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ABSTRACT

The viscometric behavior of laponite and bentonite suspensions at different concentrations in shear flow is studied. It is discovered that in the equilibrium state, a master curve of viscosity can be constructed when the applied shear stress is normalized by the respective suspension’s yield stress. The interparticle interaction controlling the yield behavior at the gel state also dominates the behavior of particles at the equilibrium flowing state. A constitutive framework is developed to describe the master curve of viscosity as a function of the shear stress normalized by the yield stress. Based on the proposed model, the effect of concentration on the viscosity of clay suspensions can be estimated via their yield stress.

I. INTRODUCTION

The rheological behavior of the clay suspension is complex due to strong interparticle forces between disk-shaped clay particles, including electrostatic and van der Waals forces, which is distinct from noncolloidal suspensions (Loisel et al., 2015; Mwasame et al., 2016; Vázquez-Quesada and Ellero, 2016; Chun et al., 2017; and Tanner, 2018). In the static state, at low ionic strength, the system forms a gel when the concentration reaches a critical value (gel point) and becomes fluidlike when a shear stress is greater than a yield stress, \( \tau_y \), giving rise to the yielding behavior. \( \tau_y \) is considered to be a very important parameter reflecting the microstructure in gel. It is often related to electrostatic forces, including the attractive forces between the faces and the edges of the clay platelets (referred to as the face-edge structure), as well as the repulsive force between the faces of the platelets (referred to as the face-face structure). Several models that originated from the DLVO (Derjaguin and Landau, Verwey and Overbeek) theory have been proposed based on this assumption, considering the face-edge attractive interactions (Laxton and Berg, 2006; Teh et al., 2009; and Leong et al., 2012) and the face-face repulsive interactions (Sakairi et al., 2005; Lin et al., 2013; and 2016), respectively. Furthermore, other approaches based on the excluded volume effects (motion of the platelet suppressed by its neighbors at high volume fractions) or the statistical hydrodynamic trapping of a particle by another (two platelets are temporarily associated by hydrodynamic trapping and move together) can also capture the yield stress and the elasticity of swelling clay suspensions (Michot et al., 2009; Paineau et al., 2011).

Besides the yield behavior, it is found that some clay suspensions, such as laponite and montmorillonite suspensions, experience an unsteady temporal behavior both in the static state and in shear flow. The temporal behavior at the static stage has been referred to as the aging of the gel (Leong et al., 2018). The microstructure in the gel is being locally adjusted in order to balance the repulsive and attractive interparticle forces and thus achieve the minimum-energy state. The time scale of this process is often in weeks, depending on the concentration of clay (Pignon et al., 1998; Au and Leong, 2015; and Leong et al., 2018). On the other hand, when a constant shear stress is applied to the system, a temporal transition can be observed, which is referred to as thixotropy (Pignon et al., 1996; 1998; and Bekkour et al., 2005). By a step shearing in shear-rate, Pignon et al. (1998) found that the time dependent behavior in shear is due to a structural change at different length scales, from the orientation of connected structures to the fragmentation of
aggregates at the length scale of $O(10^3) \mu m$; the characteristic time of orientation is about three orders of magnitude less than that of disaggregation.

A number of constitutive models have been developed to predict both the transient and steady (equilibrium) rheological behavior for complicated systems, such as clay suspensions, paints, pastes, and food products, based on both phenomenological approaches (Herschel, 1924; Powell, 1995; and Phan-Thien et al., 1997) and microstructural approaches (Nguyen and Boger, 1985; Toorman, 1997; Mujumdar et al., 2002; Coussot et al., 2002; and de Souza Mendes, 2011). The steady and transient behavior of the clay suspensions in flow has been well predicted in various degrees. However, in these models, the effect of the concentration has rarely been discussed.

In this study, the rheological behavior of laponite and bentonite suspensions is investigated in the equilibrium state. A rheological model is proposed based on the experimental results, in order to describe the shear thinning behavior of the clay suspension taking into account the clay concentration.

II. EXPERIMENT

A commercial sodium bentonite clay (Hongruitai Bentonite Technology Co., Ltd., China) and a laponite clay (BYK Additives & Instruments, UK) are used in the experiments. The clay suspensions are made by mixing the clay powder in deionized water. Samples are mixed with an overhead stirrer at 400 rpm for 30 min. The prepared samples are allowed to rest for 10 h, for bentonite suspensions, and 48 h, for Laponite suspensions, respectively, in order for the systems to achieve a stable state before measurements. The natural $pH$ of laponite and bentonite is approximately 10.1 and 9.5, respectively, which is not sensitive to the concentration in the concentration range investigated in this study.

A DHR-1 rotational rheometer from TA Instruments with a cone-plate geometry is used in the rheological measurements. The diameter of the plate is 40 mm, with a cone of cone angle of 1.983°. The cone is truncated at 48 $\mu m$ from the vertex. Both shear-stress-control and shear-rate-control modes are adopted in the test. Prehearing with a shear rate of 500 s$^{-1}$ and a shearing time of 30 s is applied. Samples are then rested for 30 s before the viscometric test. The temperature is maintained at 25°C. In order to minimize errors caused by water evaporation from the suspension, each sample loaded to the rheometer is tested once and discarded, with a testing time of about 10 min/sample.

III. RESULTS AND DISCUSSION

The transient behavior upon a steady shear stress is shown in Fig. 1. For the laponite suspension at 3.5 wt. % concentration, when a steady shear stress $\tau$ is applied to the system, and at low $\tau$, the shear rate $\dot{\gamma}$ increases and reaches a local peak value at around 0.03 s, after which $\dot{\gamma}$ falls to a low value at around 0.1 s (called the “minimal” value). At low $\tau$ (e.g., $\tau = 5$ Pa), the minimal value of $\dot{\gamma}$ is very low, reflecting the elasticity character of the gel at this stage. The peak and minimal values of $\dot{\gamma}$ become less obvious with increasing $\tau$. The behavior at this stage may be due to the deformation of the gel. After this stage, $\dot{\gamma}$ increases quickly from the minimal value. Then, two critical stresses, $\tau_1$ and $\tau_2$, may be identified. If $\tau < \tau_1$, e.g., $\tau = 5$ Pa in Fig. 1(a), $\dot{\gamma}$ decreases continuously and the equilibrium state cannot be achieved. The data are much scattered. The final $\dot{\gamma}$ reached at time 100 s is less than $10^{-4}$ s$^{-1}$. If $\tau_1 \leq \tau < \tau_2$, e.g., $\tau = 25$ Pa, $\dot{\gamma}$ appears unstable, which first decreases and then increases again and finally continuously decreases to a low value. The $\dot{\gamma}$ vs time curve is smooth, an indication that flow does occur, though unstable. Again, the equilibrium state cannot be achieved. The final $\dot{\gamma}$ within the experimental duration of 100 s is no more than $10^{-4}$ s$^{-1}$. Finally, if $\tau \geq \tau_2$, e.g., $\tau = 30$ Pa, the curve rises and approaches a steady-state value of $O(10)$ s$^{-1}$ with the overall transient time of about 10 s. Obviously, at this stage, the system yields to flow steadily. These findings are in agreement with Coussot et al. (2002). Furthermore, comparing Fig. 1(a) with Fig. 1(b), it can be seen that the time scale of the transient behavior decreases with increasing clay concentration. In this study, we focus on the viscometric behavior of clay suspensions at the equilibrium state; therefore, the transient behavior is not investigated further here.

![Fig. 1. Transient behavior of (a) 3.5 wt. % and (b) 4.5 wt. % laponite suspensions under steady shear stress.](image-url)
Viscometric data of laponite suspensions are shown in Fig. 2 using the stress control mode with step-up stress. In order for the system to reach the equilibrium state in each shear step, the shearing time is set to be 10 s and 5 s for laponite and bentonite suspensions, respectively, before the data are recorded. It can be found that \( \dot{\gamma} \) rises sharply to \( O \left( 10^{2} \right) \) s\(^{-1} \) [from a low value of \( O \left( 10^{-3} \right) \) s\(^{-1} \)] when the applied stress exceeds a critical stress, indicative of a significant yielding. The above mentioned \( \tau_1 \) and \( \tau_2 \) are close to each other because of the sharp increase in \( \dot{\gamma} \) in the vicinity of the yielding. We define a yield stress, \( \tau_y \), as a critical stress that \( \dot{\gamma} \) increases sharply. It can be found that \( \tau_y \) deduced from Fig. 2 refers to the critical stress, \( \tau_2 \), in Fig. 1. It should be noted that for \( \tau < \tau_y \), the viscometric data in Fig. 2 are, in fact, captured at the transient state as seen from Fig. 1, while for \( \tau \geq \tau_y \), the data at the equilibrium state can be achieved with a transient time of around 10 s. For bentonite suspensions, the behavior is similar to laponite suspension and the transient time at the flowing state is around 5 s. Boundary slip should be taken into account since we used the default cone-plate geometry with the roughness of 0.143 \( \mu \)m. By comparing the results from the measurements with smooth and rough plates, Pignon et al. (1998) found that the ideal shearing condition can be achieved when the shear rate exceeds 10 s\(^{-1} \) for laponite suspensions. Therefore, boundary slip is unlikely to occur when the system is in the equilibrium flowing state (\( \dot{\gamma} \geq 100 \) s\(^{-1} \)).

The yield stress, as determined from Fig. 2, at different concentrations is shown in Fig. 3 and Table I. The strong interparticle electrostatic interactions result in the formation of a network structure and consequently a gel in the macroscale. Here, clearly \( \tau_y \) increases with increasing concentrations. According to Larson (1999),

\[
\tau_y \sim \frac{\phi^2}{a^2} W'(D_y),
\]

where \( \phi \) is the volume fraction of particles, \( a \) is the particle effective radius, and \( W'(D_y) \) is the interaction potential at the particle separation distance of \( D_y \). Based on Eq. (1), Lin et al. (2015) proposed that \( \tau_y \sim \tau_0 \phi^2 / [\exp(B(\phi^{-1} - 1)) - 1] \), assuming that the main interparticle interaction is the face-face repulsive electrostatic interaction. \( \tau_0 \) and \( B \) are parameters to be determined experimentally. Obviously, \( \tau_y \) increases with increasing concentrations, a trend in agreement with our experimental results.

When \( \tau \geq \tau_y \), the network structure breaks down and the system flows steadily, reflecting in the yielding behavior. An obvious

### Table I. Yield stress of laponite and bentonite suspensions at different mass fractions.

| Mass fraction (laponite) | 3.5 wt. % | 4 wt. % | 4.5 wt. % | 5 wt. % |
|--------------------------|-----------|--------|-----------|---------|
| \( \tau_y \) (Pa)       | 45.17     | 69.22  | 108.83    | 157.68  |
| Mass fraction (bentonite) | 7.5 wt. % | 10 wt. % | 15 wt. % |
| \( \tau_y \) (Pa)       | 2.20      | 7.92   | 26.48     |

FIG. 2. Shear rate as a function of shear stress at different mass fractions in the stress-control mode for (a) laponite and (b) bentonite suspensions.

FIG. 3. Yield stress as a function of clay concentration for laponite and bentonite suspensions.
shear thinning can be observed from Fig. 2. The shear thinning is considered to be the deformation and disaggregation of the gel structure (Pignon et al., 1998), from the microscale to nanoscale range with increasing shear, or an orientation of the clay platelets, aligning with the flow (Paineau et al., 2011). The curves shift toward a higher shear stress with increasing mass fractions. In shear flow, the resistant stress against the flow is induced by the interparticle forces between clay platelets, including the face-to-face repulsive and face-to-edge attractive forces, which are complicated and difficult to be identified in detail. However, assuming that the interparticle interactions in shear flow has the same origin with the formation of gel, a simple way to quantify the rheology in flow is to relate the applied stress to the yield stress, $\tau_y$.

As shown in Fig. 4, from the viscometric curves (at the equilibrium state after yielding), the suspensions’ viscosity, $\eta$, is plotted vs the shear stress, normalized by $\tau_y$ deduced from Fig. 2. From Fig. 4,

$$\eta = \frac{r}{\gamma/\gamma_c} = K^* \gamma^{n},$$

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$$\eta = \frac{r}{\gamma/\gamma_c} = K^* \gamma^{n},$$

for all the laponite and bentonite suspensions at various concentrations, a master curve of viscosity can be constructed, especially when $\tau/\tau_y > 1$. As shown in Fig. 4(b), when $\tau/\tau_y < 1$, i.e., before yielding, the divergence in the data is obvious and is expected. In this range, the transient stage as mentioned previously is important, which varies with the concentration and clay adopted. Furthermore, shear inhomogeneity and boundary slip occur and contributed to this process (Pignon et al., 1996; 1998). Pignon et al. (1996) observed a significant shear banding for the laponite suspension near yielding. The shear banding can be deduced as

$$\tau_y = \eta \gamma_c,$$

where $K$ and $n$ are empirical parameters. The equilibrium viscosity may be expressed as

$$\eta_e = \frac{r}{\gamma/\gamma_c} = K^* \gamma^{n}.$$
### TABLE II. Parameters adopted in Eq. (4) in the fitting of experimental data.

| Parameter | $\eta_0$ | $K'$ | $m$ |
|-----------|----------|------|-----|
| Value     | 0.01     | 0.03 | -5  |

As indicated in Eq. (4), the yield stress, $\tau_y$, is included in the constitutive model. Since $\tau_y$ in the model is a function of clay concentration [Eq. (1)], the effect of clay concentration on the viscosity can be predicted. Consequently, from the master curve and $\tau_y$, the viscosity as a function of the applied shear stress can be estimated at different mass fractions. Change of $\tau_y$ with the mass fraction was estimated by, for example, Lin et al. (2015) based on Eq. (1) and assuming the interparticle interaction is due to the face-to-face electrostatic repulsive force between clay platelets.

Furthermore, a constitutive model describing the shear stress (viscosity) as a function of shear rate may be more practicable for the computation of the flow field in an engineering application. Therefore, a constitutive model based on the variable $\tau/\tau_y$, which can be straightforwardly turned to the form $\tau = \eta(\dot{\gamma})\dot{\gamma}$, is more usable and will be studied in the future.

### IV. CONCLUSION

The viscometric behavior of bentonite and laponite suspensions at the equilibrium state is investigated. It is discovered that the viscosity curves for clay suspensions at various mass fractions investigated here can be converted to a master curve when plotted against the applied stress normalized by the yield stress of the system. Therefore, it may be proposed that the factors determining the equilibrium flowing properties are the same with the factors that determine the yield behavior of the gel at the static state (i.e., the condition of interparticle interactions). Based on the experimental results, we construct a constitutive model, which describes the master viscosity curve as a function of the normalized stress. Since the yield stress is a function of clay concentration, by the model proposed here, the change of viscosity with the clay concentration can be estimated.

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