Viscoelastic Behavior of Aging Starch Gels: Effects of Concentration, Temperature, and Starch Hydrolysates on Network Properties[1]

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ABSTRACT

The time-dependent changes in network properties of aqueous starch, amylose, and waxy maize starch (amylopectin) gels were studied by small-strain oscillatory shear measurements (0.2 Hz and 2% strain) and differential scanning calorimetry. In the concentration range of 1.9–8.8%, the storage modulus (G') of amylose gels increased rapidly in the early stages but little change on long-term storage. Amylose gels were also less sensitive to storage temperatures than amylopectin and wheat starch gels. The molecular origin of waxy maize gel network development appears to lie in the crystallization of the short chains of the amylopectin molecule, as probed by differential scanning calorimetry. Waxy maize starch gelation within 24 hr of storage occurred only at high polymer concentrations (>20%, w/w). Data on the effect of temperature on gelation kinetics of this starch suggested that the overall process is nucleation controlled. Whereas small molecular weight starch hydrolysis products weakened the gel network of wheat starch gels (presumably via competitive inhibition of interchain associations between the exuded amylose chains) they enhanced the rigidity of waxy maize starch gels.

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Starch, the major reserve polysaccharide of higher plants, consists of two polydisperse α-D-glucan components, amylose and amylopectin. Amylose is linear (α-[1→4]) or lightly branched, whereas amylopectin is highly branched through additional α-(1→6) linkages (Banks and Greenwood 1975). In heated food systems, starch contributes to texture through formation of a gel network. During gelatinization, starch birefringence and crystallinity disappear, the granules swell irreversibly, and selective leaching of amylose occurs. As a consequence, the swollen granules (deformable particles) become embedded in a continuous matrix of entangled amylose molecules. Such a complex polymer composite sets as a viscoelastic gel when gelatinized starch dispersions of sufficient concentration (≥6%, w/w) are cooled (Ring 1985). Starch gels are metastable and nonequilibrium states and, therefore, undergo structure transformation (chain aggregation, recrystallization) during storage; all these changes are described by the term retrogradation. The retrogradation of starch molecules is of considerable importance to the food industry, since it has direct implications on texture and digestibility of foods containing starch. The underlying mechanisms of gelation and retrogradation of starch (Ring 1985, Miles et al 1985a) and its components (Miles et al 1984, 1985b; Ring et al 1987; Clark et al 1989) have been investigated, and some of the factors that affect these phenomena

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were revealed. The molecular interactions observed on gelation and storage of aqueous starch polysaccharide gels as they relate to polymer structure and development of shear modulus and crystallinity have been recently reviewed by Ring (1987). For gelation of amylose, it has been proposed that cross-linked network formation arises from the adoption of ordered double helical structures that act as junction zones at concentrations above the coil overlap concentration, C* ~ 1.5% (Miles et al 1985a,b). Gidley (1989) recently reported that for nearly monodisperse amyloses, gelation is observed even at concentrations lower than those leading to nondilute solution behavior (i.e., at suboverlap polymer concentrations). Recrystallization in amylose gels occurs in the polymer-rich phase by extensive helix-helix aggregation, thereby leading to crystalline domains of the B-type structure (Miles et al 1985b, Gidley 1989). The crystallinity development, as monitored by X-ray diffraction, was a much slower process than the development of shear modulus (Miles et al 1985a,b). Heterogeneous acid hydrolysis of amylose gels and retrograded amylose precipitates in conjunction with size exclusion chromatography of the amylodextrin residues suggested that interchain associations between amylose chains occur over 50 degrees of polymerization (DP) (Ring et al 1987, Jane and Robyt 1984). On the other hand, thermoreversible gelation of amylopectin (upon storage at 1°C for six weeks) is observed at concentrations above 10% (i.e., much greater than C* ~ 0.9%) and is assumed to be the result of recrystallization of short DP 15 chains constituting the ordered chain clusters of the molecule (Ring et al 1987).

Many investigations have dealt with the flow behavior of starch pastes, as reviewed by Launay et al (1986), particularly at low concentrations (<15%). However, interpretation of the rheological behavior in terms of macromolecular organization and interactions among components has not been fully elucidated. Moreover, starch gels have been studied mostly under conditions of large deformation that result in considerable damage to the gel structure. In contrast, more information about the viscoelastic properties of gels and the time-dependent consistency changes is obtained by the use of nondestructive rheological methods such as small amplitude oscillatory shear stress measurements (Wong and Lelievre 1981, Lindahl and Eliasson 1986, Muhrbeck and Eliasson 1987, Clark et al 1989). This paper examines the rheological behavior of aqueous gels of starch and its components as influenced by concentration, temperature, time, and the presence of starch hydrolysis products of varying dextrose equivalent (DE) values using small deformation mechanical measurements.

MATERIALS AND METHODS

Commercial samples of wheat and waxy maize starch (Amioca) were obtained from Ogilvie Mills (Midland, Ontario, Canada) and St. Lawrence Starch Company (Mississauga, Ontario, Canada), respectively. The amylose content of wheat starch was 21.0%, based on its iodine affinity value, according to Schoch (1964). The corresponding iodine-binding capacity of the waxy maize was <0.4 mg I_2/100 mg of starch; i.e., amylopectin content >97%. The starches were vacuum dried (80°C) and kept in a desiccator until use. Potato amylose was obtained from Aldrich Chemical Company (Milwaukee, WI). This fraction was hydrated and solubilized with hot dimethylsulfoxide in an N_2 atmosphere. The clear solution was then diluted in boiling water (0.1%, w/v) under N_2, and the polysaccharide was recrystallized twice with butan-1-ol. This material was kept in its V-hydrated form until use. The molecular characteristics of amylose were: [η] 156 ml/g in 1*N* KOH, corresponding to 1,150 DP, and iodine affinity of 18.9 g I_2/100 g. Starch hydrolysates of various DE values were provided by American Maize-Products Co., Hammond, IN (Fro-Dex 42, DE 42; Lo-Dex 15, DE 15; Lo-Dex 5, DE 5), Grain Processing Corp., Muscatine, IA (Maltrin M200, DE 20; Maltrin M150, DE 15; Maltrin 040, DE 4.7), and Staley Manufacturing Co., Decatur, IL (Star-Dri 5, DE 5; Star-Dri 1, DE 1).

Starch gels were prepared by heating aqueous starch slurries of the appropriate concentration of starch in hermetically sealed stainless steel tubes (30 mm i.d. × 65 mm height). The tubes were immersed in a 90°C water bath for 15 min to gelatinize the granular starch. After heating, the tubes were transferred to a water bath at 25°C and equilibrated for another 15 min. For rheological measurements, the gels were cut into slices 1–2 mm thick using a sharp blade. Composite gels of starch and starch hydrolysis products were prepared by first dissolving the hydrolysate in water and then adding the granular starch. Starch hydrolysis products were incorporated in the gels at a level of 20% (w/w) on a starch solids basis. Changes in gel structure were monitored by small deformation mechanical measurements obtained by a Bohlin VOR rheometer (Bohlin Rheologi, Edison, NJ). With soft gels, the cone (5.4°) and plate (30-mm diameter) fixture was used; for stiffer gels the parallel plate (30-mm diameter) was used. For concentrated gels of waxy maize starch, because of their highly viscous character, a certain amount of gel material was forced to attain the geometry of the gap by lowering the upper plate onto the sample to a preset gap width. A thin layer

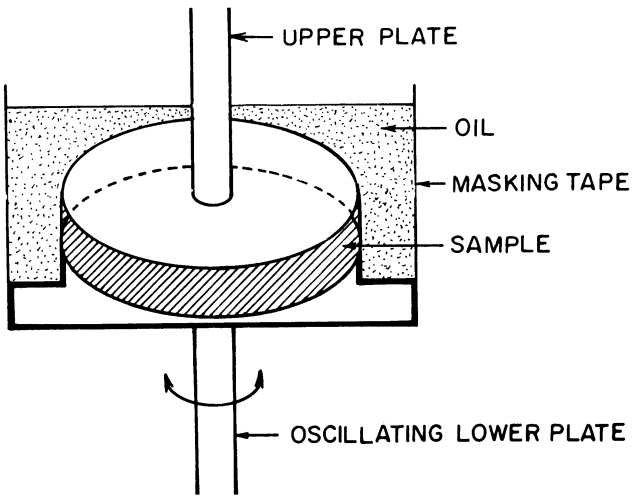

Fig. 1. Fixture geometry configuration of the measuring system indicating the positioning of the sample and the covering thin layer of mineral oil.

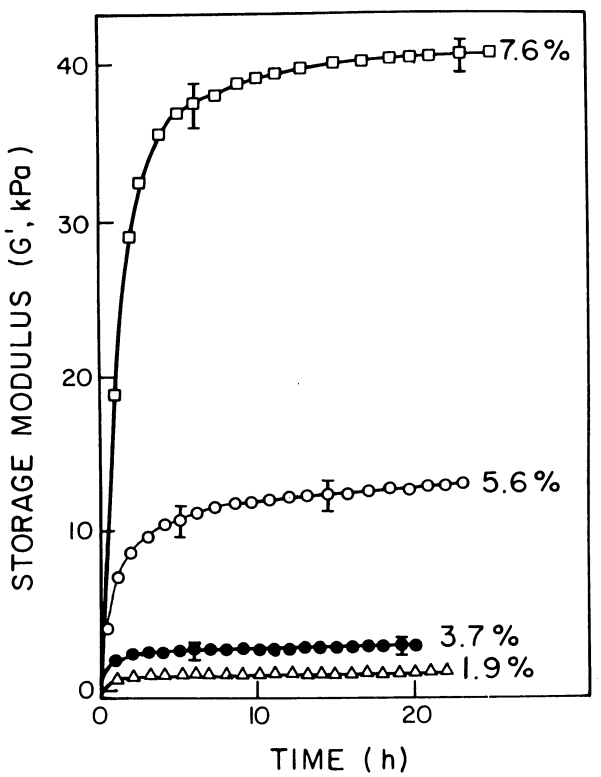

Fig. 2. Storage modulus vs. time (25°C) for gels of various concentration (w/w) of amylose. Data were obtained at 0.2 Hz and 2.0% strain.

of light mineral oil (Mallinckrodt, Inc., Paris, KY) was used to cover the parallel plates and prevent evaporative losses throughout the experiment (Fig. 1). Preliminary experiments indicated negligible contributions to the rheological parameters from the mineral oil itself. Furthermore, no migration of the oil between the sample and plate surfaces was evident that could cause slippage during the testing periods. All measurements were performed at constant temperature and data were collected at regular time intervals at 0.2 Hz and 2% strain. Data presented are averages of at least duplicate runs. The deviation in gel moduli values of repeated samples was generally less than 12%.

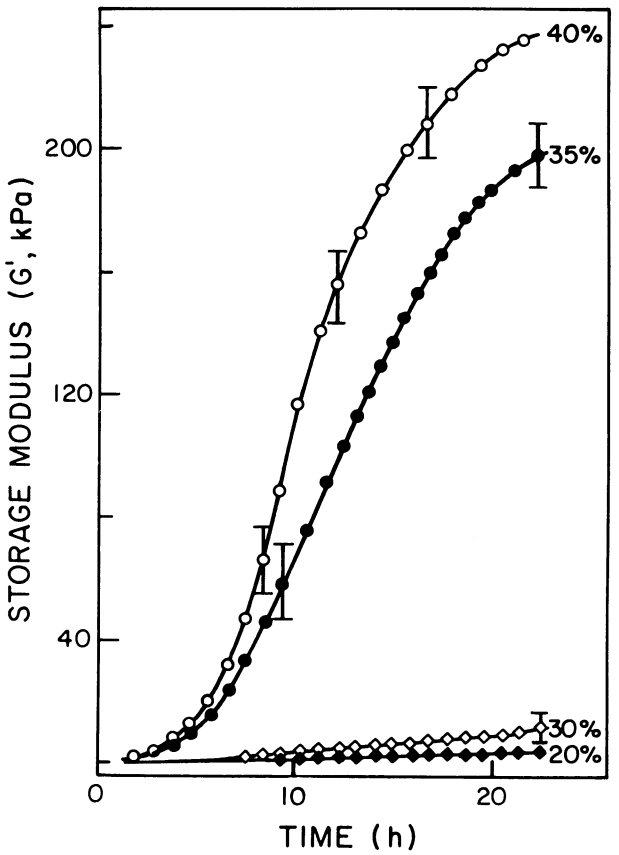

Fig. 3. Storage modulus (G') vs. time (25°C) for gels of various concentration (w/w) of waxy maize starch. Data were obtained at 0.2 Hz and 2.0% strain.

Differential scanning calorimetry (DSC) was used to assess the extent of starch retrogradation in wheat and waxy maize gels stored at 6°C. Starch samples (4.0 mg) were suspended in ~6 μl of water (i.e., 40%, w/v) or starch hydrolysate solution (hydrolysates were incorporated at 20%, w/w, of starch solids) and hermetically sealed in DuPont DSC pans. The starch suspensions were first heated (10°C/min) to 130°C to gelatinize the granules in the DSC pressure cell (1,400 kPa with N_2), cooled to room temperature, and subsequently stored for a designated period of time (2, 4, 8, 12, and 24 hr) at 6°C. The pans were then reheated to determine the magnitude of the staling (recrystallization) endotherm (J/g) observed between 50–60°C. All other DSC experimental conditions and data analyses were essentially as described by Biliaderis et al (1985).

RESULTS AND DISCUSSION

In order to characterize rheologically gels of amylose, wheat, and waxy maize starches, the effects of frequency and strain were first investigated over the concentration range used in these studies. The storage modulus (G') was found to be essentially independent of frequency (0.01–20 Hz) and strain (1–4%) in all cases. This indicated that testing starch gels at 0.2 Hz and 2% strain was within the linear viscoelastic region for these materials.

The effect of amylose concentration on time-dependent development of shear storage modulus at 25°C is shown in Figure 2. Amylose gels exhibited an initial rapid rise in modulus followed by a phase of much slower increase at longer times. Such profiles of modulus development are characteristic of aqueous biopolymer gels. According to Clark and Ross-Murphy (1987), the initial increase in modulus is due to the establishment of a three-dimensional network by interchain associations, while the subsequent slow rise in G' reflects further cross-linking due to annealing processes (rearrangements of cross-links and additional chain aggregation). It appears that after formation of a few cross-links, diffusion in the aggregated structure is significantly retarded, thereby resulting in a two-stage gelation process. Attainment of plateau values for G' was much slower in gels of higher polymer concentration (Fig. 2). Over a concentration range of 1.9–8.8%, G' (values at 24 hr) varied with concentration as $C^{3.1}$. It is interesting to note here that Ring (1985), using a pulse shearometer (200 Hz), reported a $G' \propto C^7$ dependence for amylose gels at concentrations between 1.5 and 7.0%. Recently, Clark et al (1989) made measurements on amylose gels prepared from essentially monodisperse polysaccharide chains using a mechanical spectrometer (10 rad/sec, 2% strain). For polymer concentrations within 1.0–3.0%, their experimental data indicated exponent values between 4.4 and 5.9, depending on the size of the amylose chains. The apparent inconsistencies in the observed exponent

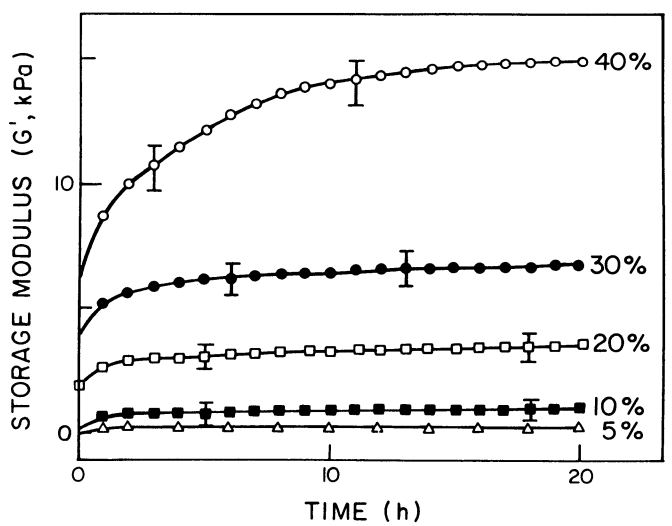

Fig. 4. Storage modulus vs. time (25°C) for gels of various concentration (w/w) of wheat starch. Data were obtained at 0.2 Hz and 2.0% strain.

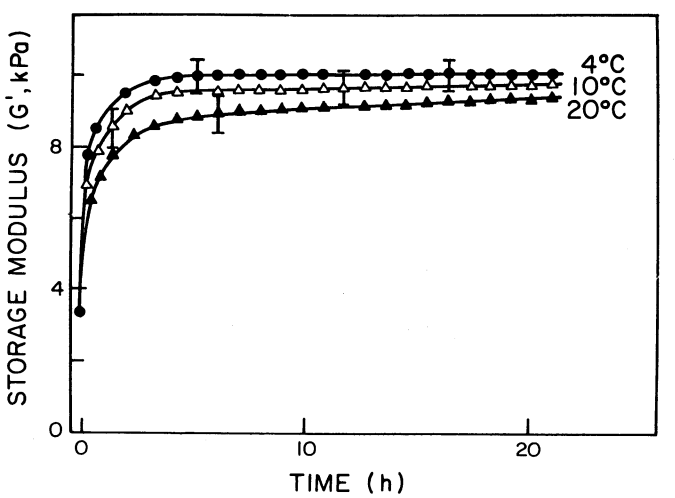

Fig. 5. Storage modulus (G') vs. time for 5% (w/w) amylose gel at various temperatures. Data were obtained at 0.2 Hz and 2.0% strain.

values among these studies may be due to differences in polydispersity, polymer concentration range as well as conditions for gel preparation. For the latter, it has been reported that the equilibrium modulus values of rapidly cooled gels are 30% less than slowly cooled gels (Miles et al 1985b). It is possible that quick quenching, as used in this study, causes "immobilization" of chains in the gel network and thus modulus values are reached very slowly thereafter. Nevertheless, these experimentally determined exponents clearly indicate the deviation from the theoretical $G' \propto C^2$ relationship predicted for biopolymer gels; according to Clark and Ross-Murphy (1987), these exponents should converge eventually to a value close to 2 and become independent of concentration as polymer concentration increases.

In contrast to amylose, waxy maize starch gelation was a much slower process (Fig. 3). Over a 24-hr period (25°C) appreciable increases in the modulus occurred only at concentrations greater than 20%. At this level, amylopectin chains are heavily entangled, since C* of this biopolymer is 0.9% (Ring et al 1987). Recent experiments conducted at 1°C by Ring et al (1987) have shown that gelation of amylopectin can occur even at 10% solutions over a period of several weeks. At 25°C (Fig. 3), the modulus did not approach a limiting value even for a 40% waxy maize starch gel. In this respect, the gelation kinetics of this material is different than that of amylose and is believed to reflect network formation via crystallization of the outer short chains (DP 15) of the amylopectin molecule (Ring and Orford 1985, Ring et al 1987).

Figure 4 shows the development of G' with time for wheat starch gels between 5 and 40% starch concentration at 25°C. Wheat starch exhibited profiles quantitatively similar to amylose profiles, although G' for the 40% gel continued to increase over identical time-temperature regimes, thus resembling the gelation behavior of amylopectin. A slow development of shear modulus for 10 and 20% pea starch gels was also observed by Miles et al (1985a) over long-term storage (seven days) and was attributed to crystallization of amylopectin. Supporting evidence was the thermal reversibility in the slow-developing component of the modulus when aged gels were heated to 95°C. In fact, the slow crystallization of amylopectin has been implicated in the long-term changes in firmness of starch gels on storage and corresponds kinetically with staling events of aging baked items (Willhoft 1973, Kulp and Ponte 1981). In terms of contributions to viscoelasticity of starch gels, in addition to the amount and viscoelastic properties of soluble amylose exuded from the swollen granules (continuous phase), the overall rheological properties of such composite systems would be also dependent on the volume fraction and rigidity of the gelatinized granules (dispersed phase). Recrystallization of amylopectin is thus expected to reinforce the gel structure by increasing particle rigidity.

The results of studies of temperature dependence of rigidity of 5% (w/w) amylose and 40% (w/w) waxy maize starch gels are presented in Figures 5 and 6, respectively. Unlike most chemical processes, the rate of change in dynamic rigidity of gels with respect to time decreases with increase in temperature, implying that gelation follows nucleation kinetics in a manner that is typical

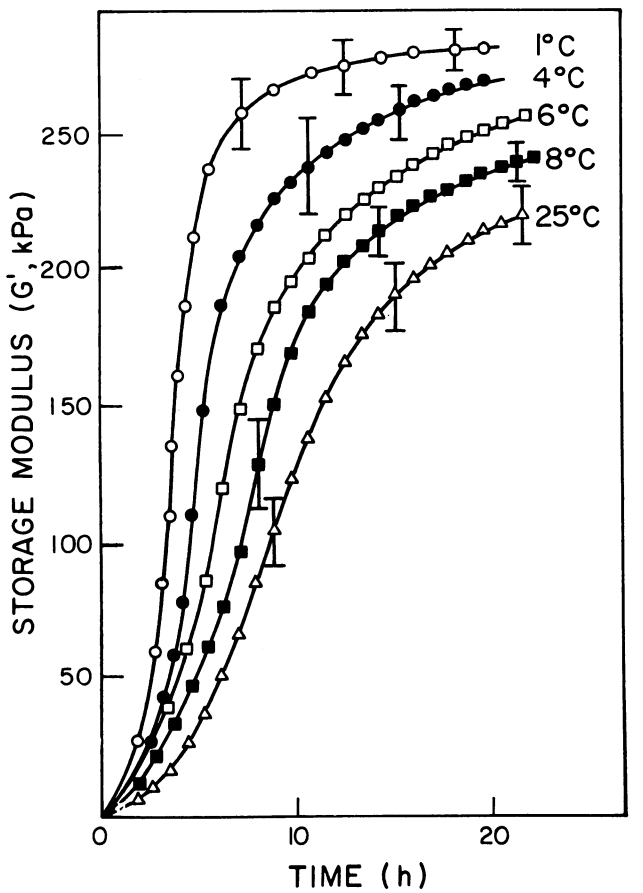

Fig. 6. Storage modulus vs. time for 40% (w/w) waxy maize starch gel at various temperatures. Data were obtained at 0.2 Hz and 2.0% strain.

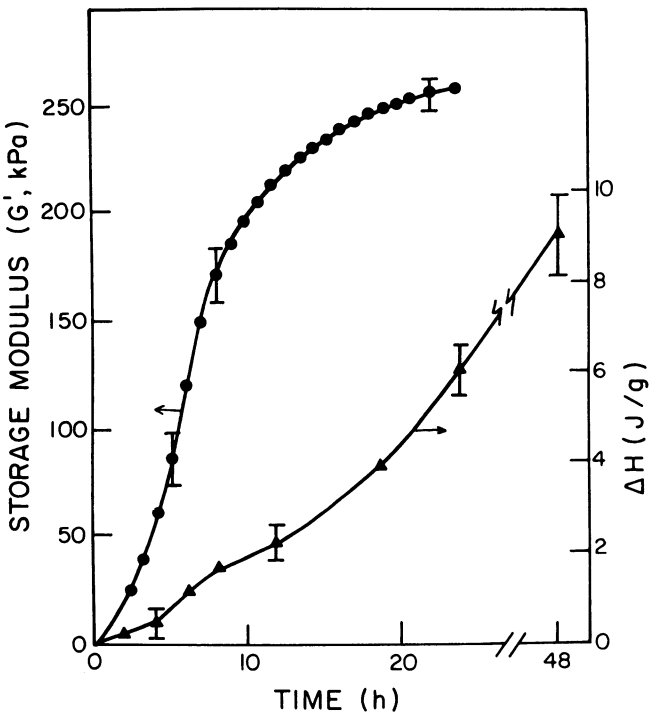

Fig. 7. Storage modulus (G') and enthalpy of gel melting (ΔH, J/g) vs. time of 40% (w/w) waxy maize (amylopectin) gels stored at 60°C.

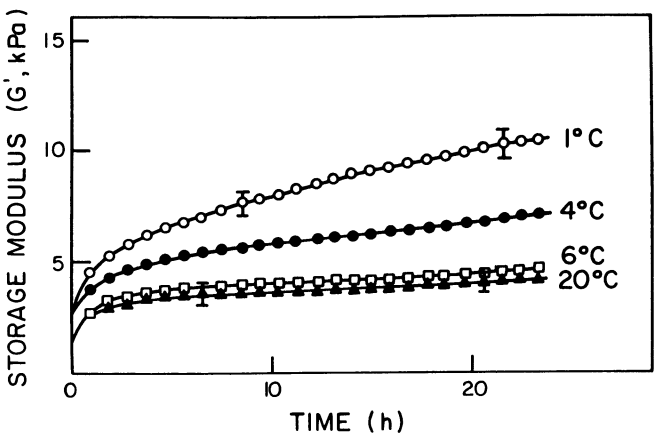

Fig. 8. Storage modulus vs. time for 20% (w/w) wheat starch gel at various temperatures. Data were obtained at 0.2 Hz and 2.0% strain.

of crystallization in polymer-diluent mixtures (Mandelkern 1964). Furthermore, the modulus of amylose gels was found to be less temperature sensitive than the waxy maize (amylopectin) gels (Fig. 5 vs. Fig. 6). These observations further support the notion that amylose gelation mainly involves rapid formation of double-helical junction zones upon cooling of amylose solutions, whereas a network-based structure for amylopectin is established mainly as a result of separation of a partially crystalline structure (Ring 1987). However, Slade and Levine (1987) pointed out that for gelation via crystallization of synthetic polymer-organic diluent systems, it is not clear whether, in addition to microcrystalline junction zones, random interchain entanglements in the amorphous regions of the network contribute to the structure and mechanical properties of the gel. Nonetheless, for solution crystallization of polymers, crystal growth is a nucleation-controlled process (Mandelkern 1964). The data in Figure 6 show that the gelation rate of amylopectin is indeed enhanced significantly at lower temperatures that favor the nucleation process. These results are in agreement with single- (Longton and Legrys 1981, Jankowski and Rha 1986, Slade and Levine 1987) or multistep- (Slade and Levine 1987) temperature regime crystallization experiments using calorimetric or rheological methods to assess the retrogradation kinetics in starch gels or cooked cereals; the DSC or elastic modulus measurements in these studies show that the rate-limiting step in retrogradation is indeed nucleation, as the theory predicts.

To follow the concurrent development of storage modulus and retrogradation endotherm, 40% (w/w) waxy maize gels were monitored continuously at 6°C for 48 hr in the rheometer and calorimeter, respectively (Fig. 7). The ΔH is generally accepted as an indicator of recrystallization of amylopectin outer chains (Nakazawa et al 1985, Zeleznak and Hoseney 1986, Roulet et al 1987, Ring et al 1987). The calorimetric and rheological measurements on aging 20% amylopectin solutions (1°C) of Ring et al (1985) suggested that the sigmoidal curves of ΔH and shear modulus development can be superimposed over the same storage period. In the present study, however, the rate of change in ΔH of these gels was much slower than the development of storage modulus (Fig. 7). Moreover, while G' reached a limiting value after 24 hr, ΔH continued to increase up to 48 hr of storage. These results would tend to suggest that on long-term storage, network rigidity is not substantially affected by further growth of crystallites. In this regard, it is also worth noting that 8% amylose gels at 6°C did not show any development of the staling endotherm over 48 hr of storage (data not shown); the junction zones in amylose gels melt at temperatures above 100°C (Biliaderis et al 1985). The results of the temperature dependence study of G' in 20% wheat starch gels are shown in Figure 8. At temperatures above 6°C, the moduli showed no appreciable changes during 24 hr of storage. At lower temperatures, however, the G'-time profiles clearly revealed the presence of a slow-developing modulus component, presumably due to amylopectin recrystallization (Fig. 8).

Since starch gels are composites in which swollen granules are embedded in an amylose network, one approach to manipulating the viscoelasticity of the system would be to interrupt the interchain associations between amylose molecules. Work published by Morris et al (1980) on carrageenan and alginate systems suggests that inclusion of short homologous chain segments of sufficient length to participate in junction zones with polymer chains would lead to weakened gel network structures; i.e., competitive inhibition to interchain associations. In this context, we have examined the effect of incorporating soluble starch hydrolysates of varying DE on the gel network development of wheat and waxy maize starches. Starch hydrolysis products were added to a level of 20% by weight on a starch basis. For wheat starch, rigidity of the composite gels was greatly reduced when hydrolysates were included (Fig. 9).

There were no clear trends regarding the magnitude of this effect in relation to the DE of the added hydrolysate. For example, gels made with Lo-Dex 5 (DE 5) and Star-Dri 1 (DE 1) exhibited the lowest G' values; this can be rationalized in terms of competitive inhibition of amylose chains. For this process, chain segments of sufficient length (i.e., hydrolysates of low DE) are required for effective participation in junction zones and thereby inhibit the formation of a continuous network of cross-linked longer amylose chains. However, wheat starch gels made with a DE 4.7 product of another manufacturer were much stiffer (Fig. 9, line 3). Chain polydispersity and degree of branching, as well as differences in the degree of granule swelling and amylose exudation during heating in the presence of each particular hydrolysate might be likely sources of such inconsistency. Clearly, further studies on gels with well-characterized fractions are required to reveal specific interactions in the amylose network, as well as between the continuous and dispersed phases of the composite gels, and thus establish relationships between structure and gel rheology. In contrast to wheat starch gels, all composite waxy maize-starch hydrolysate gels (Fig. 10) exhibited a greater rate of storage modulus development and attained higher limiting G' values after 24 hr of storage at 6°C than the control sample (waxy maize alone). These results imply that depolymerized starch chains have very little effect on gel network formation involving

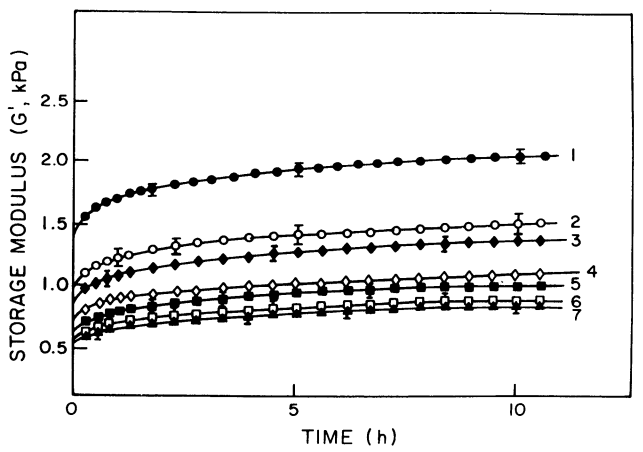

Fig. 9. Storage modulus (G') of 18% (w/w) wheat starch gels vs. time in the presence of starch hydrolysates added at 20% (w/w) of starch solids: (**1**) Control (wheat starch alone); (**2**) wheat starch/Maltrin M200 (dextrose equivalent [DE] 20); (**3**) wheat starch/Maltrin M040 (DE 4.7); (**4**) wheat starch/Fro-Dex 42 (DE 42); (**5**) wheat starch/Maltrin M150 (DE 15); (**6**) wheat starch/Lo-Dex 5 (DE 5); (**7**) wheat starch/Star-Dri 1 (DE 1). Data were obtained at 0.2 Hz, 2% strain, and 6°C.

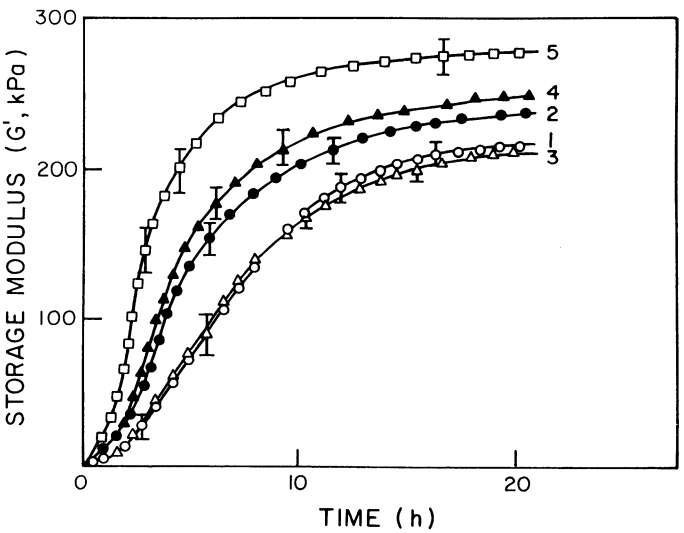

Fig. 10. Storage modulus (G') of 38% (w/w) waxy maize starch (amylopectin) gels vs. time in the presence of starch hydrolyzates added at 20% (w/w) of starch solids: (**1**) Control (waxy maize alone); (**2**) waxy maize/Fro-Dex 42 (dextrose equivalent [DE] 42); (**3**) waxy maize/Star-Dri 5 (DE 5); (**4**) waxy maize/Maltrin M200 (DE 20); (**5**) Waxy maize/Lo-Dex 15 (DE 15). Data were obtained at 0.2 Hz, 2% strain, and 6°C.

TABLE I
Recrystallization Kinetics by Differential Scanning Calorimetry (ΔH: J/g) of Aging 40%, w/w, Wheat and Waxy Maize Starch Gels in the Presence of Starch Hydrolysis Products of Varied Dextrose Equivalent (DE) Values[a]

Gel/ Storage Time (hr)	Control	Fro-Dex 42 (DE 42)	Lo-Dex 15 (DE 15)	Star-Dri 5 (DE 5)
Waxy maize				
2	0.28 ± 0.23[b]	0.85 ± 0.25	1.27 ± 0.13	1.10 ± 0.22
4	0.48 ± 0.21	2.99 ± 0.40	3.33 ± 0.27	1.96 ± 0.01
8	1.35 ± 0.16	3.46 ± 0.58	4.82 ± 0.14	2.90 ± 0.59
12	2.26 ± 0.46	5.01 ± 0.78	9.57 ± 0.79	11.23 ± 0.28
24	7.14 ± 0.67	9.00 ± 0.65	11.82 ± 0.19	12.81 ± 0.58
Wheat starch				
2	0.23 ± 0.06	0.07 ± 0.01	1.06 ± 0.44	1.52 ± 0.35
4	0.58 ± 0.07	0.09 ± 0.02	2.98 ± 0.51	1.37 ± 0.44
8	1.32 ± 0.21	1.25 ± 0.12	5.79 ± 0.75	4.40 ± 0.81
12	2.21 ± 0.43	1.85 ± 0.79	6.35 ± 0.10	7.79 ± 0.84
24	4.45 ± 0.97	2.25 ± 0.36	9.68 ± 0.01	10.53 ± 0.85

[a] Storage temperature 6°C, hydrolysates were incorporated at a level of 20% w/w of starch solids.
[b] J/g; $n = 5$.

the branched starch component at high concentrations. Ring (1987) has in fact reported that amylose and amylopectin become incompatible in concentrated aqueous solutions, thus leading to the formation of separate amylose- and amylopectin-rich phases. The data in Figure 10 are also consistent with the idea that amylopectin gelation primarily reflects intra- and intermolecular crystallization processes. To further test this hypothesis, we examined the recrystallization (staling) kinetics of wheat and waxy maize starch gels with and without added starch hydrolysates upon storage at 6°C. The DSC results of these studies are summarized in Table I. In agreement with the modulus-time data in Figure 10, crystallization of amylopectin, as monitored by the magnitude of the staling endotherm, was greatly enhanced in the presence of all three hydrolysates tested (Fro-Dex 42, Lo-Dex 15, and Star-Dri 5) compared with waxy maize alone (control). With Lo-Dex 15 and Star-Dri 5, wheat starch also showed increased staling rates by DSC (Table I), although the gel modulus data of Figure 9 suggested weakening of all composite wheat starch-starch hydrolysate gels. These observations clearly point to the fact, often not appreciated by researchers in this area, that DSC and small-deformation rheological testing examine different properties of the aging gel. First, DSC, as a probe of molecular structure, is sensitive to structural effects caused by long-range ordering of chains into microcrystalline domains. On the other hand, small-strain oscillatory shear measurements of composite starch gels, performed within the linear viscoelastic regime, reflect contributions from both elastically active aggregated amylose chains, present in little crystallographic register with one another, as well as physical cross-links established on slow recrystallization of the amylopectin short chains.

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