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Dynamic rheological measurements and analysis of starch gels

Irma Rosalina*, Mrinal Bhattacharya

Department of Biosystems and Agricultural Engineering, University of Minnesota, St. Paul, MN 55108, USA

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Abstract

The effect of starch modification and concentration on the dynamic shear properties of starch gels in water was studied. The four types of starches used were native corn starch, medium hydroxypropylated distarch phosphate, highly hydroxypropylated distarch phosphate, and distarch phosphate. Concentrations of 4, 6, 8, and 10% (w/w) in distilled water were used for each starch type. All starches showed viscoelastic solid behavior at higher concentrations (6–10% w/w). Critical gelling concentrations were found to be 4, 4, 6, and 6% for native corn starch, medium hydroxypropylated distarch phosphate, highly hydroxypropylated distarch phosphate, and distarch phosphate, respectively. Dynamic measurements were performed to study the effect of concentration and the extent of modification on starch gel properties. The linear viscoelastic region for each type of starch was determined using dynamic strain sweep. Both the elastic and viscous modulus showed only slight dependence upon frequency. The starch gels were classified as weak gels on the basis of their mechanical spectra. Viscous moduli (G'') showed a higher dependence upon frequency compared to elastic moduli (G') for all starch types. Equilibrium shear moduli (G_e) were determined by extending the spectra to zero frequency. Increasing concentration increased the values of G_e. Fractional differential model (FDM) was used to model the frequency dependence of the gels. A higher degree of cross-linking resulted in a more shear-resistant gel. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Intrinsic viscosity; Fractional differential model; Advanced rheometric expansion system

1. Introduction

Starch, in both its native and modified forms, is widely used in food processing and preparation since it is a water-soluble polymer, which can yield viscous dispersions, solutions, or gels depending on concentration and temperature conditions. The use of native starch in food processing is limited because of its tendency to retrograde and undergo syneresis. Furthermore, viscosities of native starch gels are often too high for industrial applications.

Thus, starch derivatives like ethers, esters, and depolymerized products are more widely used in industry. Some important starch ethers are hydroxyethyl and hydroxypropyl and their cationic derivatives. After modification, these starch derivatives produce gels that are stable, translucent, and have a reduced tendency to retrograde. Moreover, they also provide proper texture and are resistant to pH and temperature and hence can be used as thickeners in water- and milk-based products. Another common modification to starches is chemical cross-linking. The resulting products are usually resistant to shear, low pH, and high temperature conditions encountered during many food process operations (Wurzburg, 1986).

Hydroxypropylated starches (starch–O–CH_2–CHOH–CH_3) are prepared by reacting starch with propylene oxide to produce a low level of etherification (degree of substitution DS of 0.02–0.2, 0.2 being the maximum possible allowed). Hydroxypropyl groups are hydrophilic in nature, and when introduced into the starch granule, weaken or strain the internal bond structure holding the granule together. This reduction in bond strength is reflected in lower starch pasting temperatures. The higher the level of hydroxypropyl substitution, the lower the pasting temperature until the product became cold water swelling.

Wu and Seib (1990) compared the properties of waxy barley starch cross-linked with phosphorus oxychloride ($POCl_3$) at 25°C and cross-linked waxy maize and tapioca starches. They reported that the thickening power, hot paste stability, and clarity of optimally cross-linked waxy barley starch matched those of cross-linked waxy maize starch. Hydroxypropylation (molar substitution MS of 0.10–0.13) of cross-linked waxy barley starch gave better freeze-thaw resistance than acetylation (DS $\sim$ 0.10) and reduced the pasting temperature in amylograms of the starches by 7–10°C.

Takahashi, Maningat and Seib (1989) evaluated the properties of acetylated (DS 0.1) and hydroxypropylated (MS 0.1) distarch phosphate of wheat starch. They concluded

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* Corresponding author.

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that both types of starch gave pastes of lower consistency and gels with a lower elastic modulus but a higher elastic limit compared to those of starch from normal corn. Hydroxypropylated wheat starch (MS 0.15) formed a gel or paste at 25°C and 5–7.5% starch solids. The freeze-thaw stability of a gel of the hydroxypropylated wheat starch was intermediate between that of gels from hydroxypropylated tapioca and waxy maize starches.

Eliasson and Kim (1992) utilized rheological measurements to analyze changes in mechanical properties of hydroxypropyl potato starch pastes during freeze-thaw treatments. They compared the rheological measurements with the measurements of syneresis at different centrifugal forces (Eliasson & Kim, 1992). Kim and Eliasson (1993) investigated the effects of molar substitution (MS) and cross-linking on the freeze-thaw stability of hydroxypropyl potato starch and reported that increasing MS stabilized the complex modulus and phase angle and delayed starch paste syneresis after freeze-thaw treatments.

Starch gels can be considered as composites in which swollen gelatinized granules, containing mainly amylopectin, are embedded in and reinforced by an interpenetrating amylose gel matrix (Miles, Morris & Ring, 1985a). Gelation occured as a result of the formation of an interconnected network. Evans and Haisman (1979) studied the rheology of corn and potato starches over a moderate range of concentrations and observed a linear relationship between the elasticity modulus and concentration. Steeneken (1989) and Keetels, van Vliet and Walstra (1996) found similar concentration relationships for potato and waxy maize starches. Svegmark and Hermansson (1991) tested potato starch dispersions and reported that a similar linear relationship applied for gently sheared potato starch while a curvilinear relationship was found for the heavily sheared potato starch dispersions. Inaba, Adachi, Matsumura and Tomohiko (1994) compared gels of various starches from different botanical sources prepared under various conditions and concentrations using a compression–decompression test. Tsai, Li and Lii (1997) studied the effects of granular structures on the rheological behavior of starch pastes by comparing rice and corn starch, both cross-linked and uncross-linked.

Viscoelastic properties of the starch gels, once formed, have been measured by several researchers (Miles et al., 1985a; Miles, Morris & Orford, 1985b; Ring, Colonna, I'Anson, Kalichevsky, Miles, Morris & Orford, 1987; Orford, Ring, Carroll, Miles & Morris, 1987; Kokini, Lai & Chedid, 1992; Chedid & Kokini, 1992). Miles et al. (1985a,b) worked on the retrogradation and gelation of aqueous amylose solutions and starch dispersions. They examined the time-dependence of the ordering of amylose and amylopectin molecules and its relationship to changes in the mechanical behavior of the gel. Ring et al. (1987) studied the association of amylopectin chains in the gel by crystallization of the branches. The slow retrogradation of starch was dependent on the concentration and botanical source of the starch (Orford et al., 1987). Of the starches examined, smooth-seeded pea starch had the greatest tendency to retrograde followed by potato, maize, and wheat starch. Kokini et al. (1992) and Chedid and Kokini (1992) investigated effects of water/starch ratio, temperature, morphology, amylose/amylopectin ratio, shear, and granule size distribution on starch structure and viscoelastic properties of starch. These properties have been investigated further through the use of dynamic measurements, where the rheological response can be resolved into an elastic component and a viscous component (Myers, Knauss & Hoffman, 1962; Evans and Haisman, 1979). Myers et al. (1962) used dynamic measurements as a non-destructive means for determining mechanical properties of two differently modified starch pastes.

Dintzis and Bagley (1994) used waxy maize starch and reported both shear thickening and rheopectic behavior. da Silva and Oliveira (1997) used modified waxy maize and native maize starch. Their experiments showed that native maize starch showed shear thickening characteristics after short heating times that gradually turned to shear thinning as the heating time was increased. The modified waxy maize starch instead showed a faster and more extensive swelling and exhibited rheopectic time-dependent and shear thinning with yield stress behavior. Yield stress behavior has also been reported by Evans and Haisman (1979), Doublier (1981) and Navickis and Bagley (1983), but not by Bagley and Christiansen (1983). These differences were attributed to the difference in cooking temperatures of the starch suspensions.

The objective of this work was to identify the structural features responsible for the rheological behavior by dynamic and flow curve analysis. Experiments under oscillatory shear conditions (dynamic properties) were performed to analyze the viscoelastic properties of the gels and classify the gels into strong or weak gels. The shear-dependent behavior and results from start-up of steady shear experiments further show how the profile of the flow curve changes with increasing concentration and different degree of starch modifications.

2. Materials and methods

2.1. Materials

Both native and modified corn starches were obtained from National Starch and Chemical Company. Melojel, a common corn starch, contains about 75% amylopectin and 25% amylose. National 1658 is a medium hydroxypropylated and cross-linked corn starch while Purity 660 is a highly hydroxypropylated and cross-linked corn starch. Purity NCS-A is a highly cross-linked corn starch. The moisture content of each type of starch was estimated to be about 12% (w/w). Water used was purified using the Millipore reverse osmosis system.

2.2. Sample preparation

Weighed amounts of starch were mixed with distilled water using a spatula until a milky white solution was obtained. This usually took about 1 min of stirring. A stirrer bar was put in the jar, which was covered with a lid to avoid water loss and heated on a hot plate at about 90°C for 10 min. After the milky white solution become clear as the starch gelatinized and solubilized, stirring was stopped and the jar with the contents was transferred to a water bath thermostatted at 90°C for 30 min in order to ensure full viscosity development. It was then cooled to room temperature for approximately 2 h prior to measurement. Concentrations of 4, 6, 8, 10%(w/w) of each starch dissolved in water were used in the rheological study. In this work, concentration units are % (w/w) unless otherwise mentioned.

2.3. Rheological measurements

For dynamic rheological measurements a parallel plate fixture in the Advanced Rheometric Expansion System (ARES) rheometer (Rheometrics Inc., Piscatway, NJ) was used. The starch gel was placed on the bottom plate and the upper plate was lowered into the gel. The plate diameter was 25 mm. Expelled materials were trimmed off. The sample at the edge of the system was covered by silicone oil to prevent drying. The sample was then allowed to rest for 15 min prior to taking measurements. During this time the axis was free to rotate so that some recovery motion might occur. Sinusoidal oscillation experiments were used to analyze both elastic (G') and viscous (G'') material response simultaneously. All tests were conducted in the linear viscoelastic range. Tests were also conducted at temperatures in the range of 20–90°C and the data were shifted to construct a master curve.

2.4. Intrinsic viscosity measurements

Weighed amounts of starch (0.3 g) were mixed with a 90% (v/v) solution of DMSO in a 100 ml volumetric flask till a milky white solution was obtained. The flask was heated on a heating plate at low heat overnight until the starch dissolved. The milky white solution became clear as the starch gelatinized and solubilized. It was then cooled to room temperature and brought to volume with 90% (v/v) DMSO solution.

The solutions were filtered through a 5 μm funnel Buchner membrane system prior to loading in the viscometer. Flow times for the determination of intrinsic viscosity were obtained at 28 ± 0.1°C in a Cannon–Ubbelohde shear dilution viscometer, series 1C-B910 (Nominal constant 0.03) with working capillary diameter of $0.78 \pm 2\%$ mm. Plotting η_{sp}/c versus c, where η_{sp} was the specific viscosity and c was the concentration, and obtaining the value of the intercept on the ordinate by linear regression gave the intrinsic viscosity values. The results from the intrinsic viscosity measurements are tabulated in Table 1.

Table 1
Intrinsic viscosity and percent crystallinity for various starches

Starch	Intrinsic viscosity [η] (ml/g)	% Crystallinity
Melojel	163.75	14.16
National 1658	71.03	34.71
Purity 660	39.11	36.30
Purity NCS-A	27.04	32.86

2.5. Wide angle X-ray scattering

Wide-angle X-ray scattering was used to study structural characteristics and to identify powders, thin films, and crystals. Data collection and analysis was fully automated and phase identification was possible using the Joint Committee for Powder Diffraction Standards (JCPDS) library on CD-ROM and Bruker-AXS D5005 Diffractometer with 2.2 kW sealed Cu Source. The crystallinity data are tabulated in Table 1.

3. Results and discussions

Rheological data for each starch type and concentration were collected in replicate experiments. Two duplicate runs were done on each starch gel sample and two samples were done for each starch type and concentration. Calculated means were shown with the error bars calculated from standard deviation. Reproducible data were obtained for all samples in the linear viscoelastic region. Due to the sensitivity of rheological measurements of gel, reproducible results could not be obtained for starch gels in the nonlinear viscoelastic region. This difficulty might be due to the network rupture in the physically cross-linking starch systems under consideration.

To ensure that slip was absent during rheological measurements, tests were conducted using different gap heights as well as using a cone and plate fixture. Fig. 1 shows the effect of two gap heights (1.0 and 1.5 mm) and a cone and plate geometry on the G' and G'' versus frequency plot. The closeness of the curves using two different gap height and the cone and plate geometry is an indication of the absence of slip. The dynamic spectrum was similar for gels in the linear viscoelastic range.

The intrinsic viscosity (IV) and crystallinity (Table 1) of the native samples showed that Melojel had the highest IV but the lowest crystallinity.

3.1. Dynamic measurements

3.1.1. Limits of linear viscoelasticity

Dynamic strain sweep tests were done on the gel samples to determine the limit of linear viscoelastic region, γ_c. LVE

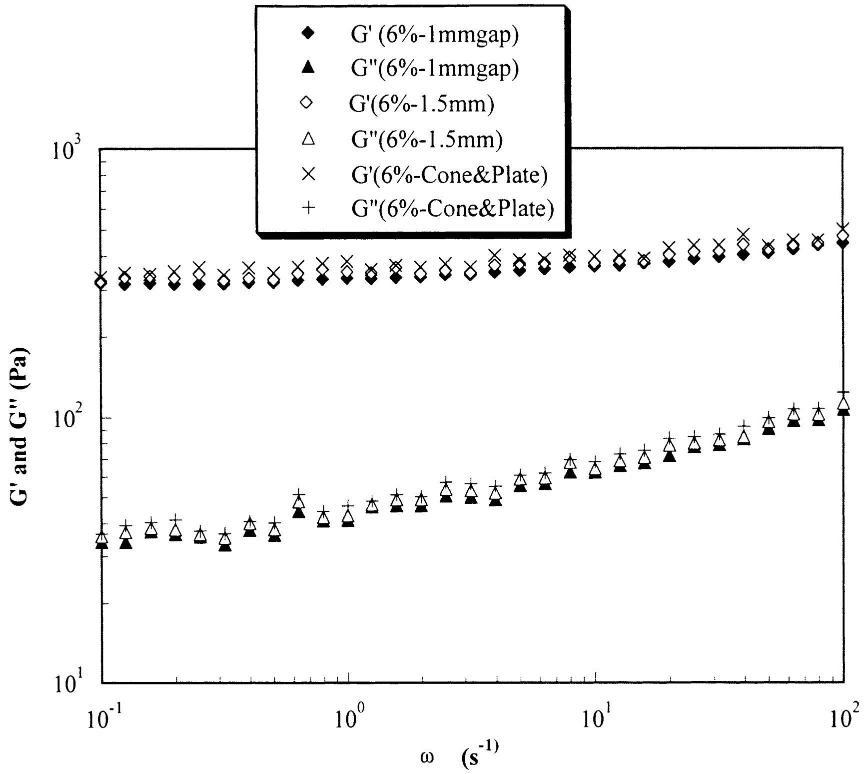

Fig. 1. Dynamic frequency sweep data for 6% Melojel using two different gap heights in a parallel plate mode and using a cone and plate fixture.

region was determined from strain region at which G' and G'' were independent of strain amplitude. Table 2 shows the limit of LVE regions.

The linear viscoelastic regions turned out to be independent of concentration at concentrations greater than C_0 (critical gelling concentration). G'' was observed to depart from linearity sooner than G'. These linear viscoelastic regions enabled an immediate distinction to be made between gels and entanglement networks, for which the linear viscoelastic region may extend to large strains, which are order of magnitude higher than gels. The viscoelastic behavior of Melojel was no longer linear after 5% strain, but the decrease of G' and G'' versus strain is definite only after 10% strain, at 1 rad/s. National 1658 has a critical strain ($\gamma_c°$) of 10%, while Purity 660 departed from linearity at 5% strain, and Purity NCS-A at 8% strain.

Table 2
LVE Region of various concentrations of four different starches at 1 rad/s

Starch type	Strain range (w/w)		
	6%	8%	10%
Melojel	0.1–10%	0.1–10%	0.1–10%
National 1658	0.1–10%	0.1–10%	0.1–10%
Purity 660	None	0.1–5%	0.1–5%
Purity NCS-A	0.1–8%	0.1–8%	0.1–8%

Tests at frequencies of 5 and 10 rad/s were also done for 8 and 10% Melojel, 10% National 1658, 10% Purity 660, and 10% Purity NCS-A to investigate the effect of testing frequency in the limit of LVE region. There were no significant differences in the linear viscoelastic region for tests done at different frequencies for any of the starch types. The curve shows that higher frequency shifted the critical strain towards a higher value.

3.1.2. Frequency dependence of G' and G''

Dynamic frequency sweep tests were done in the limit of linear viscoelastic region to determine the frequency dependence of the elastic and viscous moduli. Differences in values for the slope of $\log G'$ and $\log G''$ versus $\log \omega$ curves are summarized in Table 3. Fig. 2 shows the frequency sweep data for 6, 8, and 10% Melojel gel. 4% (w/w) concentration is determined to be a near-critical gel concentration. The elastic moduli were relatively independent on frequency (slope <0.05), while the viscous moduli were slightly dependent on frequency with $G' > G''$ ($0.1 < \text{slope} < 0.3$). This type of spectrum is sometimes associated with weak-gel behavior (Clark & Ross-Murphy, 1987). Strong and weak gels can be classified as such on the basis of their mechanical spectra.

Gels were usually classified into two major categories, the strong and the weak gels (Lapasin & Pricl, 1995). Strong gels have the characteristics of true gels where under small deformation conditions, they manifest typical behavior of

Table 3
Slope of log G' and log G'' versus log ω curves

Starch type	6% (w/w)		8% (w/w)		10% (w/w)	
	Slope of G'	Slope of G''	Slope of G'	Slope of G''	Slope of G'	Slope of G''
Melojel	0.025	0.19	0.034	0.22	0.029	0.18
National 1658	0.018	0.13	0.05	0.28	0.035	0.21
Purity 660	–	–	0.034	0.24	0.043	0.33
Purity NCS-A	0.006	0.24	0.014	0.29	0.023	0.31

viscoelastic solids and, above a critical deformation value, they rupture rather than flow. Weak gels, on the other hand, possess intermediate rheological properties between solutions and strong gels. Under small deformation, weak gels resemble strong gels in their mechanical behavior, but as deformation increases, the three-dimensional networks undergo a progressive breakdown into smaller clusters.

Fig. 3 shows the frequency dependence behavior of National 1658 at 6, 8, and 10% concentration. Data for 4% concentration were scattered due to incomplete gel formation. However, 6% concentration already shows a weak gel behavior. Therefore, the critical gel concentration for National 1658 was determined to be between 4 and 6% concentration. The hydroxypropylated and cross-linked starch gel spectrum characterizes a gel-like behavior. The storage modulus is much higher than the loss modulus. G' shows almost no dependence on frequency (slope <0.05) and G'' exhibits a minimum ($0.1 < \text{slope} < 0.3$), which is typical of a weak gel. Increasing concentration did not change the magnitude of the modulus considerably as can be seen in Fig. 3.

In Fig. 4, Purity 660 also shows weak gel behavior at high concentrations (8 and 10%). However, at 6% concentration, data were scattered which again indicates incomplete gel formation. Hence, critical gel concentration for Purity 660 was predicted to be within 6–8% concentration. The elastic modulus, G', shows almost no dependence on frequency (slope < 0.05), while the viscous modulus, G'', shows slight dependence on frequency ($0.2 < \text{slope} < 0.4$). G' values were a magnitude higher than G'' at all concentrations.

Fig. 5 shows the frequency dependence of Purity NCS-A (highly cross-linked corn starch) gels at 6, 8, and 10% concentration. The elastic modulus (G') is relatively independent of frequency (slope < 0.03) while the viscous modulus (G'') for Purity NCS-A shows a higher dependence on frequency ($0.2 < \text{slope} < 0.3$). Elastic moduli were always higher than the viscous modulus by more than 1 order of magnitude.

Frequency sweep data for 4% National 1658, 4 and 6%

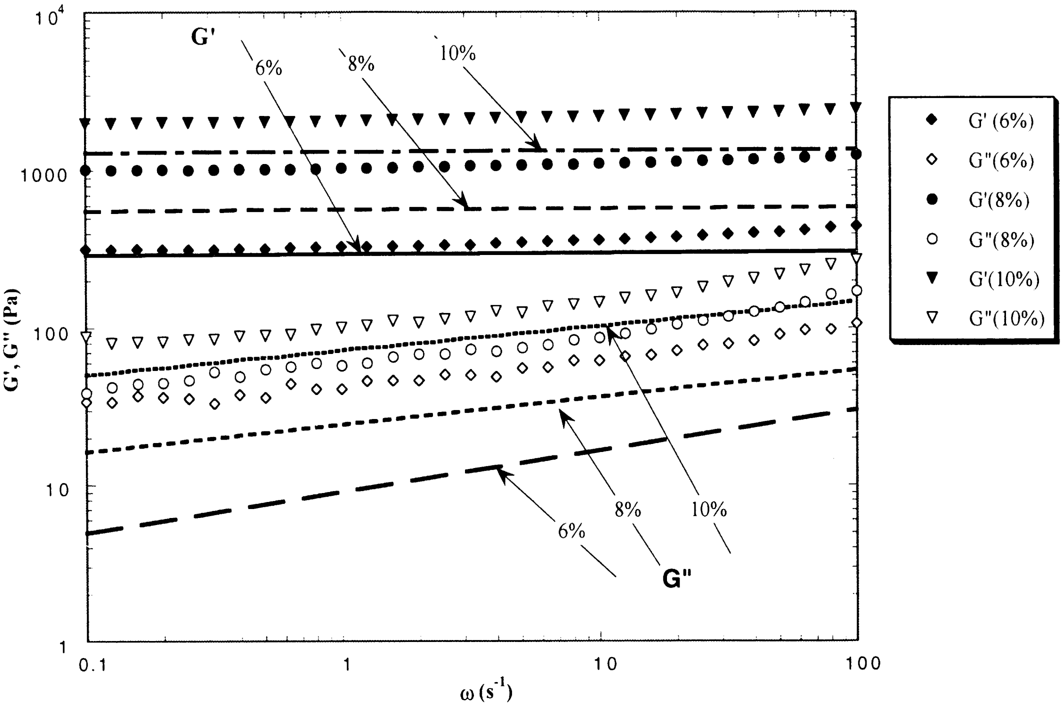

Fig. 2. Dynamic frequency sweep data for Melojel at 25°C. Numbers denote concentration in w/w. Lines are predictions from Eqs. (6) and (7).

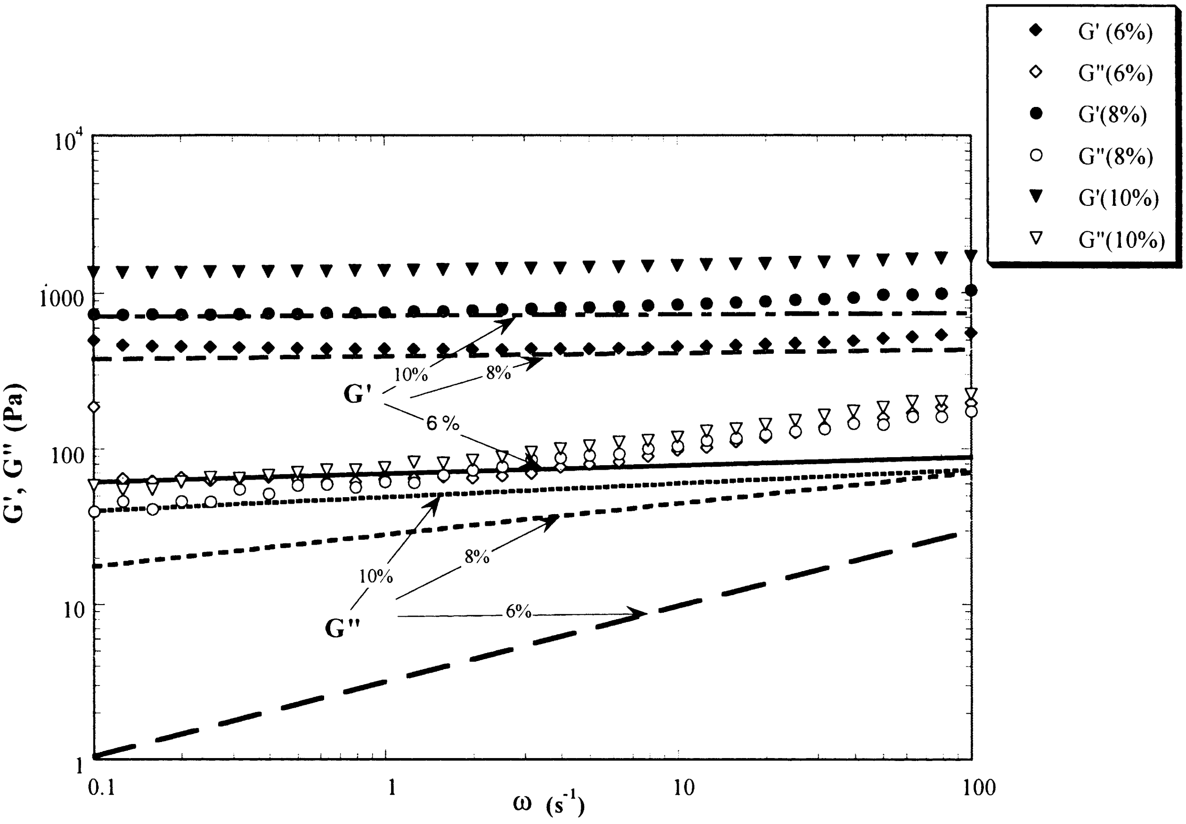

Fig. 3. Dynamic frequency sweep data for National 1658 at 25°C. Numbers denote concentration in w/w. Lines are predictions from Eqs. (6) and (7).

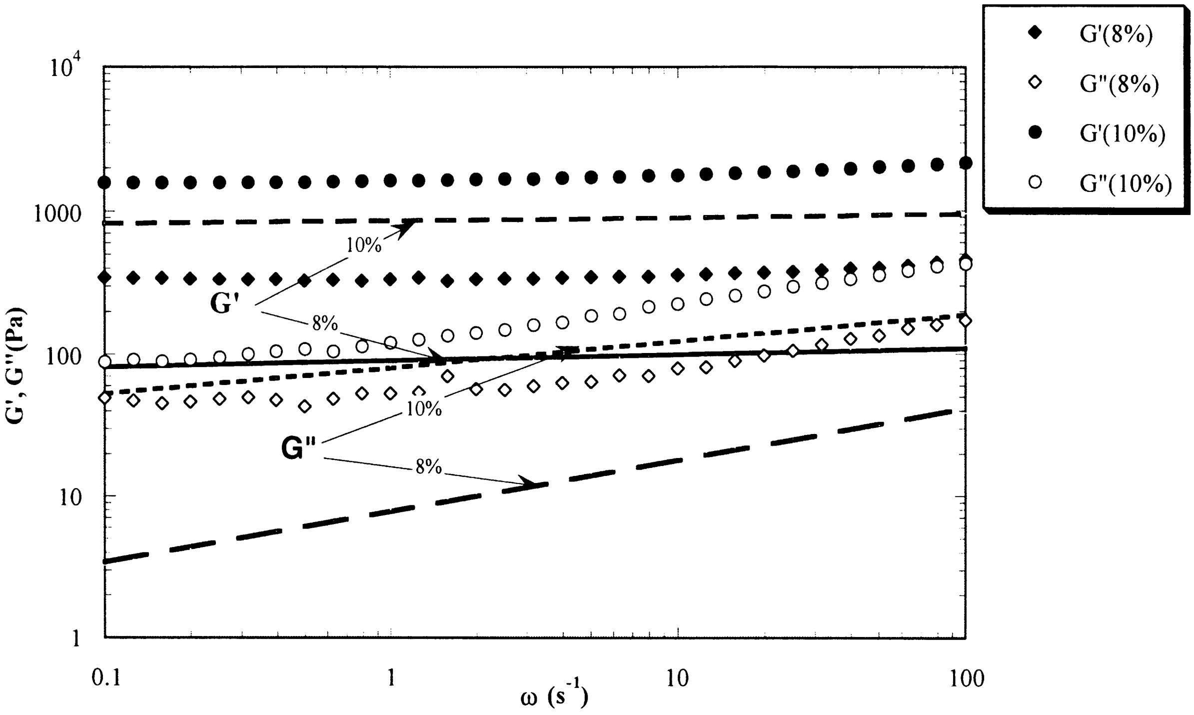

Fig. 4. Dynamic frequency sweep data for purity 660 at 25°C. Numbers denote concentration in w/w. Lines are predictions from Eqs. (6) and (7).

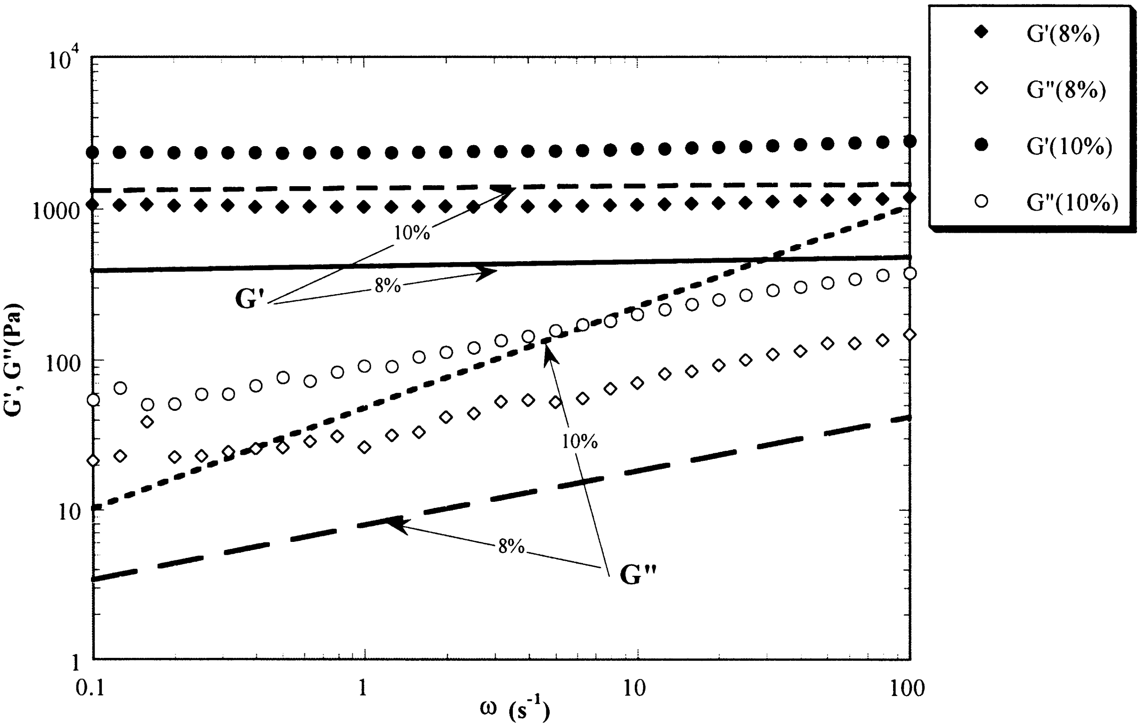

Fig. 5. Dynamic frequency sweep data for purity NCS-A at 25°C. Numbers denote concentration in w/w. Lines are predictions from Eqs. (6) and (7).

Purity 660, and 4% Purity NCS-A were scattered due to incomplete formation of the physical gels as indicated by low torque values. The concentrations above can be considered to be below the critical gelling concentrations for each starch type. When the spectra (G', G'' versus frequency) for the higher starch concentration is extended to zero frequency (on a linear scale), then the systems would be said to exhibit an equilibrium shear modulus (G_e), which is characteristic of viscoelastic solids like chemically cross-linked networks (Rosalina, 2000).

3.1.3. Modelling of material functions

There is no theoretical model that is able to describe the behaviors of physical gels in a satisfactory way. Tanaka and Edwards (1992a,b) described the rheological behavior of physically cross-linked networks under steady and unsteady flow conditions by assuming that the three-dimensional network originates from the thermally reversible association of terminal chain segments into temporary junctions. Scott-Blair, Veinoglou and Caffyn (1947) suggested that the material behavior between the Hookean solid and the Newtonian fluid could be expressed in terms of derivatives lying between the zeroth order and the first order derivative of strain. Winter and Chambon (1986) proposed to characterize the sol/gel transition in stoichiometrically balanced systems and derived from the linear theory of viscoelasticity with a relaxation function:

$$G(t) = ct^{-m} \tag{1}$$

where G is the relaxation modulus, t the time, c the material parameter, and m is a constant.

However, when applied to oscillatory shear flow, the intermediate model (Winter & Chambon, 1986) leads to simple-power law dependences on frequency for both dynamic moduli with the same exponent m. Hence, Eq. (1) cannot describe a condition other than the sol/gel transition. For this reason, Friedrich (1991) formulated an extended form of the relaxation function and demonstrated that the resulting constitutive equation with fractional derivatives can be used to represent completely the sol/gel transition as well as the other states, which precede or follow the phase transition. The formulation is then given in terms of fractional derivative of deformation (Friedrich, 1991)

$$G(t) = G_e + G_m\left(\frac{t}{\lambda}\right)^{a-b} E_{a,(a-b+1)}\left(-\left(\frac{t}{\lambda}\right)^a\right) \tag{2}$$

$E_{\alpha,\beta}(x)$ is the generalized Mittag–Lefler function defined as

$$E_{a,(a-b+1)}(x) = \sum_{k=0}^{\infty} \frac{x^k}{\Gamma(ak + (a-b+1))} \tag{3}$$

where λ is a characteristic time, G_e the equilibrium modulus, $a > 0$ and $b \leq 1$ G_m is equal to $G_0 - G_e$, where G_0 is the glassy or plateau modulus, Γ the gamma function, t the time, and $x = t/\lambda$. Eq. (3) can be simplified to (Friedrich and Braun, 1992)

$$E_{a,(a-b+1)}\left(-\left(\frac{t}{\lambda}\right)^a\right) = \frac{a_2(t/\lambda)^{a-b}}{1 + b_2(t/\lambda)^a} \tag{4}$$

Table 4
Friedrich model parameters for frequency sweep data

Starch type	Concentration (w/w) (%)	G_e (Pa)	G_m (Pa)	G_0 (Pa)	λ (s)	a	b
Melojel	6	289.72	90.46	380.19	0.04	0.49	0.59
	8	543.28	199.78	743.06	0.04	0.34	0.49
	10	1259.74	517.14	1776.88	0.07	0.52	0.56
National 1658	6	61.28	162.52	223.81	0.01	0.20	0.49
	8	366.49	272.34	638.83	0.05	0.31	0.49
	10	669.92	301.00	970.92	0.09	0.39	0.54
Purity 660	8	82.19	240.05	322.25	0.004	0.28	0.49
	10	783.67	667.09	1450.75	0.04	0.31	0.49
Purity NCS-A	8	378.90	366.07	744.97	0.05	0.22	0.49
	10	1345.44	1360.47	2705.91	0.02	0.87	0.87

where

$$a_2 = \frac{1}{\Gamma(a-b+1)} \qquad \textit{and} \qquad b_2 = \frac{1}{\Gamma(1-b)\Gamma(a)}$$

Friedrich and Heymann (1988) proposed the following generalized formulation of the fractional differential model (FDM)

$$\tau_{ij} + \lambda^a D^a(\tau_{ij}) = G_e\{\gamma_{ij} + \lambda^a D^a(\gamma_{ij})\} + G_m \lambda^b D^b(\gamma_{ij}) \tag{5}$$

The fractional differential standard solid model yields the following expressions for the storage and loss moduli:

$$G' = G_e + \frac{G_m(\lambda\omega)^b \left\{\cos\left[\frac{b\pi}{2}\right] + (\lambda\omega)^a \cos\left[(b-a)\frac{\pi}{2}\right]\right\}}{1 + 2(\lambda\omega)^a \cos\left[\frac{a\pi}{2}\right] + (\lambda\omega)^{2a}} \tag{6}$$

$$G'' = G_m \frac{(\lambda\omega)^b \left\{\sin\left[\frac{b\pi}{2}\right] + (\lambda\omega)^a \sin\left[(b-a\}\frac{\pi}{2}\right]\right\}}{1 + 2(\lambda\omega)^a \cos\left[\frac{a\pi}{2}\right] + (\lambda\omega)^{2a}} \tag{7}$$

Friedrich (1991) suggested using a FDM to describe the different behavior exhibited by the gel. Eqs. (6) and (7) were used to fit all the frequency sweep data for all starch types as can be seen in Figs. 2–5. The values of G_e, G_m, a, b, and λ were obtained from the stress relaxation data presented elsewhere (Rosalina, 2000) and fitted to Eq. (2). The values of G_e, G_m, a, b, and λ obtained are given in Table 4.

Calculated elastic modulus (G') from the Friedrich model under-predicted the experimental data within one order of magnitude for gels of all concentrations. On the other hand, the behavior of calculated viscous modulus (G'') curves was not consistent for all starch gels. The values of G'' from the FDM model under-predicted the experimental data within an order of magnitude for Melojel and National 1658 while there was a more distinct difference observed for Purity 660. Calculated values of G'' for Purity NCS-A on the other hand fit the experimental data fairly well at 8% concentration, but not at 10% concentration.

Friedrich (1993) first used the FDM for the frequency dependence behavior of polyisobutylene, galactomannan-borax gel, and polybutadiene on the glass transition region. Thus, the fact that the gels being studied here were not in their glass transition region and had characteristics of weak gels might contribute to the large deviation of experimental values from the calculated values from the FDM model.

The equilibrium shear modulus (G_e) and G_m always increase with increasing starch concentrations in the dispersions. The increase in G_e was about double to three times for every 2% increase in concentration for Melojel. For National 1658, a more drastic change was observed going from 4 to 6% concentration, and the change levels off after 6% concentration. Purity 660 exhibits a similar behavior to National 1658 where a drastic change was observed going from 6 to 8% concentration as well as with Purity NCS-A going from 4 to 6% concentration. The sudden increase of shear modulus observed at low concentrations of all the modified starches were due to the cross-linking nature of the starch. Cross-linking addition first forbids the granule to swell to its full capacity below the critical gelling concentration and then balances off afterward. The variations in characteristic time (λ) and the constants a and b in Eqs. (2)–(4) were not significant except for Purity 660 where λ goes from 0.004 to 0.04 when the concentration is increased from 8 to 10%.

Variations of the ultimate value of G' at 1% strain and 1 rad/s as a function of concentration are shown in Fig. 6. Notable differences in stiffness between the gels of the different starches are seen clearly. Melojel and Purity NCS-A gels show similar behavior in terms of concentration. At lower concentration, cross-linking in Purity NCS-A prevents full formation of gel clusters shown by lower gel stiffness. In terms of magnitude, the elastic moduli (G') of Purity NCS-A at 10% concentration are the largest (2380 Pa) compared to the other three starches. Melojel is the second largest with 2090 Pa, and Purity 660 and

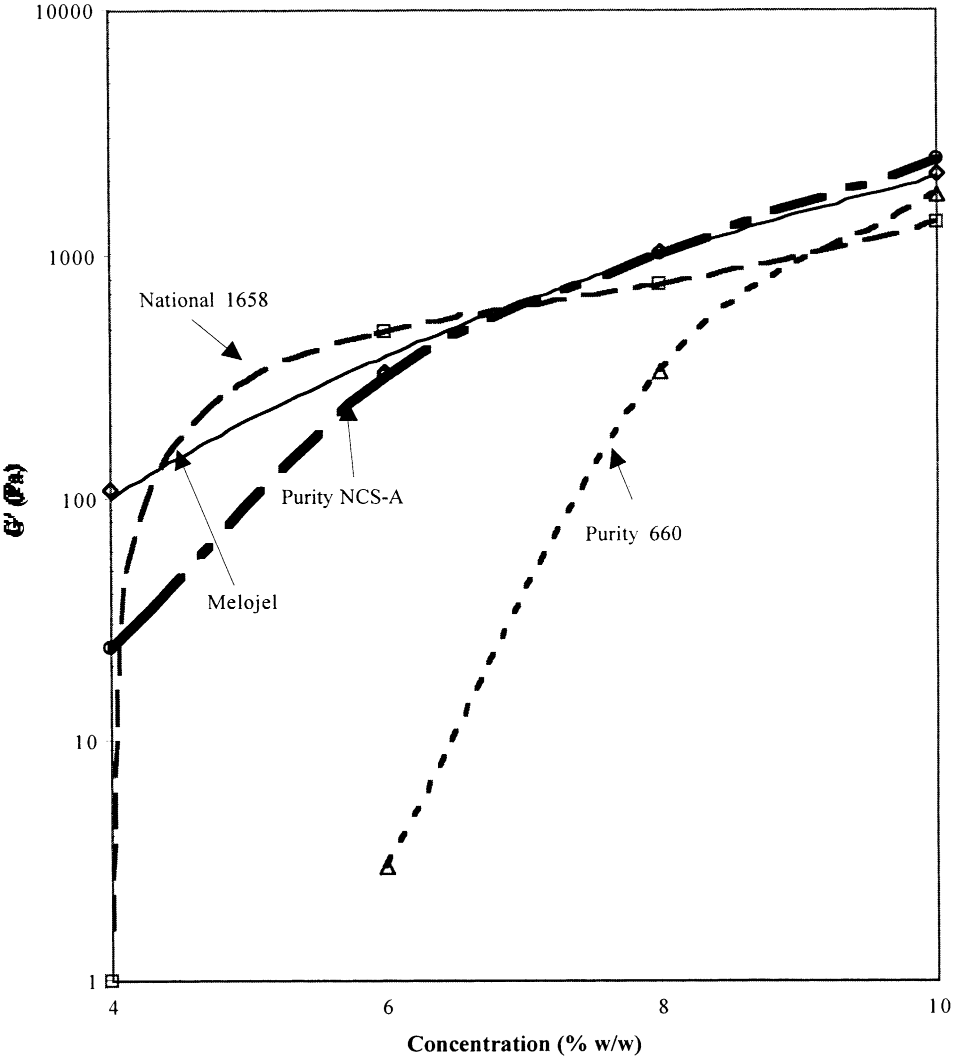

Fig. 6. G' dependence on concentration for various starches at 1% strain and 1 rad/s.

National 1658 with 1650 and 1410 Pa, respectively. At 8% concentration, however, the elastic modulus magnitude does not exhibit the same order in terms of starch types. In this case Melojel > Purity NCS-A > National 1658 > Purity 660 (1050 > 1040 > 770 > 340 Pa, respectively).

Hydroxypropylation seems to lower the gel stiffness as shown for National 1658 and Purity 660 gels. At high concentrations (C > 10% (w/w)), Purity 660 shows a higher storage modulus compared to National 1658. In this case, higher degree of cross-linking in Purity 660 acts as filler of the gel at higher concentrations. However, as the concentration goes down, cross-linking in Purity 660 prevents the starch granules from swelling up to their full capacity, resulting in lower storage modulus.

3.1.4. Frequency master curve

A master curve allows the extrapolation of data over broad temperature and frequency ranges. The storage and loss moduli were plotted versus reduced frequency (ω) making use of the reduced variables shift factor, a_T. The reduced frequency was defined as $\omega_i a_{T_i}$, where ω_i is the frequency and a_{T_i} is the value of a_T at temperature T_i. The WLF equation given below holds for any of the viscoelastic functions.

$$\log a_T = \frac{-C_1^0(T - T_0)}{C_2^0 + (T - T_0)} \tag{8}$$

where C_1^0 and C_2^0 are constants, T is the temperature, and T_0 is the reference temperature which in this study is 25°C. At high enough frequencies, the storage modulus increases into the glassy range. At low enough frequencies, any polymer will flow. As the frequency increases beyond the capability of the polymer chains to respond, the polymer is in the glassy region.

Frequency master curves were obtained for samples that were just above the critical gel concentrations. At concentrations equal to or lower than critical gel concentration, the torque levels were low and this prevented the accurate measurements at higher temperatures for the construction

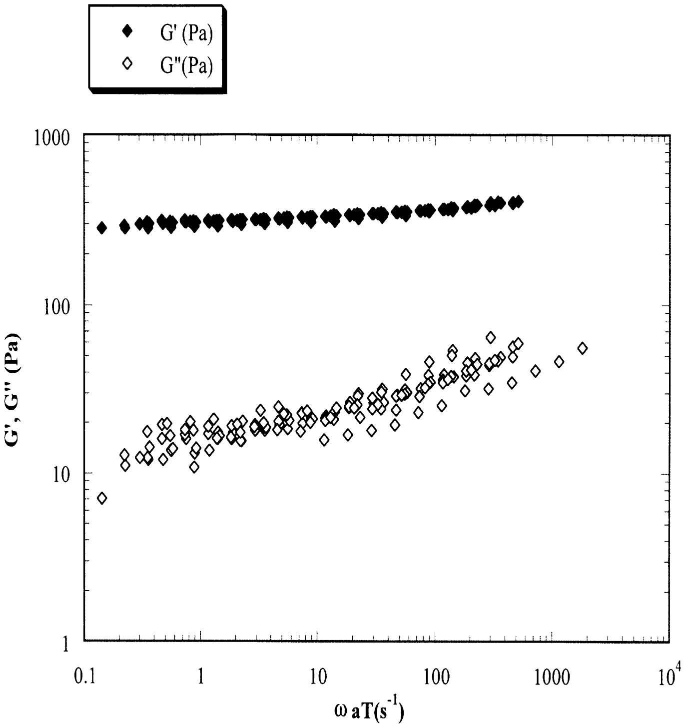

Fig. 7. Frequency master curve for 6% Melojel obtained using time-temperature superposition method.

of master curves. Figs. 7–9 show the frequency master curves for 6% Melojel, 6% National 1658, and 8% Purity 660, respectively. Physical gelation occurs as a result of intermolecular association, leading to network formation. If physical associations are to produce gelation, rather than phase separation, it is crucial that the junctions between molecules that are formed by such associations do not grow too large. The concentrations chosen were believed to indicate the critical gel concentration for each starch type. At lower concentrations, the frequency sweeps of 4% Melojel,

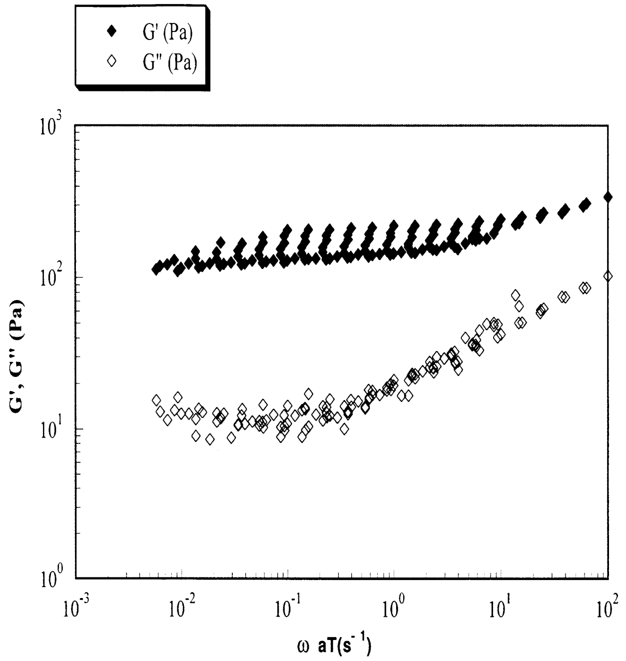

Fig. 8. Frequency master curve for 6% National 1658 obtained using time-temperature superposition method.

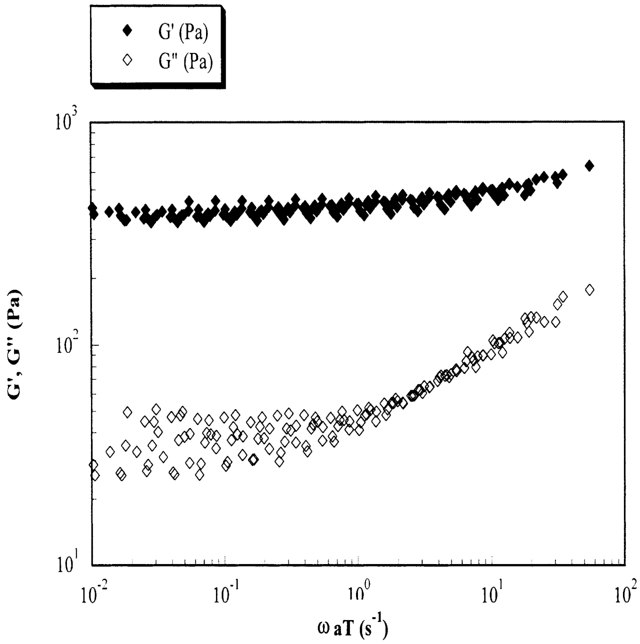

Fig. 9. Frequency master curve for 8% purity 660 obtained using time-temperature superposition method.

4% National 1658, 6% Purity 660, and 6% Purity NCS-A showed a fluid-like behavior.

Melojel starch at 6% concentration shows a fairly linear behavior towards frequency, as can be seen in Fig. 7. This is due to the characteristic of the stiff gel formed from an unmodified starch. G' is relatively independent of frequency, while there is a slight transition region seen on the G'' curve. Fig. 7 shows the end of the rubbery plateau region of a complete master curve, which is a typical case for cross-linked polymeric gel. The height of the plateau was governed by the degree of crystallinity because crystalline regions tend to behave as a filler phase and physical cross-link, tying the chains together (Sperling, 1992).

Fig. 8 shows the master curve for National 1658 starch at 6% concentration. There is a distinct increase in G'' as frequency increases at reduced frequency greater than 0.1. The portion of the master curve shown in this figure is the rubbery plateau region (lower frequency range) and part of the glass transition region (frequency > 0.1 rad/s). The glass transition region can be interpreted as the onset of long-range, coordinated molecular motion.

The frequency master curve of Purity 660 at 8% concentration is shown in Fig. 9. The elastic modulus (G') showed little dependence on frequency, which is not the case for the viscous modulus (G''). At frequencies higher than 1 rad/s, there is an increase in the G'' curve. Therefore, it can be concluded that the master curve shows part of the rubbery plateau and part of the glassy transition region.

Similar behavior was observed for National 1658 and Purity 660 with a higher transition frequency observed for Purity 660. This could be due to the fact that both starches were stabilized and cross-linked with Purity 660 undergoing a higher degree of cross-linking. A crossing over between G' and G'' can be expected at a lower frequency and the spectrum obtained within a larger frequency range may not differ very much from one for a typical macromolecular solution.

A master curve for Purity NCS-A gel was not obtained due to the difficulty in getting reproducible data. Purity NCS-A is a highly cross-linked corn starch where the cross-links somewhat prevent the starch granules from swelling and hence the characteristics of starch pastes formed were very dependent on the preparation of the sample. The Friedrich model was not used to predict the material behavior for this master curve because the values of all the parameters were temperature sensitive.

4. Conclusions

The rheological properties were assessed from dynamic and flow measurements at 25°C. Dynamic viscoelastic measurements were taken on the starch gels and the results showed different types of behavior for different modifications and concentrations. At 4% concentration (w/w), Melojel and National 1658 showed a critical gel behavior, while for Purity 660 and Purity NCS-A, this behavior was observed at 6% concentration. Critical strains were found to be independent of concentrations. The critical strain values were 0.1, 0.1, 0.05, and 0.08 for Melojel, National 1658, Purity 660, and Purity NCS-A, respectively. The elastic modulus dominated the viscous modulus for all starch types and concentrations showing a typical gel behavior. No significant differences in linear viscoelastic regions were found for tests done at different frequencies.

Both the elastic and viscous modulus shows only slight dependence upon frequency. The starch gels were classified as weak gels on the basis of their mechanical spectra. Viscous modulus (G'') showed a higher dependence upon frequency compared to elastic modulus (G') for all starch types. Equilibrium shear moduli (G_e) were determined by extending the spectra to zero frequency. Increasing concentration increased the values of G_e. FDM was used to model the frequency dependence of the gels. Notable differences in stiffness between gels of different starches were seen clearly by plotting G' as a function of concentration. Melojel and Purity NCS-A gels show similar behavior. Meanwhile, hydroxypropylation in National 1658 and Purity 660 lowered the gel stiffness. Purity 660, with a higher degree of cross-linking, showed a higher storage modulus compared to National 1658 at high concentrations while at low concentrations, the starch granules did not swell up to their full capacity, resulting in lower G'. Frequency master curve was constructed by running a frequency sweep test at different temperatures. A 6% Melojel curve showed a rubbery plateau, while 6% National 1658 and 8% Purity 660 curves showed part of the rubbery plateau region and a slight glass transition region. Higher transition frequency was observed for Purity 660 due to its higher modification.

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