Time scales for structural formation in an electrorheological suspension probed by optical and electrical responses

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Responses of the diffuse transmitted light intensity and the current passing through an electrorheological suspension to the stepwise electric field were measured in the quiescent state, and the time scales for the structural formation of the polarized particles were reported. It was found experimentally that both of the responses consist of plural modes, the faster and slower modes even in the quiescent state. The optical response was also expressed as an exponential function with two modes, which take place in succession.

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I. INTRODUCTION

The electrorheological (ER) effect of the suspension is the stress response to the electric field. It is considered that the stress response is directly related to the structural formation of the polarized particles under shear deformation. In the previous paper, we reported the stress response to the stepwise electric field, which was measured under different experimental conditions [1]. The stress response was expressed as an exponential function with three modes, mode 0, 1, and 2, which take place in succession. It is considered that mode 1 is closely related to the aggregation process of the polarized particles, and mode 2, the slowest mode among the three, corresponds to the yielding process of the aggregated chains of particles. Mode 0, the fastest mode, can be related to the polarization of the particles immediately after the application of the electric field. However, an artificial factor may also be related to mode 0 such as impulsive electrostatic attractive forces between two electrodes immediately after the onset of the electric field with a time scale of the resolution of the rheometer. It is still unclear what these modes of the stress response should be assigned to.

On the other hand, it has been clarified theoretically and experimentally by Tao *et al.* that the structure in the quiescent state is a body-centered-tetragonal (bct) lattice acting as the ground state of the ER suspension [2,3]. The structural formation of the ER suspension was also investigated theoretically in the quiescent state. Halsey and Toor considered a model of the competition between electric forces and thermal effects and they pointed out a two-step process of structural 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) [4]. Furthermore, Tao *et al.* reported the temporal evolution of three-dimensional structure in a molecular-dynamics simulation and showed the equilibrium and nonequilibrium structures. They also showed that the chain formation time (the faster response) and the solidification time (the slower response) in the ER suspension depend mainly on the ratio of the viscous force to the dipolar force [5,6]. The faster and the slower responses are predicted by theory even in the quiescent state.

Experimentally, there are only a few reports to investigate the temporal evolution of the ER suspension in the quiescent state. As described above, Tao *et al.* determined the bct lattice structure using laser beam diffraction, the mechanism of which is totally different from conventional x-ray scattering [3]. The incident laser beam propagates through the suspension of glass spheres and silicone oil via stable optic modes along a regular array of transparent spheres, and then produces diffraction patterns. Martin *et al.* performed a real-time, two-dimensional light-scattering study of the evolution of structure in a nearly index-matched single-scattering ER suspension [7]. They reported the presence of an unstable concentration fluctuation in the direction orthogonal to the electric field, indicating the slow mode for the segregation of chains into columns. In these two methods, transparent particles should be used for the suspension. On the other hand, Ginder applied the method of the diffuse transmittance of light, in which multiple scattering is taken into account, to a commercially available ER suspension, and showed that the kinetics of aggregation of the particles can be probed by an increase in the transmittance of light parallel to the electric field [8]. The obtained time scale of the aggregation of the particles was of the order of 10^{-3} s, and the increase in the diffuse transmittance was fitted to a biexponential function only when the suspension was applied to the ac electric field. Further, Ginder *et al.* also reported the current response of the ER suspensions under shear deformation and a characteristic time scale for the ER suspensions [9]. The methods of the diffuse transmittance of light and the current response would be effective for probing the structural formation in the quiescent ER suspensions, especially for the fast response, because there are no mechanical artifacts such as inertial effect in these measurements.

In the present paper, the responses of the diffuse transmitted light intensity and the current passing through an electrorheological suspension with cation exchange resin particles to the stepwise electric field were measured in the quiescent state, and the time scales for the structural formation of the polarized particles are discussed. It should be noted that both of the responses consist of plural modes, the faster and slower modes even in the quiescent state. The

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response times obtained in the present paper, especially for the faster modes, can be compared with the response times obtained by rheological measurement, because the shear deformation is negligible at the time immediately after application of the electric field. That is, the time scale of the faster modes will be much shorter than the reciprocal of the shear rate. Further, the time scale of the slower mode gives a useful piece of information, because the slower mode in the present paper is obtained without shear deformation while the slower mode of the stress response was also found under shear deformation [1].

II. THEORY

The diffuse transmittance, T, is approximately given by the following equation if the sample cell is sufficiently thick [8]: For $L \gtrsim l_{\mathrm{abs}}$,

$$T = \frac{I}{I_0} = \frac{10 l^*}{3L} \exp\left(- \frac{L}{l_{abs}} \right), \tag{1}$$

where L is the thickness of a sample cell, l^* is the transport mean free path for a random walk of photons, l_{abs} is the effective absorption length for photons diffusing in the medium, I is the intensity of the diffuse transmitted light, and I_0 is the intensity of the incident light.

Assuming that the aggregation of the particles in the suspension induced by an external electric field causes an increase in the diffuse transmittance and L is larger than l_{abs}, the normalized change in the diffuse transmittance, $\Delta T/T(0)$, or the normalized change in the transmitted light intensity, $\Delta I/I(0)$, induced by the electric field can be expressed as the following equation [8]:

$$\frac{\Delta I(t)}{I(0)} = \frac{1}{2}\left(1 + \frac{L}{l_{\mathrm{abs}}} \right) \frac{\Delta l^*(t)}{l^*(0)}, \tag{2}$$

where $\Delta X(t)[= X(t) - X(0); X = T, I, l^*]$ is the change in X obtained as a function of the time after application of the electric field, and $X(0)$ is the value of X under no electric field. In derivation of the above equation, I_0 is also assumed to be constant. In practice, we adjusted the power of the laser and checked the value of $I(0)$ and the proportional value of I_0 using an attenuator. In the present paper, the absolute value of the transmittance cannot be determined because of the absorption of light at the surface of the particles used, which are a weak pale shade of brown. Therefore, we will discuss only the normalized changes in the diffuse transmitted light intensity and the normalized changes in the mean free path of photons. However, we can discuss sufficiently the time scales for the structural formation in terms of the normalized changes in the diffuse transmitted light intensity.

III. EXPERIMENT

Cation exchange resin particles were used as reported in the previous paper [1]. The particles were suspended at a volume fraction of 0.33 in a silicone oil with a viscosity of 0.02 Pas. The suspension was sandwiched between a pair of parallel panes of glass covered with a transparent conducting layer of tin-doped indium oxides.

Figure 1 shows the block diagram of our system for the measurement of optical and electrical responses. The laser beam with a wavelength of 488 nm was generated by an argon-ion laser (Spectra-Physics, Model 2016). The power of the laser beam was adjusted to 50 mW. The beam was expanded and collimated by a pair of lenses, $L1$ and $L2$, and the diameter of the collimated light was reduced to 1 cm by an aperture. Then, the sample was illuminated by the collimated light. The incident direction of the light was perpendicular to the electrodes and parallel to the direction of the electric field. The incident light was scattered diffusely through the sample. The lens just before the detector, $L3$, was used originally in the present experiment so that the portion of the transmitted light parallel to the incident light was focused. The intensity of the focused light was detected by a photodiode instead of a photomultiplier tube (PMT) for the static measurement of the sample-thickness dependence, and by the photomultiplier tube for the dynamic measurement of the changes induced by the electric field. The signal of the intensity was amplified by a current amplifier (Keithley, Model 428) and stored in an eight-bit digital storage oscilloscope (LeCroy, LS140) as a function of time. In the present paper, the time of 0 s was defined as the time of the onset of application of the electric field. The responses obtained on each experimental condition were added at each time and averaged for the purpose of reducing random noise in the responses.

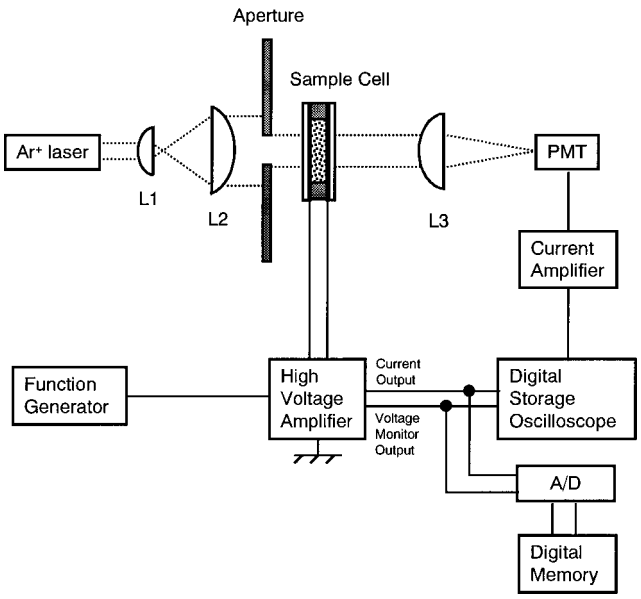

FIG. 1. Schematic representation of our system for the measurements of optical and electrical responses.

The current response was also measured in the present study. The current response was obtained from the current output of a high voltage amplifier (Treck, Model 609D-6) driven by a function generator. The gain of the high voltage amplifier is 10^3, and the bandwidth of -3 dB for small signals is guaranteed by the supplier for 35 kHz. The high voltage amplifier was also calibrated in our laboratory and the -3 dB bandwidths for input peak-to-peak voltages of 8 V, 4 V, and 2 V were 10 kHz, 20 kHz, and 35 kHz, respectively. The signal of the current was stored in a digital oscilloscope mainly for the fastest response and in a digital memory via a 12-bit analog-to-digital converter mainly for

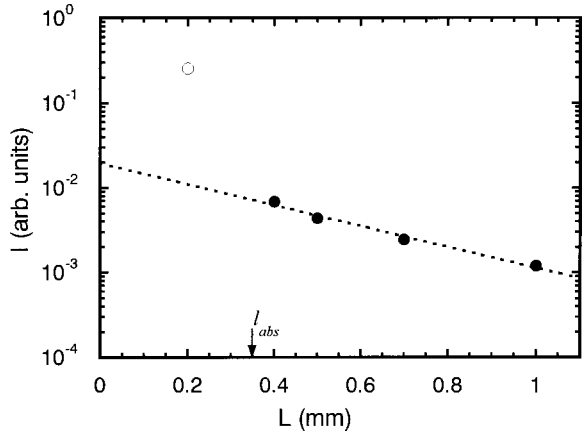

FIG. 2. The intensity of the diffuse transmitted light under no electric field plotted semilogarithmically against the thickness of the sample cells. The results with solid symbols were fitted as $I = 0.0194 \exp(-2.84L)$.

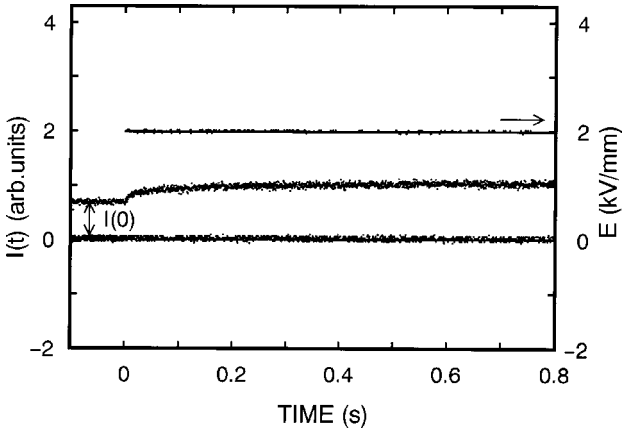

FIG. 3. The intensity of the diffuse transmitted light plotted against time. The intensity of the noise level and the applied stepwise electric field are also shown in the figure. The thickness of sample cells was 1.0 mm.

the slower responses. In the present paper, the difference between the current response of the sample in a cell and that of the empty cell was discussed for removing an artificial response of the measuring system.

IV. RESULTS AND DISCUSSION

A. Response of diffuse transmitted light intensity

Figure 2 shows the intensity of the diffuse transmitted light under no electric field plotted semilogarithmically against the thickness of the sample cells. In the figure, the results obtained with the four thicker sample cells were fitted by Eq. (1) very well. The effective absorption length calculated from the exponent was 0.35 mm, which is consistently smaller than the thickness of the sample cells fitted. Further, the effective absorption length is consistently larger than the sample thickness of the unfitted result in the figure. The diffuse transmitted light intensity of the unfitted result would be described by another equation in which the diffuse transmitted light intensity essentially varies inversely with the sample thickness in the case of $L < l_{\mathrm{abs}}$ [8]. Therefore, the thickness of the sample cells was fixed to 1.0 mm, which is much larger than l_{abs}, for the measurement of the response of the diffuse transmitted light to the electric field.

Figure 3 shows the intensity of the diffuse transmitted light plotted against time. The intensity of the noise level and the applied stepwise electric field with a strength of 2.0 kV/mm are also shown in the figure. The intensity of the diffuse transmitted light after application of the electric field increases and then saturates with time. According to Eq. (2), the increase in the intensity of the diffuse transmitted light, which was induced by the electric field, corresponds to the increase in the mean free path of photons parallel to the electric field because the sample thickness was fixed. Therefore, the diffuse transmitted light probes the aggregation of the polarized particles by the electric field in the present experiment.

Figure 4 shows the changes in the normalized intensity of the diffuse transmitted light plotted against time after application of the stepwise electric field. Similar to the rheological response [1], the normalized intensity of the diffuse transmitted light is expressed as an exponential function with two modes, which take place in succession. The plural modes are also essential for the curve fitting of the present results. The biexponential increase induced by the stepwise electric field is much different from the result reported by Ginder [8] for the response to static electric fields, and it shows that the structural formation with plural steps induced by the stepwise electric field is probed by the intensity of the diffuse transmitted light. The fitted curves by Eqs. (3) and (4) are shown in the figure. Mode 1 and mode 2 obtained at 2.0 kV/mm are also shown for example.

$$\frac{\Delta I(t)}{I(0)} = \sum_i \frac{\Delta I_i}{I(0)} \left[1 - \exp\left(- \frac{t - t_i}{\tau_i} \right) \right], \tag{3}$$

$$\frac{\Delta I_i}{I(0)} = 0 \quad \text{for} \quad t_i > t, \tag{4}$$

where $\Delta I_i / I(0)$, t_i, and τ_i are adjustable parameters of the ith mode. The parameters obtained by the curve fitting are summarized in Table I. We will discuss below the param-

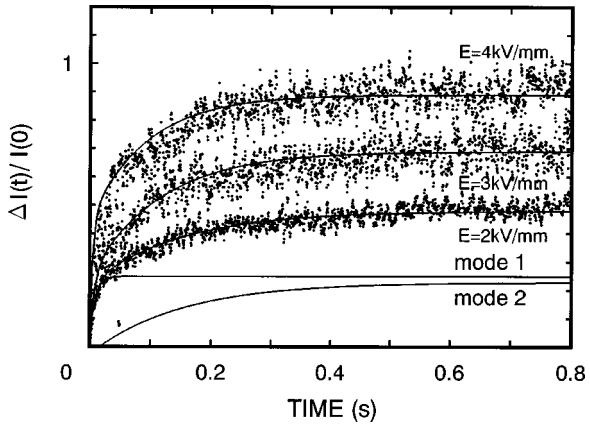

FIG. 4. The changes in the normalized intensity of the diffuse transmitted light plotted against time after application of the electric field. The thickness of the sample cells was 1.0 mm. The fitted curves by Eqs. (3) and (4) are shown in the figure. Mode 1 and mode 2 obtained at 2.0 kV/mm are also shown for example.

TABLE I. Parameters obtained by the curve fitting and the saturated value of the normalized changes in the mean free path of photons of each mode.

	2 kV/mm	3 kV/mm	4 kV/mm
τ_1 (ms)	8.3	6.5	4.7
τ_2 (ms)	150	120	94
t_1 (ms)	0	0	0
t_2 (ms)	16	11	7.0
$\Delta I_1/I(0)$	0.25	0.29	0.48
$\Delta I_2/I(0)$	0.23	0.40	0.41
$\Delta l_1^*/l^*(0)$	0.13	0.15	0.25
$\Delta l_2^*/l^*(0)$	0.12	0.21	0.21
error[a]	0.075	0.13	0.13

[a]The root mean square throughout the sampled points of data shown in Fig. 4, $0 \leqslant t \leqslant 0.8$ s, for the relative deviation of the normalized intensity measured experimentally from that calculated using Eqs. (3) and (4) with parameters listed above at each sampling point of time t, $\{[\Delta I(t)/I(0)]_{\text{meas}} - [\Delta I(t)/I(0)]_{\text{calc}}\}/[\Delta I(t)/I(0)]_{\text{calc}}$.

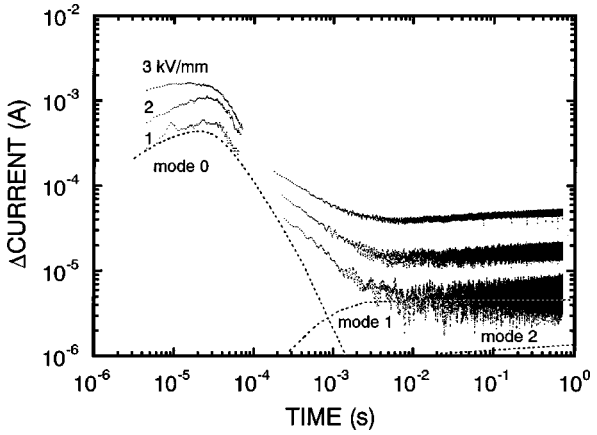

FIG. 5. The subtracted current passing through the samples plotted logarithmically against time after application of the electric field. The thickness of the sample cells was 0.5 mm, and the area of the electrodes was 5.9 cm^2. The broken lines for mode 0, 1, and 2 are speculative ones.

eters obtained, except the time scales of the structural formation in the quiescent ER suspension. Time scales such as τ_i $(i=1,2)$ are discussed separately in a later section.

In Fig. 4, it is seen that the saturated value of the overall change in the normalized intensity, $(\Delta I_1+\Delta I_2)/I(0)$, increases with an increase in the strength of the electric field. A similar tendency of the fitted parameters $\Delta I_i/I(0)$ is found for each mode. The saturated value of the overall change in the mean free path of photons, $(\Delta l_1^*+\Delta l_2^*)/l^*(0)$, is calculated to be 0.25 at 2.0 kV/mm and 0.46 at 4.0 kV/mm. The discussion above is essentially based on Eq. (2), in which the isotropic distribution of the particles is assumed. On the other hand, strongly anisotropic distribution of the particles would be induced by the electric field, especially at the highest strength of 4.0 kV/mm: The chains of the polarized particles parallel to the electric field and the two-dimensional localization of columnar structure would be induced in the suspension. Therefore, quantitative discussion that related to the mean free path of photons might be unreasonable in the present paper. Qualitatively, however, the electric-field dependence of $(\Delta I_1+\Delta I_2)/I(0)$ would be related to the aggregated structure of the polarized particles not only parallel to the electric field but also orthogonal to the electric field. In such a case, the structure would be nonequilibrium because the aggregation of the particles is so fast under strong electric fields. Further, the molecular-dynamics simulation also showed nonequilibrium structure under strong electric fields [6]. The two-dimensional localization of columnar structure orthogonal to the electric field would cause the relative increase in the mean free path of photons parallel to the electric field, to which the intensity of the diffuse transmitted light is highly sensitive.

B. Current response

Figure 5 shows the subtracted current passing through the samples plotted logarithmically against time after application of the electric field. As described in Sec. III, the subtracted current is the difference between the current response of the sample in a cell and that of the empty cell. The thickness of the sample cells was 0.5 mm and the area of the electrodes was 5.9 cm^2 in the present experiment. In the figure, the subtracted current shows a peak on the shorter time scales at a given strength of the electric field, and the subtracted current decreases with time. It should be noted that the subtracted current after the decrease is not constant but increases again gradually with time. The peak of the subtracted current is related to the polarization of the suspension, mode 0, while the gradual increase in the subtracted current is related to the conducting current passing through the suspension, mode 2. Between the peak and the gradual increase in the subtracted current, an intermediate region can be found, which would be related to the aggregation of the polarized particles induced by the electric field, mode 1. In the figure, the broken lines are also shown for modes 0, 1, and 2 as speculative ones.

Quantitatively, the bandwidths of the high voltage amplifier limit the discussion of absolute value of the subtracted current below a time scale of 10^{-5} s, because the bandwidths are 20 kHz and 35 kHz for input peak-to-peak voltages of 4 V and 2 V, respectively, and the gap between electrodes was 0.5 mm. However, the existence of the peaklike response on the shorter time scales is qualitatively evident in the present experiment. Further, the subtracted current at a given time increases with an increase in the strength of the electric field, which is consistent with the electric-field dependence of $\Delta I(t)/I(0)$ shown in Fig. 4 at a given time. (The subtracted current at 4.0 kV/mm cannot be calculated because of the electrical breakdown of the empty cell at the electric field. However, we can suppose the consistent tendency from the current response itself.) The time scales of the subtracted current will also be discussed separately in the next section.

In addition, corresponding response to the peaklike response of the subtracted current, mode 0, was not found in the normalized intensity of the diffuse transmitted light. This result consistently shows that the attribution of each mode is reasonable because the current response is highly sensitive to the response related to the polarization of the suspension, while the diffuse transmitted light is not.

C. Time scales of optical and electrical responses

The peaklike response of the subtracted current that is related to the polarization of the suspension is found as shown in Fig. 5. The time scale for the response is around 10^{-5}–10^{-4} s in our ER suspensions. Although the bandwidth of the high voltage amplifier may screen the real time scale of the response, the obtained time scale of mode 0 is the fastest among the other time scales, as discussed below. Ginder *et al.* also reported the peaklike response to bipolar excitation of the square waves and a characteristic electrical time constant τ_{el}, which was defined as a change of the transient current to decay to $1/e$ of its peak value, ranging from 10^{-4} s to 10^{-2} s [9]. The time scale obtained in our experiment is well consistent with the shorter characteristic electrical time constant. The characteristic electrical time constant was also assigned to the charging process of the ER suspensions [9].

As shown in Fig. 4 and Table I, τ_1 obtained by the normalized intensity of the diffuse transmitted light is of the order of 10^{-3} s. The time scale is consistent with not only τ_1 obtained by the rheological response, but also the time scale obtained by the electrical response of mode 1. Therefore, it is reasonable to assign mode 1 to the aggregation of the polarized particles. Further, τ_1 given in Table I is proportional to $E^{-0.8}$. The sublinear dependence of τ_1^{-1} on the strength of the electric field also suggests the electrophoretic motion [8] although no macroscopic electrophoresis was found by optical microscopic observation. The decrease in τ_1 with an increase in the strength of the electric field was predicted by Tao *et al.* in a molecular-dynamics simulation using the parameter A in which the electric field is included [6]. The tendency was also found in the rheological response, which becomes faster as the strength of the electric field increases [1,10].

In the present experiment, mode 2 was also found in the optical and electrical responses. The time scale is of the order of 10^{-1} s, which is much shorter than the time scale of 10^{2} s reported by Martin *et al.* [7]. However, the time scale of mode 2 of the optical response, τ_2, is consistent with the time scale of the gradual increase in the subtracted current shown in Fig. 5. As shown in Fig. 5, no saturation of the subtracted current is found, which shows that the response of mode 2 would be much slower. The results obtained in the present paper would sensitively probe the onset of the response of mode 2. Further, it should be noted that mode 2 was found even in the quiescent state while mode 2 of the stress response was also found under shear deformation [1]. Therefore, it should be taken into account that mode 2 is induced by shear deformation as well as other factors such as the thermal effect. In fact, a gradual increase in the subtracted (conducting) current was found in Fig. 5. The conducting current gives Joule's heat in the ER suspension. Joule's heating would induce the later densification of the aggregated chains, which causes the formation of a columnar structure.

Finally, the adjustable parameter t_2 also decreases with an increase in the strength of the electric field. The adjustable parameter t_2 is related to the onset of mode 2. In the curve fitting based on Eqs. (3) and (4), it is basically assumed that mode 2 does not occur before t_2. The assumption is essential to fit the experimental results, in good agreement with the experimental equations. Around the corresponding time in Fig. 5 to the time scale for t_2 of 10^{-2} s, the subtracted current gradually increases, which would be the onset of mode 2. Furthermore, the existence of aggregated chains should be essential before the formation of a columnar structure, which is caused by the densification of the aggregated chains. Therefore, the successive response of each mode is qualitatively reasonable to describe the structural formation in the ER suspension.

V. CONCLUSIONS

The responses of the diffuse transmitted light intensity and the current passing through an ER suspension to the stepwise electric field were measured in the quiescent state, and the time scales for the structural formation of the polarized particles were obtained. It should be noted that both of the responses consist of plural modes, faster and slower modes, which took place in succession even in the quiescent state. The time scales obtained were discussed relating to the structural formation in the ER suspension. The successive evolution of the aggregation of the particle and densification of the aggregated chains is proposed. The responses of the diffuse transmitted light and the current are effective for probing the structural formation in the quiescent ER suspensions.

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