

Rheology of concentrated xanthan gum solutions: Oscillatory shear flow behavior

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Abstract

Using a strain-controlled rheometer, the dynamic viscoelastic properties of aqueous xanthan gum solutions with different concentrations were measured over a wide range of strain amplitudes and then the linear viscoelastic behavior in small amplitude oscillatory shear flow fields was investigated over a broad range of angular frequencies. In this article, both the strain amplitude and concentration dependencies of dynamic viscoelastic behavior were reported at full length from the experimental data obtained from strain-sweep tests. In addition, the linear viscoelastic behavior was explained in detail and the effects of angular frequency and concentration on this behavior were discussed using the well-known power-law type equations. Finally, a fractional derivative model originally developed by Ma and Barbosa-Canovas (1996) was employed to make a quantitative description of a linear viscoelastic behavior and then the applicability of this model was examined with a brief comment on its limitations. Main findings obtained from this study can be summarized as follows: (1) At strain amplitude range larger than 10%, the storage modulus shows a nonlinear strain-thinning behavior, indicating a decrease in storage modulus as an increase in strain amplitude. (2) At strain amplitude range larger than 80%, the loss modulus exhibits an exceptional nonlinear strain-overshoot behavior, indicating that the loss modulus is first increased up to a certain strain amplitude ($\gamma_0 \approx 150\%$) beyond which followed by a decrease in loss modulus with an increase in strain amplitude. (3) At sufficiently large strain amplitude range ($\gamma_0 > 200\%$), a viscous behavior becomes superior to an elastic behavior. (4) An ability to flow without fracture at large strain amplitudes is one of the most important differences between typical strong gel systems and concentrated xanthan gum solutions. (5) The linear viscoelastic behavior of concentrated xanthan gum solutions is dominated by an elastic nature rather than a viscous nature and a gel-like structure is present in these systems. (6) As the polymer concentration is increased, xanthan gum solutions become more elastic and can be characterized by a slower relaxation mechanism. (7) Concentrated xanthan gum solutions do not form a chemically cross-linked stable (strong) gel but exhibit a weak gel-like behavior. (8) A fractional derivative model may be an attractive means for predicting a linear viscoelastic behavior of concentrated xanthan gum solutions but classified as a semi-empirical relationship because there exists no real physical meaning for the model parameters.

Keywords : concentrated xanthan gum solutions, rheology, oscillatory shear flow behavior, dynamic viscoelastic properties, linear/nonlinear viscoelastic behavior, fractional derivative model

1. Introduction

Xanthan gum is a high molecular weight extracellular polysaccharide produced by the bacterium *Xanthomonas campestris*. Typically, *Xanthomonas campestris* is cultivated in a well-aerated and well-agitated fermenter. The medium contains a carbohydrate source such as glucose, a suitable nitrogen source and nutrient salts. When the fermentation has finished, the broth is heated to kill the bacteria and the xanthan gum is recovered by precipitation with isopropyl alcohol. Then the polymer is dried, milled and packaged (Katzbauer, 1998).

Xanthan gum is a non-gelling biopolymer that exists in aqueous media with an ordered rigid chain conformation (Pelletier *et al.*, 2001): it is able to form highly viscous solutions even at low concentrations whose stability to temperature and pH is responsible for its great acceptance in many industries (Marcotte *et al.*, 2001; Ahmed and Ramaswamy, 2004).

Due to its exceptional rheological properties, xanthan gum is widely used as an effective stabilizer or a suitable thickener for various kinds of water-based systems. Its numerous areas of application cover a broad range including food, pharmaceutical, cosmetic, agricultural, textile, ceramic, and petroleum industries (Kang and Pettit, 1993; Schott, 1990; Garcia-Ochoa *et al.*, 2000). The most important rheological properties of xanthan gum are high vis-

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cosity at low shear rates, pronounced shear-thinning nature, and good resistance to shear degradation.

When added to fluid foods, xanthan gum increases low shear rate viscosity while having little effect on the viscosity of the food products at high shear rates (Speers and Tung, 1986). This capability gives a lot of advantages for food makers: as the viscosity is decreased with increasing shear rate, the food product becomes easy to pour, mix, pump, and moreover, the organoleptic properties are also favorably affected. This shear-thinning character of xanthan gum is more pronounced than that of other polysaccharide systems such as guar gum, locust bean gum, hydroxyethyl cellulose, and sodium carboxymethyl cellulose because of a unique rigid, rod-like conformation of xanthan gum which is more responsive to shear than a random-coil conformation (Urlacher and Noble, 1997).

Xanthan gum is bio-compatible with several gel-forming and non-gel-forming macromolecules and can form a stable gel in conjunction with suitable biopolymer systems. Therefore, xanthan gum has been explored as a potential polymer to form hydrogels (Dumitriu *et al.*, 1990; Dumitriu and Chornet, 1997; Işeki *et al.*, 2001; Alupeii *et al.*, 2002) and as an excipient for tablets in modern medicine (Talukdar *et al.*, 1998). It has also been shown by several authors that xanthan gum can play a successful role in matrix formulations for oral controlled-release drug delivery (Daskalakis, 1994; Talukdar *et al.*, 1998). Moreover, it has been proven that, as a candidate for hydrophilic matrix formulations, xanthan gum has some economical as well as pharmaceutical superiority over most other water-soluble biopolymers (Talukdar *et al.*, 1996).

One of the most important applications of xanthan gum in the field of cosmetic products is in toothpaste manufacture. A shear-thinning flow behavior of xanthan gum allows easy extrusion from the tube or from the pump dispenser. This character also ensures a toothpaste that will keep a stable stand on the brush and improves the dispersion on the teeth and rinsing from the teeth (Katzbauer, 1998).

As xanthan gum is a naturally occurring polymer, it is fully bio-degradable. Although the backbone of xanthan gum is similar to that of cellulose, it is resistant to the attack of commonly occurring cellulases. The trisaccharide chains are likely to be a barrier to enzymatic attack. Fungal cellulases are shown to catalyze cleavage of the main chain when xanthan gum is in the disordered form, but it is not attacked in the ordered helix conformation (Katzbauer, 1998). For this reason, xanthan gum can be used as a very stable thickener and stabilizer even for applications with high enzymatic activity.

As was reviewed in our previous article (Song *et al.*, 2006), there exists a relatively large amount of literature published on the rheological properties of both dilute and semi-dilute (or moderately concentrated) xanthan gum

solutions prepared from aqueous media. However, only a little attention has been given to the rheology of highly concentrated solutions of xanthan gum (Lim *et al.*, 1984; Santore and Prud'homme, 1990; Lee and Brant, 2002a, 2002b), even though these systems are much more significant from an industrial point of view (Garcia-Ochoa *et al.*, 1997; Garcia-Ochoa and Gomez, 1998; Garcia-Ochoa *et al.*, 2000). This is a main motivation that the authors have designed a comprehensive study as to the overall rheology of concentrated xanthan gum systems in aqueous media.

From our previous study (Song *et al.*, 2006) that dealt with a nonlinear rheological behavior in steady shear flow fields, it was found that: (a) concentrated xanthan gum solutions exhibit a finite magnitude of yield stress and show a marked non-Newtonian shear-thinning flow behavior; (b) the Herschel-Bulkley, Mizrahi-Berk, and Heinz-Casson models are applicable to describe the steady shear flow behavior of concentrated xanthan gum solutions; and (c) these systems exhibit a quite important elastic nature. These informations may be helpful in various industrial manufacturing processes in which xanthan gum is used as a raw material or an additive agent into other systems.

However, steady shear flow properties alone are not able to provide a sufficient information with regard to the relationship between the rheological behavior and the microstructure of a material because steady shear flow measurement is in nature a destructive technique and consequently conducted with accompanying a structural breakdown of a material. Moreover, as the deformation is too fast at high shear rates, a material cannot have enough time to respond to the applied environment of deformation.

In order to gain an insight into the microstructure of a complex material from its rheological properties, measurement should be made under the rheological ground state where a material is subjected to small deformations. This so-called dynamic test is commonly performed in oscillatory shear flow fields by applying a small amplitude of sinusoidal strain (or stress) to a material and then measuring the resulting stress (or strain) amplitude. The strain (or stress) amplitude adopted in this test should be sufficiently small in order to assure that the response of a material is within the linear viscoelastic region where the stress (or strain) is proportional to the imposed strain (or stress) and the theory of linear viscoelasticity is applicable (Macosko, 1994).

One of the most significant reasons for conducting this small amplitude oscillatory shear (SAOS) test is that it is a non-destructive technique enabling the measurement to be made without incurring structural damage to a material. This allows one to relate the dynamic rheological parameters to the molecular structure of a material. Moreover, all of the other linear viscoelastic functions can be calculated from the dynamic rheological properties using the theory

of linear viscoelasticity (Ferry, 1980; Tschoegl, 1989).

In general, an investigation employing SAOS method should begin with the determination of strain (or stress) limit for which the theory of linear viscoelasticity is applicable. To gain this end, a strain (or stress)-sweep test must be performed at a fixed frequency with increasing the amplitude of the imposed strain (or stress) and this kind of measurements is commonly called large amplitude oscillatory shear (LAOS) test. Once the linear viscoelastic limit is determined, further experiments (e.g., frequency-sweep tests) can be made at strain (or stress) amplitudes within this limit.

When conducting LAOS test, it should be kept in mind that the material functions obtained at large strain (or stress) amplitudes lose their mathematical bases since the material functions such as storage modulus and loss modulus are defined only in the linear viscoelastic region. However, as will be described in a later section (results and discussion), the results obtained from LAOS test can provide an additionally valuable information for a better understanding of the complicated rheological behavior of structured materials.

Rheological studies become particularly helpful when predictable relationships for the rheological properties of complex materials could be developed from a molecular architecture of the constituent species. However, the actual polymer molecule is an extremely complicated mechanical system with an enormous number of degree of freedom. A mechanistic basis for the interpretation of the experimentally measured data must be introduced in order to accurately understand and properly use the obtained rheological information. Such an interpretation in terms of the theoretical mechanisms provides guidelines needed to relate the rheological behavior with structure or composition and to predict or modify the textural properties of biopolymeric systems.

During the last several decades, a group of scientists has made use of the rheological constitutive equations employing the fractional derivatives to describe a viscoelastic behavior of polymeric materials. Various relaxation equations have been a central focus for their research interest. In general, these equations can be derived from well-known mechanical models (e.g., the Maxwell or the Kelvin-Voigt models) by means of substituting the time ordinary derivatives of stress and strain by derivatives of fractional order. These new models have a great advantage for quantitatively describing a linear viscoelastic behavior in the sense that fewer terms with a small number of empirical parameters may be required to develop successful fractional derivative relationships.

Sloninsky (1967) introduced fractional derivatives into the Kelvin-Voigt model to describe the relaxation processes of polymeric systems. Bagley and Torvik (1983, 1986) showed that fractional derivative models of vis-

coelastic materials are in agreement with the Rouse molecular theory. Nonnenmacher (1991) and Friedrich (1991) demonstrated that the constitutive equations using fractional order exponential functions result in a better coincidence with the experimental data on creep and stress relaxation. A four-parameter semi-empirical model was developed by Ma and Barbosa-Canovas (1996) using the fractional derivative theory. These authors used a Fourier transform approach to obtain the analytical function of the derived model. Song and Jiang (1998) developed a five-parameter modified Jeffreys model in terms of fractional derivatives and determined the constraints on the parameters. Further applications of fractional calculus ideas in rheological modeling have recently been reported by Palade *et al.* (1999), Palade and De Santo (2001), Rossikhin and Shitikova (2001), and Metzler and Nonnenmacher (2003). Most of these models have been found to be attractive as means for quantitatively describing the rheological behavior of different kinds of complex materials (Metzler and Nonnenmacher, 2003).

Based upon the above-described backgrounds, as a second step of our serial works, the objective of the present study is to systematically elucidate the dynamic viscoelastic behavior of concentrated xanthan gum systems in periodically oscillatory shear flow fields. To accomplish this end, using a strain-controlled rheometer, the dynamic viscoelastic properties of aqueous xanthan gum solutions with different concentrations were measured over a wide range of strain amplitudes and then the linear viscoelastic behavior in small amplitude oscillatory shear flow fields was investigated over a broad range of angular frequencies.

In this article, both the strain amplitude and concentration dependencies of dynamic viscoelastic behavior were firstly reported at full length from the experimental data obtained from strain-sweep tests. Secondly, the linear viscoelastic behavior was explained in detail and the effects of angular frequency and concentration on this behavior were discussed using the well-known power-law type equations. Finally, a fractional derivative model originally developed by Ma and Barbosa-Canovas (1996) was employed to make a quantitative description of a linear viscoelastic behavior and then the applicability of this model was examined with a brief comment on its limitations.

2. Fractional derivative model

It is a well-known fact that, for Newtonian viscous fluids, the following relationship is applicable:

$$\sigma = \eta \dot{\gamma} = K \frac{d\gamma}{dt} \quad (1)$$

where σ is the shear stress, γ is the shear strain, $\dot{\gamma}$ is the shear strain rate defined as $\dot{\gamma} = d\gamma/dt$, η is the viscosity, and K is a constant (here equal to the Newtonian viscosity, η).

It is also well known that, for Hookean elastic bodies, the following relationship is applied:

$$\sigma = G\gamma = K \frac{d^p \gamma}{dt^p} \quad (2)$$

where σ is the shear stress, γ is the shear strain, G is the elastic modulus defined as $G \equiv \sigma/\gamma$, and K is a constant (here equal to the elastic modulus, G).

For a material that is neither a Hookean solid nor a Newtonian fluid, Bosworth (1946) proposed the following relationship:

$$\sigma = K \frac{d^a \gamma}{dt^a} \quad (0 < a < 1) \quad (3)$$

where σ is the shear stress, γ is the shear strain, and K is a constant.

Based on Eq. (3), a general equation that describes a linear viscoelastic behavior can be developed using the Boltzmann superposition principle. By applying the Boltzmann superposition principle in combination with a fractional derivative concept, Eq. (3) has the following form:

$$\sigma(t) = \sum_{n=1}^N \left[K_n \frac{d^{a_n} \gamma}{dt^{a_n}} \right] \quad (4)$$

Eq. (4) can be rewritten in terms of a fractional operator as follows:

$$\sigma(t) = \sum_{n=1}^N K_n D^{a_n} [\gamma(t)] \quad (5)$$

Eq. (5) is a general expression for linear viscoelasticity of materials in terms of a fractional derivative. From a practical point of view, however, the material functions need to be derived implicitly from the stress-strain relations. The theory of fractional derivatives and Fourier transform would therefore be employed to manipulate these material functions based on the stress-strain relations.

Mathematically, the definition of a fractional derivative can be expressed as follows (Ross, 1975):

$$D^\alpha [x(t)] \equiv \frac{1}{\Gamma(1-\alpha)} \frac{d}{dt} \int_0^t \frac{x(t-t')}{t'^\alpha} dt' \quad (0 < \alpha < 1) \quad (6)$$

where Γ is the gamma function.

The Leibniz rule may be used to differentiate the integral in Eq. (6) and produces the following relationship:

$$D^\alpha [x(t)] = \frac{1}{\Gamma(1-\alpha)} \frac{d}{dt} \int_0^t \frac{1}{t'^\alpha} \frac{\partial}{\partial t'} x(t-t') + \frac{x(0)}{\Gamma(1-\alpha)t^\alpha} \quad (7)$$

By applying the Laplace transform to Eq. (7), the following expression is obtained:

$$L\{D^\alpha [x(t)]\} = \frac{1}{s^{1-\alpha}} \{sL[x(t)-x(0)]\} + \frac{x(0)}{s^{1-\alpha}} \quad (8)$$

Assuming that $x(0) = 0$ for all $t < 0$, Eq. (8) can then be simplified to:

$$L\{D^\alpha [x(t)]\} = s^\alpha L\{x(t)\} \quad (9)$$

By applying the Fourier transform to Eq. (9), a useful relationship is produced as follows:

$$F\{D^\alpha [x(t)]\} = (i\omega)^\alpha F[x(t)] \quad (10)$$

where $F[x(t)] = \int_{-\infty}^{\infty} x(t) \exp[-i\omega t] dt$ and $x(t) = 0$ for all $t < 0$.

By applying Eq. (10) to Eq. (5), the following expression results:

$$\sigma^*(\omega) = \sum_{n=1}^N (i\omega)^{a_n} K_n \gamma^*(\omega) \quad (11)$$

where $\sigma^*(\omega)$ and $\gamma^*(\omega)$ are the transforms of the stress and strain histories (representing the complex stress and complex strain, respectively), a_n and K_n are the constants to be determined from the experimental data, and ω is the angular frequency.

However, Eq. (11) is impractical because it involves too many constants. Hence, the first two terms on the right side of Eq. (11) are chosen for approximation of material functions:

$$\sigma^*(\omega) = [K_1(i\omega)^{a_1} + K_2(i\omega)^{a_2}] \gamma^*(\omega) \quad (12)$$

where K_1 , K_2 , a_1 and a_2 are the parameters of a simplified model.

According to the theory of linear viscoelasticity, the complex modulus, $G^*(\omega)$, is defined as the ratio of complex stress to complex strain:

$$G^*(\omega) \equiv \sigma^*(\omega) / \gamma^*(\omega) \quad (13)$$

By inserting Eq. (12) into Eq. (13), a frequency-dependent complex modulus is achieved as follows:

$$G^*(\omega) = \sigma^*(\omega) / \gamma^*(\omega) = K_1(i\omega)^{a_1} + K_2(i\omega)^{a_2} \quad (14)$$

It is customary to express the complex modulus in terms of real and imaginary parts:

$$G^*(\omega) = G'(\omega) + iG''(\omega) \quad (15)$$

where $G'(\omega)$ is the storage modulus and $G''(\omega)$ is the loss modulus, respectively.

By decomposing Eq. (14) into real and imaginary parts, the following expression is produced:

$$G^*(\omega) = \left[K_1 \omega^{a_1} \cos\left(\frac{\pi}{2} a_1\right) + K_2 \omega^{a_2} \cos\left(\frac{\pi}{2} a_2\right) \right] + i \left[K_1 \omega^{a_1} \sin\left(\frac{\pi}{2} a_1\right) + K_2 \omega^{a_2} \sin\left(\frac{\pi}{2} a_2\right) \right] \quad (16)$$

Therefore, the storage and loss moduli in Eq. (15) can respectively be rewritten with the following explicit functions:

$$G'(\omega) = K_1 \omega^{a_1} \cos\left(\frac{\pi}{2} a_1\right) + K_2 \omega^{a_2} \cos\left(\frac{\pi}{2} a_2\right) \quad (17)$$

$$G''(\omega) = K_1 \omega^{a_1} \sin\left(\frac{\pi}{2} a_1\right) + K_2 \omega^{a_2} \sin\left(\frac{\pi}{2} a_2\right) \quad (18)$$

Based on Eq. (17) and Eq. (18), additional frequency-dependent material functions including the dynamic viscosity, $\eta'(\omega)$, and the out-of-phase component of the complex viscosity, $\eta''(\omega)$, can be obtained by the following relationships:

$$\eta'(\omega) = G'(\omega)/\omega = K_1 \omega^{a_1-1} \sin\left(\frac{\pi}{2} a_1\right) + K_2 \omega^{a_2-1} \sin\left(\frac{\pi}{2} a_2\right) \quad (19)$$

$$\eta''(\omega) = G''(\omega)/\omega = K_1 \omega^{a_1-1} \cos\left(\frac{\pi}{2} a_1\right) + K_2 \omega^{a_2-1} \cos\left(\frac{\pi}{2} a_2\right) \quad (20)$$

Equations (17)–(20) can then be used to simulate a linear viscoelastic behavior of concentrated xanthan gum systems once the constants in these equations have been determined from the experimental data.

3. Experimental details

3.1. Raw materials

The xanthan gum sample used in this study is a commercially available product supplied from the Sigma-Aldrich Corporation (St. Louis, MO, USA). As was illustrated in our previous article (Song *et al.*, 2006), the primary structure of xanthan gum consists of 1, 4-linked β -D-glucose residues having a trisaccharide side chain attached to alternate D-glucosyl residues (Lapasin and Pricl, 1999). The backbone of xanthan gum is similar to that of cellulose. The side chains are β -D-mannose-1, 4- β -D-glucosyl acid-1,2- α -D-mannose, where the internal mannose is mostly O-acetylated and the terminal mannose may be substituted by a 4,6-linked pyruvic acid ketal (Stokke *et al.*, 1998). The secondary structure of xanthan gum has been shown to consist of a five-fold helical structure (Katzbauer, 1998). Most researchers (Holzwarth and Prestridge, 1977; Camesano and Wilkinson, 2001) suggest a right-handed double helical state for native xanthan gum molecule which is stabilized by intermolecular and intramolecular hydrogen bonds (Ogawa and Yui, 1998).

An accurate determination of the molecular weight of xanthan gum is extremely difficult for several reasons including its relatively high value, the stiffness of a molecule and the presence of aggregates (Born *et al.*, 2001). The weight average molecular weight of our xanthan gum is approximately estimated to be 2×10^6 g/mol (Carrier *et al.*, 1993; Katzbauer, 1998), even though its values reported in the literature are very diverse (Zirnsak *et al.*, 1999).

3.2. Preparation of solutions

Xanthan gum is soluble in both cold and hot water. Like most other hydrocolloids, xanthan gum needs an intensive agitation upon introduction into an aqueous medium in order to avoid a formation of lumps.

In this work, xanthan gum solutions with concentrations of 1, 2, 3, and 4 wt% were prepared by slowly adding the required amount of polymer powder weighed using an electronic balance (BA 210S, Sartorius, Germany) into a known volume of gently agitated medium (dust-free distilled water) filled in a glass container, which was maintained at room temperature with constant stirring using a magnetic bar for 24 hr. During stirring, the top of a glass container was sealed up with an air-tight film to prevent an evaporation of a medium.

Then, a propeller-type variable-speed homogenizer (EYELA Z-1300, Tokyo Rikakiki Co., Japan or EURO-STAR, Janke & Kunkel GmbH & Co., Germany) was used to provide a further necessary agitation of xanthan gum solutions. The agitation was continued for 3–5 hr with a rotational speed of 300 rpm until the polymer was perfectly dissolved and the solutions were lump-free. In order to complete the hydration of the polymer, the prepared solutions were kept at rest at room temperature for more than 12 hr prior to conducting the rheological measurements.

3.3. Rheological measurements

In this study, in order not only to determine the linear viscoelastic region but also to investigate the nonlinear viscoelastic behavior in large amplitude oscillatory shear flow fields, dynamic strain-sweep measurements were firstly performed for all prepared xanthan gum solutions using a strain-controlled rheometer [Advanced Rheometric Expansion System (ARES), Rheometric Scientific, Piscataway, NJ, USA] equipped with a parallel-plate fixture with a radius of 25 mm and a gap size of 2.0 mm. These strain-sweep tests were carried out at an isothermal condition of 20°C over a strain amplitude range from 0.25 to 500% with a logarithmically increasing scale at a fixed angular frequency of 1.0 rad/s.

Nextly, dynamic frequency-sweep measurements were conducted using an ARES equipped with a parallel-plate fixture with a radius of 12.5 mm and a gap size of 2.0 mm in order to elucidate the relationship between the linear viscoelastic behavior and the microstructure of concentrated xanthan gum solutions under their rheological ground state. These frequency-sweep tests in small amplitude oscillatory shear flow fields were carried out at a fixed temperature of 20°C over an angular frequency range from 0.025 to 100 rad/s with a logarithmically increasing scale at a constant strain amplitude of 1.0% (from strain-sweep tests, this strain value was confirmed to lie within the linear viscoelastic region for all prepared xanthan gum solutions).

The reasons why a parallel-plate configuration was cho-

sen as a test geometry are that: (1) cleaning is very easy after each measurement; (2) the plates can be easily covered with sandpaper; and (3) there is a relatively smaller gap error due to a larger gap size between the two plates (2.0 mm in this experiment) compared to a cone-plate fixture where the gap at the center is usually kept at 0.05 mm.

Before the xanthan gum solution was loaded, the two plates were covered with sandpaper in order to remove a wall slippage between the test material and the plates. Through a preliminary test using a direct visualization technique (Chang *et al.*, 2002, 2003) in which a straight line marker was drawn from the upper plate to the lower plate passing through the free surface of the sample solution, it was confirmed that a wall slip effect could almost be eliminated by covering the plate surfaces with sandpaper.

Special care was taken to minimize the effect of work softening when the sample solution was initially loaded on the plate each time. The sample filled up the whole gap by lowering the upper plate down to the pre-designed gap. The extra sample around the edge of the plates was trimmed with a plastic spatula.

In all measurements, a fresh sample solution was used and rested for 20 min after loading to allow material relaxation and temperature equilibration. It was found from a preliminary test that 20 min of resting time is enough for all sample solutions to be completely relaxed and to be thermally equilibrated. All measurement were made at least three times for each test and highly reproducible data were obtained within the coefficients of variation of $\pm 5\%$ in all cases.

4. Results and discussion

4.1. Nonlinear viscoelastic behavior

Fig. 1(a) shows the strain dependence of the storage modulus, $G'(\gamma_0)$, at a fixed angular frequency of 1.0 rad/s for aqueous xanthan gum solutions with different concentrations. As is obvious from Fig. 1(a), the storage modulus is gradually increased as an increase in polymer concentration over an entire range of strain amplitudes tested.

In addition, a linear region is clearly observed for all xanthan gum solutions at relatively smaller strain amplitude range ($\gamma_0 < 10\%$) in which the storage modulus exhibits a constant value regardless of strain amplitude. However, a nonlinear behavior occurs at strain amplitude range larger than 10% where the storage modulus is slightly decreased up to a certain strain amplitude ($\gamma_0 \approx 100\%$), beyond which a sharp decrease in storage modulus is observed with increasing strain amplitude, indicating a marked strain-thinning feature.

These trends are consistently seen for all xanthan gum solutions with different concentrations and more obviously observed when the reduced storage modulus [a ratio of the

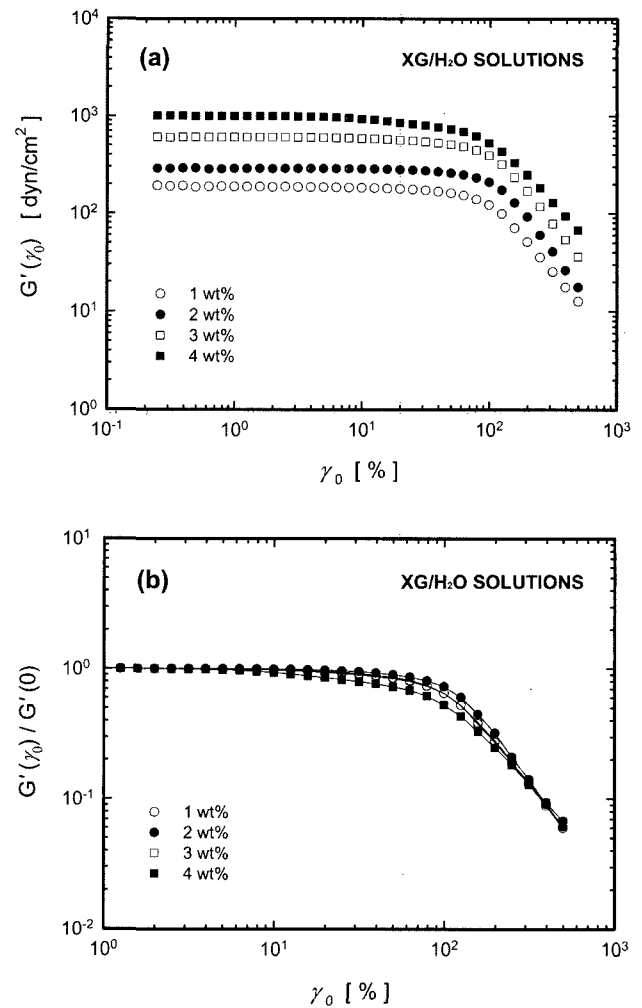


Fig. 1. (a) Storage modulus and (b) reduced storage modulus as a function of strain amplitude for aqueous xanthan gum solutions with different concentrations.

strain-dependent storage modulus, $G'(\gamma_0)$, to the strain-independent storage modulus, $G'(0)$] is plotted as a function of strain amplitude, as demonstrated in Fig. 1(b).

A strain-thinning behavior of storage modulus for concentrated xanthan gum solutions at large strain amplitudes may be interpreted by the destruction and formation of their internal structure responding to an externally imposed stimulus (Isono and Ferry, 1985; Song *et al.*, 1996). At relatively smaller strain amplitudes, the entanglement density is not changed because a balanced state is maintained between the rates of structural breakdown and rebuilding. Hence, an elastic response to an externally applied deformation exhibits a linear behavior, resulting in a constant magnitude of storage modulus.

As the strain amplitude is increased, however, since the rate of structural destruction is gradually increased whereas that of structural reformation is decreased or eliminated, an equilibrium between the two rates becomes destroyed,

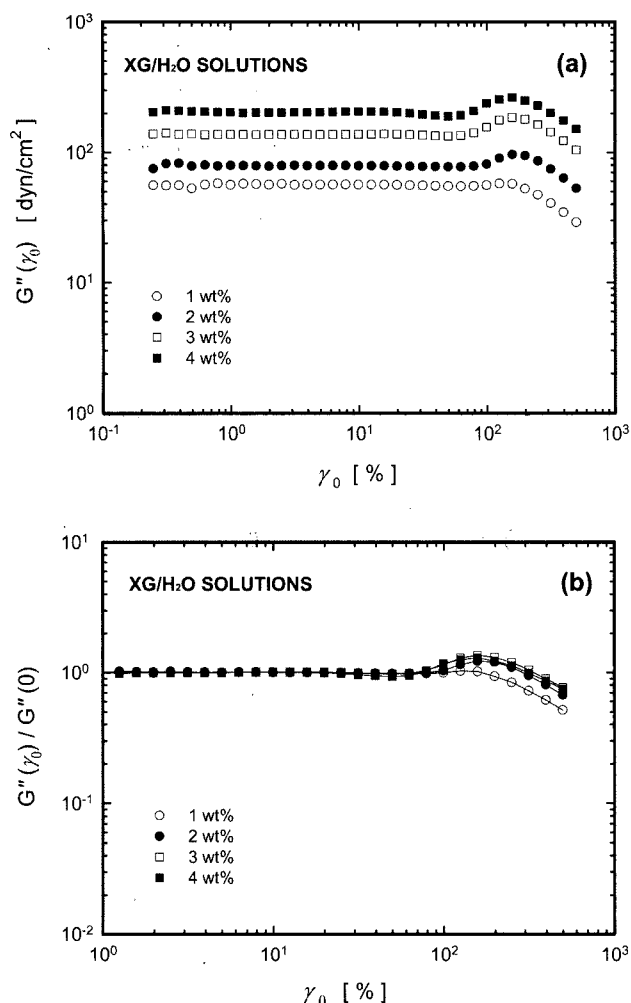


Fig. 2. (a) Loss modulus and (b) reduced loss modulus as a function of strain amplitude for aqueous xanthan gum solutions with different concentrations.

leading to a reduction in entanglement density. As a consequence, an elastic response to an externally imposed deformation exhibits a nonlinear behavior, resulting in a decrease in storage modulus.

Fig. 2(a) shows the strain dependence of the loss modulus, $G''(\gamma_0)$, at a fixed angular frequency of 1.0 rad/s for aqueous xanthan gum solutions with different concentrations. Likewise the storage modulus [Fig. 1(a)], the loss modulus is also progressively increased as an increase in polymer concentration over a whole range of strain amplitudes tested.

In addition, a linear region is clearly observed for all xanthan gum solutions at strain amplitude range smaller than 80% within which the loss modulus exhibits a constant value regardless of strain amplitude. However, an exceptional nonlinear behavior takes place at strain amplitude range larger than 80% where the loss modulus is first increased up to a certain strain amplitude ($\gamma_0 \approx 150\%$),

beyond which followed by a decrease in loss modulus with increasing strain amplitude, indicating a strain-overshoot phenomenon.

These trends are consistently observed for all xanthan gum solutions with different concentrations and more dramatically confirmed when plotting the reduced loss modulus [a ratio of the strain-dependent loss modulus, $G''(\gamma_0)$, to the strain-independent loss modulus, $G''(0)$] as a function of strain amplitude, as illustrated in Fig. 2(b).

An interesting strain-overshoot behavior of loss modulus for concentrated xanthan gum solutions at large strain amplitudes may arise from a unique structure of xanthan gum polymer chains. The structure of xanthan gum is based on a linear 1, 4- β -D-glucose backbone with charged trisaccharide side chains on every second residue (Lapasin and Pricl, 1999). These long side chains can make relatively weaker structural complexes.

In aqueous media at room temperature, the backbone of xanthan gum exists in disordered state that can be highly extended due to an electrostatic repulsion between the charged groups on the side chains. Because of this highly extended structure, the xanthan gum molecules may align and associate (partly due to hydrogen bonding) to form a weakly structured material (Rocheftort and Middleman, 1987).

When subjected to large strain amplitudes, this complex structure shows a resistance against the imposed deformation up to a certain strain amplitude, leading to an increase in loss modulus. After then, a complex structure becomes broken down by further increased deformation magnitudes above a critical strain amplitude, beyond which the polymer chains align with the flow fields, resulting in a decrease in loss modulus.

Fig. 3(a) and (b) represent both the storage modulus, $G'(\gamma_0)$, and loss modulus, $G''(\gamma_0)$, as a function of strain amplitude at a fixed angular frequency of 1.0 rad/s for 3 wt% and 4 wt% aqueous xanthan gum solutions, respectively. From a closer examination of Fig. 3(a) and (b), it is observed that the storage modulus is always greater than the loss modulus within a linear viscoelastic region, indicating that the rheological behavior in this region is in nature dominated by an elastic property rather than a viscous property. In addition, the storage modulus begins to show a nonlinear behavior at a smaller strain amplitude range than does the loss modulus.

At sufficiently large strain amplitude range ($\gamma_0 > 200\%$), however, a viscous behavior becomes superior to an elastic behavior because the storage modulus demonstrates a sharper decrease with increasing strain amplitude than does the loss modulus. The same trends are also observed for 1 wt% and 2 wt% aqueous xanthan gum solutions whose results are not displayed here on account of a space limitation.

This type of unique nonlinear viscoelastic behavior

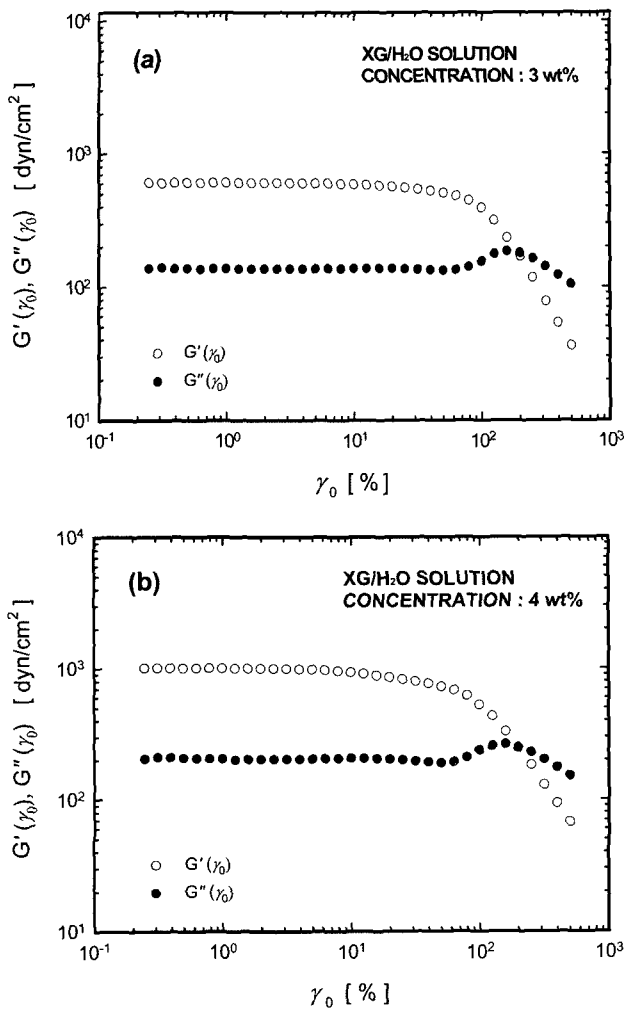


Fig. 3. Storage modulus and loss modulus as a function of strain amplitude for (a) 3 wt% and (b) 4 wt% aqueous xanthan gum solutions.

observed in this work has previously been reported for other complex materials such as carbon black-contained rubber (Roland, 1990), saponite gel system (Hoffmann and Rauscher, 1993), fumed silica suspensions (Yziquel *et al.*, 1999a), doughs (Phan-Thien *et al.*, 1997; Phan-Thien and Safari-Ardi, 1998), coating colors containing polyvinyl alcohol (Yziquel *et al.*, 1999b), oil-in-water emulsions (Bower *et al.*, 1999), electrorheological fluids (Parthasarathy and Klingenberg, 1999), magnetorheological fluids (Li *et al.*, 2004), and several semi-solid foodstuffs (Cha *et al.*, 2002).

Our findings are in agreement with the previous results reported by Hyun *et al.* (2002; 2003) who found that, through a thorough investigation as to the nonlinear viscoelastic behavior of different kinds of complex materials, there exists at least four types of large amplitude oscillatory shear flow behavior: as an increase in strain amplitude, (a) Type I [(strain-thinning) both the storage and loss moduli

are decreased]; (b) Type II [(strain-hardening) both the storage and loss moduli are increased]; (c) Type III [(weak strain-overshoot) the storage modulus is decreased whereas the loss modulus is first increased and then decreased]; and (d) Type IV [(strong strain-overshoot) both the storage and loss moduli are first increased and then decreased]. These authors also suggested that large amplitude oscillatory shear flow behavior can be used as an effective reference for classifying complex structured fluids. According to their classification, a nonlinear viscoelastic behavior of concentrated xanthan gum solutions at large strain amplitudes belongs to Type III (weak strain-overshoot).

Now it may be worth while to mention that a nonlinear viscoelastic behavior in large amplitude oscillatory shear flow fields enables a better distinction to be made between strong and weak gels because deformation dependence of these two classes of materials has been reported to be quite different (Ross-Murphy and Shatwell, 1993; Ross-Murphy, 1995). At large deformations, strong gels rupture and fail just like a solid while weak gels flow without fracture and show a recovery of solid-like character provided that a sufficiently long time is given, exhibiting a structured fluid-like behavior. This statement means that, at large strain amplitudes, the complex modulus for strong gels is essentially strain-independent (linearly viscoelastic) whereas the complex modulus for weak gels becomes strain-dependent.

Fig. 4(a) and (b) demonstrate the complex modulus, $G^*(\gamma_0)$, and the reduced complex modulus, $G^*(\gamma_0)/G^*(0)$, respectively, as a function of strain amplitude at a fixed angular frequency of 1.0 rad/s for aqueous xanthan gum solutions with different concentrations. According to the distinction described above, it is clear from Fig. 4(a) and (b) that concentrated xanthan gum solutions can be classified as a weak gel system. This ability to flow without fracture is one of the most important differences between typical strong gel systems and concentrated xanthan gum solutions. Such a nonlinear viscoelastic behavior is mainly associated with a tendency to form aggregated structures which are then broken down under the applied large strain amplitudes.

Finally, it should be noted here that, from a purely theoretical point of view, both the storage modulus, $G'(\gamma_0)$, and loss modulus, $G''(\gamma_0)$, at large strain amplitude range do not possess their mathematical foundations because these two moduli are defined only within the linear viscoelastic region. When subjected to large strain amplitudes, the stress output of a viscoelastic material becomes no longer sinusoidal and consequently the stress-strain relationship cannot be described in terms of the strain-independent storage and loss moduli due to higher harmonic contributions (Dealy and Wissbrun, 1990).

In order to analyze these higher harmonic contributions, a group of researchers (Wilhelm *et al.*, 1998; 1999; 2000;

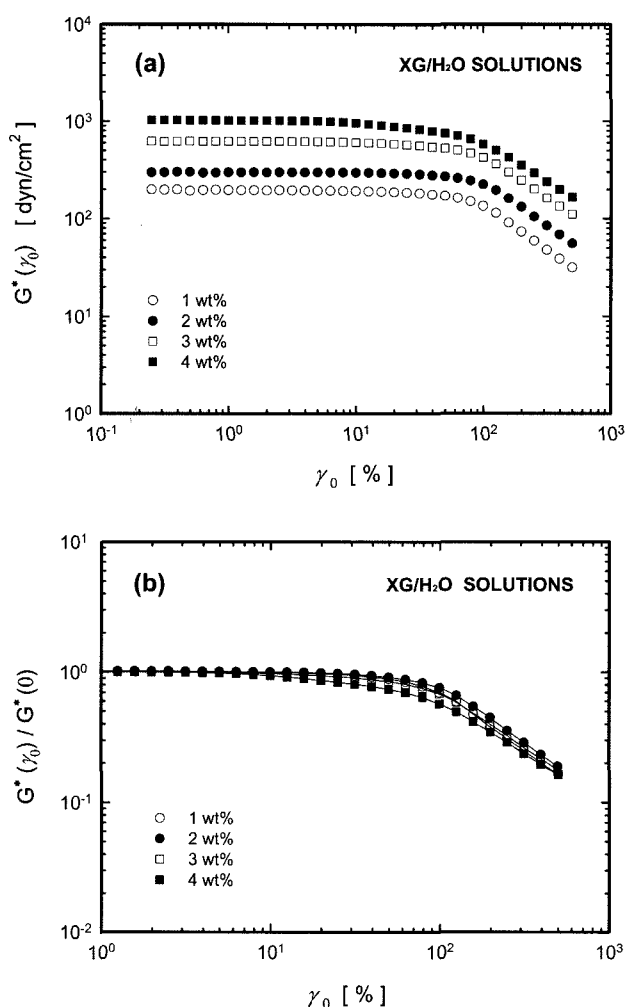


Fig. 4. (a) Complex modulus and (b) reduced complex modulus as a function of strain amplitude for aqueous xanthan gum solutions with different concentrations.

Wilhelm, 2002) has developed a Fourier transform rheology that decomposes the stress data in time domain into a frequency-dependent spectrum. We have also introduced a Fourier transform analysis to interpret a large amplitude oscillatory shear flow behavior of several kinds of polymer solutions (Song and Chang, 1998; Chang and Song, 2000). A study on the nonlinear viscoelastic behavior of concentrated xanthan gum systems in large amplitude oscillatory shear flow fields is now in progress in our laboratory and the results will be reported in the near future.

In spite of this complexity in mathematical treatments, it is true that a large amplitude oscillatory shear flow behavior can provide a plentiful information for a better understanding of the overall rheology of complex materials. In addition, large amplitude oscillatory shear test has an advantage in that it allows both the strain amplitude and time scale to be controlled independently (Yosick *et al.*, 1997). Moreover, it is relatively easy to generate flow

because this test does not involve any sudden jump in speed or position (Giacomin and Dealy, 1993).

4.2. Linear viscoelastic behavior

Fig. 5(a)~(d) show the storage modulus, $G'(\omega)$, and loss modulus, $G''(\omega)$, as a function of angular frequency for aqueous xanthan gum solutions with different concentrations of 1, 2, 3, and 4 wt%, respectively. It is first observed that, over a whole range of angular frequencies tested, the linear viscoelastic functions for all xanthan gum solutions exhibit an essentially similar behavior and both the storage and loss moduli are gradually increased with an increase in polymer concentration.

A more important point to note is that, for all concentrations, the storage modulus is always greater than the loss modulus over an entire range of angular frequencies studied, meaning that the linear viscoelastic behavior of these xanthan gum solutions is dominated by an elastic nature. In addition, both the storage and loss moduli are found to be only weak functions of angular frequency, indicating that a gel-like structure is present in these systems.

From these results, it can be understood that concentrated xanthan gum solutions form a gel-like system, as indicated by a dominance of the elastic storage modulus over the viscous loss modulus. However, the frequency dependence of the storage modulus infers that a stable (strong) gel is not formed with all concentrated solutions, demonstrating that a stable (strong) gel cannot be obtained by just increasing the xanthan gum concentration.

Such a linear viscoelastic behavior observed in concentrated xanthan gum solutions may be attributed to the occurrence of attractive interactions between helices formed by rigid xanthan macromolecules, which can give rise to a weak three-dimensional network and a complex aggregation in solutions by means of physical entanglements and hydrogen bonding (Carnali, 1992; Pal, 1995).

The frequency dependence of the storage modulus as well as the loss modulus may be quantitatively described by a power-law type relationship as follows (Jampala *et al.*, 2005; Kim and Yoo, 2006):

$$G'(\omega) = K' \omega^{n'} \quad (21)$$

$$G''(\omega) = K'' \omega^{n''} \quad (22)$$

where K' , K'' , n' , and n'' are constants; K' and K'' are the intercepts and n' and n'' are the slopes in the double logarithmic plots of the storage and loss moduli against angular frequency, respectively.

The values of the power-law parameters obtained from a linear regression analysis along with those of the determination coefficients are reported in Table 1 and Table 2. As expected, the fits of the experimentally measured data [Fig. 5(a)~(d)] to the power-law relations represent fairly

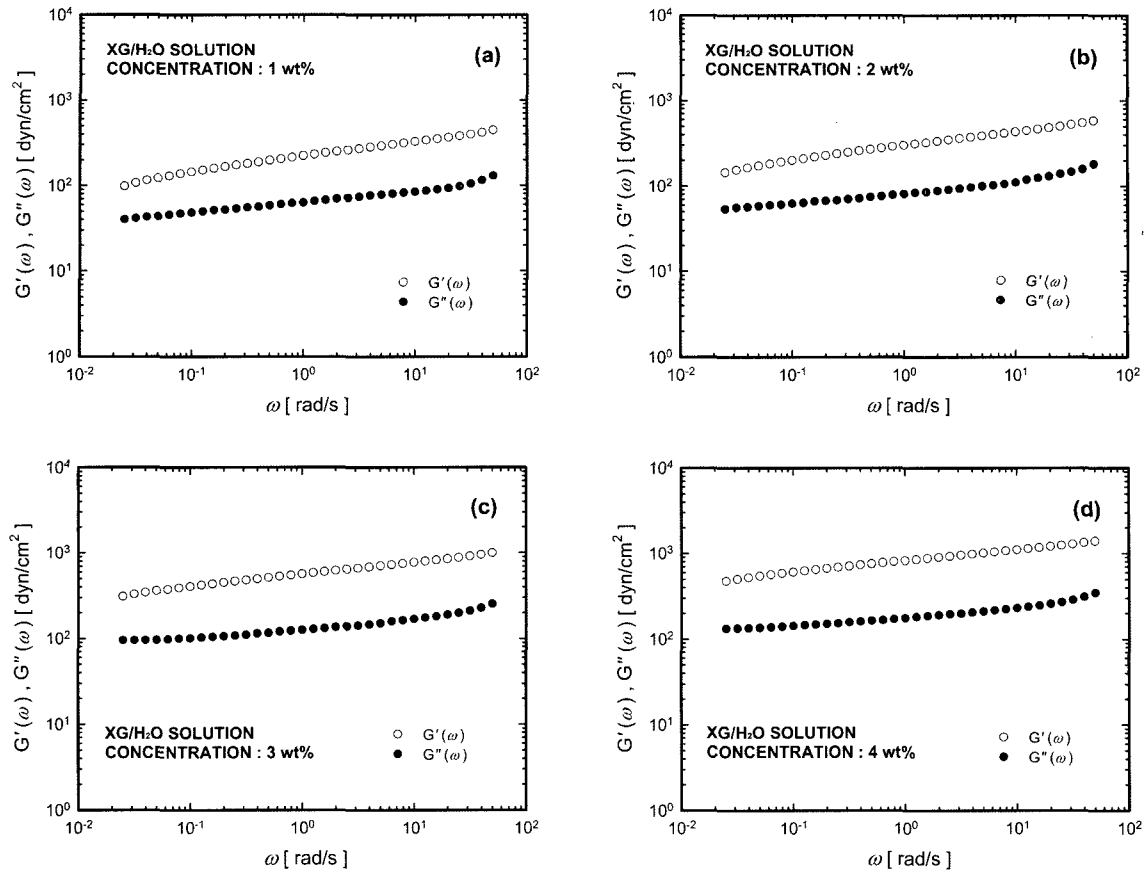


Fig. 5. Storage modulus and loss modulus as a function of angular frequency for (a) 1 wt%, (b) 2 wt%, (c) 3 wt%, and (d) 4 wt% aqueous xanthan gum solutions.

Table 1. Calculated power-law parameters of storage modulus for aqueous xanthan gum solutions with different concentrations

Concentration	K' [$\text{dyn/cm}^2 \cdot (\text{s/rad})^n$]	n' [-]	R^2
1 wt%	217	0.1842	0.9929
2 wt%	295	0.1723	0.9960
3 wt%	562	0.1450	0.9971
4 wt%	821	0.1337	0.9977

Table 2. Calculated power-law parameters of loss modulus for aqueous xanthan gum solutions with different concentrations

Concentration	K'' [$\text{dyn/cm}^2 \cdot (\text{s/rad})^n$]	n'' [-]	R^2
1 wt%	65	0.1323	0.9815
2 wt%	84	0.1382	0.9578
3 wt%	131	0.1171	0.9460
4 wt%	183	0.1122	0.9529

well the linear viscoelastic behavior of all concentrated xanthan gum solutions.

It is clear that the values of K' are much larger than those of K'' for all xanthan gum solutions, demonstrating that an elastic behavior (storage modulus) is consistently superior to a viscous behavior (loss modulus). It is also worth noting that the values of n' and n'' are gradually decreased as an increase in xanthan gum concentration, illustrating that the frequency dependence of the linear viscoelastic functions becomes weaker with increasing polymer concentration.

Both of these findings indicate that, as the polymer concentration is increased, xanthan gum solutions become more elastic and can be characterized by a slower relaxation mechanism. An additional evidence can be found by plotting their loss tangent [$\tan\delta = G''(\omega)/G'(\omega)$] as a function of angular frequency, as displayed in Fig. 6. The $\tan\delta$ becomes progressively lower for more concentrated xanthan gum solutions, exhibiting a more solid-like elastic behavior.

Now it is believed to be necessary to mention that a linear viscoelastic behavior in small amplitude oscillatory shear flow fields also enables a distinction to be made between strong and weak gels. It has been known that $n' > 0$ for a physical (weak) gel whereas $n' = 0$ for a chemical

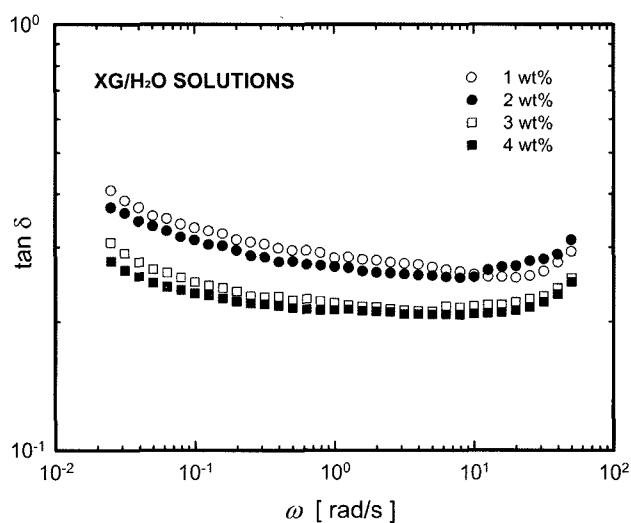


Fig. 6. Loss tangent as a function of angular frequency for aqueous xanthan gum solutions with different concentrations.

(strong) gel (Ross-Murphy and Shatwell, 1993; Ross-Murphy, 1995; Harrison *et al.*, 1999; Jampala *et al.*, 2005; Kim and Yoo, 2006). The n' value can therefore be used as a quantitative measure of the resemblance of a gel to a chemically cross-linked strong gel system. For concentrated xanthan gum solutions studied in this work, the n' values of 0.13–0.18 were obtained according to different polymer concentrations (Table 1). Hence, it can be concluded that these systems do not form a stable (strong) gel but exhibit a weak gel-like behavior. Our findings are consistent with the previously published reports (Lim *et al.*, 1984; Rochefort and Middleman, 1987; Pal, 1995; Talukdar *et al.*, 1996) where a gel-like structure was also found for highly concentrated ($c > 0.5\%$) xanthan gum solutions while it was absent for both dilute and semi-dilute concentration regimes.

By the way, several authors (Ross-Murphy *et al.*, 1983; Callet *et al.*, 1987) have suggested that, in addition to topological restraints, a structure developed in xanthan gum solutions is originated from an intermolecular association between ordered chain segments of xanthan gum. According to this suggestion, the level of intermolecular interactions may be the most important differences between ordinary polymer systems and xanthan gum solutions. The stiffness and the comparative regularity of xanthan may be the molecular parameters which stabilize rheologically relevant intermolecular interactions. This may explain why concentrated xanthan gum solutions are characterized by much longer relaxation times than most other ordinary polymer solutions with entanglement networks. In this respect, concentrated xanthan gum solutions studied in this work can be regarded as a highly elastic liquid (Giboreau *et al.*, 1994) over a wide range of time scales commonly used in dynamic tests (10^{-2} – 10^2 rad/s).

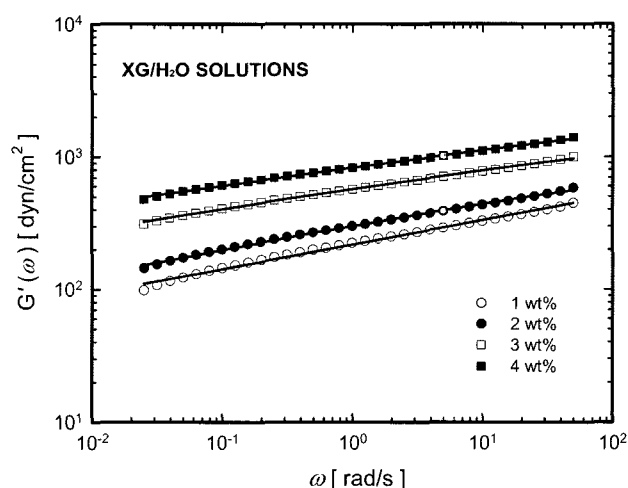


Fig. 7. Applicability of a fractional derivative model to storage modulus for aqueous xanthan gum solutions with different concentrations (solid lines are theoretically obtained curves).

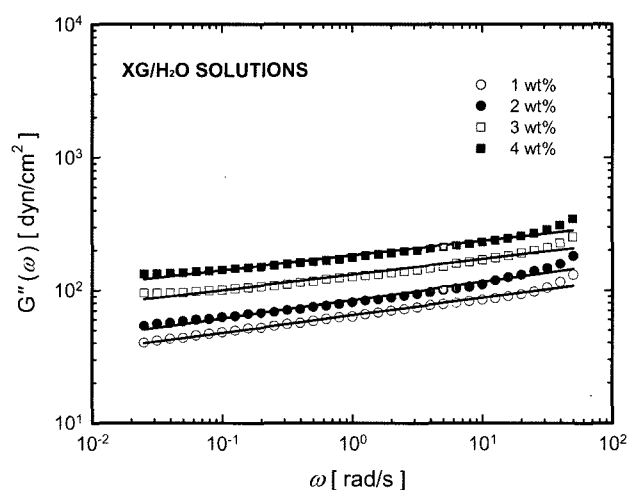


Fig. 8. Applicability of a fractional derivative model to loss modulus for aqueous xanthan gum solutions with different concentrations (solid lines are theoretically obtained curves).

4.3. Applicability of a fractional derivative model

Fig. 7 and Fig. 8 represent the simulation results of a fractional derivative model to the storage modulus and loss modulus, respectively, for aqueous xanthan gum solutions with different concentrations. As is clear from the two figures, over a whole range of angular frequencies tested, a fractional derivative model shows a fairly good applicability to describe quantitatively a linear viscoelastic behavior of all xanthan gum solutions in the sense that: (a) almost no discrepancy is observed between the experimentally obtained linear viscoelastic functions and the theoretically obtained curves; (b) both the storage and loss moduli are increased with an increase in polymer con-

Table 3. Parameters of a fractional derivative model determined from experimentally measured storage modulus and loss modulus for aqueous xanthan gum solutions with different concentrations

Concentration	$G'(\omega), G''(\omega)$	K_1	K_2	a_1	a_2	R^2
1 wt%	$G'(\omega)$	37	190	0.1838	0.1842	0.9929
	$G''(\omega)$	-289	603	0.1313	0.1318	0.9815
2 wt%	$G'(\omega)$	-347	655	0.2839	0.2304	0.9979
	$G''(\omega)$	-94	484	0.1380	0.1382	0.9578
3 wt%	$G'(\omega)$	-530	1110	0.2413	0.1905	0.9982
	$G''(\omega)$	-95	814	0.1162	0.1169	0.9460
4 wt%	$G'(\omega)$	-407	1249	0.2296	0.1646	0.9984
	$G''(\omega)$	-3992	5035	0.1123	0.1123	0.9529

centration; (c) the storage modulus is consistently larger than the loss modulus; and (d) the storage modulus as well as the loss modulus are slightly dependent on angular frequency.

In this work, a least-squares fitting method was used in order to determine the parameters (K_1, K_2, a_1, a_2) of a fractional derivative model from the experimentally measured storage and loss moduli. The values of the model parameters for all xanthan gum solutions along with those of the determination coefficients are given in Table 3.

Judging from the values of the determination coefficients ($R^2 > 0.99$ for storage modulus and $R^2 > 0.95$ for loss modulus, respectively), it can be confirmed that the simulation results are in good agreement with the experimentally measured data and consequently a fractional derivative model has a good ability to predict a linear viscoelastic behavior of all xanthan gum solutions. However, no trends are observed between the values of the model parameters, creating a doubt as to the reality of a physical meaning for these parameters.

In addition to an ability to describe accurately a linear viscoelastic behavior of concentrated xanthan gum solutions as demonstrated in this work and shown by more extensive results presented elsewhere (Ma and Barbosa-Canovas, 1996; Song and Jiang, 1998), a fractional derivative model has been reported to produce elliptical stress-strain hysteresis loops (Lissajous curves) for a sinusoidal motion of a viscoelastic material (Bagley and Torvik, 1983). For these reasons, it can be concluded that a fractional derivative model may be an attractive means for predicting the frequency-dependent stress-strain relationships of a class of viscoelastic materials.

However, a fractional derivative model may be at present regarded as a semi-empirical relationship because there exists no real physical meaning for the model parameters which are obtained from a least-squares fitting method. Therefore, this model must be used with a special caution and then applied to the situations where only a linear viscoelastic behavior is dealt with. Moreover, a further

research should be needed to reveal the physical meaning of the model parameters.

5. Conclusions

The objective of the present study is to systematically elucidate the dynamic viscoelastic behavior of concentrated xanthan gum systems in periodically oscillatory shear flow fields. To accomplish this end, using a strain-controlled rheometer, the dynamic viscoelastic properties of aqueous xanthan gum solutions with different concentrations were measured over a wide range of strain amplitudes and then the linear viscoelastic behavior in small amplitude oscillatory shear flow fields was investigated over a broad range of angular frequencies.

In this article, both the strain amplitude and concentration dependencies of dynamic viscoelastic behavior were reported at full length from the experimental data obtained from strain-sweep tests. In addition, the linear viscoelastic behavior was explained in detail and the effects of angular frequency and concentration on this behavior were discussed using the well-known power-law type equations. Finally, a fractional derivative model originally developed by Ma and Barbosa-Canovas (1996) was employed to make a quantitative description of a linear viscoelastic behavior and then the applicability of this model was examined with a brief comment on its limitations. Main results obtained from this study can be summarized as follows:

(1) The storage modulus shows a linear behavior at relatively smaller strain amplitude range ($\gamma < 10\%$) in which the storage modulus exhibits a constant value independent of the imposed deformation magnitudes. At strain amplitude range larger than 10%, however, the storage modulus demonstrates a nonlinear strain-thinning behavior, indicating a decrease in storage modulus as an increase in strain amplitude. This strain-thinning behavior of the storage modulus for concentrated xanthan gum solutions may be interpreted by the destruction and formation of their inter-

nal structure responding to an externally imposed stimulus.

(2) The loss modulus shows a linear behavior at strain amplitude range smaller than 80% in which the loss modulus exhibits a constant value regardless of the imposed deformation magnitudes. At strain amplitude range larger than 80%, however, the loss modulus demonstrates an exceptional nonlinear strain-overshoot behavior, indicating that the loss modulus is first increased up to a certain strain amplitude ($\gamma_0 \approx 150\%$) beyond which followed by a decrease in loss modulus with an increase in strain amplitude. This interesting strain-overshoot behavior of the loss modulus for concentrated xanthan gum solutions may arise from a unique structure of xanthan polymer chains which can form relatively weaker structural complexes.

(3) An elastic behavior (storage modulus) begins to show a nonlinear behavior at a smaller strain amplitude range than does a viscous behavior (loss modulus). At sufficiently large strain amplitude range ($\gamma_0 > 200\%$), however, a viscous behavior becomes superior to an elastic behavior because the storage modulus demonstrates a sharper decrease with increasing strain amplitude than does the loss modulus.

(4) An ability to flow without fracture at large strain amplitudes is one of the most important differences between typical strong gel systems and concentrated xanthan gum solutions. Such a nonlinear viscoelastic behavior is mainly associated with a tendency to form aggregated structures which are then broken down under the applied large deformation magnitudes.

(5) In small amplitude oscillatory shear flow fields, the storage modulus is always greater than the loss modulus over an entire range of angular frequencies studied, meaning that the linear viscoelastic behavior of concentrated xanthan gum solutions is dominated by an elastic nature rather than a viscous nature. In addition, both the storage and loss moduli are only weak functions of angular frequency, indicating that a gel-like structure is present in these systems. Such a linear viscoelastic behavior may be attributed to the occurrence of attractive interactions between helices formed by rigid xanthan macromolecules which can give rise to a weak three-dimensional network and a complex aggregation in solutions by means of physical entanglements and hydrogen bonding.

(6) The frequency dependence of the storage modulus as well as the loss modulus for concentrated xanthan gum solutions can be quantitatively well described by a power-law type relationship. As the polymer concentration is increased, xanthan gum solutions become more elastic and can be characterized by a slower relaxation mechanism.

(7) Concentrated xanthan gum solutions do not form a chemically cross-linked stable (strong) gel but exhibits a weak gel-like behavior, being regarded as a highly elastic liquid over a wide range of time scales.

(8) A fractional derivative model may be an attractive

means for predicting a linear viscoelastic behavior of concentrated xanthan gum solutions. However, this model may be classified as a semi-empirical relationship because there exists no real physical meaning for the model parameters.

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