Theories and Applications of Rheology, 2006 Vol.10, No. 1 95

Large amplitude oscillatory shear flow behavior of concentrated Xanthan Gum solutions : experimental investigation and fourier transform analysis

Hoa-Youn Kuk, Gap-Shik Chang and Ki-Won Song
Department of Textile Engineering, Pusan National University, Pusan 609-735, Korea

Introduction

Due to its exceptional rheological properties, xanthan gum is widely used as an effective stabilizer or a suitable thickener for various kinds of water-based systems. Its numerous areas of application cover a broad range including food, pharmaceutical, cosmetic, agricultural, textile, ceramic, and petroleum industries [1-3]. The most important rheological properties of xanthan gum are high viscosity at low shear rates, pronounced shear-thinning nature, and good resistance to shear degradation.

In the past, in order to investigate the rheological properties of xanthan gum, efforts have been mainly focused on the steady shear flow behavior as well as the frequency dependence of storage modulus and loss modulus (or dynamic viscosity) in small amplitude oscillatory shear (SAOS) deformations. On the other hand, only a few studies have been performed as to a nonlinear rheological behavior at large deformations [4,5].

A strain-sweep test may be considered to be one of the most effective rheological measurements to interpret a nonlinear viscoelastic behavior of complex materials in large amplitude oscillatory shear (LAOS) flow fields. However, it should be noted that, from a purely theoretical point of view, both the storage modulus and loss modulus at large strain amplitude range do not possess their mathematical foundations because these two moduli are defined only within the linear viscoelastic region. When subjected to large strain amplitudes, the stress output of a viscoelastic material becomes no longer sinusoidal and consequently the stress-strain relationship cannot be described in terms of the strain-independent storage and loss moduli due to higher harmonic contributions [6].

In order to analyze these higher harmonic contributions, a group of researchers [7,8] has developed a Fourier transform rheology that decomposes the stress data in time domain into a frequency-dependent spectrum. We have also introduced a Fourier transform analysis to interpret a large amplitude oscillatory shear flow behavior of several kinds of polymer solutions [9,10].

In spite of this complexity in mathematical treatments, it is true that a large amplitude oscillatory shear flow behavior can provide a plentiful information for a better understanding of the overall rheology of complex materials. In addition, large amplitude oscillatory shear test has an advantage in that it allows both the strain amplitude and time scale to be controlled independently [11].

In this work, a nonlinear viscoelastic behavior of concentrated xanthan gum solutions in LAOS flow fields has been elucidated by means of a Fourier transform analysis. In particular, the influence of nonlinear viscoelastic functions derived from the Fourier spectrum of stress response was discussed in detail.

Theoretical background

Onogi *et al.* [12] have analyzed a nonlinear viscoelastic behavior on the basis of the general theory of continuum mechanics of Green and Rivlin [13-15]. According to their analysis, when the strain is applied as a sinusoidal shear strain of $\gamma(t)=\gamma_0 \sin \omega t$, the shear stress $\sigma(t)$ is given by :

$$\sigma(t)=G_1'\gamma_0 \sin \omega t+G_1''\gamma_0 \cos \omega t$$

$$+G_3'\gamma_0^3 \sin 3\omega t+G_3''\gamma_0^3 \cos 3\omega t+\cdots\cdots \quad (1)$$

where $\sigma(t)$ is the shear stress, G_1', G_1'', G_3' and G_3'' are the nonlinear viscoelastic functions (G_1' and G_1'' are the first-harmonic shear storage modulus and loss modulus, respectively, and G_3', G_3'' are the third-harmonic shear storage modulus and loss modulus, respectively.), γ_0 is the strain amplitude and ω is the angular frequency.

If the effect of fluid inertia is negligible, the shear stress can then be represented by the following Fourier series expansion [16] :

$$\sigma(t)=\sigma_1 \sin(\omega t+\delta_1)+\sigma_3 \sin(3\omega t+\delta_3)+\cdots\cdots \quad (2)$$

Combining Eq. (1) with Eq. (2), the following sets of equations are obtained :

$$G_1'=\frac{\sigma_1}{\gamma_0}\cos\delta_1 \quad (3)$$

$$G_1''=\frac{\sigma_1}{\gamma_0}\sin\delta_1 \quad (4)$$

$$G_3'=\frac{\sigma_3}{\gamma_0^3}\cos\delta_3 \quad (5)$$

$$G_3''=\frac{\sigma_3}{\gamma_0^3}\sin\delta_3 \quad (6)$$

In addition, the fast Fourier transform (FFT) of the stress waveform may be expressed as follows [17] :

$$\sigma(k\Delta\omega)=\frac{1}{N}\sum_{n=0}^{N-1}\sigma(n\Delta t)\exp\left[-j\frac{2\pi nk}{N}\right]$$

$$k=0,1,2,\cdots,N-1 \quad (7)$$

where $\Delta\omega$ is the frequency interval (here equal to $2\pi/N\Delta t$), Δt is the time interval and j is a constant.

The nonlinear viscoelastic functions can then be calculated by inserting Eq. (3), (4), (5) and (6) into the Fourier spectrum obtained from Eq. (7).

Experimental section

The polymer selected in this study was xanthan gum (Mw $\approx$ 2×10^6 g/mol) supplied from the Sigma-Aldrich Corporation (USA). Using an Advanced Rheometric Expansion System (ARES), a sinusoidal shear strain of $\gamma(t)=\gamma_0 \sin \omega t$ at several strain amplitudes with a constant angular frequency of ω = 1 rad/s was imposed to aqueous xanthan gum solutions with various concentrations of 1, 2, 3 and 4 wt%, and then the Fourier spectrum was obtained from the fast Fourier transform (FFT) of the stress responses.

A parallel-plate fixture with a radius of 25 mm was chosen as a test geometry, and sandpaper was attached to the plate surfaces in order to eliminate a wall-slip effect. All measurements were performed at a constant gap size of 2 mm and a fixed temperature of 20 ℃.

Results and discussion

Fig. 1(a) and (b) represent the experimental stress responses to the sinusoidal strain of small amplitude (γ_0 = 10 %) and large amplitude (γ_0 = 300 %), respectively, at a fixed angular frequency of ω = 1 rad/s for 4 wt% aqueous xanthan gum solution. A linear viscoelastic behavior is indicated by a sinusoidal stress response to a small amplitude sinusoidal strain (γ_0 = 10 %). In contrast, a periodic but nonsinusoidal stress is observed as a response to a large amplitude sinusoidal strain (γ_0 = 300 %), indicating that a nonlinear viscoelastic behavior took place.

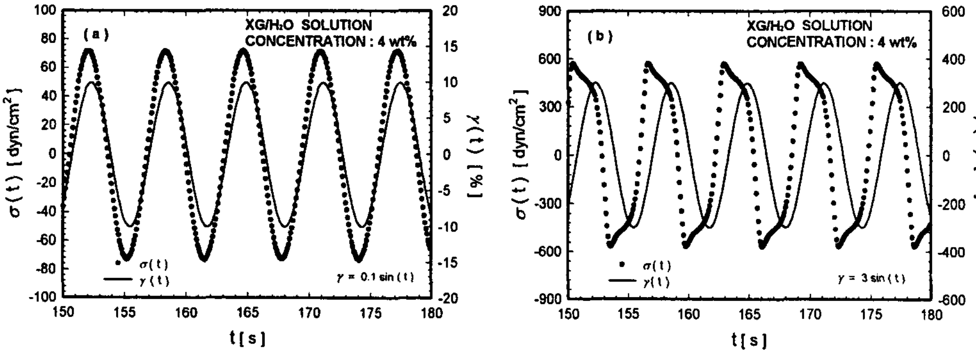

Fig. 1. Stress response to (a) small amplitude sinusoidal strain (γ_0 = 10 %) and (b) large amplitude sinusoidal strain (γ_0 = 300 %) for 4 wt% aqueous xanthan gum solution.

Fig. 2(a) and (b) show the Lissajuos curves obtained from the relation between stress and strain rate for 4 wt% aqueous xanthan gum solution. At small strain amplitude (γ_0 = 10 %), this curve maintain an elliptical form. However, when large strain amplitude (γ_0 = 300 %) was imposed, a ′ S ′ shaped curve is obtained, demonstrating a nonlinear viscoelastic behavior.

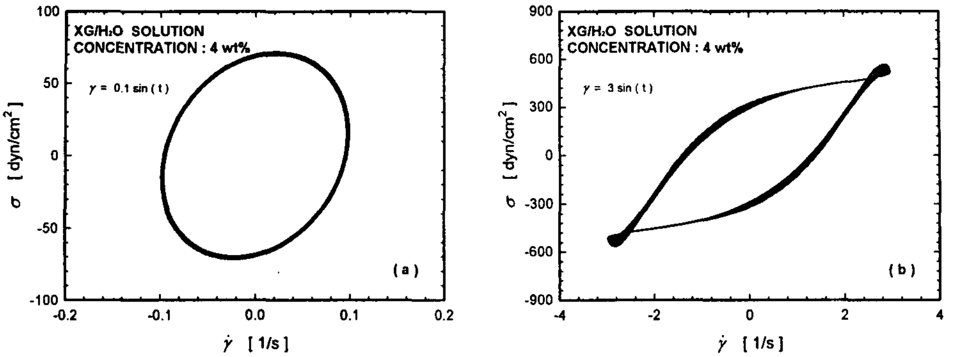

Fig. 2. Lissajous curves for 4 wt% aqueous xanthan gum solution with different strain amplitudes of (a) γ_0 = 10 % and (b) γ_0 = 300 %.

Fig. 3 displays the Fourier spectrum obtained from the FFT of the experimental stress response [Fig. 1(b)]. The Fourier spectrum consists of the first and several higher harmonic terms from the first-harmonic at angular frequency of ω = 1 rad/s to the fifth-harmonic at angular frequency of ω = 5 rad/s. Hence, the effects of higher harmonic terms should be considered to interpret a nonlinear viscoelastic behavior of this system.

As represented in Fig. 4, a nonlinear viscoelastic behavior of xanthan gum solution can be more clearly analyzed by comparing the experimental stress with the nonlinear viscoelastic functions calculated from the Fourier transform analysis.

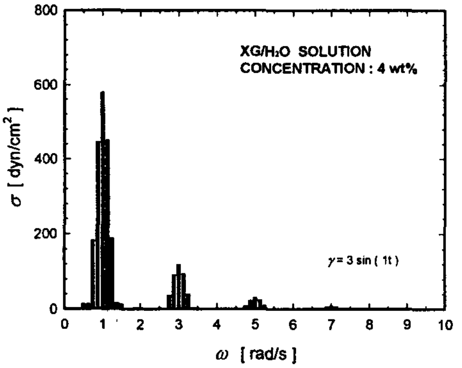

Fig. 3. Fourier spectrum of nonsinusoidal stress response for 4 wt% aqueous xanthan gum solution.

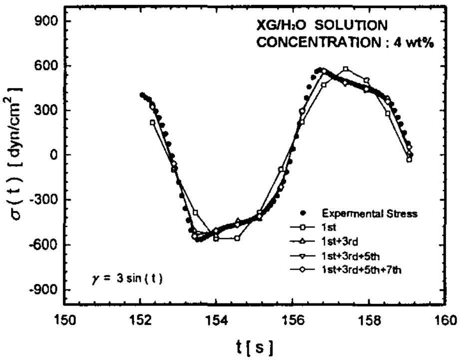

Fig. 4. Experimental stress wave compared with calculated curves for 4 wt% aqueous xanthan gum solution.

Similar trends are also observed for 1, 2 and 3 wt% aqueous xanthan gum solutions whose results are not displayed here on account of a space limitation.

References

[1] K.S. Kang and D.J. Pettit, "Industrial Gums" (R.L. Whistler and J.N. Be Miller Eds.), 3rd ed., Academic Press, New York, USA, 1993.

[2] H. Schott, 1990, "Remington's Pharmaceutical Sciences", 18th ed., Mack Publishing, Easton, PA, USA, 1990.

[3] F. Garcia-Ochoa, V.E. Santos, J.A. Casas and E. Gomez, *Biotechnol. Adv.*, **18**, 549-579 (2000).

[4] K. Hyun, S.H. Kim, K.H. Ahn and S.J. Lee, *J. Non-Newt. Fluid Mech.*, **107**, 51-65 (2002).

[5] K.W. Song, H.Y. Kuk and G.S. Chang, *Korea-Australia Rheol. J.*, **18**, in press.

[6] J.M. Dealy and K.F. Wissburn, "Melt Rheology and Its Role in Plastics Processing : Theory and Applications", Van Nostrand Reinhold, New York, USA, (1990).

[7] M. Wilhelm, P. Reinheimer, M. Ortseifer, T. Neidhöfer and H.W. Spiess, *Rheol. Acta*, **39**, 241-246 (2000).

[8] M. Wilhelm, *Macromol. Mater. Eng.*, **287**, 83-105 (2002).

[9] K.W. Song, and G.S. Chang, *Korean J. Rheol.*, **10**, 173-183 (1998).

[10] G.S. Chang and K.W. Song, *Theor. Appl. Rheol.*, **4**, 62-65 (2000).

[11] J.A. Yosick, A.J. Giacomin and P. Moldenaers, *J. Non-Newt. Fluid Mech.*, **70**, 103-123 (1997).

[12] S. Onogi, T. Masuda, and T. Matsumoto, *Trans. Soc. Rheol.*, **14**, 275 (1970).

[13] A.E. Green and R.S. Rivlin, *Arch. Rat. Mech. Anal.*, **1**, 1-21 (1957).

[14] A.E. Green and R.S. Rivlin, *Arch. Rat. Mech. Anal.*, **3**, 82-90 (1959).

[15] A.E. Green and R.S. Rivlin, *Arch. Rat. Mech. Anal.*, **4**, 387-404 (1960).

[16] D.R. Gamota, A.S. Wineman and F.E. Filisko, *J. Rheol.*, **37**, 919 (1993).

[17] A.V. Oppenheim and R.W. Schafer, "Discreate-Time Signal Procssing", Prentice-Hall, New Jersey, 1989.