a greater tendency to retrograde than the *wx* starch at 10 and 30% concentrations. Figure 9 shows the debranched commercial *du wx* starch had $\approx 3\%$ high molecular weight (DP ≈ 320) material, which was not seen in the *du wx* starches from the inbred lines (Yuan et al 1993). These long chains, whether from amylose or amylopectin, could contribute to the properties of the commercial *du wx* starch. These commercial

starches all contained blue-staining starch granules (2% for *du wx* starch and 1% for *wx* and *wx sh1* starches), indicating possible contamination by normal maize starch. However, only the *du wx* starch showed a high molecular weight peak at DP320.

For some *wx* and *du wx* samples on continued storage, the initial G' became lower than that at the previous test. For those samples, the G' increased during heating and then formed a peak at $\approx 40^\circ\text{C}$ (Figs. 2 and 4). This observation is paradoxical as it suggests the gels softened with further storage and yet stiffened during initial heating. Eliasson and Kim (1992) reported similar phenomena for starch gels that received repeated freeze-thaw treatments. In this and subsequent work (Kim et al 1993, Kim and Eliasson 1993), they suggested the behavior was related to the syneresis of the starch gels. It is not clear why syneresis of starch gels would give rise to the peak in gel modulus upon heating. Further investigation into the rheological methodology for aged starch gels is necessary to determine the underlying mechanism of this observation.

Kim and Eliasson (1993) reported that after freeze-thaw treatments, when a starch paste showed a peak in complex modulus, it also showed a thermal transition peak in DSC measurements. In the present study with constant storage temperatures, all samples that showed a peak in G' also showed a DSC endotherm, consistent with the observation of Kim and Eliasson (1993). However, a detectable retrogradation DSC peak preceded the formation of a peak in G' .

To compare the results from the rheological measurements to DSC data, the changes in initial G' (i.e., at 25°C) and ΔH over time are plotted together in Fig. 9. G' data were not plotted in Fig. 9 if the data suggested syneresis. For the *wx* and *wx sh1* starches, the development of a gel network was evidenced by the changes in G' in the first four days of storage. No retrogradation was detect-

TABLE II
Effects of Storage Time at 4°C on Retrogradation Enthalpy (ΔH , J/g) of Starch Pastes With or Without Sucrose^{a,b}

Maize Genotypes	Storage Time (days)					
	1	4	7	10	15	25
<i>wx</i>	nd ^c	nd	2.2 ± 0.2a	3.5 ± 0.2a	5.3 ± 0.2a	7.5 ± 0.4a
<i>wx sh1</i>	nd	nd	1.5 ± 0.2bc	3.0 ± 0.3a	5.0 ± 0.4a	7.7 ± 0.2a
<i>du wx</i>	2.8 ± 0.5a	7.0 ± 0.1a	9.2 ± 0.0d	9.3 ± 0.2b	10.0 ± 0.2b	11.6 ± 0.1b
<i>wx+s</i>	nd	nd	1.8 ± 0.2ac	3.2 ± 0.1a	4.4 ± 0.3c	7.0 ± 0.4c
<i>wx sh1+s</i>	nd	nd	1.5 ± 0.1b	2.3 ± 0.2c	4.2 ± 0.2c	6.5 ± 0.2d
<i>du wx+s</i>	1.9 ± 0.3b	5.8 ± 0.4b	8.3 ± 0.2e	8.6 ± 0.1d	9.6 ± 0.2d	10.9 ± 0.3e

^a 15:85 Starch-water when present, sucrose was 16.7% of total weight.

^b Values are mean ± standard deviation from three separate analyses. Values followed by the same letter in the same column are not significantly different ($P < 0.05$).

^c Not detected.

TABLE III
Characterization of Chain Length (CL) Distribution of Isoamylase-Debranched Starches from Maize Genotypes

Starch	CL Parameters ^a	Entire Sample ^b	Fraction ^c		
			I	II	III
<i>wx</i>	Peak DP		40 (39,40)	...	14 (13,14)
	DP _n	15 (15,15)	43 (42,43)	20 (20,20)	10 (10,10)
	DP _w	22 (21,23)	47 (46,47)	21 (21,21)	11 (11,11)
	wt%		22.0 (20.7,23.3)	35.2 (34.2,36.1)	42.8 (45.1,40.6)
	mole%		7.8	26.9	65.3
<i>wx sh1</i>	Peak DP		39 (39,39)	...	14 (14,14)
	DP _n	15 (15,14)	42 (41,42)	20 (20,19)	10 (10,10)
	DP _w	22 (22,22)	46 (46,45)	21 (21,21)	11 (11,11)
	wt%		20.3 (21.4,19.2)	36.9 (35.1,38.7)	42.8 (43.5,42.1)
	mole%		7.3	27.9	64.8
<i>du wx</i>	Peak DP		40 (40,39)	...	14 (15,13)
	DP _n	15 (15,15)	43 (43,42)	20 (20,20)	10 (10,10)
	DP _w	20 (20,20)	47 (46,48)	21 (21,21)	11 (11,11)
	wt%		18.4 (19.0,17.8)	38.9 (37.9,39.9)	42.7 (43.1,42.3)
	mole%		6.4	29.3	64.3

^a DP_n = Number-average degree of polymerization, DP_w = weight-average degree of polymerization, mole% based on average values of DP_n and wt%.

^b Peak at \approx DP320 for the *du wx* starch not included in calculation.

^c Values are mean from two separate analyses (shown in parentheses).

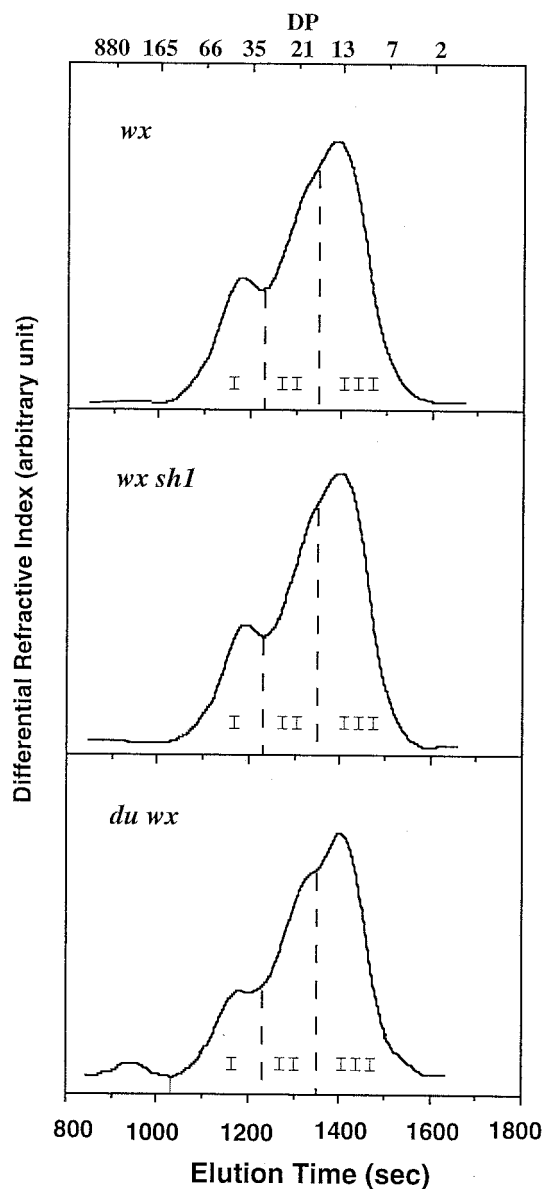


Fig. 8. High-performance size-exclusion chromatograms of debranched starches from maize genotypes *wx*, *wx sh1*, and *du wx*.

ed by DSC during the same period, indicating DSC might not be sensitive enough to detect the small proportion of amylopectin chain associations needed for gel structure. These data suggest that the initial associations responsible for establishing the three-dimensional network may involve a relatively small proportion of the amylopectin chains. At the early stages of gelation, these interactions are detected by rheological but not thermal effects. For 40% waxy starch aged at 6°C, Biliaderis and Zawistowski (1990) observed that G' developed more rapidly than did retrogradation enthalpy within 24 hr of storage. In the present work, no DSC endotherm was detected for the *wx* and *wx sh1* starch pastes (15:85 starch-water) until day 7 of storage. Between day 7 and day 15, the rate of change in G' was greater than the change in retrogradation enthalpy. For *du wx* starch much larger changes in G' than in ΔH occurred between days 1 and 4. It is plausible that at the later stages of gelation, important rheological effects may be due to reorientation of existing double helices rather than the formation of new double helices. This inference is consistent with the hypothesis that the enthalpy measured by DSC primarily reflects the loss of double-helical order rather than crystalline register (Cooke and Gidley 1992).

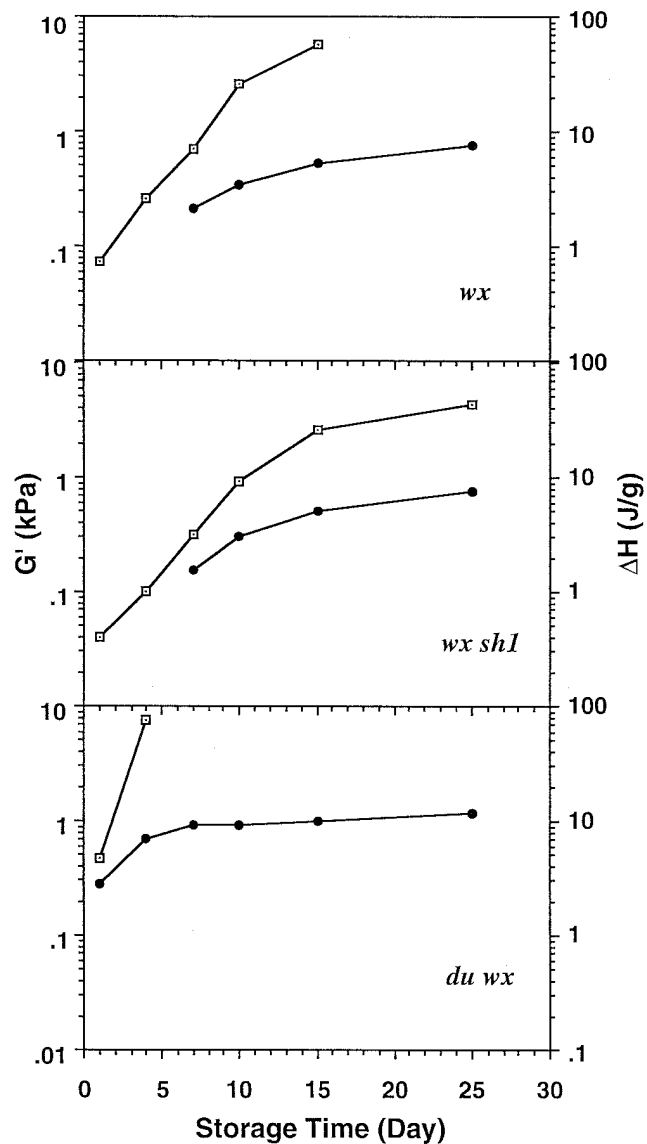


Fig. 9. Initial storage modulus (G' , \square) and retrogradation enthalpy (ΔH , \bullet) of pastes (15:85 starch-water) of *wx*, *wx sh1* and *du wx* starches as a function of storage time (days) at 4°C.

Although no significant difference in ΔH was observed between *wx* and *wx sh1* starches during most of the test periods, the *wx* sample was generally more elastic than the *wx sh1* sample throughout the storage period. Subtle differences in structure for *wx* and *wx sh1* starches might explain the different rheological behavior of starch gels with similar retrogradation enthalpy.

The addition of sucrose effectively slowed the retrogradation of *du wx* starch during the entire storage period. For the *wx* and *wx sh1* starches, the effect was only significant after 10 or 15 days of storage (Table II). Biliaderis (1992) showed the addition of sucrose, among other sugars, suppressed the development of G' and retrogradation endotherm of a waxy maize starch gel (1:0.5:1.5 starch-sugar-water), whereas fructose and glucose accelerated these processes. In the present study, sucrose apparently also delayed the onset of syneresis for the *du wx* and *wx* starches as indicated by the delayed occurrence or elimination of a G' peak upon heating.

In summary, the early development of an amylopectin gel network (15:85 starch-water) can be more easily detected rheologically than thermally. The pronounced gelling and retrogradation behavior of commercial *du wx* starch might correspond to a greater proportion of DP20–30 chains of the amylopectin, consistent with the earlier report by Shi and Seib (1992). Changes in gel

rheology and in retrogradation enthalpy of aged waxy-type starch pastes are broadly similar. However the increase in chain association (monitored by DSC) is not proportional to the increase in network structure (monitored by rheology). One might reasonably expect this relationship to vary according to starch type, concentration, and storage temperature.

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