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Scaling behavior of response times of electrorheological suspensions with cation exchange resin particles

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Stress responses of electrorheological suspensions to stepwise electric fields were measured under different experimental conditions. The stress responses could be expressed by an exponential expression with three modes, modes 0, 1, and 2. The response time of mode 1 multiplied by the shear rate ($\dot{\gamma}\tau_1$) could be roughly scaled by Mason's number (M_n) with the exponent of 0.23, while $\dot{\gamma}\tau_2$ was almost independent of M_n. The aggregation behavior of the particles is discussed in terms of theoretical expectations and our experimental results.

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An electrorheological (ER) suspension consists of polarizable particles dispersed randomly in an insulating solvent under no electric field. The ER suspension shows large increase in apparent viscosity and recovery to the original viscosity by application and removal of an external electric field, respectively. This effect of the ER suspension is called the ER effect. The temporal response of the ER effect is closely related to the aggregation of the polarized particles under shear deformation. The aggregation kinetics of the polarized particles has been studied mainly by optical methods in the quiescent state [1–5]. It is considered that the aggregation kinetics of the polarized particles in a sheared state is different from that in a quiescent state [6, and the references therein]. However, only a few measurements of the transient rheological response have been reported in a Couette flow [6–8].

On the basis of an induced dipole-dipole interaction [9], aggregation of the polarized particles is considered to be determined by the competition between induced dipole interaction forces and hydrodynamic forces by the shear deformation. Therefore, the temporal response of the ER effect is expected to be affected by an external electric field, the dielectric constant of particles, that of continuous phase of the suspension, and the intensity of hydrodynamic deformation which is applied to the suspension. These parameters are included in a general dimensionless parameter called Mason's number (M_n) [10], representing the ratio of viscous forces to induced dipole interaction forces.

$$M_n = \eta_c \dot{\gamma} / 2\varepsilon_c \varepsilon_0 (\beta E)^2, \tag{1}$$

$$\beta = (\varepsilon_p - \varepsilon_c)/(\varepsilon_p + 2\varepsilon_c), \tag{2}$$

where η_c is the viscosity of continuous phase, $\dot{\gamma}$ is the shear rate, ε_p is the dielectric constant of particles and ε_c is that of the continuous phase of insulating solvent, ε_0 is the permittivity of free space, and E is an external electric field strength. In the present paper, the dependence of temporal response of the ER suspensions with cation exchange resin particles upon the external electric field strength as well as the intensity of hydrodynamic deformation is reported, and a scaling behavior is discussed in terms of Mason's number and the response times of the ER effect of an exponential expression with plural modes multiplied by the shear rate.

Cation exchange resin particles (Amberlite IR-124) were suspended in silicone oils with viscosities of $\eta_c = 0.02$ and 0.3 Pa s, respectively. The volume fraction of the particles was 0.33 assuming the volume additivity of each silicone oil and the particles. The dielectric constant of the sample suspensions and that of silicone oil alone were measured at an electrical frequency of 1 kHz using an *LCR* meter (Hewlett and Packard 4263A). Relative dielectric mismatch of the particles and silicone oil (β) was calculated from the Maxwell relation [11] using the volume fraction of particles, the real part of the dielectric constant of sample suspensions and that of silicone oil alone. (β was around 0.22 for most sample suspensions and it changed to 0.90 for a suspension absorbing water from an atmosphere.) The electrical frequency of 1 kHz is used in the present paper because a typical response time of the ER effect is though to be on a time scale of milliseconds. However, dielectric data at 1 kHz may have no similarity to the β in effect with a static or stepwise applied electric field. β calculated from the dielectric data of the samples used in a frequency range from 100 Hz to 100 kHz decreased with an increase in the frequency below 1 kHz and it was constant above 10 kHz.

The stress responses to stepwise electric fields were measured by two rheometers of parallel plate sliding type at constant shear rate deformations. These rheometers were made in our laboratory and one of them was reported elsewhere [8,12]. In these rheometers, a mechanical sensor (a strain gage of bending type) was perpendicularly connected with an aluminum rod supported by two thin and rigid plates of phosphor bronze. The rod was also connected with one of the parallel plates of glass (upper one). Another plate (bottom one) was mounted on a translation stage to allow the appli-

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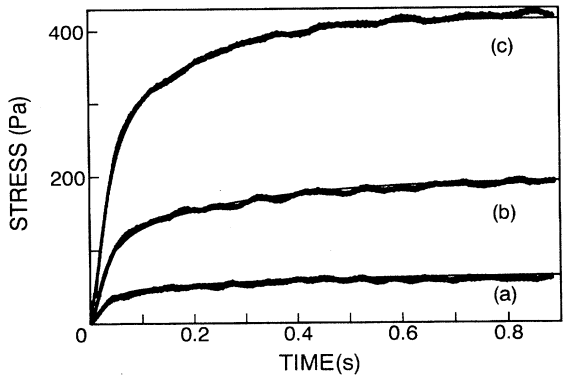

FIG. 1. Typical stress responses to stepwise electric fields with three different amplitudes of (a) 1 kV/mm, (b) 2 kV/mm, and (c) 3 kV/mm at a shear rate of 4.8 s^{-1}. Viscosity of the continuous phase was 0.02 Pa s, ε_c was 2.70 and β was 0.22. Fitted curves by Eqs. (3) and (4) are also shown in the figure.

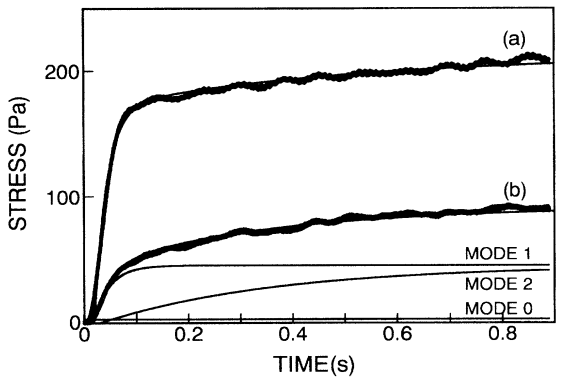

FIG. 2. Typical stress responses to a stepwise electric field at shear rates of (a) 4.1 s^{-1} and (b) 0.54 s^{-1}. Amplitude of the electric field was 2 kV/mm. Viscosity of the continuous phase was 0.02 Pa s, ε_c was 2.70, and β was 0.90. Fitted curves and the components (mode 0, mode 1, and mode 2) of the fitted curve (b) are also shown in the figure.

cation of shear deformation by sliding to one direction (x direction). The copper electrodes were attached to the glass plates. The bottom plate was slid and the displacement of the upper plate was detected by the sensor. The detected signals were digitized at a rate of 100 μs/signal by a 12-bit analog-to-digital converter, and the data were stored in a personal computer. With this detection system, any force influencing the displacement of the upper plate can be detected. For example, not only a force parallel to the x direction but also a force perpendicular to the x direction (z direction), extending or narrowing the gap between the two plates (0.5 or 1 mm), are detected as a change in a stress. The electric field was applied to the z direction. The frequency resolution of one of the rheometers [8] was 2 kHz, and that of another rheometer was about 500 Hz which was estimated from the response of the mechanical sensor connected with a parallel plate unit to a forced mechanical stimulus with a square wave. The mechanical stimulus was generated by an audio transducer driven by a pulse generator. In the present experiment, the data have not been corrected for the effect of inertia of the detection system. The stepwise electric fields were applied to the sample suspensions using a piezodrive amplifier (MESS-TEK Co., M-2628) with a 10 kHz bandwidth and it was driven by a pulse generator. The amplitude of the stepwise electric fields was up to 3 kV/mm and the shear rate was up to 5 s^{-1}.

Figures 1 and 2 show, as examples, stress responses to stepwise electric fields with three different amplitudes measured at a given shear rate and those to a stepwise electric field measured at (a) high and (b) low shear rates, respectively. The stepwise electric fields were applied at a time (t) of zero in Figs. 1 and 2. It can be roughly seen in Fig. 1 that the temporal response to reach a saturated stress (for instance, estimated from the half time to reach a saturated stress, $\tau_{1/2}$) is almost independent of the electric field strength or weakly decreases with an increase in the electric field strength (both $\tau_{1/2}$ estimated from Fig. 1 at 1 kV/mm and that at 3 kV/mm are about 45 ms; the changes in the electric field correspond to 9 times changes in M_n; nevertheless, we think from our experimental results that the temporal response of the present suspension weakly decreases with an increase in the electric field strength, which can be supported by the dependence of mode 1 as shown in Fig. 3 and its related discussion). On the other hand, temporal response measured at a high shear rate is much faster than that measured at a low one ($\tau_{1/2}$ estimated from Fig. 2 is 77 ms at 0.54 s^{-1}, and 45 ms at 4.1 s^{-1}; the changes in the shear rate correspond to 7.6 times changes in M_n, and the changes in M_n by the shear rate are comparable to those by the electric field as shown in Fig. 1). However, the shear rate dependence of the temporal response which is discussed qualitatively is opposed to an expectation from an induced dipole interaction between two particles as discussed in the next paragraph.

In the aggregation of a pair of polarized particles under shear deformation, it is considered that dipole-dipole interaction forces act as attractive forces to promote the aggregation of the particles and hydrodynamic forces act as repulsive forces to suppress the aggregation. That is, the aggregation can be suppressed when $M_n \gg 1$. Therefore, the temporal response of the ER effect is expected to become slower as M_n increases for a dilute suspension: For instance, the temporal response can be expected to become slower when the shear rate increases and the other parameters are fixed, and this expectation is opposed to the tendency of our experimental results as mentioned above. A similar opposite tendency of the shear rate dependence as shown in the present results was also reported recently by Ginder and Ceccio [6]. The aggregation of the particles in a concentrated suspension such as the present samples can follow other models in taking account of multibody effects in a shear deformation. In a concentrated ER suspension at a given volume fraction of particles, it is considered that the chance of collision of the particles increases with an increase in shear rate so that the rate for aggregation of the particles can increase. This tendency of the rate for aggregation is qualitatively consistent with the inverse relationship between the rheological response time and shear rate [6]. At the same time, it can be thought that the temporal response of the ER effect weakly decreased with an increase in the electric field strength (that is, a decrease in M_n) as discussed above. This tendency of the temporal response is qualitatively consistent with that expected by the dipole-dipole interaction between two particles. Therefore, it is expected that the temporal response (or

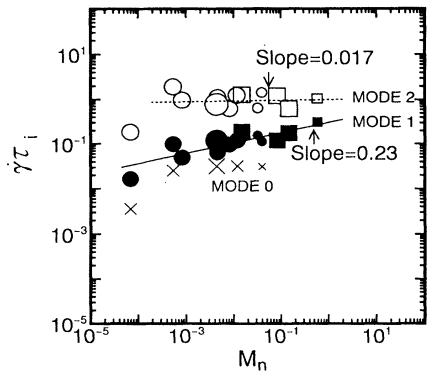

FIG. 3. Product of response times and shear rate plotted against Mason's number. The symbols × are the results of mode 0. Solid and open symbols are the results of mode 1 and those of mode 2, respectively. Square symbols are the results of suspension with $\eta_c = 0.3$ Pa s and the other symbols are those with $\eta_c = 0.02$ Pa s. Three different sizes of the symbols used in the figure represent the electric field strength of 1, 2, and 3 kV/mm in order of increasing size.

response times, τ_i, defined below) of the ER effect can be expressed as functions of M_n and the inverse of the shear rate ($\tau_i \propto \dot{\gamma}^{-1} {M_n}^m$).

As reported previously, the stress response could be well assumed to be an exponential expression with plural modes (two modes [8]) which took place in succession,

$$\sigma(t) = \sum_i \sigma_i [1 - \exp\{-(t - t_i)/\tau_i\}], \tag{3}$$

$$\sigma_i = 0 \quad (\text{for } t < t_i), \tag{4}$$

where σ_i, τ_i, and t_i are adjustable parameters of the ith mode response, respectively. In Figs. 1 and 2, it is necessary to add another mode (mode 0) so as to fit the stress response around $t = 0$. Therefore, the adjustable parameters of τ_i ($i = 0,1,2$) obtained by a curve fitting are discussed below as the response times of the ER effect. Figure 3 shows the product of the response times and shear rate plotted against M_n. It can be seen in Fig. 3 that $\dot{\gamma}\tau_1$ is roughly scaled by M_n (with the exponent of 0.23 as discussed below), while $\dot{\gamma}\tau_0$ and $\dot{\gamma}\tau_2$ are almost independent of M_n. However, there may be no specific relations with quantitative reality between $\dot{\gamma}\tau_0$ and M_n in Fig. 3. From the results of the curve fitting, τ_0 is almost constant and independent of the shear rate as well as electric field strength. Further, τ_0 is close to the time resolution of the rheometer used (about 2 ms). An artificial factor of mode 0 may also be considered such as impulsive electrostatic attractive forces between two electrodes immediately after the onset of the electric field; the gap between the parallel plates of the rheometer can be narrowed by the attractive forces of the polarized suspension with a time scale of the resolution of the rheometer. Nevertheless, it can be thought from our experimental results of mode 1 that the aggregation of the particles of the present samples is determined not only by the competition between electric forces and shearing forces but also the shear rate dependence of the chance of collision of the particles. The exponents of mode 1 and mode 2 as shown in Fig. 3 were determined as preliminary ones, respectively, by least square fitting. The exponent of mode 1 is 0.23, and that of mode 2 is on the order of 10^{-2} which indicates $\dot{\gamma}\tau_2$ is almost independent of M_n. In other words, $\dot{\gamma}\tau_1$ is roughly proportional to ${M_n}^{0.23}$ (τ_1 is roughly proportional to $\dot{\gamma}^{-3/4}$ when the other parameters are fixed) and τ_2 is roughly proportional to $\dot{\gamma}^{-1}$ alone.

It is still unclear what each of the response modes can be assigned to. Previously, two response modes, faster and slower modes, were reported [8]; the faster mode was assigned to the initial aggregation of the particles, and the slower mode was to the yield of the aggregates (clusters). Ginder and Ceccio [6] pointed out that the rheological response time (τ_{stress}) is likely controlled by the time scale for particle polarization (τ_{el}), particle aggregation (τ_{agg}), and the growth of the applied strain (τ_{strain}). It is supposed that mode 1 corresponds to the aggregation (or elongation) of particles because $\dot{\gamma}\tau_1$ depends relatively strongly on M_n. Mode 2 may correspond to the yielding process of clusters. τ_{strain} is expressed [6] as

$$\tau_{\text{strain}} \approx \gamma_y / \dot{\gamma}, \tag{5}$$

where γ_y is a yield strain [13]. As reported elsewhere, the yield strain (the larger one) estimated from the strain dependence of dynamic viscoelastic properties of an $Fe(OH)_3$ coated silica suspension is almost independent of the electric field strength [14]. This dependence of the yield strain on the electric field strength is almost consistent with that of $\dot{\gamma}\tau_2$ on M_n. Mode 0 may be related to the polarization of particles immediately after the onset of the electric field. However, other artificial factors such as the time resolution of the rheometer or the effect of the inertia of the detecting unit may also be considered as explanations of mode 0.

Further, Halsey and Toor [15] considered a model of the competition between electric forces and thermal effects and they pointed out a two-step process of structure formation of an ER suspension, initial aggregation of particles parallel to the electric field (chain formation) and later densification of the chains perpendicular to the electric field (column formation). Mode 1 and mode 2 may correspond to the chain formation and the column formation, respectively. There are alternative models reported recently which take account of the multibody effects [16,17] and upper limit of the electrostatic attractive force between nearest neighbor particles [16]. The upper limit of the chain length (the length for aggregation of particles) is determined to be proportional to the inverse of the square root of the shear rate [16]. The dependence of response time in the molecular dynamics simulation [17] correlates with our results of mode 1. At the present stage, we cannot discuss definitely which model is the better one: The plural steps (faster and slower steps) of structure formation of an ER suspension and their time scales [15] are qualitatively consistent with our results. However, the plurality and time scales were derived in a quiescent state. It is expected that the dependence of the response times upon the shear rate is shown by their model which takes account of the sheared situation as well. The model by Takimoto [17] showed only a single response time of the ER effect (τ) although the relation derived by the model, $\tau \propto (\eta_c / \varepsilon_0 E^2)^{1/4} \dot{\gamma}^{-3/4} \phi^{-1}$, where ϕ is the volume fraction of

particles, is closely related to our results of mode 1. (From our experimental results, τ_1 is roughly proportional to $\dot{\gamma}^{-3/4}$ when the other parameters are fixed and τ_2 is roughly proportional to $\dot{\gamma}^{-1}$ alone.) Further investigations are needed to discuss the applicability of these models.

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[1] K. L. Smith and G. G. Fuller, J. Colloid Interface Sci. **155**, 183 (1993).

[2] T. C. Jordan and M. T. Shaw, in *Proceedings of the 2nd International Conference on ER Fluids*, edited by J. D. Carlson, A. F. Sprecher, and H. Conrad (Technomic, Lancaster, PA, 1990), p. 231.

[3] J. M. Ginder and L. D. Elie, in *Proceedings of the 3rd International Conference on ER Fluids (Carbondal)*, edited by R. Tao (World Scientific, Singapore, 1992), p. 23.

[4] J. E. Martin, J. Odinek, and T. C. Halsey, Phys. Rev. Lett. **69**, 1524 (1992).

[5] J. M. Ginder, Phys. Rev. E **47**, 3418 (1993).

[6] J. M. Ginder and S. L. Ceccio, J. Rheol. **39**, 211 (1995).

[7] A. Hosseini-Sianaki, W. A. Bullough, R. Firoozian, J. Makin, and R. C. Tozer, in *Proceedings of the 3rd International Conference on ER Fluids (Carbondal)*, edited by R. Tao (World Scientific, Singapore, 1992), p. 219.

[8] K. Tanaka, T. Yoshida, and K. Koyama, in *Proceedings of the 3rd International Conference on ER Fluids (Carbondal)*, edited by R. Tao (World Scientific, Singapore, 1992), p. 289.

[9] H. See and M. Doi, J. Rheol. **36**, 1143 (1992).

[10] L. Marshall, C. F. Zukoski, and J. W. Goodwin, J. Chem. Soc. Farady Trans. 1 **85**, 2785 (1989).

[11] G. Schwarz, J. Phys. Chem. **66**, 2636 (1962).

[12] K. Mingawa, T. Watanabe, M. Munakata, and K. Koyama, J. Non-Newton. Fluid Mech. **52**, 59 (1994).

[13] R. T. Bonnecaze and J. F. Brady, J. Rheol. **36**, 73 (1992).

[14] K. Tanaka, K. Koyama, and T. Watanabe, Polym. Prepr. **34** (2), 339 (1994).

[15] T. C. Halsey and W. Toor, Phys. Rev. Lett. **65**, 2820 (1990).

[16] J. Takimoto, in *Proceedings of the 3rd International Conference on ER Fluids (Carbondal)*, edited by R. Tao (World Scientific, Singapore, 1992), p. 53.

[17] J. Takimoto (unpublished), and private communication.