잔탄 검 농후계의 정상유동 함수와 동적 점탄성 함수의 상관관계

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Correlations between viscometric functions (nonlinear behavior) and dynamic viscoelastic functions (linear behavior) for concentrated Xanthan Gum solutions

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Introduction

Rheological properties of viscoelastic materials can be characterized by well-defined classical rheometrical techniques performed in steady shear and/or oscillatory shear flow fields. It may be greatly desirable to interrelate material properties obtained from different types of experiments because some inevitable limitations in steady shear rheometry (for instance, wall slippage and sample migration) can be overcome by using a different type of experiment and then relating the obtained material properties back to the framework of interest.

Previous studies as to the rheology of polymeric systems have suggested that there exist some relationships between material functions describing the steady shear flow properties and those describing the dynamic viscoelastic properties. An important feature of these findings is that a nonlinear behavior in steady shear flow fields in which the deformations are large could be mathematically correlated with a linear behavior in small amplitude oscillatory shear (SAOS) flow fields in which the deformations are small.

Some of the most difficult material properties of viscoelastic materials to experimentally determine are viscometric functions or steady shear rheological properties. On the other hand, linear viscoelastic functions in SAOS flow fields can be measured relatively with ease and with a good reproducibility over a reasonably wide range of frequencies.

In this work, the correlations between steady shear flow (nonlinear behavior) and dynamic viscoelastic (linear behavior) properties for concentrated xanthan gum solutions were derived using the modified forms of the Cox-Merz rule and the DeWitt relation as well as comparing the primary normal stress coefficient with the corresponding dynamic data. In addition, the applicability of the Rutgers-Delaware relation was examined in detail.

Research background

DeWitt [1] derived theoretically the relationship between the steady shear viscosity, $\eta(\dot\gamma)$, and the dynamic viscosity, $\eta'(\omega)$, written as follows :

$$\eta(\dot\gamma) = \eta'(\omega) \quad \text{at} \quad \dot\gamma = \omega \tag{1}$$

where $\dot\gamma$ is the shear rate and ω is the angular frequency. However, nowadays it is a well-known fact that while $\eta(\dot\gamma)$ and $\eta'(\omega)$ coincide well with each other at low

shear rates and frequencies, $\eta'(\omega)$ decreases more rapidly than $\eta(\dot{\gamma})$ does at high shear rates and frequencies [2].

Cox and Merz [3] recommended a useful empirical relationship based on their work on polystyrene melts. This empiricism predicts that $\eta(\dot{\gamma})$ should be matched with the absolute value of the complex viscosity, $|\eta^*(\omega)|$, at equal values of shear rate and frequency, expressed as follows :

$$\eta(\dot{\gamma}) = |\eta^*(\omega)| \quad \text{at} \quad \dot{\gamma} = \omega \tag{2}$$

This relationship is sometimes called the 'Cox-Merz empirical rule' because it has been confirmed for most polymer systems by many authors. However, some studies showing deviations from the Cox-Merz rule have been published [4] especially for colloidal systems, physically crosslinked systems, and associating polymer systems.

Doraiswamy *et al.* [5] developed a non-linear rheological model to describe the steady shear flow behavior of yield stress fluids and proposed an apparent extension of the Cox-Merz rule applied to these fluids. This model predicts the superimposition of $\eta(\dot{\gamma})$ and $|\eta^*(\omega)|$ as functions of shear rate, $\dot{\gamma}$ and of an effective shear rate (that is, equal to the product of the strain amplitude, γ_m and angular frequency, ω), respectively.

$$\eta(\dot{\gamma}) = |\eta^*(\gamma_m \omega)| \tag{3}$$

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 [6], even though its values reported in the literature are very diverse [7].

In this work, xanthan gum solutions with concentrations of 1, 2, 3, and 4 wt% were prepared by slowly adding the required amount of polymer powder into a known volume of 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.

The rheological properties of prepared xanthan gum solution were measured using a strain-controlled rheometer [Advanced Rheometric Expansion System (ARES), Rheometric Scientific, 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 ℃. The steady shear flow properties were measured over a wide range of shear rates from 0.025 to 500 1/s with a logarithmically increasing scale. Nextly, the dynamic and complex viscosities in small and large amplitude oscillatory shear flow fields were measured over a wide range of angular frequencies from 0.025 to 100 rad/s with a logarithmically increasing scale at constant strain amplitudes of γ_0 = 5, 10, 20, 50, 100, 200, 300, 400, 500, 600 %.

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. 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.

Results and discussion

As shown in Fig. 1 and Fig. 2 together with Table 1, while all of the steady, complex and dynamic viscosities for aqueous xanthan gum solutions follow the power-law behavior with respect to shear rate and frequency, the experimentally obtained results demonstrate indicating that the complex viscosity is larger than the steady shear viscosity that the Cox-Merz rule is not applicable to these systems. However, as reported in Table 2 and Table 3, both the complex and dynamic viscosities are correlated successfully to the steady shear viscosity for concentrated xanthan gum solutions using a nonlinear modification of the Cox-Merz rule and the DeWitt relation expressed as the following forms, respectively [8,9].

$$| \eta^*(\omega)| = C \cdot \eta(\dot{\gamma})^{\alpha} \quad \text{at} \quad \dot{\gamma} = \omega \tag{4}$$

$$\eta'(\omega) = C' \cdot \eta(\dot{\gamma})^{\alpha'} \quad \text{at} \quad \dot{\gamma} = \omega \tag{5}$$

Table 1. Power law parameter for aqueous XG/H_2O solutions with various concentrations.

Concentration	$\eta(\dot{\gamma})$			$\eta'(\omega)$			$\|\eta^*(\omega)\|$		
	k $(P \cdot s^{n-1})$	n (-)	r^2	k' $(P \cdot s^{n'-1})$	n' (-)	r^2	k* $(P \cdot s^{n^*-1})$	n* (-)	r^2
1 wt%	85.516	0.1401	0.9997	65.28	0.1308	0.9999	261.3	0.2374	0.9993
2 wt%	201.430	0.1334	0.9999	80.27	0.1070	0.9999	336.8	0.2076	0.9997
3 wt%	310.382	0.1299	0.9996	113.6	0.0492	0.9998	622.4	0.1730	0.9998
4 wt%	455.168	0.1275	0.9996	163.3	0.0581	0.9998	901.9	0.1597	0.9998

Otherwise, the Rutgers-Delaware relation is greatly acceptable at large strain amplitudes, as illustrated in Fig. 3 and Fig. 4.

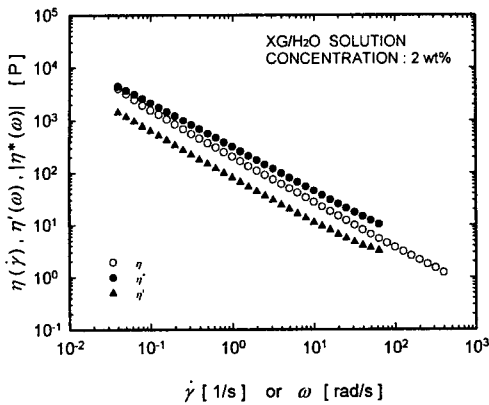In addition, as depicted in Fig. 5 and Fig. 6, the primary normal stress coefficient

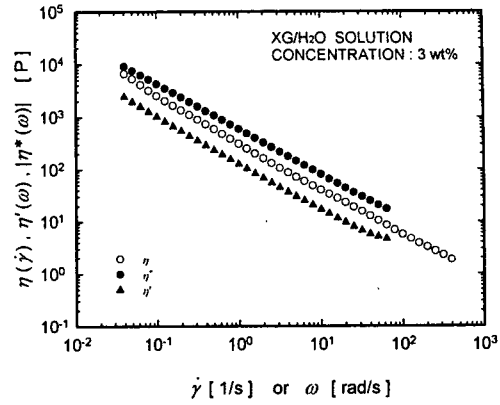Fig. 1. Comparison of $\eta(\dot{\gamma})$ with $|\eta^*(\omega)|$ and $\eta'(\omega)$ for 2 wt% XG/H2O solution.

Fig. 2. Comparison of $\eta(\dot{\gamma})$ with $|\eta^*(\omega)|$ and $\eta'(\omega)$ for 3 wt% XG/H2O solution.

Table. 2. Empirical correlation constants between $\eta(\dot{\gamma})$ and $\eta^*(\omega)$.

Concentration	C $(P^{1-\alpha})$	α (-)	r^2
1 wt%	5.005	0.8770	0.9991
2 wt%	2.293	0.9286	0.9998
3 wt%	2.838	0.9318	0.9997
4 wt%	2.099	0.9776	0.9998

Table. 3. Empirical correlation constants between $\eta(\dot{\gamma})$ and $\eta'(\omega)$.

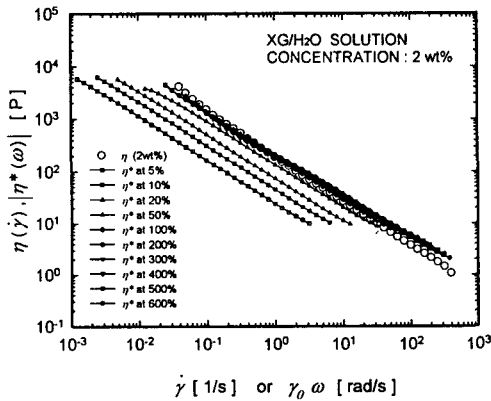| Concentration	C' $(P^{1-\alpha'})$	α' (-)	r^2
1 wt%	1.022	0.9438	0.9994
2 wt%	0.3990	1.001	0.9998
3 wt%	0.4106	0.9972	0.9998
4 wt%	0.3057	1.032	0.9998

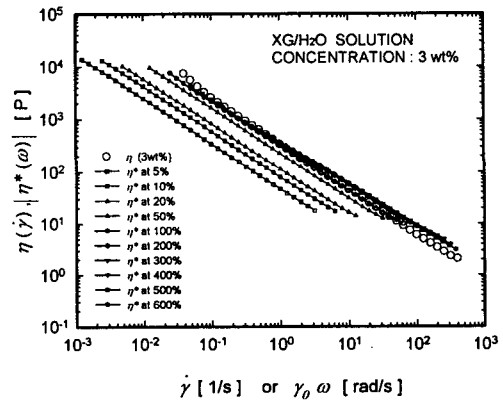Fig. 3. Applicability of the Rutgers-Delaware relation for 2 wt% XG/H2O solution.

Fig. 4. Applicablity of the Rutgers-Delaware relation for 3 wt% XG/H2O solution.

versus shear rate as well as G'/ω^2 versus frequency also follow the power-law

behavior and the two material functions may be correlated as follows over a tested range of shear rates and frequencies.

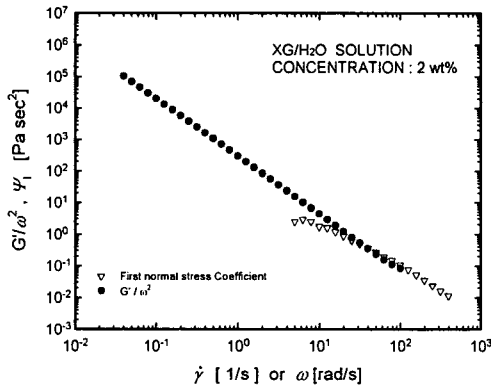$$G'(\omega)/\omega^2 = C^*[\Psi(\dot{\gamma})]^{a^*} \quad \text{at} \quad \dot{\gamma} = \omega \tag{6}$$

Fig. 5. Comparison of $\Psi_1(\dot{\gamma})$ with $G'(\omega)/\omega^2$ for 2 wt% XG/H$_2$O solution.
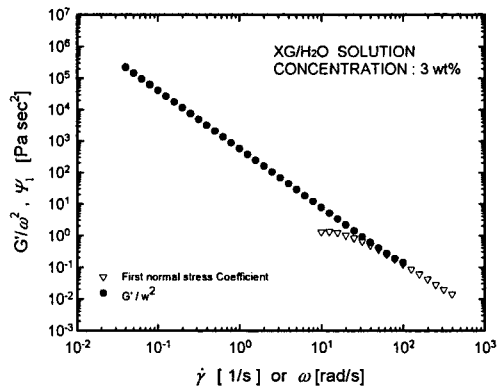
Fig. 6. Comparison of $\Psi_1(\dot{\gamma})$ with $G'(\omega)/\omega^2$ for 3 wt% XG/H$_2$O solution.

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