Expanded Discrete Relaxation Model for Konjac Glucomannan Hydrocolloid

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Rheological storage and loss moduli (G' and G'') of a Konjac glucomannan (KGM) hydrocolloid were measured by a rheometer AR500 with variations of angular frequency and temperature at different concentrations. The results show that angular frequency sweep curves of G' and G'' mainly looked like ascending curves on the double logarithmic diagram. Moduli versus angular frequency curves were fitted to the power law, Spriggs, and Oldroyd models with standard errors much higher than the reasonable value (about 5%), while the discrete relaxation model gave a standard error of 0.81%. On the basis of the discrete relaxation model and experimental results, expanded formulae that include the angular frequency, temperature and concentration as independent variables were proposed. The obtained result can help the designer, fabricator, and consumer in optimizing their formulation with the KGM hydrocolloid.

Keywords   discrete relaxation, hydrocolloid, Konjac glucomannan, rheological model

INTRODUCTION

Konjac glucomannan (KGM), a highly viscous and soluble fiber originating in Asia, is obtained from the tuber of *Amorphophallus konjac*. The many hydroxides of glucomannan molecules make it easy to dissolve in water and form a hydrocolloid [1]. As a raw polymeric material from agriculture, KGM acquired great technical importance in recent years because of the great number of

possible applications in the food, cosmetics, chemistry, petroleum, and medicine industries [2–4].

Understanding the behavior of the konjac glucomannan hydrocolloid is an essential first step in understanding more complex KGM systems of technological significance. Of particular importance are their rheological properties, as they define the flow and deformation behavior as well as the viscosity and the elasticity of the KGM hydrocolloid. An effective method to describe the rheological properties may be the model that establishes relations among the rheological variables. With the use of viscoelastic moduli as the chief variables, a few studies concerning the rheological properties of KGM systems can be found in the literature. Synergistic and complement interactions of mixture of KGM with acetan or carrageenan were demonstrated by rheological evidence [5,6]. Upon dynamic viscoelastic measurements and differential scanning calorimetry, interaction and sol-gel transition in aqueous solutions of gellan gum and KGM with different molecular weights have been showed to behave like dilute and concentrated polymer solutions, which exhibite different gelation characteristics in small amplitude oscillatory shear flow [7–9]. After the liquid crystalline behavior of the KGM aqueous solutions was determined by polarized optical microscopy and circular dichroism, rheological properties of the liquid crystalline solutions of KGM were found to exhibit a pseudoplastic behavior [10]. Viscoelastic shear moduli of water dispersions of KGM and polysaccharides (such as corn starch and bacterial polysaccharide) were measured as a function of mixing ratio and storage time, showing behaviors either intermediate between a concentrated polymer solution and a weak gel [11] or synergistic gelation [12]. A KGM aqueous solution oscillated in direct-current electric field undergoes an electrorheological effect, which is attributed to the KGM's ability to absorb moisture, its intrinsic polarity and its molecular weight; increasing water content and polarity increases the effect, but increased molecular weight decreases it [13]. The rheological moduli and gelation temperature were observed to decrease when the electrolyte was present, with divalent cations having a greater effect than monovalent cations [14]. Based on rheological and thermal studies, the heat-setting gelation of KGM and curdlan solution is thermo-irreversible. So, hydrogen bonding is believed to play an important role in this irreversible network formation [15], and in a general KGM solution [16]. Recently, the modeling method was found to be effective and interesting in the investigations on gum solutions [17]. Aqueous konjac glucomannan dispersions with soybean protein and xanthan gum mixture as the sustained release material of the matrix tablet and sorption of Pb(II) by konjac glucomannan solution beads were tested by rheological instrument [18–20]. Although important progress has been made, challenging problems about the rheology of the konjac glucomannan hydrocolloid still exist. To our knowledge, a multi-variable rheological model that is practically significant

for the application of the KGM hydrocolloid by the designer, fabricator and consumer in optimizing the formulation has not been established.

The objective of this paper is to measure the shear storage and loss moduli of the konjac glucomannan hydrocolloid with variations of angular frequency and temperature at different concentrations, to introduce theoretical models for fitting the experimentally recorded data of the KGM hydrocolloid, and to establish a three-variable function of the angular frequency, temperature and concentration for the KGM hydrocolloid by combining the experimental curves and the time temperature superposition (TTS) results [21].

EXPERIMENTAL

Materials

The konjac glucomannan sample used in our experiment was supplied by Hubei Enshi Hongye Konjac Development Co., Ltd., and had these principal properties: granularity $\leq 220\,\mu m$, glucomannan content $\geq 95\%$, protein content $< 0.6\%$, ash content $< 3\%$. The molecular structure of the konjac glucomannan contains glucose and mannose in a molar ratio of 1:1.6 with β-1-4 linkages and a little β-1-3 branches. The weight-average molecular weight is about 1.1×10^6.

Konjac glucomannan hydrocolloid samples were prepared by intense mechanical mixing of KGM powder in distilled water for 3 h at 50°C. Rheological data of these samples were thus reproducible and did not change with time. KGM concentrations of those samples were 0.6, 0.8, 1.0, 1.2, 1.5, 1.8, and 2.0 wt%. The concentration was generally controlled below 2.0 wt%, owing to the superb sticking capability of the KGM. High concentration will result in a gel state at which the experiment cannot be carried out at room temperature.

For those hydrocolloid samples, dynamic viscoelastic measurements were carried out with a rheometer AR500 by TA instruments as soon as they returned to room temperature. A standard steel parallel plate with 1000 µm gap and 40 mm diameter was chosen. The shear storage and loss moduli, G' and G'', were recorded as functions of either angular frequency from 0.1 to 100.0 rad/sec or temperature from 10 to 50°C. The oscillatory strain was 1%, which is located in the linear region. The recorded data were processed by TA Instruments software, named the Rheology Advantage Data Analysis (v3.0.24).

Methods

According to the definition of the discrete relaxation spectrum, we selected the finite five terms (fit to experimental data) to write the following relaxation

function as a primary model to describe the konjac glucomannan hydrocolloid during the data processing,

$$G(t) = \sum_{j=1}^{5} G_j \exp(-t/\tau_j) \tag{1}$$

whose corresponding equations for the shear storage and loss moduli are

$$G'(\omega) = \sum_{j=1}^{5} G_j \frac{(\omega\tau_j)^2}{1 + (\omega\tau_j)^2} \tag{2}$$

$$G''(\omega) = \sum_{j=1}^{5} G_j \frac{(\omega\tau_j)}{1 + (\omega\tau_j)^2} \tag{3}$$

where, t is time, G_j and τ_j are parameters to be fitted. The fitting results were evaluated by a standard error defined in Equation (4).

$$\frac{\sqrt{\frac{\sum (x_m - x_c)^2}{n-2}}}{range} \tag{4}$$

where x_m is the measured value and x_c is the calculated value of x for each data point, n is the number of data points, and the range is the maximum value of x_m minus the minimum value. Generally speaking, a reasonable fit gives a standard error of $\leq 5\%$ owing to a ≥ 95 wt% glucomannan content of the KGM sample.

While modeling thermorheological properties, the time-temperature superposition (TTS) principle [21] can enormously simplify the problem. According to this rule, the time (frequency) and temperature dependences of polymeric materials that exhibit thermorheological simple behavior can be simplified as functions of ($a_T\omega$), otherwise independent of temperature. In this case, $G' = G'(a_T\omega)$ and $G'' = G''(a_T\omega)$. Here a_T is a function of temperature and is called shift factor. This indicates that the temperature dependence of G' and G'' is realized only through the same shift factor which is obtained by a model. The commonly used model is the Arrhenius equation [21]:

$$a_T = A \exp\left(\frac{E_a}{RT}\right) \tag{5}$$

where, E_a is the activation energy (in J) associated with the relaxation, $R = 8.31$ is the gas constant (in J/K), T is the absolute temperature in K, A is a dimensionless constant. The Arrhenius model implies that the temperature dependence of the polymer exhibits decreasing viscoelastic behavior with temperature. As shown by Yang et al. [22], konjac glucomannan hydrocolloid undergoes the simple behavior. It is thus reasonable to choose this model to predict the thermorheological properties of KGM hydrocolloid, such as calculating the temperature dependence of G' and G''.

RESULTS AND DISCUSSION

Angular Frequency Dependence

Typical results for the storage and loss moduli (G′ and G″) as well as their ratio tan $\delta = G''/G'$, as functions of angular frequency ω (in rad/sec) at 30°C for the konjac glucomannan hydrocolloid sample with a concentration of 1.5 wt %, are shown in Figure 1. Both G′ and G″ increased with the angular frequency, while tanδ decreased. At lower angular frequency, G″ was six times more than G′, which meant the KGM hydrocolloid appeared dominated by the viscous property that reflected a fluid character.

In order to quantitatively analyze the measured result, we selected the commonly used rheological models to fit the data in Figure 1. They were the Power law, Spriggs [23], and Oldroyd [24] models, and discrete relaxation spectrum (the multi-element Maxwell model). Mathematically, each model was presented as a function of the angular frequency ω, which may have several parameters. The parameters for each model were obtained by optimizing the error to minimum by the Rheology Advantage Data Analysis (v3.0.24). Numerical results for the parameters and standard errors for these models are listed in Table 1, where, constant k and law index n were defined in the form: $G'' = k\omega^n$, $G' = k\omega^n/tan(n\pi/2)$. The equations of the Spriggs model [25] have three parameters: viscosity, time and alpha. There are also three parameters in the Oldroyd model [26], which are called viscosity, time1 and time2. Comparing the numerical results in Table 1, one can find that only the discrete relaxation spectrum (solid lines in Figure 1) accurately fitted the rheological curves of the konjac glucomannan hydrocolloid in Figure 1. Errors of $\geq 35\%$
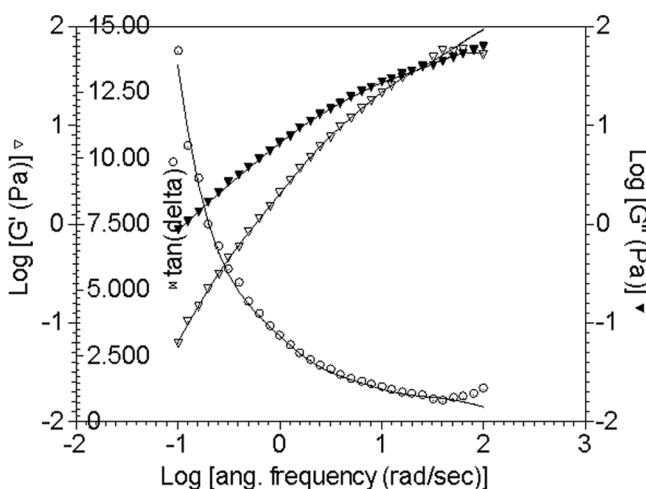
Figure 1: The dependence of G′ and G″ as well as tan δ on the angular frequency (data points) at 30°C for the Konjac glucomannan hydrocolloid sample at concentration of 1.5 wt%. Solid lines are plotted by the discrete relaxation model.

Table 1: Optimized parameters and standard errors of rheological models fitting to the measured data of the Konjac glucomannan hydrocolloid at 1.5wt% concentration.

Model	Optimized parameters for each model					Standard error (%)
Power law	Constant = 3.36 Pa.s$^{0.549}$	Law index = 0.549				39
Spriggs	Viscosity = 24.2 Pa.s	Time = 34.3 s	Alpha = 1.39			35
Oldroyd	Viscosity = 18.6 Pa.s	Time 1 = 2.57 s	Time 2 = 0.130 s			46
Discrete relaxation spectrum	G_1 = 101 Pa τ_1 = 0.0115 s	G_2 = 27.0 Pa τ_2 = 0.888 s	G_3 = 7.84 Pa τ_3 = 0.397 s	G_4 = 0.455 Pa τ_4 = 1.45 s	G_5 = 0.466 Pa τ_5 = 3.06 s	0.81

for the Power law, Spriggs and Oldroyd models were not suitable for the rheological description of KGM hydrocolloid, since they were far beyond any reasonable value. In this case, we chose the discrete relaxation spectrum as the base for further modeling. Eqs. (1–3) of the discrete relaxation model only have one independent variable (either the time or angular frequency), therefore they are called the one-variable model for the KGM hydrocolloid.

Temperature Dependence

The temperature dependence of the konjac glucomannan hydrocolloid can be demonstrated more clearly by temperature ramp data of G′ and G″. Figure 2 illustrated the data recorded at 10 Hz for the KGM hydrocolloid sample with a concentration of 1.5 wt%. It was clear that the G′ and G″ decreased as the temperature increases from 10 to 50°C. Both data in Figures 1 and 2 indicated that the storage and loss moduli were not only functions of angular frequency, but also of temperature.

To better understand the data in Figures 1 and 2, we quantitatively analyze them with the TTS rule [18]. Based on the TTS theory, Eqs. (2) and (3), which denote the shear storage and loss moduli of the konjac glucomannan hydrocolloid, can be rewritten as
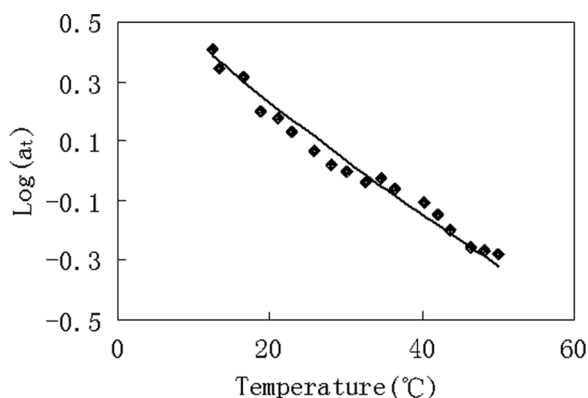
$$G'(\omega, T) = \sum_{j=1}^{5} G_j \frac{(\omega a_T \tau_j)^2}{1 + (\omega a_T \tau_j)^2} \tag{6}$$

$$G''(\omega, T) = \sum_{j=1}^{5} G_j \frac{(\omega a_T \tau_j)}{1 + (\omega a_T \tau_j)^2} \tag{7}$$
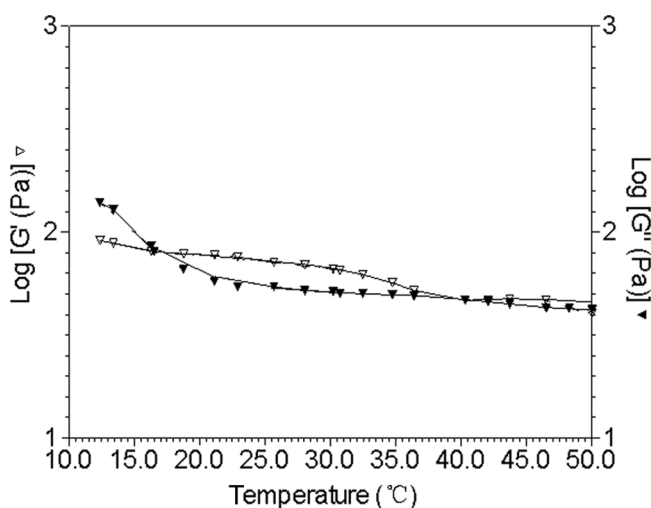
Figure 2: Temperature ramp data (points) of the G′ and G″ at 10 Hz for the Konjac glucomannan hydrocolloid sample with a concentration of 1.5 wt%. Lines are the fitted results with the corresponding shift factor.

Figure 3: The calculated shift factor (data points) and fitted line with Eq. (5).

where, both G_j and τ_j (in sec) are independent of temperature, and take the values in Table 1. Eq. (5) shows a trend that a_T decreases with rising temperature. This behavior brings about the same trend for Eqs. (6) and (7) at a fixed angular frequency, which qualitatively agrees with the curves in Figure 2. We checked out that Eqs. (6) and (7) fit the data in Figure 2 with a standard error of less than 3%. The corresponding calculated relation between a_T and T was shown in Figure 3. The dots in Figure 3 were the calculated data from Figure 2. The solid line was the fitting result to Eq. (5) with $Ea = 3.30 \times 10^4$ (Joules), $A = 2.20 \times 10^{-6}$ and standard error 1.1%. The corresponding calculated G' and G'' functions of temperature are presented by the lines in Figure 2. It is clear that Eqs. (6) and (7) have two independent variables (angular frequency and temperature), therefore they can describe the thermoviscoelastic properties since the KGM hydrocolloid was shown as a thermorheological simple material [22].

Concentration Dependence

In order to present the influence of the Konjac glucomannan concentration more clearly, we chose three typical sets of data with concentrations of 1.2, 1.5, and 1.8 wt% to avoid the duplications of the data sets at 0.6, 0.8, and 1.0 wt% to the data at 1.2 wt% when plotting them on the LogG' and LogG'' versus temperature diagram. The temperature ramp data of G' and G'' for the KGM hydrocolloid sample at these concentrations are illustrated in Figure 4(a) and (b). It showed that both G' and G'' at the testing concentrations decreased with increasing temperature. The values of G' and G'' at higher concentration were consistently higher than the values at lower concentration.

The dependences of G' and G'' on the concentration may be shown more clearly on the diagram of modulus versus concentration. Figure 5 was the result which clearly demonstrated the modulus monotonously ascended with
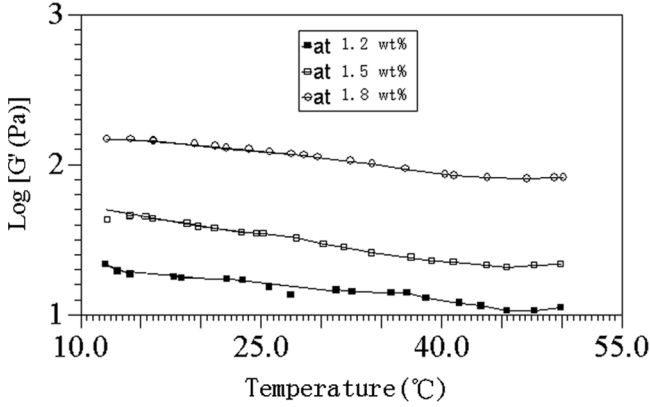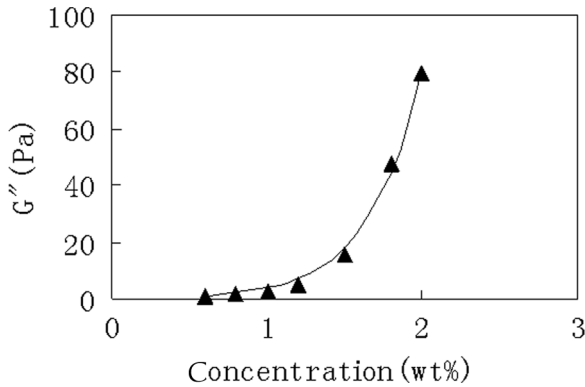
(a)
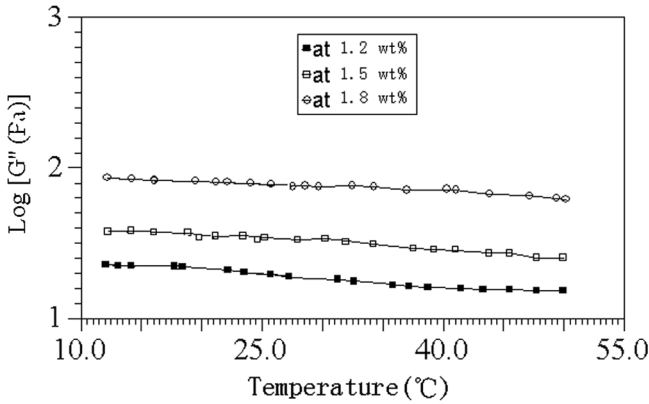
(b)

Figure 4: The temperature ramp data (points) of G' (a) and G'' (b) for the Konjac glucomannan hydrocolloid sample with various concentrations of 1.2, 1.5,1.8 wt% at 10 Hz. Lines are the fitted results with the corresponding shift factor.

Figure 5: G'' versus concentration for the Konjac glucomannan hydrocolloid sample at angular frequency 12.57 rad/sec and 30°C.

TABLE 2: Constants of the three-variable model for the KGM hydrocolloid.

$G_{01} = 1.13\,\text{Pa}$	$G_{02} = 0.306\,\text{Pa}$	$G_{03} = 0.0886\,\text{Pa}$	$G_{04} = 0.00512\,\text{Pa}$	$G_{05} = 0.00524\,\text{Pa}$	$Ea = 3.30 \times 10^4\,\text{J}$
$\tau_1 = 0.0115\,\text{s}$	$\tau_2 = 0.888\,\text{s}$	$\tau_3 = 0.397\,\text{s}$	$\alpha\ \tau_4 = 1.45\,\text{s}$	$\alpha\ \tau_5 = 3.06\,\text{s}$	$A = 2.20 \times 10^{-6}$

concentration at 12.57 rad/sec and 30°C. A simple mathematical formula in the following form can fit these data:

$$G = G_0 e^{\alpha c} \tag{8}$$

where, α is a dimensionless constant, c denotes the concentration in wt%, and G presents either G' or G''. For the data in Figure 4(b), if $\alpha = 3.0$ and $G_0 = 0.20\,\text{Pa}$, an optimized fit can be obtained as a solid line in Figure 5.

Accumulating the preceding results, we propose the following expanded equations to model the konjac glucomannan hydrocolloid:

$$G'(\omega, T, c) = \sum_{j=1}^{5} G_{0j} e^{3c} \frac{(\omega a_T \tau_j)^2}{1 + (\omega a_T \tau_j)^2} \tag{9}$$

$$G''(\omega, T, c) = \sum_{j=1}^{5} G_{0j} e^{3c} \frac{(\omega a_T \tau_j)}{1 + (\omega a_T \tau_j)^2} \tag{10}$$

$$a_T = 2.20 \times 10^{-6} \exp\left(\frac{3.30 \times 10^4}{R(273 + t)}\right) \tag{11}$$

where, t is temperature in °C, G_{0j} and τ_j (in sec) are constants shown in Table 2. These equations have three independent variables (angular frequency, temperature and concentration), and are then called the three-variable model for the KGM hydrocolloid. They completely describe the variations of the moduli with angular frequency, temperature and concentration for the KGM hydrocolloid, which forms a base for the concentration-thermorheological study into the KGM hydrocolloid using only the 12 parameters in Table 2. It was proved that these formulae fitted all of our recorded data within standard error of $\leq 3\%$ by adapting the constants.

CONCLUSIONS

Through experimental and numerical study, practically and theoretically valuable results were obtained as follows:

1. With rheological storage and loss moduli (G' and G'') measurements of a konjac glucomannan (KGM) hydrocolloid by a rheometer AR500 with variations of angular frequency and temperature at different concentrations, it was found that angular frequency sweep curves of G' and G'' mainly looked like ascending curves on the double logarithmic diagram.

The Power law, Spriggs, and Oldroyd models could not fit the experimental data, while the discrete relaxation model fit them with a standard error of 0.81%.

2. On the basis of the discrete relaxation model and experimental results, expanded formulae that include the angular frequency, temperature and concentration as independent variables were proposed. These equations present the relations of the modulus to angular frequency, temperature and concentration, which is of practical importance for industries concerning the KGM hydrocolloid.

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