Rheology of Concentrated Xanthan Gum Solutions : Steady Shear Flow Behavior

Ki-Won Song*, Yong-Seok Kim, and Gap-Shik Chang

School of Chemical Engineering, Pusan National University, Pusan 609-735, Korea

Abstract: Using a strain-controlled rheometer, the steady shear flow properties of aqueous xanthan gum solutions of different concentrations were measured over a wide range of shear rates. In this article, both the shear rate and concentration dependencies of steady shear flow behavior are reported from the experimentally obtained data. The viscous behavior is quantitatively discussed using a well-known power law type flow equation with a special emphasis on its importance in industrial processing and actual usage. In addition, several inelastic-viscoplastic flow models including a yield stress parameter are employed to make a quantitative evaluation of the steady shear flow behavior, and then the applicability of these models is also examined in detail. Finally, the elastic nature is explained with a brief comment on its practical significance. Main results obtained from this study can be summarized as follows : (1) Concentrated xanthan gum solutions exhibit a finite magnitude of yield stress. This may come from the fact that a large number of hydrogen bonds in the helix structure result in a stable configuration that can show a resistance to flow. (2) Concentrated xanthan gum solutions show a marked non-Newtonian shear-thinning behavior which is well described by a power law flow equation and may be interpreted in terms of the conformational status of the polymer molecules under the influence of shear flow. This rheological feature enhances sensory qualities in food, pharmaceutical, and cosmetic products and guarantees a high degree of mixability, pumpability, and pourability during their processing and/or actual use. (3) The Herschel-Bulkley, Mizrahi-Berk, and Heinz-Casson models are all applicable and have equivalent ability to describe the steady shear flow behavior of concentrated xanthan gum solutions, whereas both the Bingham and Casson models do not give a good applicability. (4) Concentrated xanthan gum solutions exhibit a quite important elastic flow behavior which acts as a significant factor for many industrial applications such as food, pharmaceutical, and cosmetic manufacturing processes.

Keywords: Concentrated xanthan gum solutions, Rheology, Steady shear flow behavior, Yield stress, Steady shear viscosity (viscous behavior), Viscoplastic flow models, Primary normal stress difference (elastic nature)

Introduction

Xanthan gum is a natural polysaccharide and one of the most important industrial biopolymers. Xanthan gum was first discovered in the late 1950s at the Northern Regional Research Laboratories (NRRL) of the United States Department of Agriculture (USDA) [1]. Since then, xanthan gum produced by the bacterium *Xanthomonas campestris* has been extensively studied because of its exceptional properties that would allow this biopolymer to supplement other known natural and synthetic water-soluble polymers. Today, xanthan gum is regarded as the most significant microbial polysaccharide from a commercial stand-point.

Xanthan gum has been used in a wide variety of food materials for a number of important reasons including emulsion stabilization, temperature stability, compatibility with food ingredients, and its pseudoplastic rheological properties [2]. Xanthan gum is also used in pharmaceutical formulations, cosmetics, and agricultural products as a dispersing agent and a stabilizer of emulsions and/or suspensions because of its ability in thickening aqueous solutions [3]. Xanthan gum is further used in textile printing pastes, ceramic glazes, slurry explosive formulations, and rust removers [4]. In addition, high viscosity of solutions and water solubility of

this biopolymer have created important applications in the petroleum industry where it is commonly used in drilling fluids and in enhanced oil recovery processes [5].

The unique rheological properties induced by xanthan gum have prompted its industrial success and are responsible for its wide-spread use in various applications, as mentioned above. The rheological behavior of xanthan gum reflects the ordered conformation and consequent intermolecular interactions usually adopted in aqueous solutions [6]. Likewise other biopolymeric materials, rheological studies of this polysaccharide can provide a lot of significant informations with regard to [7] : (a) quality control of either raw materials or final products; (b) process engineering; (c) optimization of formulations on the basis of the relationships between micro-structure and physical properties; and (d) objective texture analysis of commercial products.

As will be reviewed in the next section, it was realized from our rigorous literature survey that, while there exists a reasonably substantial amount of literature published on the rheological properties of dilute and semi-dilute (or moderately concentrated) xanthan gum solutions prepared from aqueous media, only a little attention has been given to the rheology of concentrated solutions of xanthan gum, even though these systems are far more important from an industrial point of view. During the production of xanthan gum, for instance, more concentrated solutions (up to 3 wt%) occur in the fermen-

---

*Corresponding author: kwsong@pusan.ac.kr

tation process [8,9]. The strongly non-Newtonian character of concentrated xanthan gum solutions is essential for mixing, heat transfer, and oxygen mass transfer requirements of xanthan gum fermentation reactors [10]. Fermentation broths that are further concentrated up to 13 wt% xanthan gum are already available in the commercial market.

Based upon the above-described backgrounds, we have designed a comprehensive study as to the overall rheology of concentrated xanthan gum systems in aqueous media. As a first step of our works, the objective of the present study is to systematically investigate the nonlinear rheological behavior of concentrated xanthan gum solutions in steady shear flow fields. Using a strain-controlled rheometer, the steady shear flow properties of aqueous xanthan gum solutions with different concentrations were measured over a wide range of shear rates.

In this article, both the shear rate and concentration dependencies of steady shear flow behavior were reported from the experimentally obtained data. In particular, the viscous behavior was quantitatively discussed using a well-known power law type flow equation with a special emphasis on its importance in industrial processing and actual usage. In addition, several inelastic-viscoplastic flow models including a yield stress parameter were employed to make a quantitative evaluation of the steady shear flow behavior, and then the applicability of these models was also examined in detail. Finally, the elastic nature was explained with a brief comment on its practical significance.

Literature Review

In the past, the rheological properties of xanthan gum in both dilute and semi-dilute (or moderately concentrated) solutions have been extensively studied. The determination of concentration regimes has been an important aspect of the previous works because xanthan gum systems demonstrate a differently complicated rheological behavior according to the concentration regime. In this section, selected publications most pertinent to our study are now reviewed briefly.

An early valuable article on this subject appeared in 1978. Through a thorough investigation of the steady shear flow properties of aqueous solutions of xanthan gum over a wide range of shear rates and concentrations, Whitcomb and Macosko [11] reported that sufficiently dilute xanthan gum solutions show a region of the Newtonian viscosity at low shear rates and that more concentrated solutions appear to exhibit a yield stress. Moreover, they speculated that, by modeling their intrinsic viscosity data, the conformation of xanthan gum in solution is rod-like having a flexibility to some extent.

A first theoretical as well as experimental approach on the viscoelastic properties of xanthan gum was made by Thurston and Pope in 1981 [12,13]. These authors reported that the same relaxation processes are responsible for both the steady

and oscillatory flow behaviors and are sufficient to describe the change in viscoelasticity with angular frequency and the change in steady flow viscosity with shear rate.

Later, from a wide range of rheological experiments, Ross-Murphy et al. [14,15] concluded that, in aqueous solution, xanthan gum may be regarded as a highly extended worm-like chain interacting by noncovalent association to develop a weak-gel network, which can be readily reversible under shear flow. As a representative example of their suggestion, they showed that a well-known Cox-Merz rule is no more obeyed even in semi-dilute xanthan gum solutions. A similar behavior was found by Cuvelier and Launay [16]. These authors investigated both the steady shear flow and dynamic viscoelatic properties of xanthan gum solutions with various concentration regimes in which different master curves are obtained and deduced that this may be due to a change in the density of the junction zones of the elastic network formed by side-by-side associations.

The influences of salt, temperature, and strain on the structure of xanthan gum solutions were studied by Rochefort and Middleman [17] using both the steady and oscillatory shear experiments. Their conclusions are very similar to the previous ones. Nevertheless, a master curve of dynamic properties covering six decades of frequency has been obtained in highly saline solution and the frequency-temperature superposition allows a characterization of the conformational transition induced by temperature change.

Tiu et al. [18-20] investigated the steady and dynamic shear properties of dilute solutions of xanthan gum in aqueous media at different concentrations and temperatures. They reported that these solutions exhibit both shear-thinning and elastic characteristics even at extremely low concentrations and the temperature-concentration superposition principle using reduced variables are applicable to both steady and dynamic shear data, and moreover, the Cox-Merz relation is valid only in low shear rate and frequency regions. The existence of a yield stress in biopolymer/water systems was thoroughly discussed by Giboreau et al. [21]. In the same article, these authors also proved that the Cox-Merz relation does not hold (the complex viscosity is larger than the steady shear viscosity) through comparing the steady and dynamic shear data.

Hatakeyama et al. [22-24] have investigated the viscoelastic properties of aqueous xanthan gum solutions and hydrogels formed by annealing in the sol state followed by subsequent cooling using both a parallel-plate and a cone-plate type rheometers. Based on their experimental results, these authors showed the structural change of the solution in the annealing process and the structure of gels.

Solutions of xanthan gum obtained by a dissolution at moderate temperature tend to exhibit a pseudoplastic behavior with high viscosity even at low concentrations [25]. It has been reported that concentration has a considerable effect on the rheological characteristics of xanthan gum solutions whereas temperature as well as pH do not [26,27].
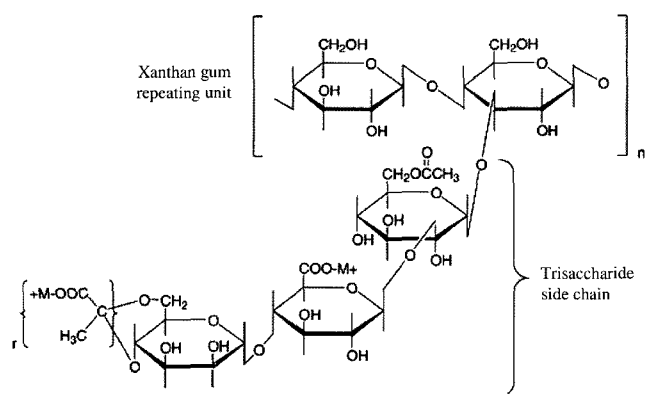
Figure 1. Structure of xanthan gum.

Experimental Details

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 illustrated in Figure 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-glucose residues [28]. 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 [29]. The secondary structure of xanthan gum has been shown to consist of a five-fold helical structure [30]. Most researchers [31,32] suggest a right-handed double helical state for native xanthan gum molecule which is stabilized by intermolecular and intramolecular hydrogen bonds [33].

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 [34]. The approximate weight average molecular weight of our xanthan gum is estimated to be 2×10^6 g/mol [35], even though its values reported in the literature are very diverse [36].

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, xathan 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 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.

Rheological Measurements

The steady shear flow properties of prepared xanthan gum solutions were measured 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 12.5 mm and a gap size of 2.0 mm. All measurements were performed 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.

The reasons why a parallel-plate configuration was chosen 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 [37] 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 over a shear rate range tested 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 measurements were made at least three times for each test and highly reproducible data were obtained within the coefficients of variation of ±5 % in all cases.

Results and Discussion

Yield Stress and Flow Curves

Figure 2 shows the flow curves (representation of the shear stress as a function of shear rate) for aqueous xanthan gum solutions with different concentrations. As is obvious from Figure 2, for all xanthan gum solutions, the shear stress tends to level off and approach a limiting constant value as a decrease in shear rate towards zero at low range of shear rates, indicating that these polymer systems exhibit a finite magnitude of yield stress. It is also clearly observed that the larger values of yield stress are obtained with increasing polymer concentration. Moreover, the shear rate dependence of the shear stress is not so strong as that of most other ordinary water-soluble polymer solutions over a whole range of shear rates tested.

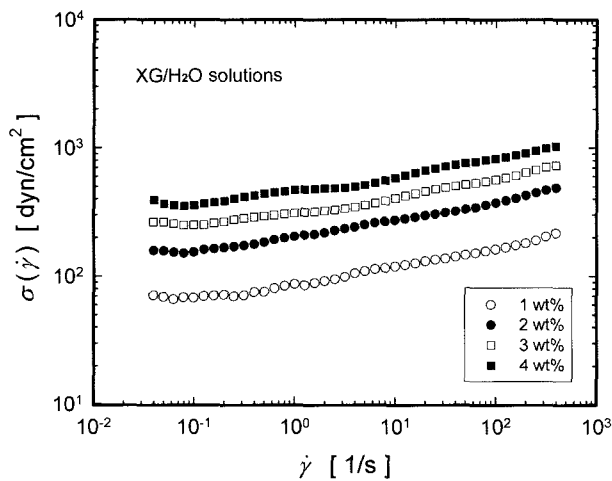These results are more dramatically manifested when plotting

Figure 2. Flow curves for aqueous xanthan gum solutions of different concentrations.
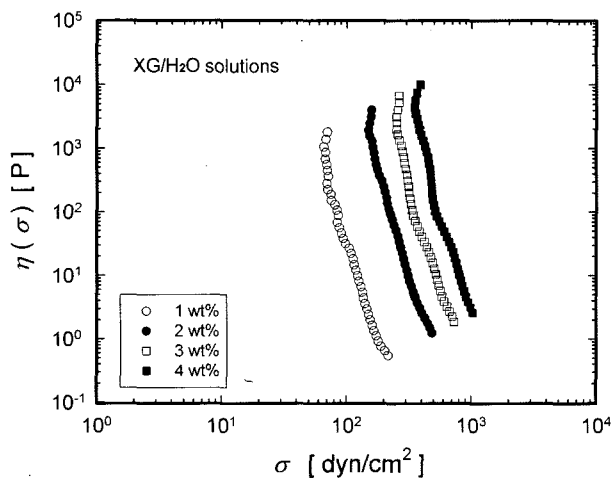
the steady shear viscosity as a function of shear stress rather than shear rate, as demonstrated in Figure 3. Two distinctive regions are clearly seen for each xanthan gum solution : (1) the existing region of a yield stress reflected by a viscosity that continues to rise at relatively lower range of shear stresses; and (2) the shear-thinning region where the viscosity is substantially decreased with increasing shear stress. Furthermore, these flow curves are shifted to the right side as an increase in polymer concentration, indicating an increase in yield stress. These characteristics are quite different from the typical flow behavior of most other ordinary polymer solutions [38].

The appearance of a yield stress for xanthan gum solutions may originate from the fact that a large number of hydrogen bonds in the helix structure result in a stable configuration that can exhibit a resistance to flow [39]. Only when a sufficient magnitude of shear stress (larger than a yield stress) is applied, this structure becomes broken down. Subsequently, orientation of the polymer chains takes place, resulting in a shear-thinning flow behavior at higher shear rates in a similar manner to that encountered in ordinary polymer solutions.

Our findings are in agreement with the previous results reported by Marcotte *et al.* [26] who mentioned that the appearance of a yield stress followed by a shear-thinning nature is a typical behavior of concentrated xanthan gum systems. These authors also suggested that this behavior may be caused by an intermolecular association due to acetate residues.

Steady Shear Viscosity

Figure 4 shows the shear rate dependence of the steady shear viscosity for aqueous xanthan gum solutions with different concentrations. As is clear from Figure 4, while the Newtonian viscosity region is not observed at low shear rates, the steady shear viscosity of all solutions is sharply decreased as an increase in shear rate, demonstrating that
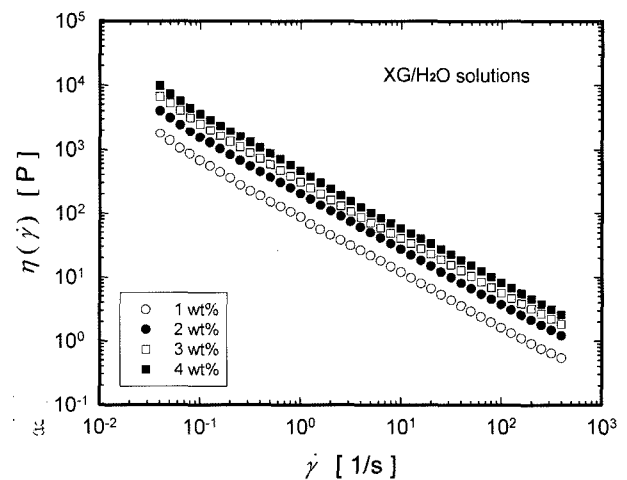

Figure 3. Steady shear viscosity as a function of shear stress for aqueous xanthan gum solutions of different concentrations.

Figure 4. Shear rate dependence of steady shear viscosity for aqueous xanthan gum solutions of different concentrations.
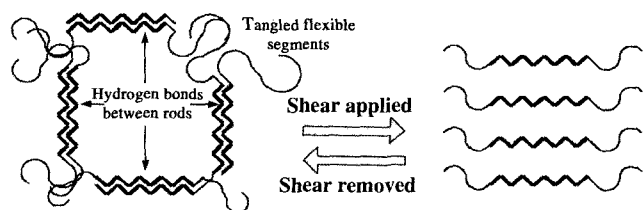
Figure 5. Schematic representation of the effect of shear on xanthan gum polymer network.

these systems exhibit a marked non-Newtonian shear-thinning behavior.

A shear-thinning flow behavior may be the most common rheological similarity between diverse fluid systems including polymer melts/solutions, suspensions, and emulsions. This behavior is generally explained to arise from chain orientation or alignment of micro-structure with the flow direction, thus reducing the local drag [39]. As the shear rate is further increased, the alignment of flow becomes more complete and consequently the shear viscosity is further decreased. The intermolecular interactions (particulary the entanglements) may be reduced due to a microstructural anisotropy resulting from the shear deformation.

A pronounced shear-thinning behavior of xanthan gum solutions may be interpreted by the conformational status of the polymer molecules [40]. As schematically depicted in Figure 5(a), the large molecules of xanthan gum form aggregates through hydrogen bonding and polymer entanglement, resulting in a high shear viscosity at low shear rates or at rest. However, under the influence of high shear rates, the steady shear viscosity of xanthan gum solutions is decreased due to the disentanglement of the polymer network and the partial alignment of the individual macromolecules in the direction of the shear flow, as schematically drawn in Figure 5(b), resulting in a low shear viscosity at high shear rate region. Upon the removal of shear, the network structure reforms rapidly and hence the viscosity is recovered almost instantaneously.

This rheological feature enhances sensory qualities in food, pharmaceutical, and cosmetic products and guarantees a high degree of mixability, pumpability, and pourability during their processing and/or actual use [35]. These are just inevitable reasons why xanthan gum is widely used as a suitable thickener or an efficient stabilizer for suspensions and emulsions in many industries [4].

The shear rate dependence of steady shear viscosity seems to be well described by a well-known power-law (or Ostwald-de Waele) equation expressed as follows:

$$\eta(\dot{\gamma}) = K\dot{\gamma}^{n-1} \tag{1}$$

where $\eta(\dot{\gamma})$ is the shear rate-dependent viscosity, $\dot{\gamma}$ is the shear rate, K is the consistency index, and n is the flow

Table 1. Calculated power law parameters for aqueous xanthan gum solutions of different concentrations

Concentration	K (P·s^{n-1})	n (−)	R^2
1 wt%	85.5159	0.1401	0.9997
2 wt%	201.430	0.1334	0.9999
3 wt%	310.382	0.1299	0.9996
4 wt%	455.168	0.1275	0.9996

behavior index. As n tends to 1, the shear-thinning nature becomes less pronounced, so that a Newtonian behavior is achieved when n equals to 1.

The values of the power-law parameters obtained by a linear regression analysis along with those of the determination coefficients are tabulated in Table 1. As expected, the fits of the experimentally measured data (Figure 4) to the power-law equation represent quite well the viscous behavior of all concentrated xanthan gum solutions. It is also clear that, while the consistency index is increased with concentration as a consequence of the expected development of a stronger structure, the flow behavior index is gradually decreased with concentration, indicating a progressive increase in shear-thinning nature.

Furthermore, it should be pointed out that the different values of the flow behavior index are responsible for the fact that the influence of xanthan gum concentration on steady shear viscosity is also dependent on the shear rate, as can be seen in Figure 4. It is already known that, in concentrated polysaccharide systems, an increase in viscosity with concentration is less pronounced as the shear rate is increased [28]. This feature is necessary for their practical applications because marked differences in viscosity must be required over a different range of shear rates associated with their performance as a stabilizer or a thickener with several operations such as mixing, pumping, and pouring [7].

Applicability of Viscoplastic Flow Models

The yield stress of a material is defined as the minimum shear stress that must be applied to a material to induce flow. The physical meaning and the real existence of a true yield stress has long been a subject of serious debate among rheological scientists [41-50] on the grounds that any material will flow provided that a sufficiently long time is given. Barnes and Walters [41] initiated this debate in their article titled "The yield stress myth?" in which they stated that "if a material flows at high shear stresses, it will also flow, however slowly, at low stresses". This statement means that there exists no real yield stress since, even at an infinitesimally small stress, any material will flow if the time scale of the observation is sufficiently long. Nevertheless, the engineering reality of a yield stress [42], which depends on the time scale of the measurement, is a useful as well as a desirable concept because there are many industrial and practical problems that can smoothly be solved with considering a yield stress

of a raw material or a final product.

It is true that, given a sufficient amount of time within which to initiate flow, most materials would not exhibit a yield stress from a purely theoretical point of view. Because of the dependence of all material processes on strict time limitations, however, the concept of a yield stress is helpful for process design/control and modeling. In fact, many material processes (pipeline transport of raw materials, for a typical example) generally involve a residence time which is significantly shorter than that required to support the theoretical view-point.

The determination of a yield stress in any material system is difficult. When dealing with a yield stress as a true material parameter, two key-points should be kept in mind; the obtained yield stress value is usually dependent not only on the accuracy of the instrument/equipment but also on the time scale of the observation. Therefore, there exists no generally accepted standard procedure to determine a yield stress value. Many techniques have been devised for the measurement of a yield stress during the past several decades [51-60]. One of the most common techniques is an indirect measurement which involves an extrapolation of the shear stress-shear rate data obtained from conventional rheometers to zero shear rate. This can be done either without or with the use of a rheological model. The extrapolated yield stress relies on the accurate experimental data at low shear rate range.

In this study, several inelastic-viscoplastic flow models including a yield stress parameter were employed to make a quantitative evaluation of the steady shear flow behavior of concentrated xanthan gum solutions, and then the applicability of these models was also examined in detail.

A general viscoplastic flow model having a yield stress term may be expressed by the following form:

$$\sigma^{n_1} = \sigma_y^{n_1} + k\dot{\gamma}^{n_2} \qquad (2)$$

where σ is the shear stress, σ_y is the yield stress, $\dot{\gamma}$ is the shear rate; n_1 and n_2 are material parameters related to the material's flow behavior, and consequently, each flow model is determined according to the conditions of n_1 and n_2.

Table 2 summarizes the viscoplastic flow models [61-65]

adopted in this study and their flow characteristics. Here σ_y is the yield stress of each model and k is the consistency index related to a high-shear limiting viscosity, η_∞, as the shear rate is increased towards infinity. n is the flow behavior index; a material parameter that determines the shear-thinning nature of a material. In order that the models summarized in Table 2 could predict a shear-thinning behavior, both n_1 and n_2 must be a positive value and n_1 should be larger than n_2 or equivalent to n_2.

In this study, in order to determine the material parameters of each model, a linear regression analysis was used for both the Bingham and Casson models, while a nonlinear regression analysis adopting the Levenberg-Marquardt method was used for the Herschel-Bulkley, Mizrahi-Berk, and Heinz-Casson models.

The values of the material parameters calculated from the viscoplastic flow models along with those of the determination coefficients are reported in Table 3. As expected, both the yield stress and consistency index values are progressively increased as an increase in xanthan gum concentration for all flow models. The value of a flow behavior index provides a reference for the assessment of a shear-thinning nature; as this value becomes closer to zero, a more pronounced shear-thinning behavior is observed. As is clear from Table 3, all of the xanthan gum solutions exhibit a marked shear-thinning behavior regardless of their concentrations.

The Bingham model gives a poor ability for predicting the flow behavior of concentrated xanthan gum solutions because this model follows a Newtonian behavior once the yield stress is exceeded. Judging from the values of the determination coefficients, the Casson model could not show a good applicability, either. This is due to an unreality of the assumptions introduced when this model was theoretically developed. One of the important assumptions of the Casson model was that solid particles form a one-dimensional chain-like structure in a two-phase suspension when dispersed in Newtonian media, disregarding other configurations or interactions. However, the large molecules of xanthan gum in aqueous media are believed to form a three-dimensional network structure (aggregates) based on intermolecular hydrogen bonding and polymer entanglement to the extent allowed by a mutual

Table 2. Viscoplastic flow models used in this study and their characteristics

Flow model	Equation	n_1	n_2	η_∞	Shear-thinning condition
Bingham [61]	$\sigma = \sigma_y + k\dot{\gamma}$	1	1	k	-
Casson [62]	$\sigma^{1/2} = \sigma_y^{1/2} + k\dot{\gamma}^{1/2}$	0.5	0.5	k^2	-
Herschel-Bulkley [63]	$\sigma = \sigma_y + k\dot{\gamma}^n$	1	n	0; k, if $n = 1$	$0 < n \leq 1$
Mizrahi-Berk [64]	$\sigma^{1/2} = \sigma_y^{1/2} + k\dot{\gamma}^n$	0.5	n	0; k^2, if $n = 0.5$	$0 < n \leq 0.5$
Heinz-Casson [65]	$\sigma^n = \sigma_y^n + k\dot{\gamma}^n$	n	n	$k^{1/n}$	$0 < n$

Table 3. Calculated flow model parameters for aqueous xanthan gum solutions with different concentrations

Flow model	Concentration	σ_y (dyn/cm^2)	k (P·s^{n-1})	n (−)	R^2
Bingham	1 wt%	83.05	0.497	-	0.6184
	2 wt%	193.8	1.128	-	0.6172
	3 wt%	306.2	1.631	-	0.6581
	4 wt%	466.0	2.252	-	0.6243
Casson	1 wt%	75.73	0.373	-	0.8450
	2 wt%	176.9	0.558	-	0.8452
	3 wt%	279.8	0.653	-	0.8823
	4 wt%	408.6	0.763	-	0.8546
Herschel-Bulkley	1 wt%	43.76	41.9	0.230	0.9889
	2 wt%	94.27	106.6	0.213	0.9950
	3 wt%	202.7	105.3	0.273	0.9923
	4 wt%	266.2	185.8	0.239	0.9879
Mizrahi-Berk	1 wt%	36.58	3.220	0.162	0.9882
	2 wt%	77.40	5.386	0.148	0.9950
	3 wt%	185.7	3.949	0.208	0.9915
	4 wt%	236.0	5.925	0.176	0.9875
Heinz-Casson	1 wt%	28.78	0.182	0.109	0.9876
	2 wt%	58.06	0.186	0.096	0.9950
	3 wt%	170.7	0.239	0.164	0.9909
	4 wt%	205.4	0.216	0.130	0.9871

repulsion of the negatively charged side chains.

Our result is not in agreement with the previous one reported by Garcia-Ochoa and Casas [66] who stated that the Casson model describes well the rheological behavior of xanthan gum solutions. This difference in observations is probably due to a sensitivity of the rheometrical instrument, a range of shear rates tested, and the concentration regimes.

On the other hand, the Herschel-Bulkley, Mizrahi-Berk, and Heinz-Casson models give an excellent ability to describe the flow behavior of concentrated xanthan gum solutions. All of these three models have the values of determination coefficients greater than 0.98 and show a clear tendency that the yield stress values are increased as an increase in xanthan gum concentration.

By the way, it should be considered here that, even though similar values of the determination coefficients are obtained for different flow models, there exists a possibility for each model to provide a dissimilar ability to predict the flow behavior of a material [67]. In order to confirm this matter, all models used in this study were directly applied to the experimentally measured shear stress-shear rate data for all xanthan gum solutions. The obtained results for 2 wt% and 3 wt% xanthan gum solutions are displayed in Figure 6.

Both the Bingham and Casson model show a relatively large discrepancy between the obtained results and the experimentally measured data over an entire range of shear rates tested, and moreover, represent a larger yield stress than experimentally measured.
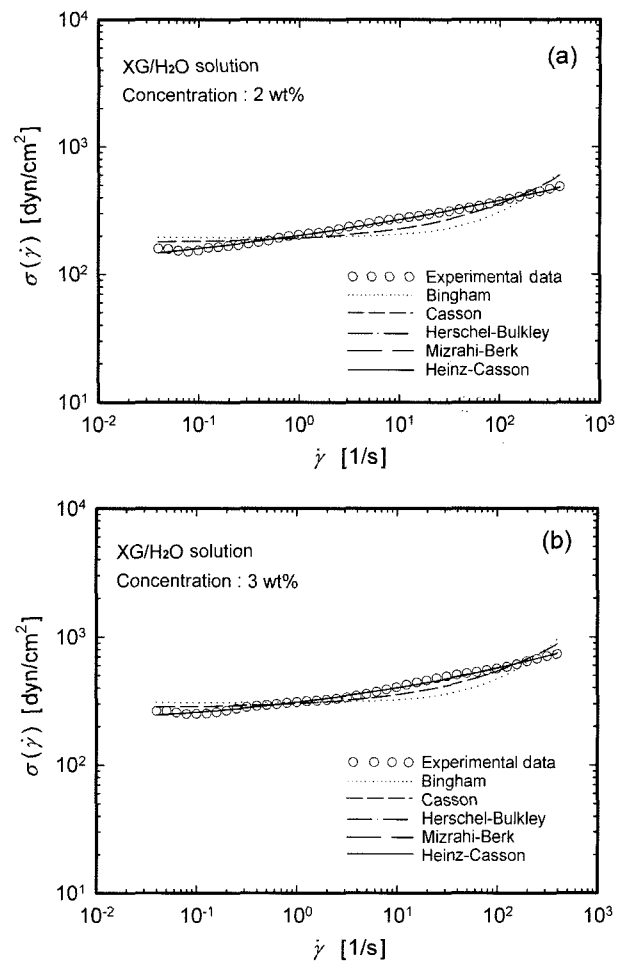

Figure 6. Applicability of viscoplastic flow models to (a) 2 wt% and (b) 3 wt% aqueous xanthan gum solutions.

On the other hand, the Herschel-Bulkley, Mizrahi-Berk, and Heinz-Casson models are all in good agreement with the experimentally measured data over a whole range of shear rates tested. Furthermore, no discrepancy is observed between these three models, indicating that they have almost an equivalent ability to predict the flow behavior of concentrated xanthan gum solutions. These trends are also observed for 1 wt% as well as 4 wt% xanthan gum solutions whose results are not shown here on account of a space limitation.

From these results, it can be concluded that these three (Herschel-Bulkley, Mizrahi-Berk, and Heinz-Casson) models are regarded as the most useful relationships to quantitatively evaluate the steady shear flow behavior of concentrated xanthan gum solutions.

Primary Normal Stress Difference

The primary normal stress difference in steady shear flow fields is an important material function that allows the evaluation of the elastic flow properties of a material. This material function is defined as follows:
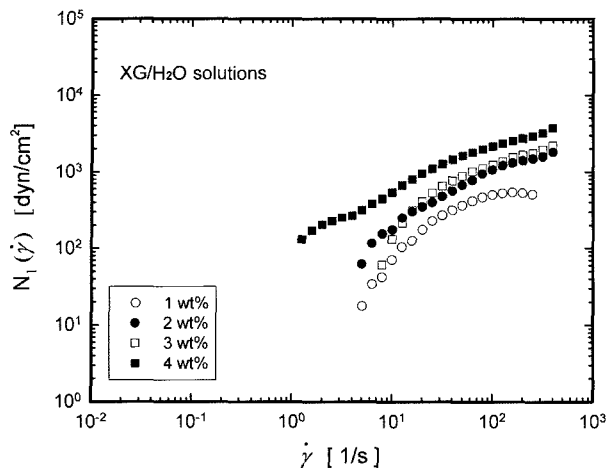
Figure 7. Shear rate dependence of primary normal stress difference for aqueous xanthan gum solutions of different concentrations.

Figure 8. Primary normal stress difference as a function of shear stress for aqueous xanthan gum solutions of different concentrations.

$$N_1(\dot{\gamma}) = \sigma_{11} - \sigma_{22} = \Psi_1(\dot{\gamma})\dot{\gamma}^2 \qquad (3)$$

where $N_1(\dot{\gamma}) = \sigma_{11} - \sigma_{22}$ is the primary normal stress difference and $\Psi_1(\dot{\gamma})$ is the primary normal stress coefficient.

In general, when making a rheological measurement by means of a conventional rheometer, most viscoelastic liquids do not exhibit measurable normal force except at high shear rates [68]. In our experiments, the primary normal stress differences of all xanthan gum solutions showed negative values at low shear rates, indicating that the inertia effects are dominant to the elastic properties. However, it was possible to report here the elastic behavior of concentrated xanthan gum solutions because reliable data could be obtained at relatively higher range of shear rates ($\dot{\gamma} > 1$ 1/s) and these data were confirmed to have a high reproducibility through our several repeated measurements.

Figure 7 shows the shear rate dependence of the primary normal stress difference for aqueous xanthan gum solutions with different concentrations. It is clear that these systems exhibit quite important elastic flow properties in steady shear flow fields. As expected, the primary normal stress difference is gradually increased as an increase in xanthan gum concentration in a given shear rate range. However, these elastic properties are comparable with those shown by ordinary polymer solutions, such as polyethylene oxide or polyisobutylene, which exhibit a linearly increasing trend of the primary normal stress difference at high shear rates [69].

An elastic behavior of concentrated xanthan gum solutions is more interestingly observed when plotting the primary normal stress difference as a function of shear stress rather than shear rate, as illustrated in Figure 8. These elastic flow properties of xanthan gum solutions may be quite significant for many industrial applications such as food, pharmaceutical, and cosmetic manufacturing processes. For example, several
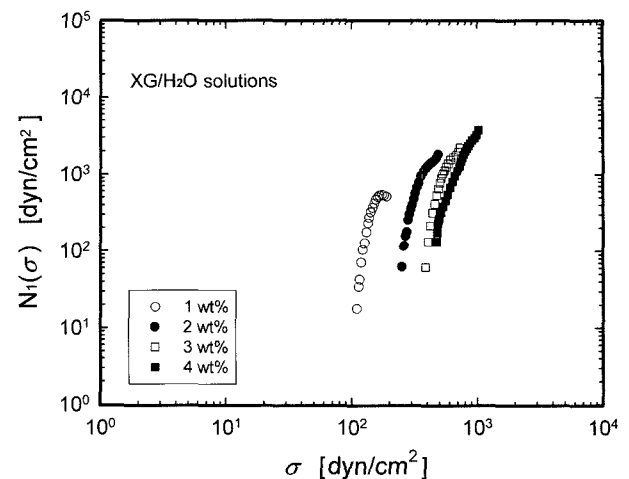
applications of xanthan gum in foods (mayonnaises, salad dressings, syrups, sauces, and dairy products), pharmaceuticals (controlled-release drug-delivery agents), and cosmetics (shampoos, lotions, and creams) are mainly based on the elastic properties of this biopolymer. It was therefore considered to be necessary to evaluate the elastic behavior of concentrated xanthan gum solutions in the steady shear flow fields.

Conclusions

The objective of the present study is to systematically investigate the nonlinear rheological behavior of concentrated xanthan gum systems in steady shear flow fields. Using a strain-controlled rheometer, the steady shear flow properties of aqueous xanthan gum solutions with different concentrations were measured over a wide range of shear rates.

In this article, both the shear rate and concentration dependencies of steady shear flow behavior were reported from the experimentally obtained data. In particular, the viscous behavior was quantitatively discussed using a well-known power law type flow equation with a special emphasis on its importance in industrial processing and actual usage. In addition, several inelastic-viscoplastic flow models including a yield stress parameter were employed to make a quantitative evaluation of the steady shear flow behavior, and then the applicability of these models was also examined in detail. Finally, the elastic nature was explained with a brief comment on its practical significance. Main results obtained from this study can be summarized as follows:

1. Concentrated xanthan gum solutions exhibit a finite magnitude of yield stress. The appearance of a yield stress may come from the fact that a large number of hydrogen bonds in the helix structure result in a stable configuration that can show a resistance to flow.

2. Concentrated xanthan gum solutions show a marked non-Newtonian shear-thinning behavior which is well described by a power law flow equation and may be interpreted by the conformational status of the polymer molecules under the influence of shear flow. This rheological feature enhances sensory qualities in food, pharmaceutical, and cosmetic products and guarantees a high degree of mixability, pumpability, and pourability during their processing and/or actual use.

3. The Herschel-Bulkley, Mizrahi-Berk, and Heinz-Casson models are all applicable and have an equivalent ability to describe the steady shear flow behavior of concentrated xanthan gum solutions, whereas both the Bingham and Casson models do not give a good applicability.

4. Concentrated xanthan gum solutions exhibit a quite important elastic flow behavior which acts as a significant factor for many industrial applications such as food, pharmaceutical, and cosmetic manufacturing processes.

Acknowledgement

References

1. A. Margaritis and J. E. Zajic, *Biotechnol. Bioeng.*, **20**, 939 (1978).
2. K. S. Kang and D. J. Pettit in "Industrial Gums", 3rd ed. (R. L. Whistler and J. N. Be Miller Eds.), pp.341-398, Academic Press, New York, USA, 1993.
3. H. Schott, "Remington's Pharmaceutical Sciences", 18th ed., p.1308, Mack Publishing, Easton, PA, USA, 1990.
4. F. Garcia-Ochoa, V. E. Santos, J. A. Casas, and E. Gomez, *Biotechnol. Adv.*, **18**, 549 (2000).
5. G. Gallino, M. Migliori, and B. de Cindio, *Rheol. Acta*, **40**, 196 (2001).
6. E. Pelletier, C. Viebke, J. Meadows, and P. A. Williams, *Biopolymers*, **59**, 339 (2001).
7. J. Moreno, M. A. Vargas, J. M. Madiedo, J. Munoz, J. Rivas, and M. G. Guerrero, *Biotechnol. Bioeng.*, **67**, 283 (2000).
8. F. Garcia-Ochoa, V. E. Santos, and A. Alcon, *Chem. Biochem. Eng. J.*, **11**, 69 (1997).
9. J. A. Casas, V. E. Santos, and F. Garcia-Ochoa, *Enzyme Microbial Technol.*, **26**, 282 (2000).
10. F. Garcia-Ochoa and E. Gomez, *Biochem. Eng. J.*, **1**, 1 (1998).
11. P. J. Whitcomb and C. W. Macosko, *J. Rheol.*, **22**, 493 (1978).
12. G. B. Thurston, *J. Non-Newt. Fluid Mech.*, **9**, 57 (1981).
13. G. B. Thurston and G. A. Pope, *J. Non-Newt. Fluid Mech.*, **9**, 69 (1981).
14. S. B. Ross-Murphy, V. J. Morris, and E. R. Morris, *Faraday Symp. Chem. Soc.*, **18**, 115 (1983).
15. R. K. Richardson and S. B. Ross-Murphy, *Intern. J. Biol. Macromol.*, **9**, 257 (1987).
16. G. Cuvelier and B. Launay, *Carbohydr. Polym.*, **6**, 321 (1986).
17. W. E. Rochefort and S. Middleman, *J. Rheol.*, **31**, 337 (1987).
18. K. C. Tam and C. Tiu, *J. Rheol.*, **33**, 257 (1989).
19. K. C. Tam and C. Tiu, *J. Non-Newt. Fluid Mech.*, **46**, 275 (1993).
20. A. K. Podolsak, C. Tiu, T. Saeki, and H. Usui, *Polym. Intern.*, **40**, 155 (1996).
21. A. Giboreau, G. Cuvelier, and B. Launay, *J. Texture Studies*, **25**, 119 (1994).
22. T. Yoshida, M. Takahashi, T. Hatakeyama, and H. Hatakeyama, *Polymer*, **39**, 1119 (1998).
23. J. Fujiwara, T. Iwanami, M. Takahashi, R. Tanaka, T. Hatakeyama, and H. Hatakeyama, *Thermochimica Acta*, **352/353**, 241 (2000).
24. T. Iseki, M. Takahashi, H. Hattori, T. Hatakeyama, and H. Hatakeyama, *Food Hydrocolloids*, **15**, 503 (2001).
25. B. Urlacher and O. Noble in "Thickening and Gelling Agents for Food : Xanthan Gums", (A. Imeson Eds.), pp.284-312, Blackie Academic & Professional, London, UK, 1997.
26. M. Marcotte, A. R. Taherian-Hoshahili, and H. S. Ramaswamy, *Food Res. Intern.*, **34**, 695 (2001).
27. T. Ahmed and H. S. Ramaswamy, *Food Hydrocolloids*, **18**, 367 (2004).
28. R. Lapasin and S. Pricl, "Rheology of Industrial Polysaccharides : Theory and Applications", Aspen Publishers, Gaithersburg, MD, USA, 1999.
29. B. T. Stokke, B. E. Christensen, and O. Smidsrod in "Polysaccharides : Structural Diversity and Functional Versatility - Macromolecular Properties of Xanthan", (S. Dumitriu Eds.), pp.433-472, Marcel Dekker, New York, USA, 1998.
30. R. Moorhouse, M. D. Walkinshaw, and S. Arnott, *Amer. Chem. Soc. Symp. Ser.*, **45**, 90 (1977).
31. G. Holzwarth and E. B. Prestridge, *Science*, **197**, 757 (1977).
32. T. A. Camesano and K. J. Wilkinson, *Biomacromolecules*, **2**, 1184 (2001).
33. K. Ogawa and T. Yui in "Polysaccharides : Structural Diversity and Functional Versatility-X-ray Diffraction Study of Polysaccharides", (S. Dumitriu Eds.), pp.101-130, Marcel Dekker, New York, USA, 1998.
34. K. Born, V. Langendorff, and P. Boulenguer, "Biopolymers", Vol. 5, pp.259-291, Wiley-Interscience, New York, USA, 2001.
35. B. Katzbauer, *Polym. Degrad. Stability*, **59**, 81 (1998).
36. M. A. Zirnsak, D. V. Boger, and V. Tirtaatmadja, *J. Rheol.*,

43, 627 (1999).

37. G. S. Chang, J. S. Koo, and K. W. Song, *Korea-Australia Rheol. J.*, **15**, 55 (2003).

38. K. W. Song, T. H. Kim, G. S. Chang, S. K. An, J. O. Lee, and C. H. Lee, *J. Korean Pharm. Sci.*, **29**, 193 (1999).

39. G. Harrison, G. V. Franks, V. Tirtaatmadja, and D. V. Boger, *Korea-Australia Rheol. J.*, **11**, 197 (1999).

40. T. Moschakis, B. S. Murray, and E. Dickinson, *J. Colloid Interf. Sci.*, **284**, 714 (2005).

41. H. A. Barnes and K. Walters, *Rheol. Acta*, **24**, 323 (1985).

42. J. P. Hartnett and R. Y. Z. Hu, *J. Rheol.*, **33**, 671 (1989).

43. G. Astarita, *J. Rheol.*, **34**, 275 (1990).

44. I. D. Evans, *J. Rheol.*, **36**, 1313 (1992).

45. G. Astarita, *J. Rheol.*, **36**, 1317 (1992).

46. J. Schurz, *J. Rheol.*, **36**, 1319 (1992).

47. H. A. Barnes, *J. Non-Newt. Fluid Mech.*, **81**, 133 (1999).

48. C. Balan, *Appl. Rheol.*, **9**, 58 (1999).

49. H. A. Barnes, *Appl. Rheol.*, **9**, 262 (1999).

50. D. Hadjistamov, *Appl. Rheol.*, **13**, 209 (2003).

51. Q. D. Nguyen and D. V. Boger, *Ann. Rev. Fluid Mech.*, **24**, 47 (1992).

52. P. V. Liddel and D. V. Boger, *J. Non-Newt. Fluid Mech.*, **63**, 235 (1996).

53. M. A. Rao and J. F. Steffe, *Food Technol.*, **51**, 50 (1997).

54. C. W. Pernell, E. A. Foegeding, and C. R. Daubert, *J. Food Sci.*, **65**, 110 (2000).

55. P. H. Huh, G. S. Chang, J. O. Lee, K. W. Song, and C. H. Lee, *Theor. Appl. Rheol.*, **4**, 45 (2000).

56. H. A. Barnes and Q. D. Nguyen, *J. Non-Newt. Fluid Mech.*, **98**, 1 (2001).

57. G. P. Roberts, H. A. Barnes, and C. Carew, *Chem. Eng. Sci.*, **56**, 5617 (2001).

58. P. O. Brunn and H. Asoud, *Rheol. Acta*, **41**, 524 (2002).

59. J. R. Stokes and J. H. Telford, *J. Non-Newt. Fluid Mech.*, **124**, 137 (2004).

60. P. H. T. Uhlherr, J. Guo, C. Tiu, X. M. Zhang, J. Z. Q. Zhou, and T. N. Fang, *J. Non-Newt. Fluid Mech.*, **125**, 101 (2005).

61. E. C. Bingham, "Fluidity and Plasticity", pp.215-218, McGraw-Hill, New York, USA, 1922.

62. N. Casson in "Rheology of Disperse Systems" (C. C. Mill Eds.), p.84, Pergamon Press, London, UK, 1959.

63. W. H. Herschel and R. Bulkley, *Kolloid Zeit.*, **39**, 291 (1926).

64. S. Mizrahi and Z. Berk, *J. Texture Studies*, **3**, 69 (1972).

65. W. Heinz, *Material Prüfung*, **1**, 311 (1959).

66. J. A. Garcia-Ochoa and J. A. Casas, *Chem. Eng. J.*, **53**, B41 (1994).

67. K. W. Song and G. S. Chang, *Korean J. Rheol.*, **11**, 143 (1999).

68. P. J. Carreau, D. C. R. De Kee, and R. P. Chhabra, "Rheology of Polymeric Systems : Principles and Applications", pp.84-102, Hanser/Gardner Publications, Cincinnati, OH, USA, 1997.

69. M. E. Ortiz, D. C. R. De Kee, and P. J. Careau, *J. Rheol.*, **38**, 519 (1994).