Examination of the interrelations between linear viscoelastic functions (dynamic moduli, stress relaxation modulus and discrete relaxation spectrum) for concentrated Xanthan Gum solutions

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Introduction

Xanthan gum is a natural polysaccharide and one of the most important industrial biopolymers. Due to its unique properties such as emulsion stabilization, temperature stability, compatibility with food ingredients, and pseudoplastic rheological properties, xanthan gum has been used in a wide variety of food materials. In addition, its remarkable characters (i.e., high viscosity in solution state, ability to thicken an aqueous solution, and water solubility) have created important applications in many industries including pharmaceuticals, cosmetics, textiles, and agricultural products.

In general, when a finite magnitude of strain is imposed to a viscoelastic material like xanthan gum, the stress relaxation behavior occurs, indicating that the stress is gradually decreased with time. At small strain magnitudes, the stress relaxation behavior can be represented by the linear relaxation modulus, $G(t)$, and $G(t)$ may be expressed using the relaxation spectrum, $H(\lambda)$.

The relaxation spectrum, $H(\lambda)$, can be divided into two kinds. One is the continuous relaxation spectrum and the other is the discrete relaxation spectrum. The calculation of relaxation modulus from the continuous relaxation spectrum is represented as follows :

$$G(t) = \int_{-\infty}^{\infty} H(\lambda)[\exp(-t/\lambda)]d(\ln\lambda) \tag{1}$$

As can be seen in Eq. (1), an integration from -∞ to +∞ is required to calculate the relaxation modulus from the continuous relaxation spectrum, although the relaxation modulus data are never available over an entire range of time scales from zero to infinity.

The approximation methods to calculate the relaxation spectrum have been developed by some authors. Laun [1] and Baumgaertel and Winter [2] suggested the methods to calculate the discrete relaxation spectrum by using linear regression and nonlinear regression, respectively. However, these calculation procedures cause an ill-posed problem in that the modulus strength, G_i, becomes negative. Therefore, the number of relaxation times should be restricted to avoid this problem. Once the discrete relaxation spectrum is determined from these methods, the relaxation modulus or dynamic moduli can be calculated. On the other hand, Kamath and Mackley [3] obtained the relaxation modulus by direct conversion of the frequency domain of dynamic moduli to the time domain by using the Fourier transform. Inversely, Schwarzl [4] proposed a method to directly obtain the dynamic moduli from the stress relaxation modulus.

In this study, the dynamic moduli and relaxation modulus of concentrated xanthan gum solutions were obtained by using the above-mentioned methods and then the experimentally measured data were compared with these results.

Theoretical background

The experimentally measured data of storage and loss moduli can be used to determine the discrete relaxation spectrum. Laun [1] suggested a linear regression as a simple method to calculate the discrete relaxation spectrum, that is, if using M sets of data [$G'(\omega_j)$, $G''(\omega_j)$] to determine N sets of model parameters, (G_i, λ_i), N values of λ_i are specified such that they are equally distributed on a logarithmic time scale within the range of experimentally applied frequencies. And then, N sets of G_i can be determined by a linear regression using the least-squares method that the average square deviation between the predicted G', G'' values and measured G', G'' data should be minimum :

$$\sum_{j=1}^{M}\left[\left\{\sum_{i=1}^{N}\frac{1}{G'(\omega_j)}G_i\frac{(\omega_j\lambda_i)^2}{1+(\omega_j\lambda_i)^2}-1\right\}^2+\left\{\sum_{i=1}^{N}\frac{1}{G''(\omega_j)}G_i\frac{\omega_j\lambda_i}{1+(\omega_j\lambda_i)^2}-1\right\}^2\right]=\min \tag{2}$$

This method needs to specify previously the relaxation time, λ_i, and then determine, G_i, by a linear regression.

Otherwise, Baumgaertel and Winter [2] introduced a nonlinear regression to keep not only all G_i but also all λ_i freely adjustable. They could avoid an ill-posed problem by the restriction to a small number of relaxation times.

In general, the complex modulus, $G^*(\omega)$, can be expressed as follows :

$$G^*(\omega)=i\omega\int_{-\infty}^{\infty}G(t)\exp(-i\omega t)dt \tag{3}$$

The inverse Fourier integral transform of Eq. (3) becomes the continuous relaxation modulus. Kamath and Mackley [3] calculated the discrete relaxation modulus using the discrete Fourier transform of the continuous relaxation modulus :

$$G(t)=\frac{1}{\pi}\frac{\omega_{\max}}{N}\sum_{m=0}^{N-1}\frac{G^*(\omega)}{i\omega}\exp(i2\pi mk/N) \tag{4}$$

The relaxation modulus of a viscoelastic material may be expressed from a Maxwell model. However, due to the fact that a Maxwell model is not enough to tell the real relaxation behavior of a viscoelastic material, the relaxation modulus is described by using a generalized Maxwell model as follows :

$$G(t)=\sum_{i=1}^{N}G_i[\exp(-t/\lambda_i)] \tag{5}$$

In order to calculate the discrete relaxation spectrum, a linear regression described above may be used. When using a linear regression, N sets of G_i, making the average square deviation between the predicted $G(t)$ values and measured $G(t)$ data should be minimum, can be calculated as follows :

$$\sum_{j=1}^{M}\left[\sum_{i=1}^{N}G_i\exp(-t_j/\lambda_i)-G(t_j)\right]^2=\min \tag{6}$$

In the case of calculating the dynamic moduli from the relaxation modulus, a nonlinear regression may also be used in the similar manner as mentioned above. Otherwise, the dynamic moduli can be directly obtained from the relaxation modulus using a Schwarzl interconversion as follows :

$$G'(\omega)=G_e+\omega\int_0^{\infty}[G(t)-G_e]\sin\omega t dt \tag{7}$$

$$G''(\omega) = \omega \int_0^\infty [G(t) - G_e] \cos \omega t dt \tag{8}$$

Experimental section

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 ℃. Both the storage and loss moduli in small 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. Nextly, a constant strain magnitude of γ_0 = 10 % was applied to sample solutions and then the resulting relaxation modulus was detected with time in stress relaxation test.

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

The relaxation modulus can be expressed in the form of Eq. (5) by using the discrete relaxation spectrum which was calculated from the measured dynamic moduli by means of both a linear and a nonlinear regression. In addition, the Fourier transform was used to directly calculate the relaxation modulus from the dynamic moduli.

Fig. 1 illustrates the experimentally measured $G(t)$ for 3 wt% aqueous xanthan gum solutions compared with the results obtained from the above-mentioned methods. The relaxation modulus directly calculated from the measured dynamic moduli using the Fourier transform is well coincident with the experimentally measured $G(t)$. On the other hand, the relaxation modulus obtained from the discrete relaxation spectrum using both a linear and a nonlinear regression methods does not agree with the experimentally measured $G(t)$. In particular, a larger discrepancy is found in the case

of using a linear regression method. This may be due to an ill-posed problem occurring during the calculation procedures of the discrete relaxation spectrum. Although the results are not shown here, it is also observed that the values of $G(t)$ become greater as a larger number of sets, (G_i, λ_i), was adopted when using a linear regression.

The two dynamic moduli, $G'(\omega)$ and $G''(\omega)$, were calculated from the relaxation modulus using a Schwarzl interconversion. The discrete relaxation spectrum was obtained from $G(t)$ using both a linear and a nonlinear regressions, and then, $G'(\omega)$ and $G''(\omega)$ were calculated by integration.

In Fig. 2, the experimentally measured dynamic moduli, $G'(\omega)$ and $G''(\omega)$, for 3 wt% aqueous xanthan gum solutions are compared with the results obtained from the above-described methods. All of the results agree well with the experimentally measured $G'(\omega)$ and $G''(\omega)$. In the case of obtaining the dynamic moduli with a Schwarzl interconversion, however, there exists a problem that this method gives results in a frequency range shorter than the time scale of the stress relaxation data. Because of this truncation, in order to obtain the results over a wide enough frequency range, it is recommended to adopt the method that obtains the dynamic moduli from the discrete relaxation spectrum which is calculated from $G(t)$ using a linear and/or a nonlinear regression.

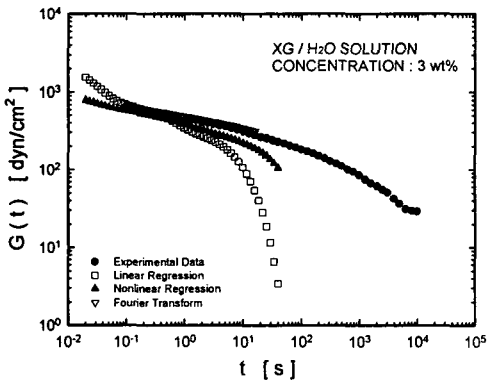

Fig. 1. Relaxation modulus versus time for 3 wt% XG/H_2O solution.

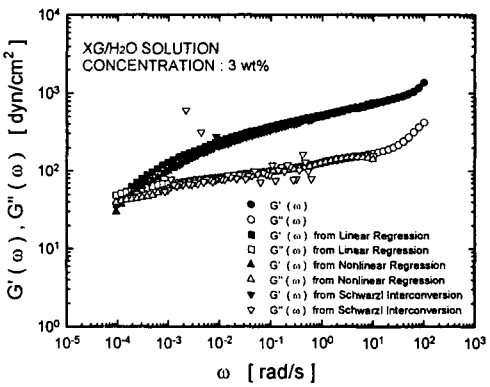

Fig. 2. Storage and loss moduli versus anglular frequency for 3 wt% XG/H_2O solution.

Acknowledgments

One of the authors (Y.S. Kim) is grateful to the Moo-Jin Science & Technology Scholarship Foundation for the financial support provided during his whole master course of Graduate School (from March, 2006 to February, 2008).

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