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Structural viscoelasticity of a water-soluble polysaccharide extract

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A B S T R A C T

Two structural changing processes are incorporated into a traditional viscoelastic model to characterize and predict the shear thickening rheological behaviors of a polysaccharide mucilage of black tree fern. The shear-dependent structure effect could cause varying linear viscoelasticity, and the relaxation spectrum in the model was modified by an empirical sigmoidal function and a structure parameter. The steady shear viscosity of the mucilage was fitted to obtain the parameters in the empirical function. The step rate experimental data was fitted to obtain the structural formation and disruption information. According to the varying spectrum in steady shear state, the extract shows slight shear strengthening of linear viscoelasticity at low shear rate, then steep strengthening in 3–6 s^{-1}, and last large strengthening at the shear rate higher than 10 s^{-1}. Both the time-dependent shear thickening viscosity and the shear hysteresis behavior of the mucilage can be predicted using the developing structure.

1. Introduction

The mucilage extracted from the fronds of black tree fern of New Zealand can be consumed as food or pharmaceutical for some disease, and its shear rheological behaviors has attracted some attention [1–3]. In the recent experimental work, Wee et al. [3] introduced a detailed research on the time-dependent shear thickening behavior for the water-soluble extract, which is attributed to the effect of non-starch polysaccharide in the extracted mucilage. The polysaccharide has a large molecular weight and a semi-flexible random coil conformation. The intermolecular associations or the interaction of hydrogen-bonding was presumed to be responsible for the shear-thickening [1,3], and a cooperative zipping mechanism of stretched polysaccharide chains [3] was used to illustrate the shear-thickening, a shear-induced structural effect. Abundant rheological experimental data of the polysaccharide extract provides an excellent foundation for understanding the shear-thickening viscosity with model.

The structural kinetic equation usually used in the description on the time-dependent viscosity decreasing phenomenon under constant shear rate, i.e. thixotropy, is, [4–6].

$$\frac{d\zeta}{dt} = -k_1\dot{\gamma}\zeta + k_2(1-\zeta) \tag{1}$$

where k_1 and k_2 are the constants for structure breakdown and buildup, respectively, ζ is a scalar structure parameter, t is a time variable, $\dot{\gamma}$ is the shear rate. The breakdown is caused by shear rate, and the buildup or structure formation is due to Brownian motion. A generalized structural kinetic equation with more parameters [5,7] is written as,

$$\frac{d\zeta}{dt} = -k_1\dot{\gamma}^r\zeta^u + k_2\dot{\gamma}^s(1-\zeta)^v \tag{2}$$

where the powers r, s, u and v are either directly specified in the model or obtained by fitting the data [4,5,7,8]. This kind of structure equation can be combined with the upper-convected Maxwell constitutive equation or other viscoelastic equation to characterize the nonlinear viscoelasticity [4–7,9–14]. Moreover, the structure equation can also be adopted to describe the antithixotropy and shear-thickening in principle [6,11,12,15] though such work is much less than that on thixotropy. Eq. (2) could be used to describe the time-dependent viscosity and shear thickening of the polysaccharide mucilage [3] due to the fact that the buildup term contains the structure effect induced by shear.

Another kind of kinetic equation, i.e. population balance model, can also be used to explain the time-dependent viscosity of fluid, which can be written as [16–18],

$$\frac{dN_i}{dt} = \sum_{j=1}^{i-2} 2^{j-i+1}\xi_{i-1,j}N_{i-1}N_j + \frac{1}{2}\xi_{i-1,i-1}N_{i-1}^2 - N_i\sum_{j=1}^{i-1} 2^{j-i}\xi_{i,j}N_j - N_i\sum_{j=i}^{i_{max}-1}\xi_{i,j}N_j - S_iN_i + \sum_{j=i}^{i_{max}}\Gamma_{i,j}S_jN_j \tag{3}$$

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where N_i is the number concentration of flocs or aggregates with volume V_i, i is the number from 1 to i_{max}, $i = 1$ represents the primary flocs or aggregates with volume V_1, i_{max} used is 30 [19] or 40 [16], j is the number similar to i, and ξ, *S*, and *Γ* are the parameters. The parameter ξ can include the effect of shear rate [16,17,19,20] or of both shear rate and Brownian motion [18,21], and *S* usually only includes the effect of shear rate [16–21]. Thus, the first two terms of the right-hand side describe the formation of size-V_i flocs due to the aggregation of smaller aggregates caused by shear rate and Brownian motion, the next two terms account for the loss of size-V_i flocs due to the aggregation with other aggregates caused by shear rate and Brownian motion, and the 5th term accounts for the loss of size-V_i flocs due to the breakage caused by shear rate, and the 6th term describes the formation of size-V_i flocs due to the breakage of larger aggregates caused by shear rate. It is apparent that the change of microstructure in fluid described by population balance model can be added into viscosity model [16–18,20] or viscoelastic model [21] to present the time-dependent viscosity, and it is possible that population balance model have the capability to describe the time-dependent shear thickening of the polysaccharide mucilage [3] because the model has the structure effect induced by shear.

In the earlier work of the polysaccharide extract of the New Zealand black tree fern, Goh et al. [22] analyzed the mechanism of shear thickening of the mucilage and also introduced some viscoelastic models, such as the Tanaka-Edwards model [23] and the model of Marrucci et al. [24], which could be capable of describing the thickening behavior of the mucilage. In the recent work of Wee et al. [3], the energetically crosslinked transient network (ECTN) model of Lele and Mashelkar [25] was introduced to qualitatively explain the thickening of the mucilage. However, in the present paper, a structuralized viscoelastic model, containing the PSM-type KBKZ model [26], an empirical function, and a structure equation, was proposed to characterize the rheological behavior of the polysaccharide mucilage [3]. The paper is organized as follows. The theoretical models are provided firstly, and then the parameters of the model are obtained and the rheological properties of the mucilage are characterized. The shear-rate- and time-dependent viscosities of the mucilage are predicted using the model. The results are summarized in the last section.

2. Materials and methods

2.1. Experimental data

Most of the experimental data of the polysaccharide mucilage used here are from the paper of Wee et al. [3], which include the shear viscosity curves at different shear time intervals, the single step rate curves with both rate-up and rate-down cases, and the multistep rate curves. Another group of the data is the shear complex viscosity obtained by dynamic shear, which is from the earlier work of the authors [1].

The freeze-dried mucilage [3] consists of 11% (w/w) non-starch polysaccharide, 10.3% (w/w) starch, 49% (w/w) sugars, 2.2% (w/w) crude protein, 18% (w/w) ash, and 0.2% (w/w) fat, in which the key component of influencing the flow behavior of the fern mucilage, i.e. non-starch polysaccharide [1], consists of 73% (w/w) uronic acid, 14.3% (w/w) galactose, 7.1% (w/w) xylose and 3.1% (w/w) arabinose. The mucilage solution used in most of the rheological experiments contains 5% (w/w) freeze-dried mucilage, which was prepared by hydrating in Milli-Q water at 20 °C [3]. The concentration of the mucilage influences the shear thickening behavior of the solution, which was indicated by introducing a small amount of experiments at 2% (w/w) and 10% (w/w) in Wee et al. [3]. For simplicity, the concentration effect was not considered in the present work, and the shear rate- and time-dependent viscosity of the 5% (w/w) mucilage at 20 °C was described.

2.2. Viscoelastic model

The modified separable KBKZ integral-type model is,

$$\boldsymbol{\tau} = \int_{-\infty}^{t} m(t-t', f, \zeta) \cdot h(I) \cdot C_t^{-1}(t')dt', \tag{4}$$

where $m(t-t', f, \zeta)$ is the time- and shear-rate-dependent memory function with the structure effect induced by shear, $h(I)$ is the strain-dependent damping function, *I* is a generalized strain invariant, C_t^{-1} is the Finger strain tensor, i.e. the inverse of the Cauchy-Green strain tensor C_t, *t* and *t′* are the present and the past time, respectively.

The memory function $m(t-t', f, \zeta)$ is written as,

$$m = \sum_i \frac{g_i \cdot f(\dot{\gamma}) \cdot \zeta}{\lambda_i} \cdot e^{\left(-\frac{t-t'}{\lambda_i}\right)}, \tag{5}$$

where λ_i and g_i are the relaxation times and the relaxation modulus coefficients, respectively, at low shear rate, i is the number of relaxation spectrum here, $f(\dot{\gamma})$ reflects the effect of shear rate on the structure and the linear viscoelastic spectrum of the mucilage in steady shear status, which can be of the form,

$$f(\dot{\gamma}) = \sum_j \frac{n + le^{-k_j\dot{\gamma}}}{1 + ae^{-b_j\dot{\gamma}}}, \tag{6}$$

where *n*, *l*, k_j, *a* and b_j are the parameters, *n*, *l* and *a* are the dimensionless constants, the unit of k_j and b_j is second, j is the number of the parameters k_j and b_j here. The scalar parameter *ζ* reflects the effect of both shear rate and shear time on the structure change of viscoelastic fluid in step rate experiment, which has the form,

$$\zeta = x/c, \tag{7}$$

where *x* is relative structure, $c = f/f^*$ is a transform coefficient, and f^* is a *f* value at a reference shear rate. The relative structure *x* obeys the following kinetic equation,

$$\frac{dx_w}{dt} = -p_w(\dot{\gamma})x_w^3 + q_w(\dot{\gamma})x_w, \tag{8.1}$$

$$x = \prod_{w=1} x_w, \tag{8.2}$$

where x_w is the *w*-th component of the structure parameter, p_w and q_w are the constants for structure breakdown and buildup, respectively, at a specified shear rate, and the maximum *w* is 2 for the step rate test with the increasing shear rate or 1 with the decreasing shear rate. The structure buildup term in one-component Eq. (8.1), proportion to *x*, is different from that in structure equation, Eq. (1) or (2), which is proportion to $(1-\zeta)$ or $(1-\zeta)^N$. The mechanism of the buildup term in Eq. (8.1) is that buildup is related to structured part, which indicates that the current structure could promote to produce more and larger structure and then cause larger drag in flow; while the buildup term in Eq. (1) or (2) indicates the effect of unstructured part. The one-component Eq. (8.1) with the power of 2 for the structure parameter in breakdown term is the logistic law of population growth introduced by Verhulst in 1837 [27,28]. The present structure equation has some property of Eq. (3) and the concise merit of Eq. (1) or (2).

The damping function employed is the PSM-type [26],

$$h(I) = \frac{\alpha}{\alpha + (I-3)}, \tag{9}$$

where α is a material constant. The generalized strain invariant *I* is written in the form,

$$I = \beta I_{C^{-1}} + (1-\beta)I_C, \tag{10}$$