

주기적 진동전단 유동장에서 잔탄검 농후계의 선형 및 비선형 점탄성 거동

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Linear and nonlinear viscoelastic behavior of concentrated Xanthan Gum solutions in periodically oscillatory shear flow fields

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Introduction

Xanthan gum is a high molecular weight extracellular polysaccharide produced by the bacterium *Xanthomonas campestris*. Xanthan gum is a non-gelling biopolymer that exists in aqueous media with an ordered rigid chain conformation [1] : it is able to form highly viscous solutions even at low concentrations whose stability to temperature and pH is responsible for its great acceptance in many industries [2,3].

From our previous study [4] that dealt with a nonlinear rheological behavior in steady shear flow fields, it was found that : (a) concentrated xanthan gum solutions exhibit a finite magnitude of yield stress and show a marked non-Newtonian shear-thinning flow behavior; (b) the Herschel-Bulkley, Mizrahi-Berk, and Heinz-Casson models are applicable to describe the steady shear flow behavior of concentrated xanthan gum solutions; and (c) these systems exhibit a quite important elastic nature. These informations may be helpful in various industrial manufacturing processes in which xanthan gum is used as a raw material or an additive agent into other systems.

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

Experimental section

The xanthan gum sample used in this study is a commercially available product supplied from the Sigma-Aldrich Corporation (St. Louis, MO, USA). The weight average molecular weight of our xanthan gum is approximately estimated to be 2×10^6 g/mol [5,6], even though its values reported in the literature are very diverse [7].

Xanthan gum solutions with concentrations of 1, 2, 3, and 4 wt% were prepared by slowly adding the required amount of polymer powder weighed using an electronic balance 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 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.

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

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

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. In all measurements, a fresh sample solution was used and rested for 20 min after loading to allow material relaxation and temperature equilibration.

Results and discussion

Fig. 1 shows the strain dependence of the storage modulus, $G'(\gamma_0)$, at a fixed angular frequency of 1.0 rad/s for aqueous xanthan gum solutions with different concentrations. A linear region is clearly observed for all xanthan gum solutions at relatively smaller strain amplitude range ($\gamma_0 < 10$ %) in which the storage modulus exhibits a constant value regardless of strain amplitude. However, a nonlinear behavior occurs at strain amplitude range larger than 10 % where the storage modulus is slightly decreased up to a certain strain amplitude ($\gamma_0 \approx 100$ %), beyond which a sharp decrease in storage modulus is observed with increasing strain

amplitude, indicating a marked strain-thinning feature. A strain-thinning behavior of storage modulus for concentrated xanthan gum solutions at large strain amplitudes may be interpreted by the destruction and formation of their internal structure responding to an externally imposed stimulus [8,9].

Fig. 2 shows the strain dependence of the loss modulus, $G''(\gamma_0)$, at a fixed angular frequency of 1.0 rad/s for aqueous xanthan gum solutions with different concentrations. A linear region is clearly observed for all xanthan gum solutions at strain amplitude range smaller than 80 % within which the loss modulus exhibits a constant value regardless of strain amplitude. However, an exceptional nonlinear behavior takes place at strain amplitude range larger than 80 % where the loss modulus is first increased up to a certain strain amplitude ($\gamma_0 \approx 150\%$), beyond which followed by a decrease in loss modulus with increasing strain amplitude, indicating a strain-overshoot phenomenon. An interesting strain-overshoot behavior of loss modulus for concentrated xanthan gum solutions at large strain amplitudes may arise from a unique structure of xanthan gum polymer chains. The structure of xanthan gum is based on a linear 1,4- β -D-glucose backbone with charged trisaccharide side chains on every second residue [10]. These long side chains can make relatively weaker structural complexes.

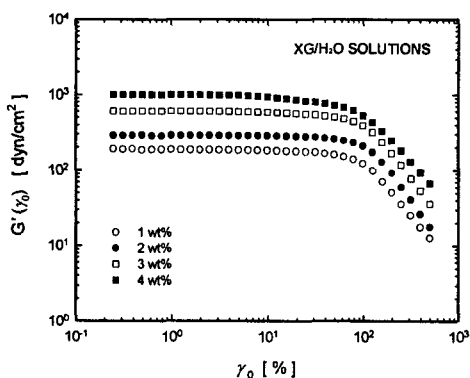


Fig. 1. Storage modulus as a function of strain amplitude for aqueous xanthan gum solutions with different concentrations.

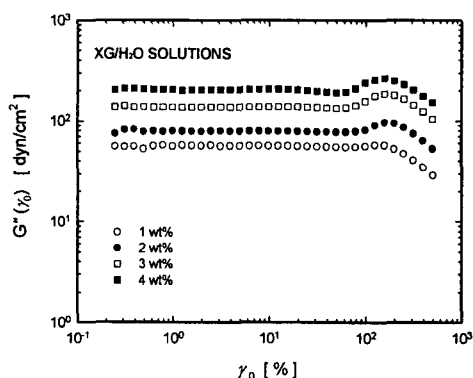


Fig. 2. Loss modulus as a function of strain amplitude for aqueous xanthan gum solutions with different concentrations.

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

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

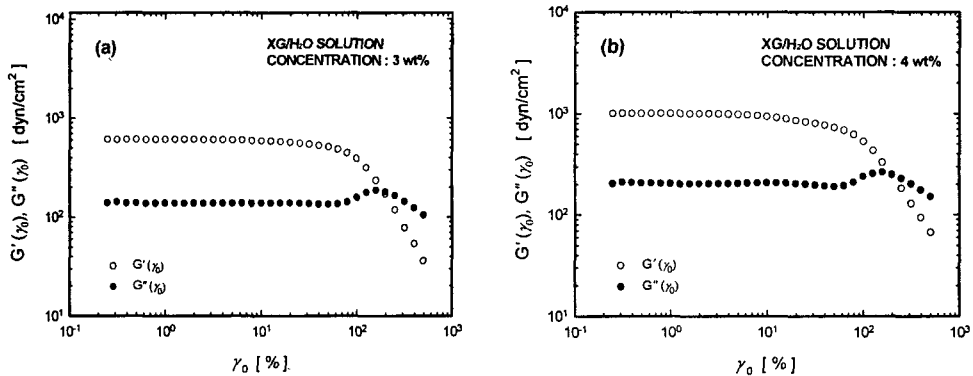


Fig. 3. Storage modulus and loss modulus as a function of strain amplitude for (a) 3 wt% and (b) 4 wt% aqueous xanthan gum solutions.

Fig. 4(a) and (b) show the storage modulus, $G'(\gamma_0)$, and loss modulus, $G''(\gamma_0)$, as a function of angular frequency for aqueous xanthan gum solutions with different concentrations of 1 and 2 wt%, respectively. An important point to note is that the storage modulus is always greater than the loss modulus over an entire range of angular frequencies studied, meaning that the linear viscoelastic behavior of these xanthan gum solutions is dominated by an elastic nature. In addition, both the storage and loss moduli are found to be only weak functions of angular frequency, indicating that a gel-like structure is present in these systems.

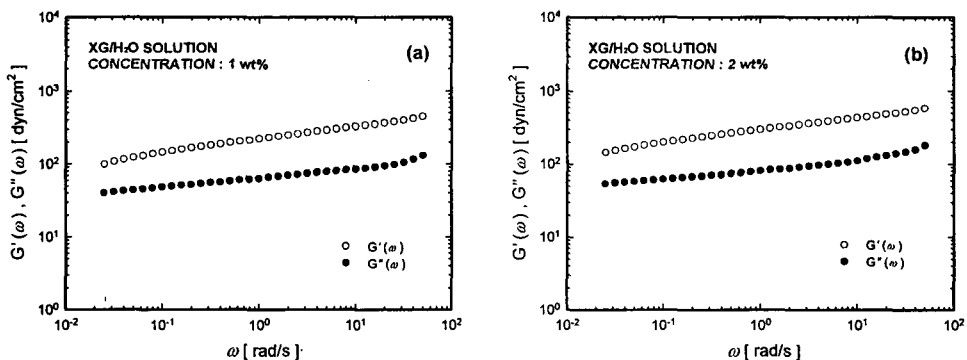


Fig. 4. Storage modulus and loss modulus as a function of angular frequency for (a) 1 wt% and (b) 2 wt% aqueous xanthan gum solutions.

Such a linear viscoelastic behavior observed in concentrated xanthan gum solutions may be attributed to the occurrence of attractive interactions between helices formed by rigid xanthan macromolecules, which can give rise to a weak three-dimensional network and a complex aggregation in solutions by means of physical entanglements and hydrogen bonding [11,12].

The frequency dependence of the storage modulus as well as the loss modulus may be quantitatively described by a power-law type relationship as follows [13,14] :

$$G'(\omega) = K' \omega^{n'} \quad (1)$$

$$G''(\omega) = K'' \omega^{n''} \quad (2)$$

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

The values of the power-law parameters obtained from a linear regression analysis along with those of the determination coefficients are reported in Table 1 and Table 2. As expected, the fits of the experimentally measured data to the power-law relations represent fairly well the linear viscoelastic behavior of all concentrated xanthan gum solutions.

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

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

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

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

It is clear that the values of K' are much larger than those of K'' for all xanthan gum solutions, demonstrating that an elastic behavior (storage modulus) is consistently superior to a viscous behavior (loss modulus). It is also worth noting that the values

of n' and n'' are gradually decreased as an increase in xanthan gum concentration, illustrating that the frequency dependence of the linear viscoelastic functions becomes weaker with increasing polymer concentration.

Finally it is believed to be necessary to mention that a linear viscoelastic behavior in small amplitude oscillatory shear flow fields enables a distinction to be made between strong and weak gels. It has been known that $n' > 0$ for a physical (weak) gel whereas $n' = 0$ for a chemical (strong) gel [15,16]. The n' value can therefore be used as a quantitative measure of the resemblance of a gel to a chemically cross-linked strong gel system. For concentrated xanthan gum solutions studied in this work, the n' values of 0.13 ~ 0.18 were obtained according to different polymer concentrations (Table 1). Hence, it can be concluded that these systems do not form a stable (strong) gel but exhibit a weak gel-like behavior.

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