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Dynamic and extensional properties of starch in aqueous dimethylsulfoxide

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Abstract

The effect of starch composition and concentration on the rheological properties of starch in a mixed solvent, water–DMSO, was investigated in dynamic shear and extensional mode. High amylose corn starch containing 70% amylose and 30% amylopectin, common corn starch containing 25% amylose and 75% amylopectin, and waxy corn starch containing about 99% amylopectin were used in this study. Concentrations of 2, 4, 6, and 8% (w/v) in 10% water-90% DMSO (v/v) were used for each starch type. An increase in the amylopectin content of starch from 30 to 99% caused a change in behavior from semidilute solution to viscoelastic solid at a concentration of 8% (w/v). At a concentration of 2%, an increase in the amylopectin content of starch from 30 to 99% caused a change from Newtonian to incipient gel-like behavior. Behavior at intermediate concentrations of 4 and 6% (w/v) varied from semidilute to critical gel-like with increasing amylopectin content. A power-law relaxation was observed for all concentrations of common and waxy corn starches with the slope decreasing with increase in concentrations. A 2% waxy corn starch solution displayed extension thinning behavior, while a 2% high amylose corn starch solution displayed Newtonian behavior. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Dynamic and extensional properties; Starch; Aqueous dimethylsulfoxide; Rheological properties

1. Introduction

A growing awareness of environmental concerns and depleting oil reserves have led to increasing use of natural polymers in various applications. Starch is a reserve polysaccharide substance occurring naturally as minute granules (2–100 μm particle size) in the roots, seeds, and stems of several types of plants including rice, wheat, barley, tapioca, millet, corn, and potatoes. It is a blend of two structurally distinct polysaccharides, amylose and amylopectin. Amylose is a linear polymer of α-D-glucose linked together through 1 → 4 linkages. Amylopectins, on the other hand are branched polymers containing short chains that are interlinked via α-(1 → 6). Starch granules have a complex packing arrangement of the two constituent polymers which has not been established conclusively. Granule size, shape, and composition (i.e. amylose/amylopectin content) vary with the plant source. Small amounts of non-carbohydrate components like lipids, proteins, and ash are also present (Whistler & Daniel, 1984; Young 1984). Starch owes much of its functionality to these two polysaccharide components.

While mostly used as foodstuffs, the versatility of starch allows its use in a multitude of non-food uses. These include its use in formulation of products such as adhesives, detergents, ceramics, paper coatings, aids in textile industry, and in oil recovery operations. To further improve its versatility, chemical modification of polysaccharide chains are the focus of current research in order to derive products with “tailor-made” characteristics for a variety of applications. Homogeneous processes using organic solvents can be used to obtain derivatives from native starch with uniform and selective substitution (Lapasin & Pricl, 1995). As an example, water-soluble potato amylose acetates, propionates, and butyrates have been prepared by homogeneous reactions in dimethyl sulfoxide (DMSO) in the presence of triethylamine catalyst (Rutenberg, Jarowerko & Ross, 1962). Waxy milo starch and corn starch anthranilates have been prepared by reaction with isatoic anhydride in DMSO (Parmerter, 1971). DMSO is a solvent for both starch and many synthetic polymers, and is used to solubilize a number of graft copolymers (Lapasin & Pricl, 1995).

The mixed solvent system, water–DMSO, has been used as a solubilizing agent for starch and its components (Dintzis & Tobin, 1969). Amylose has been reported to form a stable solution in DMSO. While starch solutions in water are unstable, with the phenomena of retrogradation being observed, solutions in aqueous DMSO have been reported to

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be relatively stable (Gidley, 1989). There have been studies of the solution conformation of amylose in aqueous DMSO (Dintzis & Tobin, 1969). The molecular weight dependence of viscosity for amylopectin in pure DMSO has also been investigated (Salemis & Rinaudo, 1984). There have been some studies of the rheological properties of starch dispersed in aqueous DMSO (Dintzis & Bagley, 1995a,b). There is a need for the rheological characterization of starch dispersed in aqueous DMSO for the prediction of flow behavior in starch modification processes as this is the solvent of choice for several starch modification process. In this paper, we present a detailed study of the behavior of starches of various compositions (different amylose to amylopectin ratio) and concentration in DMSO under dynamic shear and extensional deformation.

2. Experimental procedure

2.1. Materials

Three types of native starches with different compositions were obtained from the American Maize Products Company. The approximate compositions were known (Delgado, Gottnied & Ammeraal, 1991). Amylomaize VII, a high amylose corn starch, contained about 70% amylose and 30% amylopectin. Amioca, a waxy corn starch, contained about 99% amylopectin while common corn starch contained about 75% amylopectin and 25% amylose. The moisture content of each type of starch was determined to be about 10% on a weight by weight basis.

Certified grade DMSO with water content less than 0.2% was obtained from Fisher Scientific. Water used was purified using the Millipore reverse osmosis system.

2.2. Sample preparation

Weighted amounts of starch were mixed with a 90% (v/v) solution of DMSO with water using a spatula until a milky white dispersion was obtained. This usually took about 1 min of stirring. A stirrer bar was put in the beaker which was covered with aluminum foil and placed in a water bath at 96–98°C. This corresponded to a sample temperature of approximately 85–87°C. The beaker was heated by stirring for 15 min at 50 rpm, after which stirring was stopped and the beaker heated for an additional 15 min. The milky white dispersion became clear as the starch gelatinized and solubilized. The weight was checked to ensure that no evaporation of solvent had occurred. The solution was then cooled to room temperature and loaded onto the rheometer. The effect of storage time of the samples prior to loading in the rheometer was determined by testing samples of the same concentration with different storage times.

Concentrations of 2, 4, 6, and 8% (w/v) of each starch dissolved in aqueous DMSO (90% DMSO, 10% water) were used in the rheological study. In this work, concentrations units are % (w/v) unless otherwise mentioned.

2.3. Intrinsic viscosity

The samples were prepared in an identical fashion to that used in the measurement of rheological parameters as described above. After the sample cooled to room temperature, it was transferred to a 100 ml volumetric flask, and brought to volume with washings from the beaker. The solutions were filtered through a 5 μm polycarbonate disposable membrane prior to loading in the viscometer. Flow times for the determination of intrinsic viscosity were obtained at 22 ± 0.1°C in a Canon-Ubbelohde shear dilution viscometer, series 1C-B855. Intrinsic viscosities were obtained by plotting η_{sp}/c versus c, where η_{sp} was the specific viscosity and c the concentration, and obtaining the value of the intercept on the ordinate by linear regression.

2.4. Rheological measurements

2.4.1. Experiments in shear

A Rheometrics Fluids Spectrometer (RFS-II) manufactured by Rheometrics Inc., Piscataway, NJ, was the strain controlled rheometer used. The apparatus consists of a rotating outer cylinder (cup) into which the sample was transferred initially. The inner cylinder (bob) was suspended from an air bearing and torque was measured using transducers with a range of 0.002–100 g cm. The diameters of the cup and bob were 34 and 32 mm, respectively, and the bob length was 33 mm. Temperature control (in the range ~10–90°C) was achieved by using a circulating fluid bath. This apparatus can be used for both steady shear and dynamic flow measurements, typically for fluids having viscosities in the range $\sim 10^{-3}$–10^{5} Pa s.

The expression for shear stress on the inner cylinder for the case of rotating outer cylinder is given by

$$\tau_{r\theta} = \frac{M_\mathrm{i}}{2\pi R_\mathrm{i}^2 L} \qquad (1)$$

where M_i is the torque measured on the inner cylinder, and R_i and L are the radius and length of the inner cylinder, respectively.

Equations for shear rate for the case of an outer rotating cup is given by Krieger, 1968 and Krieger and Elrod, 1953. The working equations given in the operating manual of RFS-II are strictly valid for a Newtonian fluid, n = 1. The use of this approximation leads to an error given by

$$\left.\frac{\dot\gamma_\mathrm{power}}{\dot\gamma_\mathrm{Newt}}\right|_{R_\mathrm{i}} = \frac{1-\kappa^2}{n(1-\kappa^{2/n})} \qquad (2)$$

where $\kappa = R_1/R_2$, R_1 is the radius of the bob and R_2 the radius of the cup.

The error estimate from Eq. (2) increases with decrease in the value of n. The lowest value of n was 0.652 for 2% waxy starch. Thus the error in using the Newtonian approximation for shear experiments on the RFS-II is less than 3.3% from Eq. (2).

All samples were loaded at room temperature and allowed to equilibrate for approximately 15 min. This was done to allow temperature equilibration and relaxation of any induced stresses during loading. All measurements were carried out at 21–23°C.

2.4.2. Experiments in extension

An opposed nozzle device, the Rheometrics RFX Fluid Analyzer, was used to measure the extensional viscosity of 2% (w/v) solutions of native starch in aqueous DMSO. Higher concentrations were not used due to experimental problems such as cavitation for high viscosity samples and gel-like behavior for waxy starch solutions. The opposed nozzle device is an extensional viscosity indexer, rather than a rheometer as pointed out by Dontula, Pasquali, Scriven and Macosko (1997). The flow is not homogeneous, but has a strong extensional component (Macosko, 1994). The device attempts to create a uniaxial extensional flow by drawing fluid through two opposed nozzles mounted on rigid arms by the action of two syringes driven by a stepper motor. The left nozzle arm can rotate about a pivot, while the other arm is fixed. The flow of fluid through the nozzles into the syringes results in a force that tends to pull the nozzles together. Torque is measured by a rebalance transducer which maintains the gap constant. The torque M applied to keep the gap constant can be used to define an effective extensional viscosity η_E of the fluid as

$$\eta_E = \frac{M}{\pi R^2 L \dot{\epsilon}} \tag{3}$$

where L is the distance from the pivot of the left nozzle arm and the plane of symmetry through the nozzles and R is the radius of the nozzles.

The assumption of steady homogeneous uniaxial flow between the nozzles leads to the definition of the apparent extension rate as

$$\dot{\epsilon} = \frac{Q}{\pi R^2 h} \tag{4}$$

where $2Q$ is the total flow rate into both nozzles, and $2h$ is the total separation between the nozzles. A nozzle gap to diameter ratio of 1 was used. Five pairs of nozzles of 1, 2, 3, 4, and 5 mm diameter were used. Smaller nozzle diameters give higher apparent extension rates at the same liquid flow rate.

3. Results and discussion

3.1. Reproducibility

Reproducibility of data was determined by conducting at least two replicates of each experiment and by using at least two duplicate samples. Thus there were a minimum of four data sets for each measurement. In the plots of the dynamic frequency sweeps the calculated mean values are used. Error bars are depicted on all the frequency sweep data. In other plots, multiple data sets are overlaid to highlight specific effects. Reproducible data sets were obtained for all the samples except 6% and 8% waxy corn starch, and 8% common corn starch. For these three samples, viscoelastic properties were strongly dependent on the method of preparation. Taking care to minimize variations in sample preparation, reproducible data sets were obtained for viscoelastic properties within the linear viscoelastic regime. Waxy corn starch samples of 6% and 8% concentration, and common corn starch samples of 8% concentration had dynamic properties analogous to those of crosslinking polymeric systems near the gel point as reported in the literature (Chambon & Winter, 1987; Winter & Chambon, 1986). It was observed that experiments on gels were difficult to reproduce with precision (Larson, 1999). Gels were disordered materials that were kinetically frozen, with the consequent sensitivity of viscoelastic properties on the method of preparation. Venkataraman and Winter (1990) reported that a polymer crosslinked beyond the gel point could be reduced from a viscoelastic solid to a critical gel, or to a viscoelastic liquid with increasing magnitude of shear strain. This effect was attributed to the rupture of the network structure of the crosslinking polymer by shear strains above a magnitude of 2 (Venkataraman & Winter, 1990). This lead to the difficulty in obtaining reproducible data sets for nonlinear viscoelastic properties and could be attributed to network rupture in the physically crosslinking starch systems under consideration.

Experiments on different rheometers should yield the same value for a particular material function provided none of the assumptions made in deriving the working equations for the test geometry have been violated, secondary flow effects are negligible, transducers have been properly calibrated, and there are no changes in the sample. Cone and plate geometry offers the advantage of measuring normal forces. However, edge failure was observed at shear rates less than 1.0 s^{-1}, even for the lower concentration samples. This led to poor reproducibility of data among even replicate runs. Higher torque sensitivity was the reason behind the use of the couette geometry for high amylose corn starch. In order to make sure data collected were not an instrument artifact, linear viscoelastic transformations (Ferry, 1980) were employed to check material function data and extend the time scale covered.

4. Solvent viscosity

The solvent behaves like a Newtonian fluid with a viscosity of 3 mPa s. Torque values were below transducer sensitivity for shear rates below 10 s^{-1}. In a frequency sweep, solvent contributes only to the loss modulus G'', while the solute contributes to both the loss modulus and the storage modulus G'. In the case of pure solvent, there is no solute. Hence only the loss modulus is significant, and is given by

$$G'' = \omega \eta_s \tag{5}$$

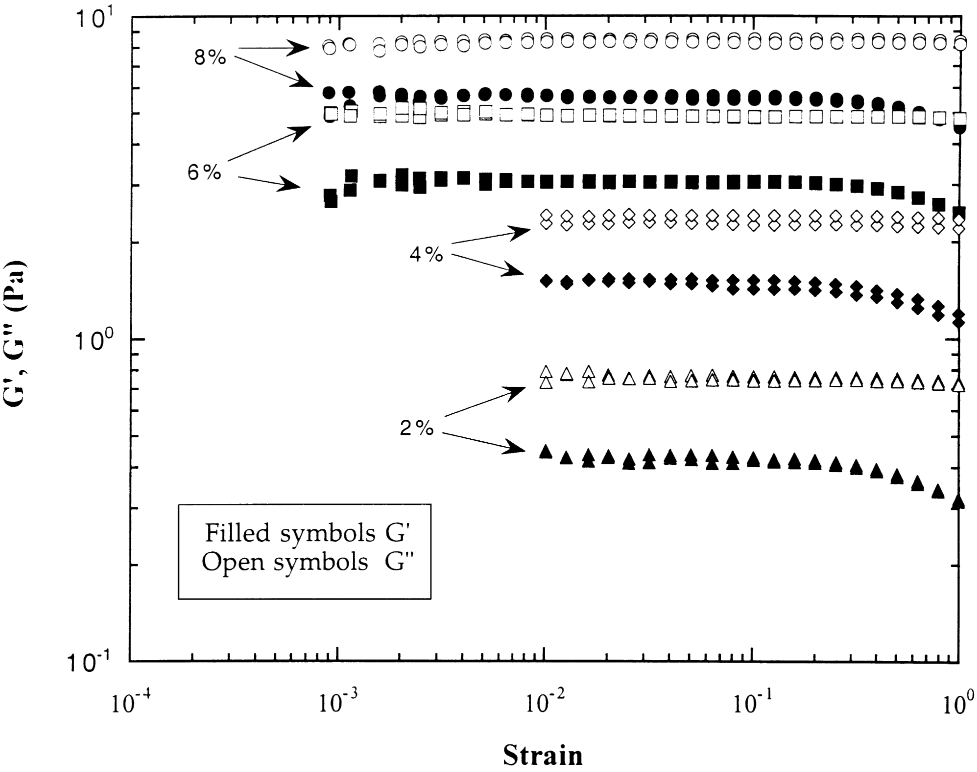

Fig. 1. Dynamic strain sweep data for common corn starch. Numbers denote concentration in % (w/v).

Thus, viscosity obtained from the intercept of a log G''–log ω plot would serve as a check of the viscosity value obtained from steady shear experiments. A value of 2.93 mPa s was obtained for η_s by linear regression from a log G''–log ω plot for the solvent 90% DMSO–10% water. This value is within 3% of the value from steady shear experiment. A value of 3 mPa s for η_s was used in data analysis. The density of the solvent was 1.09 g ml^{-1}, determined by measuring the mass of known volume of solvent using a calibrated volumetric flask.

4.1. Intrinsic viscosity

Polymer solutions can be classified into dilute, semidilute, and concentrated solutions based on the extent of coil overlap and entanglement effects. The coil overlap parameter $c[\eta]$ is commonly used in literature to determine whether a polymer solution is dilute, semidilute, or concentrated. Polymer solutions having a value of $c[\eta] < 1$ are termed dilute. Concentration effects become important at a value of $c[\eta]$ close to unity, and intermolecular interaction seem to be dominated by coil overlap in the semidilute range $1 < c[\eta] < 10$. Entanglement effects become important in solutions above a value of $c[\eta] = 10$, and these solutions are termed as concentrated.

Intrinsic viscosity for waxy, common corn, and high amylose corn starch were determined to have values of 119, 105, and 79 ml g^{-1}, respectively at a temperature of 22°C. Intrinsic viscosity of starch solutions have been reported to be dependent on the method of preparation (Dintzis & Bagley, 1995b). The procedure for sample preparation outlined in the experimental section was followed throughout this study to ensure a consistent basis for data analysis. The values for waxy and high amylose corn starch were lower than the values reported by Dintzis and Bagley (1995b) for starch solutions in the same solvent (90% DMSO–10% water) at a temperature of 25°C. The shear rate at the wall also affects the value of the intrinsic viscosity. Dintzis and Bagley (1995b) reported wall shear rates of the order of 20 s^{-1} with a capillary size of 0.078 cm. In this study, the capillary diameter used was 0.078 cm. Thus, the difference in $[\eta]$ values could be due to a longer exposure time to high temperature and differences in the stirrer speeds used during sample preparation. This leads to lower molecular weight as indicated in the work of Millard, Dintzis, Willet and Klavons (1997). The value of the parameter $c[\eta]$ was calculated for the different concentrations used in the study, and ranged from 2.3–9.5, 2.1–8.4, and 1.5–6.3 for waxy, common corn, and high amylose corn starch respectively, depending on concentration.

5. Dynamic measurements

5.1. Limits of linear viscoelasticity

A dynamic strain sweep was used to determine the limit of strain γ_c for linear viscoelasticity. For common corn and

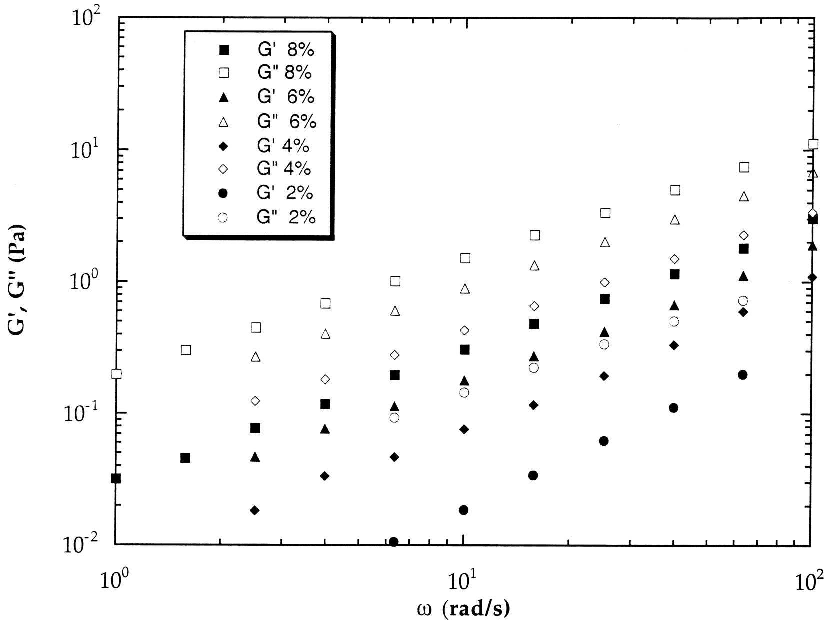

Fig. 2. Frequency sweep data for high amylose corn starch. Numbers denote respective concentration in % (w/v).

waxy corn starch, sinusoidal strains with a range of amplitudes typically from 0.001 to 1.0, each at constant frequency (10 rad s^{-1}) were applied and the dynamic moduli G' and G'' measured. For high amylose corn starch, the range of strain amplitude was higher, from 0.01 to 8.0. This was done to keep the torque signal above the lower limit of the transducer. Plots of the dynamic moduli as a function of strain are shown in Fig. 1 for common corn starch. Similar plots were also obtained for the other two types of starches. Multiple points represent replicate runs. The LVE region was determined from the portion of the curve where the values of G' and G'' were independent of strain amplitude. It was observed that the value of G' was more sensitive to strain amplitude, and at a certain value γ_c, the magnitude of G' decreased with increasing strain amplitude. The value of γ_c was found to be independent of the concentration, and was about 0.15 for common corn starch, 0.1 for waxy corn starch, and between 0.15 and 0.20 for high amylose corn

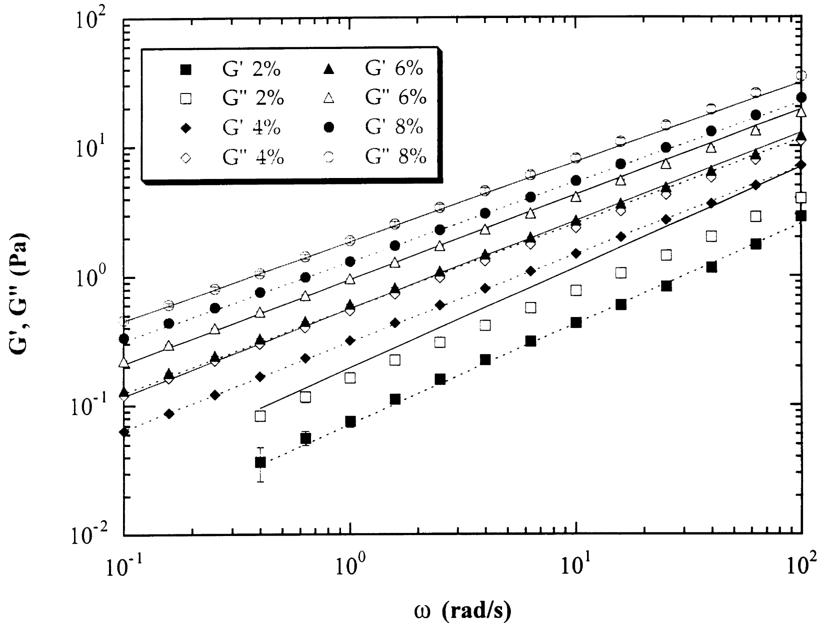

Fig. 3. Frequency sweep data for common corn starch. Numbers denote respective concentration. Lines (Dashed: G', Solid: G'') are predictions from Eqs. (14) and (15).

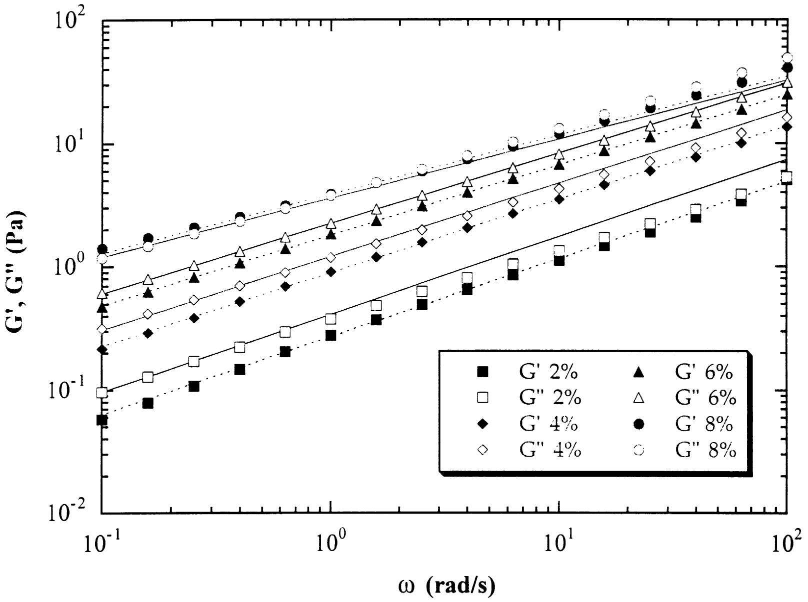

Fig. 4. Frequency sweep data for waxy starch. Numbers denote respective concentration. Lines (Dashed: G', Solid: G'') are predictions from Eqs. (14) and (15).

starch. As indicated in the plots, low-torque signal and phase angle resolution become limiting at low-strain amplitudes, and were the cause of scatter in data.

5.2. Frequency dependence

5.2.1. Effect of concentration

Data for the elastic modulus (G') and the viscous modulus (G'') are plotted as a function of frequency with concentration as a parameter for the three starch types in Figs. 2–4. The G' and G'' curves were essentially linear on log–log scale for high amylose and common corn starch. A linear dependence of log G'' on log ω was also observed for waxy corn starch. However, the slope of the terminal region of G' data decreased with increasing concentration for waxy corn starch, from a downward slope at low frequency observed for 2 and 4% concentration to the flat curve observed for 8% concentration. Values for the slope of log G' and log G'' versus log ω curves are summarized in Table 1 for the three starch types. Dynamic moduli for high amylose corn starch are plotted in Fig. 2. G'' is greater than G' for all the concentrations, similar to that observed for the common corn starch. Low-torque signal and phase angle resolution became limiting at frequencies below 5 rad s^{-1}. G' and G'' curves for the 8% concentration sample are parallel to those for the 6% concentration sample, with a slope of 0.99 and 0.87, respectively. The slope of the G' and G'' curves increase to a value of 1.08 and 0.90, respectively, for the 4% concentration sample, and 1.29 and 0.89, respectively, for the 2% concentration sample. The shape of the G' and G'' curves for high amylose corn starch suggested the applicability of dilute solution molecular theory to model the experimental data.

A number of phenomenological and molecular models have been proposed to describe the rheological behavior of polymer solutions, and have been documented elsewhere (Bird, Armstrong & Hassager, 1987; Ferry, 1980). Most of the molecular models available have been derived for very dilute polymer solutions in which molecules are treated as essentially isolated from each other, with no intermolecular interaction. However, sensitivity limitations of instruments require experimental data to be generated at finite concentrations. Consequently, comparison to molecular theory requires the extrapolation of experimental data to infinite dilution.

Typically, the storage modulus and the loss modulus are the viscoelastic functions considered, and the corresponding quantities extrapolated to infinite dilution are the intrinsic

Table 1
Slope of log G' and log G'' versus log ω curves

	High amylose corn starch		Common corn starch		Waxy corn starch	
	G'	G''	G'	G''	G'	G''
2%	1.29	0.89	0.76	0.69	0.63	0.57
4%	1.08	0.90	0.65	0.67	0.59	0.56
6%	0.99	0.87	0.65	0.63	0.57	0.56
8%	0.99	0.87	0.61	0.63	0.49	0.54

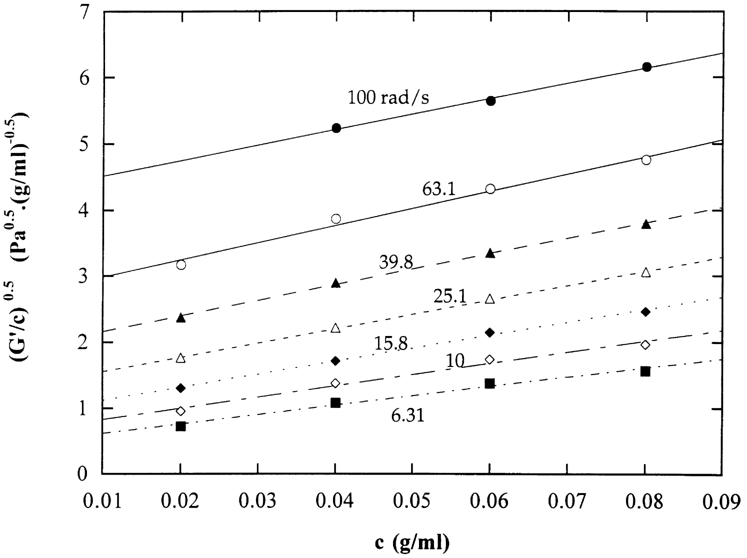

Fig. 5. Plot to determine $[G']$ for high amylose starch by extrapolation to c = 0. Numbers denote the frequency in rad s^{-1}.

storage and loss modulus

$$[G'] = \lim_{c\to 0} \frac{G'}{c} \tag{6}$$

$$[G''] = \lim_{c\to 0} \frac{(G'' - \omega\eta_s)}{c} \tag{7}$$

where ω is the frequency in rad s^{-1} and η_s is the solvent viscosity.

The reduced dimensionless intrinsic moduli are defined as

$$[G']_R \equiv \frac{[G']M}{RT} \tag{8}$$

$$[G'']_R \equiv \frac{[G'']M}{RT} \tag{9}$$

where M is the molar mass of the polymer (assumed monodisperse), R the gas constant, and T the absolute temperature. The theory of Rouse (1953) was developed for a dilute solution of a monodisperse, linear viscoelastic polymer in a theta solvent. In this theory, hydrodynamic interactions between the beads are ignored. Hydrodynamic interaction between the beads was included in the theory of Zimm (1956). The expressions obtained for the dynamic moduli in both Rouse and Zimm theory are given as

$$[G']_R = \sum_{i=1}^{N} \frac{\omega^2\lambda_i^2}{1 + \omega^2\lambda_i^2} \tag{10}$$

$$[G'']_R = \sum_{i=1}^{N} \frac{\omega\lambda_i}{1 + \omega^2\lambda_i^2} \tag{11}$$

where λ_i are the relaxation times, which are different for the two models.

In the Rouse model,

$$\lambda_i = \frac{6[\eta]\eta_s M}{\pi^2 i^2 RT} \tag{12}$$

The relaxation time corresponding to i = 1 is termed as the longest or terminal relaxation time.

Dynamic data obtained for the high amylose corn starch was plotted as $(G'/c)^{1/2}$ and $(G'' - \omega\eta_s)/c$ versus c, and extrapolated to c = 0 using linear regression as shown in Figs. 5 and 6, respectively. Intrinsic moduli values obtained are tabulated in Table 2.

Using the value of 79 ml g^{-1} obtained from experiment for the intrinsic viscosity, and the value of 3.2×10^6 g mol^{-1} for M_w from data available in the literature (Fishman & Hoagland, 1994; Fishman, Cooke, White & Damert, 1995; Fishman, Rodriguez & Chau, 1996), the longest relaxation time was calculated to be 1.89×10^{-4} s for the high amylose corn starch from Eq. (12). This value of λ_i was used in Eqs. (10) and (11) with N = 6 to calculate Rouse theory predictions for the reduced intrinsic dynamic moduli. The prediction from Rouse theory when compared to experimental data indicates that $[G'']_R$ matches prediction from Rouse theory very closely. However, experimental data for $[G']_R$ is higher than the Rouse model prediction by a factor of about 100. The Rouse theory was developed for dilute solutions of monodisperse linear polymer molecules. High amylose corn starch is known to be a mixture of polydisperse linear and branched polymers, with the linear fraction comprising about 70% by weight of the mixture (Delgado et al., 1991). The presence of a molecular weight distribution, excluded volume effects, and branching causes the lack of agreement of experimental data with molecular theory. A plot of the zero shear viscosity versus the parameter $c[\eta]$ for the various concentrations has a slope of 1.9 on log–log scale which is higher than the value of unity

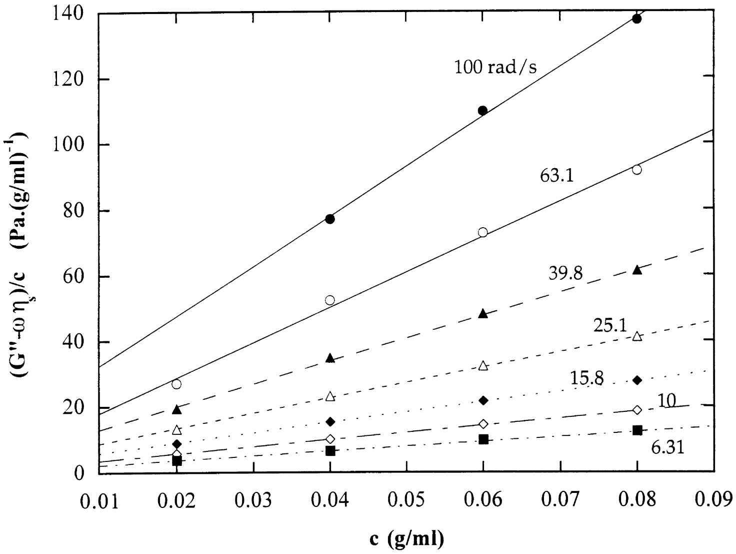

Fig. 6. Plot to determine $[G'']$ for high amylose starch by extrapolation to c = 0. Numbers denote the frequency in rad s^{-1}.

predicted by Rouse theory. It can therefore be inferred that the high amylose corn starch solutions are in the semidilute regime.

Dynamic moduli for common corn starch are plotted in Fig. 3. G'' is greater than G' for all the concentrations. Data for 2% concentration were limited at low frequency by low-torque signal. The G' and G'' curves are essentially linear on log–log scale for the concentrations studied. The slope of the G' curve decreases from a value of 0.76 to 0.61 with increasing concentration, while the slope of the G'' curve decreases from 0.69 to 0.63 with increasing concentration. When tan δ is plotted as a function of frequency for common corn starch, it is observed that for 2% concentration tan δ decreases with increasing frequency, which is typical for a viscoelastic liquid. Tan δ for 4% and 6% concentration common corn starch decreases with increasing frequency till about 15 rad s^{-1}, and is essentially independent of frequency for $\omega > 15$ rad s^{-1}. Tan δ increases with increasing frequency for 8% concentration common corn starch, which is typical of a viscoelastic solid. The plateau value for tan δ is the same for both 6% and 8% concentration common corn starch. Thus 6% concentration common corn starch can be considered to be near the gel point, while 8% concentration common corn starch is just beyond the gel point. At the gel point, the loss tangent has been reported to be independent of the frequency (Chambon & Winter, 1987; Izuka, Winter & Hashimoto, 1992; Winter & Chambon, 1986). A system at the gel point is termed a critical gel. Power-law relaxation over five decades of frequency for chemically crosslinking polymers at the gel point has also been reported (Chambon & Winter, 1987; Izuka et al., 1992; Winter & Chambon, 1986). Similar power-law relaxation behavior has been reported for a commercial linear low-density polyethylene at intermediate frequencies over a limited range of frequency (Larson, 1985). A method for the rheological determination of the gel point has been proposed based on the detection of a loss tangent independent of frequency (Chambon & Winter, 1987; Winter & Chambon, 1986). The relaxation modulus for critical and near-critical gels is given by Winter and Chambon (1986), Chambon and Winter (1987), and Larson (1985).

$$G(t) = ct^{-m} \tag{13}$$

The storage modulus (G') and the loss modulus (G'') are given by Larson (1985)

$$G' = \omega \int_0^\infty G(t) \sin \omega t \, dt = \frac{c\pi\omega^m}{2\Gamma(m) \sin(m\pi/2)} \tag{14}$$

$$G'' = \omega \int_0^\infty G(t) \cos \omega t \, dt = \frac{c\pi\omega^m}{2\Gamma(m) \cos(m\pi/2)} \tag{15}$$

where $\Gamma(m)$ is the gamma function. The loss tangent is then given by

$$\tan \delta \equiv \frac{G''}{G'} = \tan(m\pi/2)$$

The slope of the G' and G'' vs ω on a log–log plot is a measure of the parameter m for the critical gel. The two values of m, one from the G'curve and the other from the G'' curve are close, indicating parallel lines for critical gels. It should also be noted that where the slopes from the G' and

Table 2
Intrinsic dynamic moduli for high amylose corn starch

ω (rad s^{-1})	$[G']$ Pa (g ml)$^{-1}$	$[G'']$ Pa (g ml)$^{-1}$
100	18.39	17.31
63.1	7.44	7.29
39.3	3.71	6.08
25.1	1.81	4.23
15.8	0.87	2.72
10	0.45	1.56
6.31	0.24	0.81

Table 3
Model parameters for common corn and waxy starch

Concentration (%)	Common corn starch		Waxy corn starch	
	c	*m*	*c*	*m*
2	0.05	0.78	0.21	0.63
4	0.23	0.68	0.70	0.59
6	0.43	0.66	1.41	0.57
8	0.99	0.61	3.13	0.48

G'' curves are different, we have a 'non-critical' gel as seen from Table 1.

The exponent m has a value in the range $0 \leq m \leq 1$ depending on molecular composition and crosslinking conditions, and the prefactor c is a measure of the strength of the critical gel (Chambon & Winter, 1987; Izuka et al., 1992; Winter & Chambon, 1986). As expected, c increases with an increase in the concentration for both common and waxy corn starch (Table 3). A material exhibiting such power-law relaxation has an infinitely long relaxation time. For a chemically crosslinking system, the exponent m decreases, and the gel strength c increases, as the stoichiometric ratio of crosslinker to precursor is increased (Izuka et al., 1992). Entanglements among the precursor polymer molecules may result in a decrease in the value of m (Izuka et al., 1992) and this is also observed from our data (Table 3). Gelation due to formation of a network of physical bonds between molecules has been observed for several systems (Larson, 1999). Local helical structures, microcrystallites, and nodular domains have been proposed as the interactions that give rise to physical gelation (Lin, Mallin, Chien & Winter, 1991). However, the junctions in physical gels have a finite lifetime, and the formation of physical crosslinks is reversible. The typical power-law scaling observed for chemical crosslinking systems has been reported to hold for physical gelation processes as well (Rochas, Brulet & Guenet, 1994). Thus, the power-law behavior observed for starch in water–DMSO in this study could be attributed to the formation of physical crosslinks. Starch has an abundance of hydroxyl groups, and the phenomena of retrogradation and syneresis in starch–water systems has been attributed to hydrogen bonding. The conformation of amylose in various solvents is that of a locally helical and flexible chain (Kapoor, 1998). The thermoreversible gelation of the polysaccharide agarose in water–DMSO mixtures has been attributed to the formation of helical structures (Adolf & Martin, 1990). However, the exact structure of the proposed helical associations has yet to be ascertained (Adolf & Martin, 1990; Larson, 1999). The power-law behavior of starch–water–DMSO systems could be attributed to the formation of helical structures leading to physical crosslinks.

The power-law scaling for crosslinking systems near gel point can be attributed to the fractal scaling properties of gel clusters (Chambon & Winter, 1987; Larson, 1999). Adolf and Martin (1990) derived the value of the scaling exponent m using a dynamic scaling theory for the viscoelasticity of systems near gel point as $m = D/(2 + D_f) = 2/3$, where $D_f = 2.5$ is the fractal dimensionality of the clusters formed by the fractal aggregates, and $D = 3$ is the dimensionality of space. The theoretical value for m of 2/3 was observed for a crosslinked epoxy at various degrees of cure and a time-cure superposition was observed to hold for the data. The m values for the common corn starch at 4% and 6% correspond to the theoretical value of $m = 0.67$. However, deviations from the theoretical value of 2/3 for m have also been reported (Adolf & Martin, 1990; Chambon & Winter, 1987; Izuka et al., 1992; Rochas et al., 1994; Winter & Chambon, 1986).

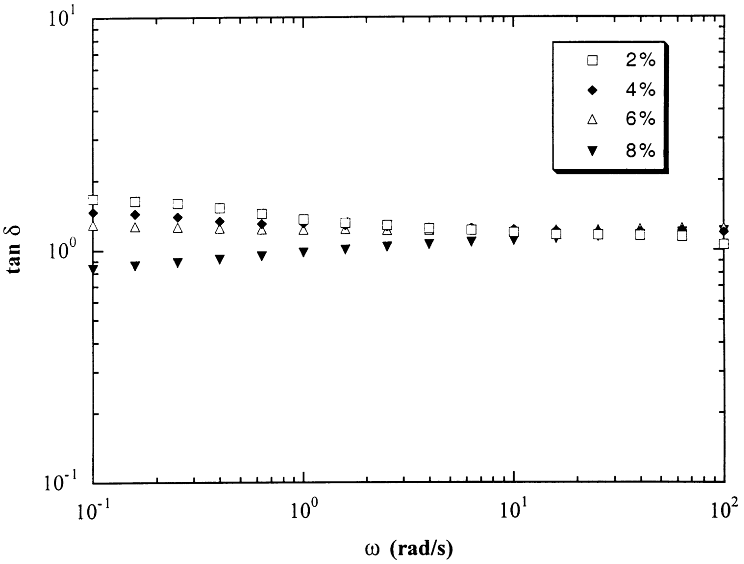

Fig. 7. Variation of the loss tangent with concentration for waxy starch.

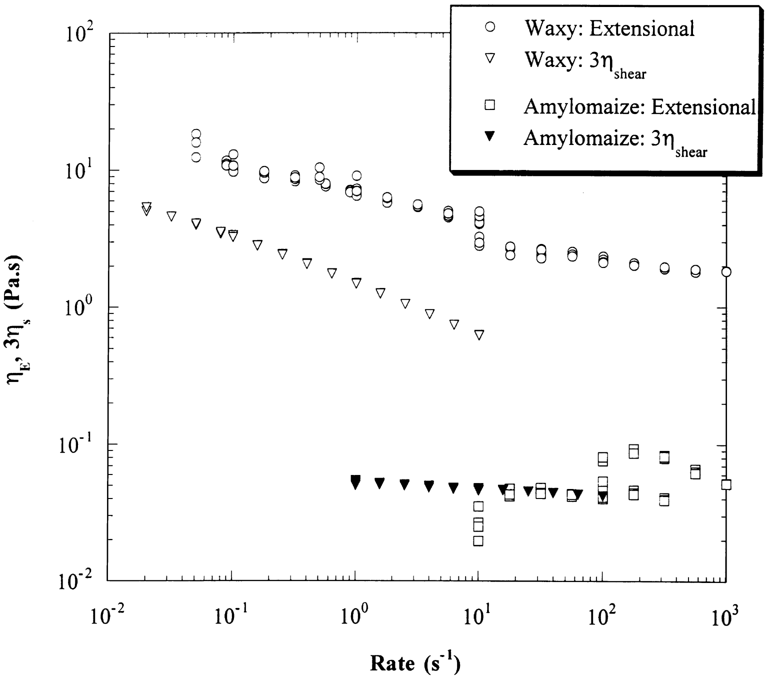

Fig. 8. Apparent extensional viscosity of 2% waxy and 2% high amylose starch. Shear viscosity data shown for determining Trouton ratio.

The dynamic moduli for the waxy corn starch, which is essentially pure amylopectin, are plotted in Fig. 4. It can be seen that G'' is greater than G' over the entire range of frequency and concentration except at a concentration of 8% (w/v), where G' is greater than G'' at low frequency and a crossover occurs at $\omega = 1.58$ rad s^{-1}. The curves of G' and G'' are parallel only for a concentration of 6%, and have a slope of 0.56 which is constant over the entire frequency range. Data for 2% and 4% concentrations show a downward slope at low frequency, which is indicative of fluidlike behavior. Thus waxy corn starch exhibits fluidlike behavior at concentrations below 6% and solidlike behavior above concentrations of 6%. Thus, a 6% concentration waxy corn starch exhibits critical gel behavior with a power-law behavior throughout the frequency regime investigated. The reported dependence of viscoelastic behavior of a chemically crosslinking system on magnitude of shear strain was observed for the physically crosslinking starch systems in this study. As a representative example, increasing shear time in preparation from 15 to 20 min reduced the 6% critical gel to a viscoelastic liquid, as was observed from dynamic data in the low frequency (Kapoor, 1998). Data for a sample with extra 5 min of stirring during preparation have a downward slope at low frequency. Tan δ is plotted as a function of frequency for waxy corn starch in Fig. 7. Tan δ for 2% and 4% concentration waxy corn starch decreases with increasing frequency, which is typical for a viscoelastic liquid. Tan δ is independent of frequency for the critical gel (6% w/v), and increases with increasing frequency for 8% concentration waxy corn starch, which is typical of a viscoelastic solid.

5.2.2. Effect of starch composition

The magnitude of the dynamic moduli is highest for waxy corn starch and lowest for high amylose corn starch at a given frequency and concentration. The slopes of the G' and G'' curves are lowest for waxy corn starch and highest for high amylose corn starch. This trend can be explained due to the high molecular weight and high branching of the amylopectin as compared to amylose. Waxy corn starch consists of approximately 99% amylopectin, and thus has a greater proportion of high molecular weight molecules than either common corn starch (~75% amylopectin) or high amylose corn starch (~30% amylopectin). Ferry (1980) observed that the magnitude of G' depended on the contour rearrangements possible within the period of oscillatory deformation. Contour rearrangements of the highly branched and high molecular weight amylopectin would be expected to be slower than those for the essentially linear and lower molecular weight amylose, leading to higher magnitudes of G' with increasing amylopectin content at the same frequency. The formation of self similar clusters give rise to power-law relaxation in common corn and waxy corn starch, in contrast to the semidilute solution behavior of high amylose corn starch.

6. Extensional measurements

Apparent extensional viscosity (η_E) data for 2% concentration waxy and high amylose corn starch are depicted in Fig. 8. Experiments were planned to detect differences between the two extreme molecular composition. The values of $3\eta_s$, where η_s is the shear viscosity of the starch

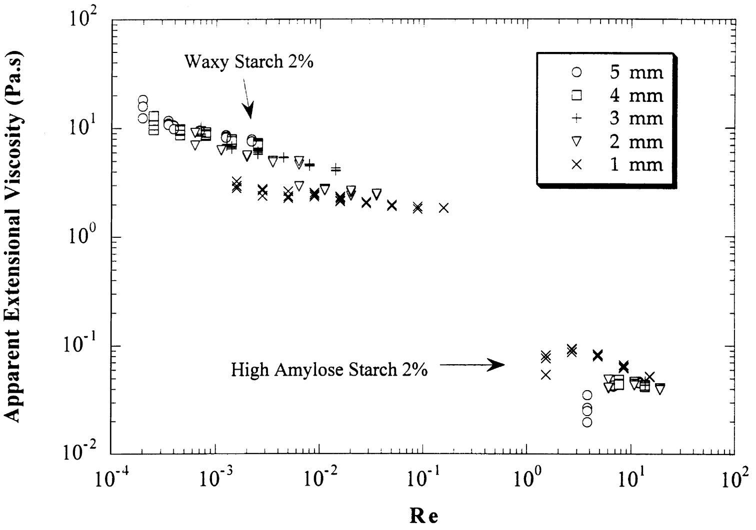

Fig. 9. Apparent extensional viscosity versus Reynolds number for different nozzle sizes. Numbers denote nozzle size in mm.

solutions at a shear rate equal in magnitude to the extension rate, have also been shown for comparison. η_E values for 2% concentration waxy corn starch were higher than those for high amylose corn starch of the same concentration. The value of η_E decreases with increasing extension rate for waxy corn starch. There is scatter in η_E data in the range of extension rate between 100 and 300 s^{-1} for 2% concentration high amylose corn starch. From shear viscosity data, it was observed that 2% concentration high amylose corn starch was essentially a Newtonian fluid with a η_s value of 18 mPa s. Waxy corn starch solution of 2% concentration shows shear thinning behavior, with a shear viscosity of 1.73 Pa s at the lowest shear rate of 0.02 s^{-1}. The values of η_E and $3\eta_s$ match for 2% concentration high amylose corn starch at rates between 17.78 and 100 s^{-1} while those of waxy corn starch solution of similar concentration has a value of about 15 for the ratio η_E/η_s at rates below 0.1 s^{-1}.

In this study, reproducibility of the measurements was examined by using different nozzle sizes at the same extension rate. In the case of 2% concentration waxy corn starch, values of η_E agree within 10% at rates up to 10 s^{-1}. At a rate of 10 s^{-1}, there is a discontinuity in the curve, with the value of η_E at higher rates matching for two different nozzle sizes, 1 and 2 mm. For 2% concentration high amylose corn starch, there is a mismatch in η_E data at rates higher than 100 s^{-1} for different nozzle sizes. This was because torque did not attain a steady state value during measurements. The lack of a steady state has also been reported for a 0.95% by weight polyethyleneoxide (PEO) solution in water at extensional rates greater than 2000 s^{-1} (Dontula et al., 1997), and was attributed to the low (<50 mPa s) shear viscosity of the solution.

Dontula et al. (1997) studied the extensional viscosity of glycerin–water mixtures at various glycerin volume fractions, and PEO solutions in water at concentrations from 0.05 to 1.89% by weight. It was concluded that at Reynolds numbers $Re = (\rho Q h/\eta_s \pi R^2) = (\rho \dot{\epsilon} h^2/\eta_s)$ greater than unity, fluid mechanical effects become important and measurements were affected by dynamic pressure, shear on the nozzles, and liquid inertia. It was also observed that reliable measurements of extensional viscosity of fluids having shear viscosity less than about 50 mPa s were not possible due to high Reynolds number (Re) effects and transducer sensitivity. The extensional viscosity of the waxy and high amylose corn starch solutions are plotted versus Reynolds number in Fig. 9. It was observed that $Re > 1$ for all the nozzle sizes and extensional rates for 2% concentration high amylose corn starch, while $Re < 1$ for waxy corn starch of the same concentration. Thus, the lack of reproducibility for 2% concentration high amylose corn starch data could be explained by fluid mechanical effects and force values being close to the limit of transducer sensitivity. This was a consequence of the low-shear viscosity (18 mPa s) of 2% concentration high amylose corn starch. From Fig. 9, two levels of extensional viscosity were observed for 2% concentration waxy corn starch. The discontinuity of the data at the lower level were obtained at extension rates greater than 10 s^{-1}. Waxy corn starch is comprised of the highly branched, high molecular weight amylopectin. Data generated from the extensional experiments could be indicative of material behavior. However, instrument effects have been reported to be significant in opposed nozzle experiments (Dontula et al., 1997; Macosko, 1994), and limited conclusions could be drawn from the data.

7. Conclusions

The rheological properties of starch in a mixed solvent water–DMSO produced stable solutions and varied with starch composition and concentration. The limit of strain in the linear viscoelastic region was determined to be between 0.15 and 0.20 for high amylose corn starch, 0.15 for common corn starch, and 0.1 for waxy corn starch. Loss modulus was greater than storage modulus in the frequency range 0.1–100 rad s^{-1} for all samples except 8% concentration waxy corn starch, where a crossover was observed at a frequency of 1.58 rad s^{-1}. High amylose corn starch at a concentration of 2% (w/v) was essentially a Newtonian liquid with a viscosity of 18 mPa s. The applicability of Rouse theory to high amylose starch data was limited by the presence of branching and polydispersity, which resulted in the underprediction of elastic moduli.

Rheological properties of common corn starch changed from a viscoelastic liquid at 2% concentration to a near-critical gel at 8% concentration. The proportion of amylopectin in starch dictated whether ‘gel-like’ viscoelastic behaviors were observed. A power-law relaxation was observed for all concentrations of common corn starch, with the slope of the G' and G'' curves decreasing with an increase in concentration. Power-law behavior was also observed for waxy corn starch, with the slope of the G' and G'' curves decreasing from 0.63 and 0.57, respectively, at 2% concentration, to a value of 0.49 and 0.54, respectively at 8% concentration. Waxy corn starch was a viscoelastic liquid at 2% and 4% concentration, a near-critical gel at 6% concentration, and a viscoelastic solid at 8% concentration. The power-law relaxation observed could be due to the formation of self-similar clusters near the gel point. The relaxation exponent m (Eq. (13)) had values of 0.776, 0.678, 0.655, and 0.612 for 2%, 4%, 6%, and 8% concentration common corn starch, respectively. Waxy corn starch had m values of 0.629, 0.594, 0.569, and 0.477 for concentrations of 2%, 4%, 6%, and 8%, concentration, respectively. Rheological properties of 8% concentration common corn starch, and 6% and 8% concentration waxy corn starch were sensitive to variation in the preparation method, and network rupture effects were observed at a strain magnitude greater than 2. Extensional thinning was observed for 2% concentration waxy corn starch. Extensional viscosity data for 2% concentration high amylose corn starch were dominated by fluid mechanical and instrument effects, and limited conclusions could be drawn from the extensional data.

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