Effect of Fractal Dimension of Floc Size in a Constitutive Model Based on a Population Balance Equation for Floc-Forming Suspensions on Shear Rheology

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A viscoelastic constitutive model for floc-forming suspensions developed in a previous study couples a population balance equation for the floc aggregation-breakage and a White-Metzner-type viscoelastic model. In the White-Metzner model, the viscosity and the relaxation time were respectively represented by a Krieger-Dougherty model and a power-law model, which depend on the effective volume fraction of flocs. The relation between the effective floc radius and the length of a monomer, which is the minimum unit of a fiber, was described using the mass to radius fractal dimension \( d_f \). The present study considered the effect of \( d_f \) on the rheological properties of the proposed model and analyzed its shear property by simulating startup shear flows. The steady shear viscosity is larger for suspensions of smaller \( d_f \) and shows a shear-thinning property, which appears more strongly with decreasing \( d_f \). The first normal stress coefficient shows fractal-dimension dependence and is larger for smaller \( d_f \). These phenomena are relevant to a characteristic of the present model whereby the effective volume fraction is larger for suspensions of flocs of smaller \( d_f \). Furthermore, analyses of the transient behavior of shear rheology revealed that the change in the floc size distribution proceeded in a much shorter time as compared to the relaxation time \( \lambda \) of the White-Metzner model, and hence the growth of macroscopic properties, such as shear viscosity and the first normal stress coefficient, was mainly dominated by the steady-state value of \( \lambda \), although it depends on temporal change in the floc size distribution of flocs.

Key Words: Fiber flocs / Population balance equation / Fractal dimension / Effective volume fraction / Shear rheology

1. INTRODUCTION

In the manufacturing process of products using cellulose nanofibers (CNFs), flows of CNF suspensions often appear and their flow behavior affects the quality of products. Furthermore, the rheology of CNF suspensions is complicated because of the aggregation-breakage behavior of fiber flocs in flows, and hence the flow of CNF suspensions shows characteristic behavior. The flow of CNF suspensions is therefore an important issue from both engineering and rheological points of view. Numerical simulation will be a strong tool for the analysis of the flow of floc-forming suspensions, such as CNF suspensions. Consequently, we developed a White-Metzner-type viscoelastic model for floc-forming suspensions based on a population balance equation (PBE) for fiber floc size proposed by Puisto et al. to provide a constitutive model for floc-forming suspensions that can describe the floc aggregation-breakage and is applicable to macro flow simulations.

In the proposed model, the floc size distribution is computed using the PBE, and the effective volume fraction of flocs is estimated. The effect of the effective volume fraction on the viscoelastic properties of CNF suspensions is introduced in the model through the viscosity and the elastic modulus. The viscosity is modeled by the Krieger-Dougherty model, and the volume fraction dependence of the elastic modulus is approximated by a power-law model. We numerically investigated the shear behavior of the developed model and confirmed that the model can describe shear-thinning viscosity and the first normal stress difference depending on the effective volume fraction of flocs.

In the previous investigation, the value of the fractal dimension, which is one of the model parameters, was fixed. However, the fractal dimension characterizes the formation of flocs and the effective volume fraction of flocs depends on the fractal dimension, and hence understanding of the effect of the fractal dimension is important. The investigation of the effect of the fractal dimension in the previously proposed model was a remaining problem. We therefore considered the effect of the fractal dimension on the rheological property of this model. In the present study, the startup shear flow was numerically simulated by varying the fractal dimension in order to inves-
tigate the dependence of the shear rheology of this model on the fractal dimension. We focused on the effect of the fractal dimension in the present paper. Hence, the constitutive model, simulated problems, and the values of model parameters except for the fractal dimension were fixed to the same values in the previous paper. Steady shear rheology and temporal responses in both shear stress and the first normal stress difference were investigated.

2. MODEL OF CELLULOSE NANOFIBER SUSPENSIONS

Here, we briefly introduce a previously proposed constitutive model for CNF suspensions. In this model, the White-Metzner model is coupled with a PBE for fiber floc aggregation-breakage, and the viscosity function of the White-Metzner model is described by the Krieger-Dougherty model. In addition, the elastic modulus is approximated by a power-law model.

We applied a PBE-based model proposed by Puisto et al. to a model of suspensions of CNFs, which is a floc-forming suspension. In this model, the mass balance of fibers is described by the following equations:

$$\frac{dn_i}{dt} = \frac{1}{2} \sum_{j=1}^{i-1} k^{(a)}(i-j, j)n_{i-j}n_j - \sum_{j=i+1}^{\infty} k^{(a)}(i, j)n_in_j - k^{(b)}(i)n_i + \sum_{j=i+1}^{\infty} \beta(i, j)k^{(b)}(j)n_j,$$

where $i$ and $j$ denote the numbers of monomers for different size classes of flocs. Here, the monomer refers to the minimum unit composing a floc. Moreover, $n_i$ is the number of flocs consisting of $i$ monomers per unit volume, $k^{(a)}$ and $k^{(b)}$ are aggregation and fragment kernels, respectively, and $\beta$ represents a fragment distribution function. We used the aggregation and fragmentation kernels proposed by Vanni:

$$k^{(a)}(i, j) = c_v \frac{4}{3} \gamma (r_i + r_j)^3,$$

where $c_v$ is a collision efficiency factor, which was set to 0.03, $\gamma$ is the shear rate, and

$$k^{(b)}(i) = \gamma \exp \left( -\frac{2F_c}{3\pi\eta\gamma^2} \right),$$

where $F_c$ is the aggregate effective internal bond force, and $\eta$ is the viscosity of the suspension. These kernels are functions of the radius of a floc consisting of $i$ monomers, $r_i$, defined by

$$r_i = r_0 i^{1/d},$$

where $r_0$ is the length of a monomer, and $d$ is the mass to radius fractal dimension. The floc size depends on the fractal dimension $d$, and its effect on the rheological property is analyzed in the present paper. We used the discretization method proposed by Kumar and Ramkrishna and assumed uniform binary fragmentation $14)^\beta = 2/(j - 1)$ to solve Eq. 1.

The discretized equation was solved using the Euler forward differential method. Furthermore, we assumed that the total number of monomers ($\sum n_i$) is conserved.

Both the viscosity $\eta$ and the elastic modulus $G$ are represented by functions of the effective volume fraction $\varphi_{\text{eff}}$:

$$\varphi_{\text{eff}} = \sum_i n_i v_i = \frac{4}{3} \pi r_0^3 \sum_i n_i i^3,$$

where $v_i$ is the volume of a floc consisting of $i$ monomers. Similarly to the previous model, the viscosity is evaluated using the Krieger-Dougherty model:

$$\eta(\varphi_{\text{eff}}) = \eta_0 \left( 1 - \frac{\varphi_{\text{eff}}}{\varphi_m} \right)^{-k},$$

where $\eta_0$ is the solvent viscosity, $\varphi_m$ is the maximum packing volume fraction, and $k$ is a power index. Moreover, the elastic modulus function $G(\varphi_{\text{eff}})$ is assumed to be described by a power-law model:

$$G(\varphi_{\text{eff}}) = G_m \left( \frac{\varphi_{\text{eff}}}{\varphi_m} \right)^m,$$

where $G_m$ is an elastic constant, and $m$ is a power-index. The relaxation time $\lambda$ is evaluated by $\lambda(\varphi_{\text{eff}}) = \eta(\varphi_{\text{eff}})/G(\varphi_{\text{eff}})$.

These models are introduced in the White-Metzner model as follows:

$$\tau + \lambda(\varphi_{\text{eff}}) \frac{\delta \tau}{\delta t} = 2\eta(\varphi_{\text{eff}}) \mathbf{D},$$

where $\tau$ is the extra stress tensor, and $\mathbf{D}$ is the rate-of-deformation tensor. The differential operator $\delta/\delta t$ indicates the upper-convected derivative.

3. SIMPLE SHEAR FLOWS

We numerically simulated startup flows of simple shear at prescribed shear rates $\dot{\gamma}$ in order to evaluate the rheological properties of floc-forming suspensions. In the initial state, the
fluid is at rest and the number density distribution of flocs is assumed to be uniform. Moreover, simple shear is imposed on the fluid at time \( t = 0 \). The shear and the normal stresses \( \tau_{xy} \), \( \tau_{xx} \), and \( \tau_{yy} \) are computed, and the shear viscosity \( \eta \) and the first normal stress difference \( N_1 \) are evaluated by \( \eta = \tau_{xy}/\dot{\gamma} \) and \( N_1 = \tau_{xx} - \tau_{yy} \), respectively.\(^{10}\) Here, \( x \) and \( y \) indicate the directions of flow and the velocity gradient, respectively.

We adopted the same values for the model parameters\(^{11}\) as those used in our previous study:\(^{9,10}\) \( \rho_0 = 1.550 \text{ kg/m}^3 \), \( \rho_s = 1.000 \text{ kg/m}^3 \), \( F_c = 1.2 \text{ nN} \), \( \dot{\varepsilon}_{\text{eff}} = 5.3 \), \( \eta_s = 1.05 \text{ \( \mu \)m} \), \( m_p/m_s = 0.01 \), \( G_m = 0.05 \text{ Pa} \), \( m = 4 \), \( \varphi_m = 0.64 \), \( k = 2.0 \), and \( \eta_0 = 0.001 \text{ Pa} \cdot \text{s} \). Moreover, the total number of monomers per unit volume, the radius of the maximum floc, and the radius \( r_k \) of a floc in the \( k \)th class were set to be the same as in our previous simulations.\(^{9,10}\) In the present analysis, the fractal dimension \( d_f \) is varied as \( d_f = 2.65, 2.7, 2.75, \) and \( 2.8 \). For suspensions of small \( d_f \), the floc size evaluated using Eq. 4 is large, and the effective volume fraction \( \varphi_{\text{eff}} \) computed using Eq. 5 increases. In addition, \( \varphi_{\text{eff}} \) possibly exceeds \( \varphi_m = 0.64 \), which corresponds to the maximum packing volume fraction for random packing of spheroidal particles and is often applied in the Krieger-Dougherty model. Consequently, it is necessary to apply larger \( \varphi_{\text{eff}} \) for small \( d_f \). We therefore chose relatively large values of \( d_f \) in the present simulation.

4. RESULTS AND DISCUSSION

4.1 Steady shear properties

Figure 1 shows the dependence of both shear viscosity \( \eta \) and the first normal stress difference \( N_1 \) at steady states on \( d_f \). The shear viscosity is larger for smaller \( d_f \) and has a shear-thinning property for every \( d_f \). A previous study\(^9\) revealed that the occurrence of the shear thinning was due to the fact that the ratio of small flocs increases with increasing shear rate. The first normal stress difference \( N_1 \) increases with increasing \( \dot{\gamma} \) and is larger for smaller \( d_f \). The values of model parameters except for \( d_f \) used in the present simulation were determined to describe rheological properties of CNF suspensions and when \( d_f = 2.75 \), the shear viscosity predicted by the present model agrees well with the corresponding experimental measurements.\(^1,11\) On the other hand, to the author’s knowledge, experimental data of rheology of CNF suspensions for other fractal dimensions were unavailable. Hence we cannot compare the predicted results with the corresponding experimental measurements of real CNF systems. However, the dependence of viscosity on \( d_f \) qualitatively agrees with the counterpart of other floc-forming suspensions.\(^{17,18}\) Weston et al.\(^{17}\) investigated the agglomerate morphology and rheology of Boehmite nanocrystal suspensions at two pH conditions. They found that shear viscosity of suspensions decreases with increasing the fractal dimension of the agglomerate nanocrystals. Moreover, Barthelmes et al.\(^{18}\) carried out the numerical simulation of shear-induced coagulation and fragmentation of suspensions of polydisperse particles that form fractal structures and reported that shear viscosity decreased with increasing the fractal dimension.

The difference in viscosity with \( d_f \) is relevant to the dependence of \( \varphi_{\text{eff}} \) on \( d_f \). Figure 2 plots \( \varphi_{\text{eff}}/\varphi_m \) for each \( d_f \) as a function of \( \dot{\gamma} \). Here, \( \varphi_{\text{eff}} \) is smaller for larger \( d_f \). Consequently, as known from Eq. 6, the viscosity of suspensions of large \( d_f \) is small.

We analyze the mechanism of the dependence of \( \varphi_{\text{eff}} \)
on $d_f$. Figure 3 shows the floc size distribution for each $d_f$ at $\dot{\gamma} = 0.1$ s$^{-1}$, 1 s$^{-1}$, 10 s$^{-1}$, and 100 s$^{-1}$. The existing probabilities of flocs belonging to each class, $P$, scaled by that when the floc size is uniformly distributed, $P_0$, are indicated. The peak position shifts to the small-floc-size side as the shear rate increases for every $d_f$ because flocs tend to be broken by shear deformation more frequently at higher shear rates. Furthermore, the peak position shifts to the large-floc-size side, and the peak value decreases as $d_f$ increases. These results are relevant with respect to the fractal-dimension dependence of the fragmentation kernel $k^{(b)}$. As indicated in Fig. 4, the value of $k^{(b)}$ is smaller for larger $d_f$, which means that the breakage rate of the same size floc decreases as $d_f$ increases. Consequently, in Fig. 3, the peak position of $P/P_0$ for large $d_f$ exists in larger-floc side, as compared to suspensions of small $d_f$. However, the effective volume fraction is smaller for suspensions of larger $d_f$, which can be explained as follows. As known from Eq. 4, flocs of large $d_f$ consist of more monomers, as compared to those of smaller $d_f$ for the same size. Therefore, when the total number of monomers is fixed, the number of flocs decreases, and hence the effective volume fraction also decreases, even though the population of large-size flocs is relatively large.

Next, we consider the elastic properties. The difference in the elastic property due to $d_f$ is clearly seen in the first normal stress coefficient $\Psi_1$. We therefore analyze the behavior of $\Psi_1$ instead of $N_1$. In a Maxwell-type constitutive model including the White-Metzner model, $\Psi_1$ is described by $\Psi_1 = N_1 / 2\dot{\gamma}^2 = 2\nu \eta / (G \dot{\gamma}^2)$. Here, $\Psi_1$ is constant for the upper-convected Maxwell model, while, in the present model, both $\eta$ and $G$ depend on $\varphi_{\text{eff}}$ as per Eqs. 6 and 7.

Figure 5 plots the first normal stress coefficient $\Psi_1$ as a function of shear rate $\dot{\gamma}$. Here, $\Psi_1$ is larger for smaller $d_f$ and shows the shear-thinning behavior for every $d_f$. The steady state value of $\varphi_{\text{eff}}$ increases with decreasing $d_f$, as shown in Fig. 2, and $\lambda$ increases in a relatively large $\varphi_{\text{eff}} / \varphi_{\text{m}}$ region, as shown.

![Fig. 3 Distributions of floc size at shear rates $\dot{\gamma} = (a) 0.1$ s$^{-1}$, (b) 1 s$^{-1}$, (c) 10 s$^{-1}$, and (d) 100 s$^{-1}$ at steady states for fractal dimensions $d_f = 2.65, 2.7, 2.75,$ and 2.8. The existing probabilities of flocs belonging to each class, $P$, scaled by that when the floc size is uniformly distributed, $P_0$, are plotted.](image-url)
When the floc size is uniformly distributed, probabilities of flocs belonging to each class, \( P_k \) of the fragmentation kernel are relevant with respect to the fractal-dimension dependence \( d \) breakage rate of the same size floc decreases as \( d \) increases for every \( \gamma \). The peak position shifts to the small-floc-size side as the shear rate \( \dot{\gamma} \) increases. Consequently, in Fig. 3, the peak position of \( d \) and the peak value decreases as \( \dot{\gamma} \) increases. These results increase in a relatively large \( \dot{\gamma} \). In a Maxwell-type constitutive model including \( \Psi \), the value of \( \Psi \) approaches a constant value as per Eqs. 6 and 7.

\[
\Psi = \frac{\eta_0 \dot{\gamma}}{\eta(\dot{\gamma})} = \frac{\eta_0 \dot{\gamma}}{\eta(\dot{\gamma})} = \frac{\eta_0 \dot{\gamma}}{\eta(\dot{\gamma})} = \frac{\eta_0 \dot{\gamma}}{\eta(\dot{\gamma})}
\]

Fig. 4 Reduced fragmentation kernel \( k^{(b)} \) as a function of floc size at shear rates \( \dot{\gamma} = (a) 0.1 \text{ s}^{-1}, (b) 1 \text{ s}^{-1}, (c) 10 \text{ s}^{-1}, \) and (d) 100 \text{ s}^{-1} at steady states for fractal dimensions \( d_f = 2.65, 2.7, 2.75, \) and 2.8.

in Fig. 6. Consequently, \( \Psi_1 \) is larger for suspensions of smaller \( d_f \). In addition, the value of \( \Psi_1 \) approaches a constant value at high shear rates for each \( d_f \). When the fractal dimension is large, at \( d_f = 2.8 \), \( \Psi_1 \) slightly depends on the shear rate and is approximately constant.

\[\Phi_{\text{eff}, \phi} / \Phi_{\text{m}} = \frac{1 - (\Phi_{\text{eff}, \phi} / \Phi_{\text{m}})^k}{(\Phi_{\text{eff}, \phi} / \Phi_{\text{m})}^m}\]

\( \lambda = (\eta_0 / G_{\text{m}}) [1 - (\phi_{\text{eff}} / \phi_{\text{m}})^{-k}] / (\phi_{\text{eff}} / \phi_{\text{m})}^m \)

Fig. 5 First normal stress coefficient \( \Psi_1 \) as a function of shear rate \( \dot{\gamma} \) for \( d_f = 2.65 \) (circles), 2.7 (squares), 2.75 (triangles), and 2.8 (lozenges).

Fig. 6 Relaxation time \( \lambda = (\eta_0 / G_{\text{m}}) [1 - (\phi_{\text{eff}} / \phi_{\text{m}})^{-k}] / (\phi_{\text{eff}} / \phi_{\text{m})}^m \) as a function of \( \phi_{\text{eff}} / \phi_{\text{m}} \) at \( \eta_0 = 0.001 \text{ Pa s}, G_{\text{m}} = 0.05 \text{ Pa}, m = 4, \) and \( k = 2.0 \).
4.2 Transient shear properties

We analyze the dependence of the transient shear properties of the present model on \( d_f \). The temporal behavior of the present model suspension is dominated by two mechanisms: the temporal change in the floc size distribution and the relaxation process characterized by the relaxation time \( \lambda \).

After the startup of shear, flocs repeat aggregation and breakage, and hence the floc size distribution changes with time, resulting the temporal change in the effective volume fraction \( \phi_{\text{eff}} \). Since the effective volume fraction in the initial state, \( \phi_0 \), varies with \( d_f \), we consider the normalized effective volume fraction \( \phi_{\text{eff}} / \phi_0 \) in order to compare the rate of the temporal change from the initial state. Figure 7 shows the temporal changes in \( \phi_{\text{eff}} / \phi_0 \) at \( \dot{\gamma} = 1 \text{ s}^{-1} \) and \( 10 \text{ s}^{-1} \) for each \( d_f \). The volume fraction quickly decreases to reach a steady state, and the rate of decrease is faster at higher shear rates and for smaller fractal dimensions. The time necessary for the effective volume fraction to reach a steady state value is on the order of \( 10^{-1} \text{ s} \). Furthermore, the decrease from the initial value is larger for smaller \( d_f \). Consequently, the shear thinning in viscosity in Fig. 1 appears more strongly for suspensions of smaller \( d_f \).

Although the relaxation time \( \lambda \) depends on the floc size distribution through \( \phi_{\text{eff}} \), the growth of macroscopic properties such as \( \eta \) and \( \Psi_1 \) is considered to be mainly dominated by the steady state value of \( \lambda \). As shown in Fig. 6, \( \lambda = (\eta_0/G_m)(1 - \phi_{\text{eff}} / \phi_m)^{\frac{1}{2}} / (\phi_{\text{eff}} / \phi_m)^m \) is on the order of 1 s because, in the present simulation, \( \phi_{\text{eff}} / \phi_m \) ranges from approximately 0.45 to 0.9. Figures 8 and 9 show temporal changes in \( \eta \) and \( \Psi_1 \), respectively, at \( \dot{\gamma} = 1 \text{ s}^{-1} \) and \( 10 \text{ s}^{-1} \). In both cases of \( \eta \) and \( \Psi_1 \), it takes longer to reach a steady state for suspensions of smaller \( d_f \). Furthermore, the time required is much longer than time necessary for the change in the floc size distribution.

These results indicate that the growth of both \( \eta \) and \( \Psi_1 \) is dominated by the relaxation time \( \lambda \). In floc-forming suspensions, the macroscopic relaxation process originates from the deformation of flocs. Although the present model does not describe the deformation of flocs directly, this model can represent the effect of floc deformation on the relaxation process via the relaxation time \( \lambda \) in the White-Metzner model.
state in a short time, as compared to the relaxation time \( \lambda \). Consequently, the growth of macroscopic properties, such as \( \eta \) and \( \Psi_1 \), is mainly dominated by the steady-state value of \( \lambda \), although this value depends on the temporal change in the floc size distribution through \( \varphi_{\text{eff}} \). Furthermore, both \( \eta \) and \( \Psi_1 \) grow faster for suspensions of larger \( d_f \). The present model can adjust the growth of the floc size distribution by controlling the value of \( d_f \). In addition, although the present model does not describe the deformation of flocs directly, the model can represent its effect on the macroscopic relaxation process of stress via the relaxation time \( \lambda \).

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