

Transient rheological behavior of natural polysaccharide xanthan gum solutions in start-up shear flow fields: An experimental study using a strain-controlled rheometer

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The objective of the present study is to experimentally investigate the transient rheological behavior of concentrated xanthan gum solutions in start-up shear flow fields. Using a strain-controlled rheometer, a number of constant shear rates were suddenly imposed to aqueous xanthan gum solutions with different concentrations and the resultant shear stress responses were measured with time. The main findings obtained from this study can be summarized as follows: (1) For all shear rates imposed, however low it may be, the shear stress is rapidly increased with time (stress overshoot) upon inception of steady shear flow before passing through the maximum stress value and then gradually decreased with time (stress decay) until reaching a steady state flow. (2) As the imposed shear rate is increased, a more pronounced stress overshoot takes place and the maximum stress value becomes larger, whereas both times at which the maximum stress is observed and needed to reach a steady state flow are shortened. (3) The maximum shear stress is linearly increased with shear rate in a double logarithmic scale and becomes larger with increasing concentration at equal shear rates. In addition, the time at which the maximum stress occurs exhibits a linear relationship with the inverse of shear rate in a double logarithmic scale for all xanthan gum solutions, regardless of their concentrations. (4) The shear stress is sharply increased with an increase in strain until reaching the maximum stress at small range of deformations. The maximum stress is observed at similar strain values, irrespective of the imposed shear rates lower than 10 1/s. (5) The Bird-Leider model can be successfully used with regard to quantitatively predicting the transient behavior of concentrated xanthan gum solutions. However, this model has a fatal weakness in terms of describing a decrease in shear stress (stress decay).

Keywords: xanthan gum, transient rheology, start-up shear flow, stress overshoot, stress decay, Bird-Leider model

1. Introduction

Polysaccharides are polymers made up of many monosaccharides joined together by glycosidic linkages. They are therefore very large, often branched, macromolecules. Bacteria and many microbes, including fungi and algae, often secrete polysaccharides as an evolutionary adaptation to help them adhere to surface and to prevent them from drying out. Microbial exopolysaccharides have a significant commercial value, particularly in regard to the production of gels and modification of the rheological properties of aqueous systems. Nowadays, they are replacing the plant and macroalgae exopolysaccharides traditionally used in the food, pharmaceutical, textile and oil industries (Palaniraj and Jayaraman, 2011; Jang *et al.*, 2015).

Among microbial exopolysaccharides, one of the most important industrial biopolymers may be xanthan gum because of its exceptional properties that allow this bio-

polymer to supplement other natural and synthetic water-soluble polymers. Xanthan gum was first discovered in the late 1950s at the Northern Regional Research Laboratories (NRRL) of the United States Department of Agriculture (USDA). These laboratories discovered that the bacterium *Xanthomonas campestris* found on cabbage plants produces an extracellular polysaccharide (Margaretis and Zajic, 1978).

The knowledge of rheological properties of xanthan gum aqueous systems is of great importance and their correct measurements provide a lot of useful informations with regard to engineering applications, formulation of commercial products, design and process evaluation, quality control, and storage stability, because rheological characteristics affect the flow behavior during processing as well as the mechanical properties of the final products (Lapasin and Prici, 1999).

Due to the fact that manufacturing process is made very fast, transient rheological phenomena become particularly important and these phenomena are known to be sensitive to changes in the microstructure of a material during pro-

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cessing. In order to investigate a transient rheological behavior, one of the most widely-used traditional test methods has been to impose a step-strain deformation to a material. However, it is impossible to generate an ideal step-strain deformation that can be made only under the condition of an infinite velocity and a massless test material (Dealy and Wissbrun, 1990). Furthermore, it is also actually impossible to generate an instantaneous deformation, and consequently the actual strain history will be a certain function of time that depends on the mechanical design and the control system of the instrument used (Dealy and Wissbrun, 1990).

On the contrary, a start-up of steady shear flow is relatively easy to generate. It is the velocity rather than the position of the moving surface that must be controlled, and this velocity is always finite (Carreau *et al.*, 1997). For this reason, the most reasonable test method for studying a transient rheological behavior is to track the stress as a function of time in flows involving a steady simple shear.

Because of its paramount importance in a wide variety of industrial applications, a lot of studies have been conducted during the past several decades in order to investigate the rheological properties of both dilute and semi-dilute (or moderately concentrated) xanthan gum solutions prepared from aqueous media by means of a steady/dynamic shear rheometry (Whitcomb and Macosko, 1978; Rochefort and Middleman, 1987; Tam and Tiu, 1989; Milas *et al.*, 1990; Rodd *et al.*, 2001; Wyatt and Liberatore, 2009; Choppe *et al.*, 2010; Xu *et al.*, 2013), creep/creep recovery tests (Giboreau *et al.*, 1994; Pal, 1995; Ma and Barbosa-Canovas, 1997), stress relaxation tests (Richardson and Ross-Murphy, 1987), and large amplitude oscillatory shear measurements (Carmona *et al.*, 2014). However, a little attention has been given to the rheological characterization of highly concentrated solutions of xanthan gum (Lim *et al.*, 1984; Santore and Prudhomme, 1990; Song *et al.*, 2006a; Song *et al.*, 2006b), even though these systems are much more significant from an industrial view-point (Garcia-Ochoa *et al.*, 2000).

In particular, there exists only a few literature that dealt with the rheology of concentrated xanthan gum solutions in transient flow conditions such as a sudden inception of steady shear flow (Ross-Murphy and Shatwell, 1993; Ross-Murphy, 1995). In fact, such a rheological information is far more essential because transient flow is directly related to the real conditions usually encountered at an initial stage of actual material processings. Based upon the above-described backgrounds, we have designed a comprehensive study as to the transient rheology of concentrated xanthan gum systems in aqueous media.

As a first step of our serial works, the objective of the present study is to experimentally investigate the transient rheological behavior of concentrated xanthan gum solu-

tions in start-up shear flow fields. To this end, using a strain-controlled rheometer, a number of constant shear rates were suddenly imposed to aqueous xanthan gum solutions with different concentrations and the resultant shear stress responses were measured with time.

In this article, a pronounced stress overshoot behavior was firstly reported on the basis of the experimentally obtained results, and then explained by comparing with a similar behavior found for concentrated polymer systems. Next, the effects of shear rate, concentration and strain on this behavior were discussed in depth. In addition, the Bird-Leider empirical model was selected to quantitatively predict the transient rheological behavior of concentrated xanthan gum solutions, and then the applicability of this model was examined in detail.

2. Experimental Details

2.1. Raw materials

The xanthan gum sample used in this study was a commercially available product supplied from the Sigma-Aldrich Corporation (St. Louis, MO, USA). As illustrated in Fig. 1, 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

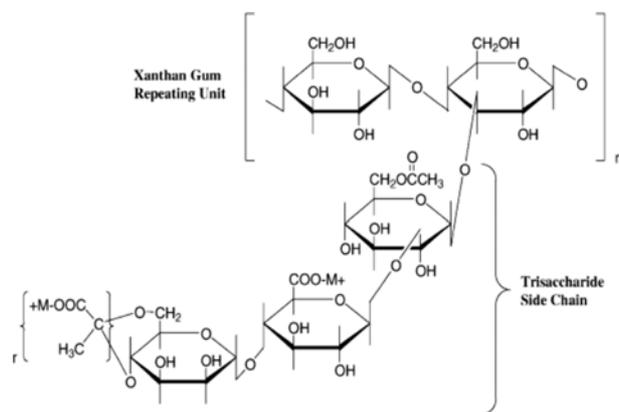


Fig. 1. Structure of xanthan gum.

including its relatively high value, the stiffness of a molecule and the presence of aggregates (Born *et al.*, 2001), resulting in very diverse values reported in the literature (Zirnsak *et al.*, 1999). In fact, such various ranges of its molecular weight are originated mainly from the difference in either manufacturers or suppliers. This is because the molecular weight of xanthan gum is determined by the degree of microbial fermentation steps (or culture time), just as the molecular weight of synthetic polymers is dependent on the degree of polymerizations. Fortunately, the weight average molecular weight of our xanthan gum is found to be 1.13×10^6 g/mol in the literature (Chun and Park, 1994; Chun *et al.*, 2009; Chun and Ko, 2012). This value has been determined by a full analysis of the experimentally measured rheological (viscometric) data and is thus believed to be a very reliable data.

2.2. Preparation of sample 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 different concentrations of 1, 2, 3, and 4wt% 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.

After then, a propeller-type variable-speed homogenizer (EYELA Z-1140, Tokyo Rikakiki Co., Japan or EUROSTAR, 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.

2.3. Rheological measurements

The rheological measurements have been conducted using an Advanced Rheometric Expansion System (ARES) (Rheometric Scientific, Piscataway, NJ, USA). ARES is a well-known strain-controlled rheometer that is capable of subjecting a test material to either a dynamic or a steady shear strain and then measuring the resultant torque values expended by the sample in response to the imposed shear strain. When operating this instrument, the dynamic/steady shear strain is applied by the step-motor and the torque

value is measured by the force rebalance transducer (FRT).

In this study, the transient rheological behavior of prepared xanthan gum solutions was investigated in start-up shear flow fields using an ARES equipped with a parallel-plate fixture having a radius of 12.5 mm and a gap size of 2.0 mm. A number of constant shear rates ($\dot{\gamma} = 0.01, 0.025, 0.05, 0.1, 0.25, 0.5, 1, 2.5, 5, 10, 25, 50,$ and 100 1/s) were suddenly imposed at time $t = 0$ to sample solutions that were initially subjected to a rest state and then the resultant shear stress responses were detected with time until a steady state was reached. All investigations were performed at an isothermal condition of 20°C .

In addition, in order to characterize the steady shear flow properties of prepared xanthan gum solutions, steady rate-sweep measurements were nextly performed using an ARES equipped with the same parallel-plate fixture as adopted when transient rheological investigation was made. These rate-sweep tests were carried out at a fixed temperature of 20°C over a wide range of shear rates from 0.025 to 500 1/s with a logarithmically increasing scale.

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.*, 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 investigations, 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 measurements 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.

3. Results and Discussion

3.1. Stress overshoot behavior

A typical transient behavior of a viscoelastic material at start-up of steady shear flow with different shear rates may be schematically displayed in Fig. 2a. When the steady shear flow with a constant shear rate is suddenly imposed to a viscoelastic material, the shear stress, $\sigma^+(t, \dot{\gamma})$, is rapidly increased with time until reaching the maximum (or

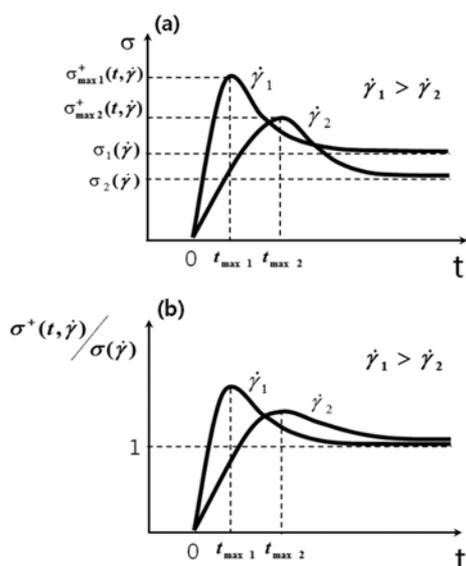


Fig. 2. Schematic representation of typical transient behavior at start-up of steady shear flow with different shear rates: (a) Shear stress vs. time and (b) reduced shear stress vs. time relationships.

peak) stress value, $\sigma_{\max}^+(t, \dot{\gamma})$, at a time, t_{\max} , and then gradually decreased with time towards its steady-state value, $\sigma(\dot{\gamma})$. This temporal sequence has usually been referred to as a stress overshoot behavior (or phenomenon) among

rheological specialists (Bird *et al.*, 1987; Tanner, 2000).

In general, a discrepancy in transient behaviors of the variation of shear stress values corresponding to the imposed shear rates becomes larger as the higher shear rates are applied to a material. Because this fact is bound to bring about a difficulty in analyzing and comparing the transient behaviors with different shear rates, the reduced shear stress defined as a ratio of the shear stress $\sigma^+(t, \dot{\gamma})$ measured during a whole period of experimental times to the shear stress $\sigma(\dot{\gamma})$ obtained after reaching a steady state is employed in this study, as depicted in Fig. 2b, in order to easily characterize a transient behavior of aqueous xanthan gum solutions.

Figs. 3a-3d show the transient behavior represented by the reduced shear stress as a function of time at various shear rates for aqueous xanthan gum solutions with different concentrations of 1, 2, 3, and 4wt%, respectively. It is commonly observed for all xanthan gum solutions that, regardless of the imposed shear rates, however low it may be, the shear stress is sharply increased with time at an initial stage upon inception of steady shear flow before passing through the maximum stress value and then progressively decreased with time. After sufficiently long time has passed, the shear stress reaches a steady state where xanthan gum solutions eventually exhibit a completely viscous flow behavior with showing a constant

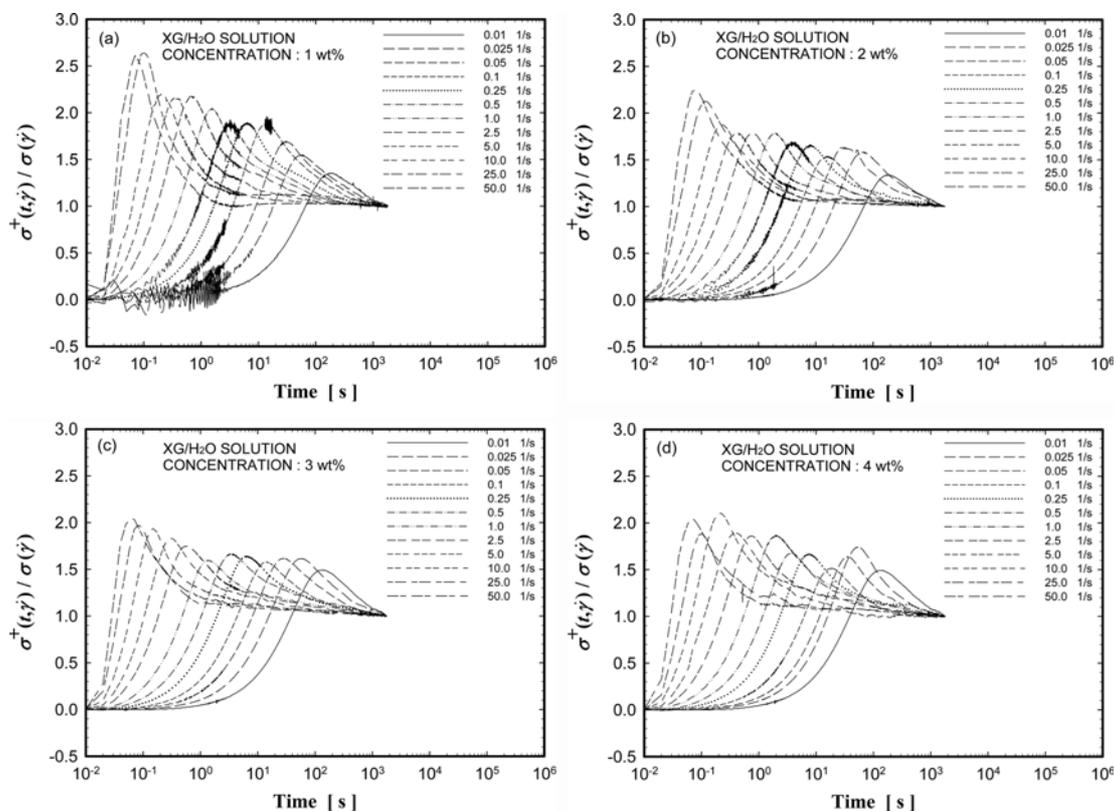


Fig. 3. Reduced shear stress as a function of time at various shear rates for XG/H₂O solutions with different concentrations of (a) 1wt%, (b) 2wt%, (c) 3wt%, and (d) 4wt%.

shear stress that becomes no longer dependent on time.

In other words, a transient behavior of our xanthan gum solutions can be characterized by a stress overshoot followed by a stress decay towards a steady state for all shear rates applied; (i) step 1: a stress overshoot behavior on account of a contribution of a strong elastic nature, (ii) step 2: a stress decay behavior that represents a viscoelastic response accompanied with a structural breakdown, and (iii) step 3: a steady-state viscous flow behavior.

In addition, as the imposed shear rate is increased, a more pronounced stress overshoot behavior takes place and the maximum stress value becomes larger, whereas both times at which the maximum stress is observed and needed to reach a steady state are shortened. These results may originate from the fact that rearrangement of xanthan gum molecules occurs faster with an increase in shear rate. Such a trend is consistently observed for all xanthan gum solutions used in this study, irrespective of their concentrations.

This type of transient rheological behavior has previously been reported for other complex materials including amorphous polymers (Van Melick *et al.*, 2003a; Van Melick *et al.*, 2003b), emulsions (Partal *et al.*, 1999; Krishnan *et al.*, 2002), microgels (Islam *et al.*, 2004), nanocomposites (Letwimolnun *et al.*, 2007), and colloidal suspensions (Mahaut *et al.*, 2008; Koumakis and Petekidis, 2011). All of these materials are known to have a yield stress; they show an elastic-plastic-viscous property of turning from a solid-like behavior at rest or at very small shear stresses into a liquid-like behavior above a certain magnitude of shear stress called a yield stress.

By the way, a stress overshoot behavior has also been frequently found for viscoelastic fluids such as polymer melts (Boukany *et al.*, 2009) and concentrated polymer solutions (Osaki *et al.*, 2000; Islam and Archer, 2001; Tezel *et al.*, 2009; Bae *et al.*, 2013); these polymer systems do not exhibit a yield stress. In this respect, it would be meaningful to interpret a transient rheological behavior observed in xanthan gum solutions by comparing with a similar behavior reported for polymer systems having no yield stress.

For polymer melts and concentrated solutions, the appearance of a stress overshoot has been microscopically accounted for both by an elastic deformation of polymer chains (polymer stretching) before reaching the maximum stress and by a disentanglement of polymer chains (structural breakdown and subsequent rearrangement) after passing through the maximum stress (Wang *et al.*, 2007; Wang and Wang, 2009).

However, no stress overshoot is observed when low shear rates are imposed to these polymer systems (Osaki *et al.*, 2000; Islam and Archer, 2001; Boukany *et al.*, 2009; Tezel *et al.*, 2009; Bae *et al.*, 2013). This is because, at low shear rates (*i.e.*, at long time scales), the rheology of

polymer melts and concentrated solutions is governed by a viscous nature rather than an elastic nature (Song *et al.*, 1998; Song *et al.*, 1999). Only when the shear rates higher than a certain critical value above which an elastic feature becomes dominant are applied, these polymer systems exhibit a stress overshoot behavior due to a contribution of an elastic property.

In the case of our xanthan gum solutions, on the other hand, an elastic nature is consistently superior to a viscous nature over a wide range of time scales. This is verified by the fact (Song *et al.*, 2006b) that the storage modulus, $G'(\omega)$, is always greater than the loss modulus, $G''(\omega)$, over a broad range of angular frequencies with the values of the power-law parameters $K'[G'(\omega) = K' \omega^n]$ being always larger than those of $K''[G''(\omega) = K'' \omega^n]$ for all xanthan gum solutions used in this study, regardless of their concentrations. Such viscoelastic properties of aqueous xanthan gum solutions may be attributable to the occurrence of attractive interactions between helices formed by rigid xanthan macromolecules, giving rise to a weak three-dimensional network and a complex aggregation in solutions by means of physical entanglements and hydrogen bonding (Song *et al.*, 2006a; Song *et al.*, 2006b).

In addition, both of the storage modulus and loss modulus are only a weak function of angular frequency (Song *et al.*, 2006b), indicating that a gel-like structure is present in aqueous xanthan gum solutions and that a very slow relaxation mechanism is expected for these systems (Lee *et al.*, 2012; Huang *et al.*, 2014). This fact seldom allows the difference between the two moduli to be closer to each other and therefore can be a main reason why a stress overshoot behavior takes place even at very low shear rates (*i.e.*, at very long time scales) where an elastic nature still plays a role in deforming (stretching) the xanthan gum polymer chains.

3.2. Concentration-dependent behavior

Fig. 4 demonstrates the maximum shear stress, $\sigma_{\max}^+(t, \dot{\gamma})$, as a function of shear rate for aqueous xanthan gum solutions with different concentrations. It is clearly observed that, for all concentrations, the maximum stress is linearly increased with an increase in shear rate in a double logarithmic scale and that the maximum stress becomes larger with increasing concentration when equal shear rates are imposed. It is also of interest that the increasing rate of the maximum stress against shear rate seems to show a little variation with concentration.

In order to elucidate the influence of concentration on the maximum stress in more detail, the slope of the maximum stress against shear rate in terms of concentration is illustrated in Fig. 5 for all aqueous xanthan gum solutions. It is obviously confirmed that the slope exhibits an almost equal value of approximately 0.2, which is nearly independent of concentration. This indicates that the stress

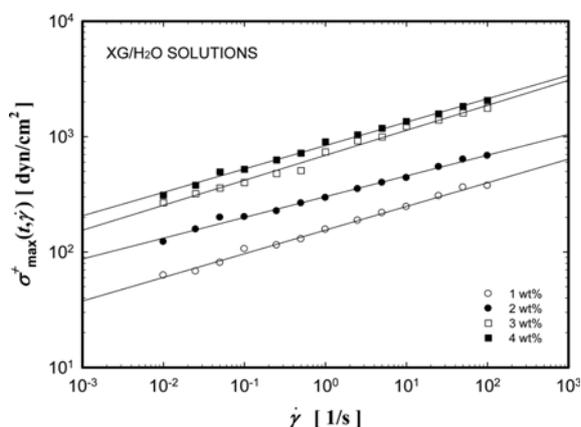


Fig. 4. Maximum shear stress as a function of shear rate for XG/H₂O solutions with different concentrations.

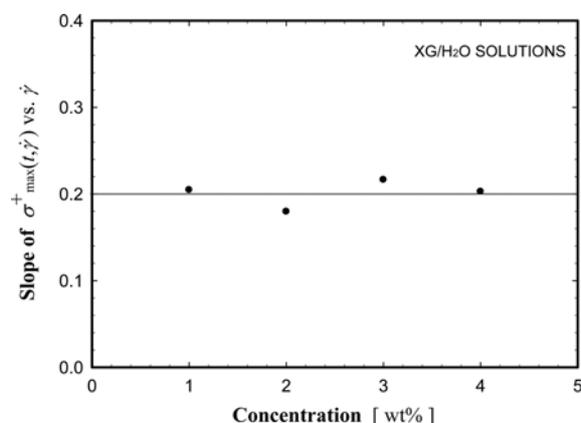


Fig. 5. Slope of $[\sigma_{\max}^+(t, \dot{\gamma}) \text{ vs. } \dot{\gamma}]$ against concentration for XG/H₂O solutions.

overshoot behavior of xanthan gum solutions is mainly dependent on the applied shear rate, regardless of their concentrations.

Such a tendency has never been reported for concentrated polymer solutions (Bae *et al.*, 2013) whose increasing rate of the maximum stress against shear rate becomes smaller as an increase in concentration and consequently whose slope of the maximum stress against shear rate is decreased with increasing concentration. For concentrated polymer solutions, as the concentration is increased, more elaborate physical entanglements of the polymer chains are formed, giving rise to a stronger elastic feature to the polymer systems. This leads to a less destruction of the network structure persisted by an elastic nature and a subsequent less rearrangement of the polymer chains. For these reasons, as the concentration is increased, the dependency of shear rate on the maximum stress becomes weaker.

In the case of our xanthan gum solutions, on the contrary, a highly elastic nature due to a complex aggregation of polymer chain entanglements and hydrogen bonding is

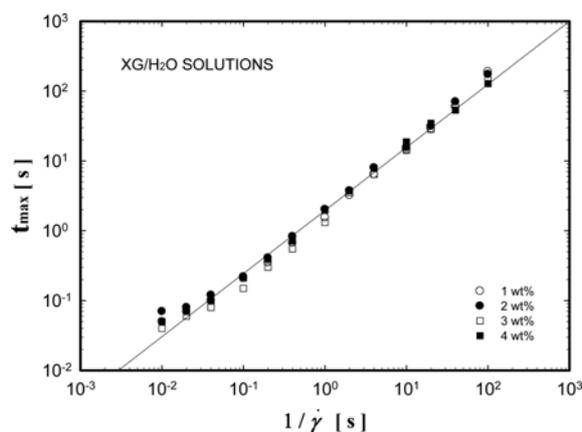


Fig. 6. t_{\max} against inverse of shear rate for XG/H₂O solutions with different concentrations.

already present even for the solution with the lowest concentration of 1wt%. As the concentration is increased, an elastic property naturally becomes stronger with a viscous property being also increased. However, the difference between these two properties (*i.e.*, a ratio of the elasticity to the viscosity) is expected to remain almost unchanged over a wide range of time scales tested in this study, even though the concentration is increased. This may be an important reason why the shear rate dependence of the maximum stress exhibits a little deviation with concentration.

Fig. 6 shows the time, t_{\max} , at which the maximum stress occurs as a function of the inverse of shear rate for aqueous xanthan gum solutions with different concentrations. The t_{\max} exhibits a highly linear relationship with the inverse of shear rate in a double logarithmic scale for all xanthan gum solutions, indicating that the t_{\max} of xanthan gum solutions is mainly dependent on shear rate, irrespective of their concentrations. This is in agreement with the result which will be obtained from the prediction using the Bird-Leider model in the later section.

3.3. Strain-dependent behavior

Due to the fact that total strain can be expressed as a product of shearing time and imposed shear rate $[\gamma(t) \equiv \int \dot{\gamma} dt = \dot{\gamma}t]$, a transient behavior (or stress overshoot behavior) may be described in terms of strain. Figs. 7a-7d show the transient behavior represented by the reduced shear stress as a function of strain at various shear rates for aqueous xanthan gum solutions with different concentrations of 1, 2, 3, and 4wt%, respectively. For all xanthan gum solutions, regardless of their concentrations, the shear stress is sharply increased until reaching the maximum stress value with an increase in strain at small range of deformations. Such a remarkable appearance of stress overshoot is due to a finite response of the microstructure up to a critical level of deformation beyond which a

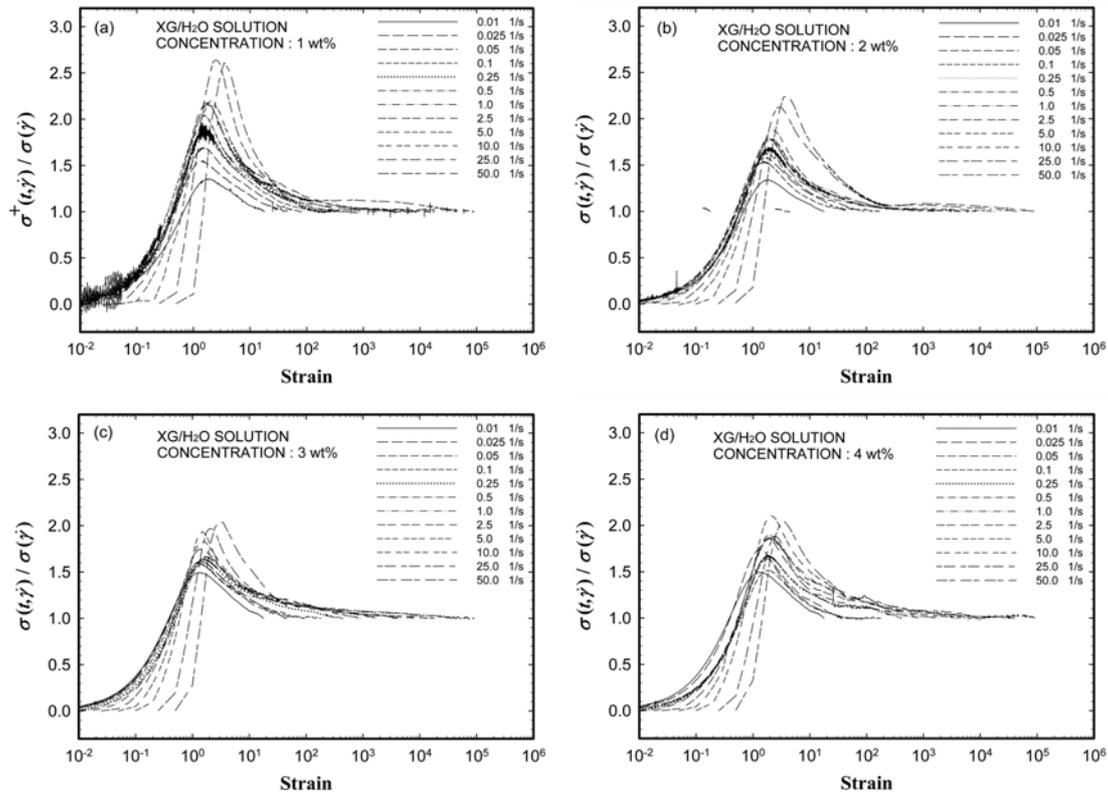


Fig. 7. Reduced shear stress as a function of strain at various shear rates for XG/H₂O solutions with different concentrations of (a) 1wt%, (b) 2wt%, (c) 3wt%, and (d) 4wt%.

monotonic stress decay concomitant with a structural destruction is followed.

It is more interesting that the maximum stress is found at similar strain values of approximately between 1.0~2.0, irrespective of the imposed shear rates lower than 10 1/s. This is a more typical response of an elastic solid rather than a viscoelastic liquid, confirming once again that our xanthan gum solutions are a highly elastic liquid showing a solid-like behavior. When shear rates higher than 10 1/s are applied, however, the strain value at which the maximum stress is observed is rapidly increased with an increase in shear rate. This result may be attributed to an insufficient time for xanthan gum solutions to respond to an externally applied larger stimulus concurrent with an increase in shear rate.

In the past, Mewis and Moldenaers (1987) suggested that the transient stress curves could be reduced to a single master curve by plotting the normalized (or reduced) stress in terms of total deformation. As can be seen in Figs. 7a-7d, however, this scaling is not valid for xanthan gum solutions subjected to higher shear rates ($\dot{\gamma} > 10$ 1/s) and similar results have been reported for other structured materials (Krishnan *et al.*, 2002). Such a disagreement is originated from the fact that the earlier studies were restricted to a relatively lower range of shear rates, even in the Newtonian region.

At small strain range, a sharp rise in reduced stress can be considered as a consequence of an elastic nature of a material, and the value of the maximum stress can be taken to be a quantitative measure for the original level of the microstructure of a material. Therefore, the strain at which the maximum stress is observed may be regarded as a strain limit up to which the microstructure of a material is able to maintain its undestroyed state.

Upon the basis of these considerations, the strain limit in

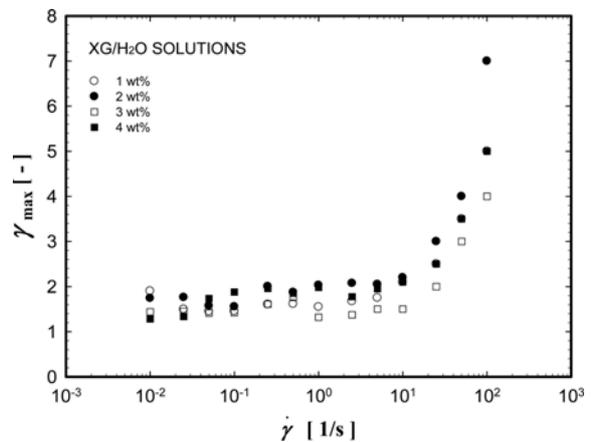


Fig. 8. Strain limit as a function of shear rate for XG/H₂O solutions with different concentrations.

terms of shear rate for aqueous xanthan gum solutions with different concentrations is illustrated in Fig. 8. As expected from the above-mentioned discussions, the strain limit for all shear rates lower than 10 1/s exhibits a similar value with each other within a narrow range from 1.2 to 2.0, irrespective of concentrations. Once the imposed shear rate exceeds 10 1/s, however, the strain limit is sharply increased with an increase in applied shear rate for all xanthan gum solutions tested in this study.

3.4. Prediction using the Bird-Leider model

In this study, the Bird-Leider model (Leider and Bird, 1974; Leider, 1974) was chosen to quantitatively predict the transient (stress overshoot) behavior of concentrated xanthan gum solutions. The Bird-Leider model is an empirical viscoelastic flow equation whose material properties are obtained by fitting the steady shear stress, steady normal stress and the transient shear stress data. This model has been proved to be useful in regard to describing a stress overshoot phenomenon observed in several semi-solid food materials (Navarro *et al.*, 1995; Navarro *et al.*, 1997) and lubricating greases (Delgado *et al.*, 2009).

The Bird-Leider model has the following form (Leider and Bird, 1974; Leider, 1974):

$$\tau(t, \dot{\gamma}) = p(\dot{\gamma})^q [1 + (h\dot{\gamma}t - 1)\exp(-t/gq\lambda)] \tag{1}$$

where $\tau(t, \dot{\gamma})$ is the shear stress, p and q are viscous power-law parameters, h and g are adjustable parameters, t is time, $\dot{\gamma}$ is imposed shear rate, and λ is time constant.

The time constant, λ , is calculated by assuming both the steady shear viscosity, $\eta(\dot{\gamma})$, and the first normal stress coefficient, $\Psi_1(\dot{\gamma})$, to follow a power-law behavior:

$$\eta(\dot{\gamma}) = p(\dot{\gamma})^{q-1}, \tag{2}$$

$$\Psi_1(\dot{\gamma}) = p'(\dot{\gamma})^{q'-2} \tag{3}$$

where p' and q' are elastic first normal stress power-law parameters.

The time constant is then constructed as follows:

$$\lambda = \left[\frac{p'}{2p} \right]^{1/(q'-q)}. \tag{4}$$

Using these power-law parameters and the time constant, the Bird-Leider model can be reduced to the following relationship expressed by the reduced shear stress:

$$\frac{\sigma^+(t, \dot{\gamma})}{\sigma(\dot{\gamma})} = \frac{p(\dot{\gamma})^q [1 + (h\dot{\gamma}t - 1)\exp(-t/gq\lambda)]}{\dot{\gamma} \eta(\dot{\gamma})} = 1 + (h\dot{\gamma}t - 1)\exp(-t/gq\lambda) \tag{5}$$

where $\sigma^+(t, \dot{\gamma})$ is the shear stress measured during a whole period of experimental times and $\sigma(\dot{\gamma})$ is the shear stress obtained after reaching a steady state.

The Bird-Leider model incorporates an elastic response

in its $\dot{\gamma}t$ term. At very short times and at a constant shear rate, this model reduces to

$$\tau = \text{constant}(h\dot{\gamma}t). \tag{6}$$

The term, $\dot{\gamma}t$, represents the total strain to which a material is subjected. Eq. (6) can be thought of as an initial elastic response in which a sharp increase in shear stress to the maximum stress value occurs when a constant shear rate is suddenly imposed to a material.

A time constant, λ , may be regarded as a relative indicator of the viscoelasticity of a material. Material parameters obtained from steady shear stress and normal stress measurements are combined to generate a property with the dimension of time similar to the relaxation time for a Maxwell viscoelastic fluid.

A distinct advantage of the Bird-Leider model is that, when a sufficiently long time has passed, this equation converges to a power-law flow behavior commonly observed in many kinds of structured viscoelastic materials. In addition, the Bird-Leider model is quite flexible in predicting a transient behavior since this equation contains two adjustable parameters besides the power-law parameters and the time constant.

Fig. 9 shows the shear rate dependence of the steady shear viscosity and the regression result by a viscous power-law relationship [Eq. (2)] for aqueous xanthan gum solutions with different concentrations. The steady shear viscosity for all xanthan gum solutions is sharply decreased with an increase in shear rate, indicating that these systems exhibit a pronounced shear-thinning flow behavior. It is also clearly observed that the steady shear viscosity obeys a prominent power-law behavior over a wide range of shear rates. This confirms that one of the key assumptions [Eq. (2)] of the Bird-Leider model is well satisfied with the experimentally measured data.

Fig. 10 demonstrates the shear rate dependence of the

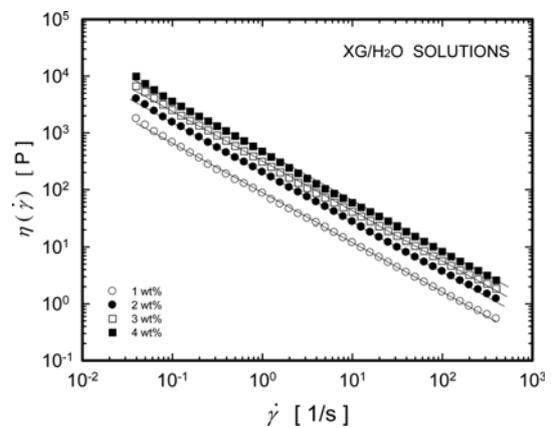


Fig. 9. Shear rate dependence of steady shear viscosity and regression result by a viscous power-law relationship for XG/H₂O solutions with different concentrations.

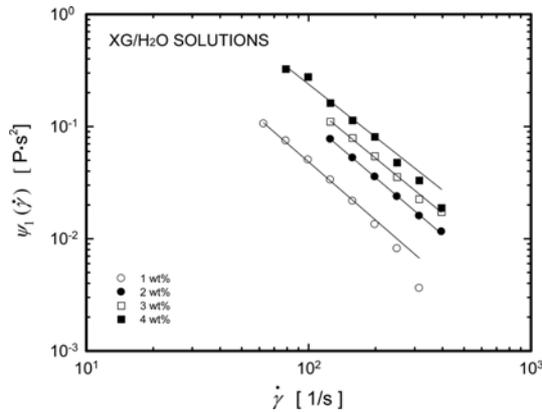


Fig. 10. Shear rate dependence of first normal stress coefficient and regression result by an elastic power-law relationship for XG/H₂O solutions with different concentrations.

first normal stress coefficient and the regression result by an elastic power-law relationship [Eq. (3)] for aqueous xanthan gum solutions with different concentrations. Unlike the case of the steady shear viscosity, the first normal stress coefficient obeys a power-law behavior within a limited range of shear rates. This is because reliable data could be obtained at relatively higher range of shear rates.

Table 1. Calculated values of power-law parameters and time constants for XG/H₂O solutions with different concentrations.

Parameter	1wt%	2wt%	3wt%	4wt%
p	85.5159	201.430	310.382	455.168
q	0.1401	0.1334	0.1299	0.1275
p'	133.730	266.285	289.315	322.205
q'	0.2787	0.3134	0.3729	0.4340
λ	0.1695	0.1002	0.0432	0.0338

In general, when making steady shear flow measurements by means of a conventional rotational-type rheometer, measurable normal forces are seldom obtained except at high shear rates, due to a dominance of an inertia effect to an elastic property of a material at low shear rates. In spite of such a limited result, it may be accepted that another key assumption of the Bird-Leider model [*i.e.*, a power-law behavior of the first normal stress coefficient, Eq. (3)] is also effective for our xanthan gum solutions.

For reference, all of the calculated values of the power-law parameters for steady shear viscosity and first normal stress coefficient together with those of the time constants are reported in Table 1 for all aqueous xanthan gum solutions tested in this study. The slope of each curve in Figs.

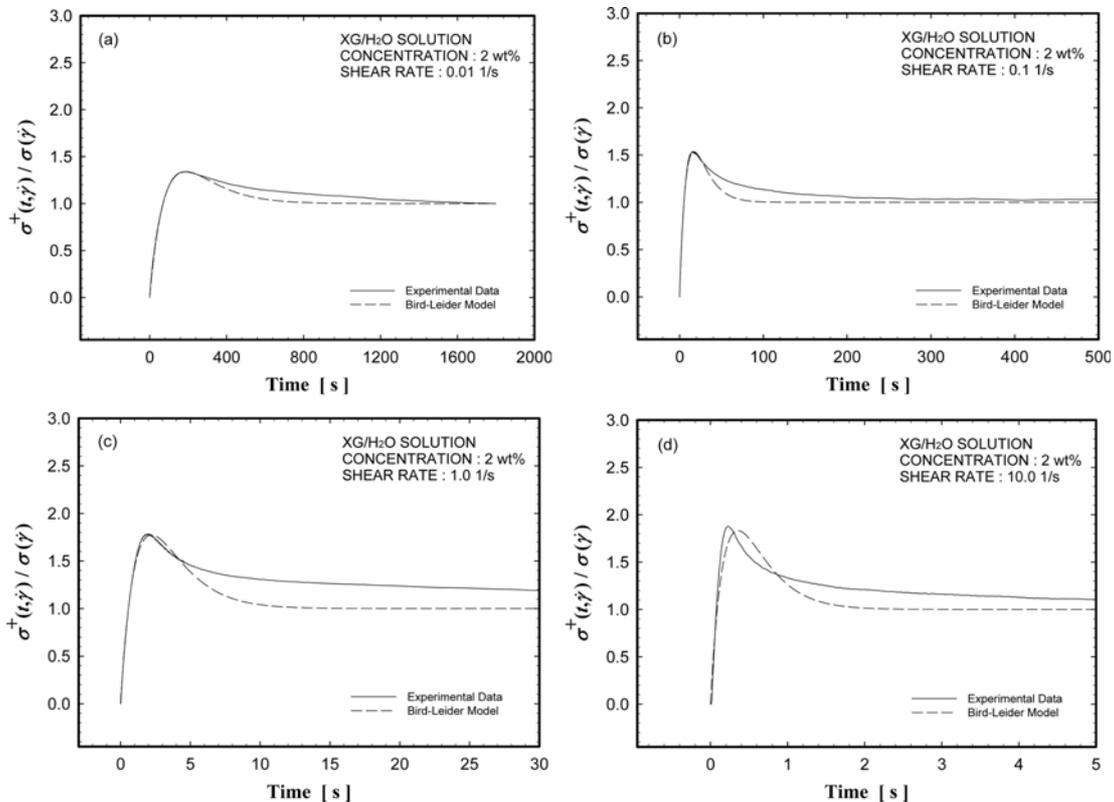


Fig. 11. Comparison between experimentally obtained reduced shear stress and prediction from Bird-Leider model for 2wt% XG/H₂O solution at various shear rates of (a) 0.01 1/s, (b) 0.1 1/s, (c) 1 1/s, and (d) 10 1/s.

9 and 10 becomes equivalent to $q - 1$ and $q' - 2$, respectively.

Figs. 11a-11d show a comparison of the experimentally obtained reduced shear stress with the prediction result from the Bird-Leider model for 2wt% aqueous xanthan gum solution at various shear rates of 0.01, 0.1, 1, and 10 1/s. As can be seen from these figures, a choice of the Bird-Leider model is found to be a successful attempt with regard to quantitatively describing the transient behavior of concentrated xanthan gum systems. In particular, when relatively lower shear rates ($\dot{\gamma} = 0.01$ and 0.1 1/s) are applied, the Bird-Leider model has a more excellent ability to express a rapid increase in shear stress (*i.e.*, stress overshoot) to the maximum stress value as well as the time at which the maximum stress occurs. Such a tendency is consistently observed for other concentrated (1wt%, 3wt%, and 4wt%) xanthan gum solutions whose results are not displayed in this article on account of a space limitation.

Nevertheless, this model has a fatal weakness in terms of describing a decrease in shear stress (*i.e.*, stress decay) which always exhibits a slower decrease than does the predicted result from the Bird-Leider model. In other words, while an experimentally observed actual stress decay is very progressive, the Bird-Leider model predicts a sharper decrease from the maximum stress to a steady state stress value. This may be fundamentally attributable to the incompleteness of the exponential term in the equation, $\exp(-t/gq\lambda)$, that plays a role in characterizing a stress relaxation until a steady state is reached. The Bird-Leider model adopts a single exponential term to express the evolution of shear stress with time, leading to its ability to be limited. This weak point is thought to be improved by considering a series of relaxation terms instead of a single exponential term, which is out of the scope of this study.

Now it would be necessary to confirm an important result reported in the former section that the t_{\max} is mainly dependent on shear rate, regardless of concentration, by using the Bird-Leider model.

Mathematical expressions for the t_{\max} are obtained as follows by differentiating Eq. (1) with respect to time at a constant shear rate and then equating the derivative to zero:

$$t_{\max} = gq\lambda + \frac{1}{h\dot{\gamma}} \quad (7)$$

From Eq. (7), it can be known that the t_{\max} shows a linear relationship with the inverse of shear rate. This indicates that the t_{\max} is mainly dependent on shear rate, irrespective of concentration, being in coincidence with the experimentally obtained result (Fig. 6).

Finally, it should be noted here that the Bird-Leider model is not a true constitutive equation but an empirical equation. This model predicts the most appropriate form

of a transient behavior by numerically determining the adjustable parameters, h and g , with a nonlinear regression using stress overshoot data. In this respect, prediction of a transient behavior by means of a time-strain separable integral-type constitutive equation (the so-called Wagner model) (Wagner, 1976) is now in progress in our laboratory and the results will be reported in the near future.

4. Conclusions

In spite of their paramount importance in a wide variety of industrial applications, a little attention has been given to the rheological characterization of concentrated xanthan gum systems. Moreover, there exists only a few literature that dealt with the rheology of highly concentrated xanthan gum solutions in transient flow fields including a sudden inception of steady shear flow. From an industrial point of view, however, such a rheological information becomes much more necessary, since transient flow is directly associated with the real conditions frequently faced with at an initial stage of actual material processings.

The principal objective of the present study has been to experimentally investigate the transient rheological behavior of concentrated xanthan gum solutions prepared from aqueous media in start-up shear flow fields. With this aim, using a well-known strain-controlled rheometer [Advanced Rheometric Expansion System (ARES)], a number of constant shear rates were suddenly imposed to prepared xanthan gum solutions with different concentrations and then the resultant stress responses were measured with time.

For all shear rates imposed, however low it may be, the shear stress is rapidly increased with time (stress overshoot behavior) upon inception of steady shear flow before passing through the maximum stress value and then gradually decreased with time (stress decay behavior) until reaching a steady state flow. Such a transient behavior is mainly attributed to the fact that an elastic nature is always dominant to a viscous nature over a wide range of time scales for all xanthan gum solutions, irrespective of their concentrations, and particularly due to the fact that an elastic feature still plays its role in deforming (stretching) the xanthan gum polymer chains even at very low shear rates (at very long time scales).

As the imposed shear rate is increased, a more pronounced stress overshoot takes place and the maximum stress value becomes larger, whereas both times at which the maximum stress is observed and needed to reach a steady state flow are shortened. Such a result is originated from the fact that rearrangement of xanthan gum molecules occurs faster with an increase in imposed shear rate.

The maximum shear stress is linearly increased with shear rate in a double logarithmic scale and becomes larger

with increasing concentration at equal shear rates. However, the increasing rate of the maximum stress against shear rate shows a little variation with concentration. In addition, the time at which the maximum stress occurs exhibits a linear relationship with the inverse of shear rate in a double logarithmic scale for all xanthan gum solutions, regardless of their concentrations. These results indicate that a stress overshoot behavior of concentrated xanthan gum solutions is mainly dependent on the applied shear rate, being almost independent of concentration.

The shear stress is sharply increased with an increase in strain until reaching the maximum stress at small range of deformations. Such a remarkable appearance of stress overshoot is due to a finite response of the microstructure up to a critical level of deformation beyond which a monotonic decrease in shear stress (stress decay) is followed concomitant with a structural destruction.

The maximum stress is observed at similar strain values of approximately 1.0~2.0, irrespective of the imposed shear rates lower than 10 1/s. This is a more typical response of an elastic solid rather than a viscoelastic liquid. When shear rates higher than 10 1/s are applied, however, the strain value at which the maximum stress is observed is rapidly increased with an increase in shear rate for all xanthan gum solutions. This may be attributed to an insufficient time for xanthan gum solutions to respond to an externally applied larger stimulus concurrent with an increase in shear rate.

The Bird-Leider model can be successfully used with regard to quantitatively predicting the transient behavior of concentrated xanthan gum solutions. This is due to the fact that this model predicts the most appropriate form of a transient behavior through a numerical determination of the adjustable parameters with a nonlinear regression using stress overshoot data. When relatively lower shear rates are applied, this model shows a more excellent ability for expressing a rapid increase in shear stress (stress overshoot) to the maximum stress value as well as the time at which the maximum stress is observed.

The Bird-Leider model has a fatal weakness in terms of describing a decrease in shear stress (stress decay) which always exhibits a slower decrease than does the prediction from the model. This may be attributable to the incompleteness of a single exponential term in the equation that plays a role in characterizing a stress relaxation until a steady state is reached.

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