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Electrorheology of Neat Poly(Ethylene Glycol) Suspensions

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We studied particle size, shape, molecular weight and temperature dependencies of ER effect of poly(ethylene glycol) (PEG) suspensions. The particles were dispersed in low-viscosity silicon oil. We obtained flow curves and dynamic yield stresses by increasing shear rate and compared these with static yield stresses in our previous study (obtained by increasing shear stress). The yield stress under a dc electric field increased by decreasing molecular weight and increasing particle concentration, and did not change with particle size or shape. In addition, significant differences between static and dynamic yield stresses disappeared in absolute value and electric field intensity dependence. And the static yield stress increased with temperature and the dynamic yield stress showed a maximum value at near room temperature. We also measured transient behavior of a PEG suspension at various temperatures and found that it took about 30 seconds to reach the constant viscosity on the application or removal of electric fields. It can be thought that this relatively long response time to create chain structures causes sudden flowing by increasing shear stress gradually and different results between static and dynamic yield stresses.

Key Words: Electrorheology / Yield Stress / Poly(Ethylene Glycol) / Suspension / Bingham Fluid

1. INTRODUCTION

Poly(ethylene glycol) (PEG) is well-known as biocompatible, nontoxic, and hydrophilic polymers¹⁾ and used as drugs and cosmetics. When electric fields are applied to the PEG/silicon oil suspensions, chain structures are created between electrodes and ER effect appears.²⁻⁴⁾ Before applying an electric field, the PEG particles in the suspension aggregate at lower negative electrode in several minutes. After applying an electric field, parts of particles go up from the negative electrode to upper positive electrode and chain networks appear.^{2,3)} These chain networks can be seen by naked eyes.²⁾

In addition, we studied ER effect of PEG/poly(vinyl alcohol) (PVA) binary blend particle suspensions and found that the blend (PVE 10-25 wt%) suspensions showed higher yield stresses (σ_y) than neat PEG suspensions even if the neat PVA suspension did not show the ER. At this time, chain networks of the blend increased and migrating particles decreased compared with neat PEG suspensions.²⁾

In this study, we studied the particle size, shape, concentration, molecular weight and temperature dependencies of ER effect for PEG suspensions. In previous studies,^{2,4,5)} we investigated

the molecular weight and temperature dependencies of σ_y for PEG particle suspensions. However, when chain networks were broken by shear stress, the suspensions flew immediately and the networks disappeared. It was difficult to detect σ_y by increasing shear rate and detecting shear stress (dynamic yield stress). Therefore, the shear stress was increased at a rate of 0.1 Pa s^{-1} and we measured shear rate. From these measurements, we took the stress value when these particle chains broke down and shear rate jumped as σ_y (static yield stress). In this study, we used low-viscosity silicon oil as a dispersion medium to activate the reassembling of PEG particles and measured the dynamic yield stress. It is expected that the chain structuring processes in shear fields are different from those in a quiescent state because the flow behavior of ER suspensions is governed by a balance between electric and hydrodynamic forces.⁶⁾ In addition, we studied the temperature dependence of transient behavior in dc electric fields under external stress and compared the rate of creation and breaking of chain structures.

2. MATERIALS AND METHODS

2.1 Materials

Characteristics of crushed PEG particles were shown in Table 1. PEG-4k, 20k and 2M were obtained from Wako

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Pure Chemical Industries Ltd. (Osaka, Japan). PEG-200k was purchased from Polysciences, Inc. PEG-4k and 20k were crushed by ball mill with zirconia balls (diameter is 5 mm) over 24 h. On the other hand, PEG-200k and 2M were not crushed because these samples were sold as granulated powders. All PEG samples were sifted on a 200 mesh (75 μm) sieve. In Table 1, the weight and number average molecular weights (M_w and M_n) of PEG-4k and 20k were measured by gel permeation chromatography using a calibration curve for poly (methyl methacrylate) standards. To calculate viscosity-average molecular weights (M_v) of all samples, we measured viscosities of aqueous PEG solutions (5.0-20 g/l) using a vibratory viscometer (SV-10 manufactured by A&D Co. Ltd., Tokyo) at 298 K. Each particle diameters were calculated from micrographs of digital optical microscope (KEYENCE VH-6200) as Heywood diameter, that is defined as the diameter of a circle having the same area of the segmented defect.⁷⁾ To measure particle shape dependencies of ER, we prepared sphere PEG-4k particles. To obtain them, we suspended crushed PEG-4k particles in high viscosity silicon oil, heated them to 353 K to melt, cooled to room temperature,³⁾ and washed by *n*-hexane. Average diameter of sphere PEG-4k was 29.6 μm . Micrographs of crushed and sphere PEG-4k were shown in Fig. 1. The densities were measured by Archimedes' method in the silicon oil (TSF-451-10, GE Toshiba Silicones Co., Tokyo, Japan) at 298 K. The glass transition temperatures (T_g) and melting points (T_m) were determined by a differential scanning calorimeter (DSC-60, Shimadzu Co., Kyoto, Japan).

The PEG samples were kept in a vacuum desiccator until the ER measurement and the percentage of moisture contents for all samples were less than 0.3 wt%. These samples were suspended in TSF-451-10. The viscosity of this oil is 1.0×10^{-2} Pa s at 298 K.

Table I. Characteristics of crushed PEG samples.

Characteristics	PEG-4k	PEG-20k	PEG-200k	PEG-2M
M_n^*	4.14×10^3	2.70×10^4		
M_w^*	4.38×10^3	2.87×10^4		
M_w/M_n^*	1.06	1.06		
M_v^*	5.5×10^3	2.91×10^4	2.64×10^5	2.14×10^6
Average Diameter/ μm	13.0	12.3	16.6	20.4
Density/ g cm^{-3}	1.21	1.21	1.20	1.15
T_g/K	207.8	209.9	213.1	214.1
T_m/K	333.3	341.7	341.8	343.7

*calculated by PMMA calibration curve.

2.2 Methods

Rheological properties were measured using a parallel plate geometry on a stress-controlled rheometer (Haake, RheoStress RS100). We modified this rheometer for ER measurements. The upper plate (positive electrode) is isolated from the shaft by ceramics and connected by copper wire. A dc voltage was applied by a technique of frictionless contact to the upper plate, which was insulated from the shaft. The diameters of two plates were 35 mm and the gap between two plates was 1.0 mm. This device was also used in our previous studies.^{2,4,5)}

The shear rates in steady-flow experiments were from 1.0 to $1.0 \times 10^3 \text{ s}^{-1}$. For studying transient behavior of PEG suspensions, we used 2.0 wt% crushed and sphere PEG suspensions to which 5.0 Pa steady shear stress was applied.

3. RESULTS AND DISCUSSION

3.1 Particle Shape Dependence

Figure 2 shows the flow curves for crushed and sphere PEG-4k suspensions (at a particle concentration of 5.0 wt%) in 0, 1.0, 2.0 and 3.0 kV/mm dc electric fields. The flow curves

Fig. 1. Micrographs of crushed and sphere PEG-4k particles.

of crushed and sphere PEG-4k suspensions were almost the same. For 3.0 wt% suspensions, this correspondence was also observed. As shown in Fig. 1, there are significant differences in shape and size between crushed and sphere PEG-4k. In particular, crushed particles have many edges and charges are biased. But these effects did not influence the ER for PEG suspensions.

Ko et al.⁸⁾ pointed that there are no consistent relationship between ER effect and particle size. When particle size increases, ER effect becomes stronger in some cases^{9,10)} and weaker in other cases.¹¹⁾ In addition, the suspension of PEG-4k crushed roughly by a pestle (average diameter is 21.0 μm) showed similar σ_y to PEG-4k (13.0 μm). As mentioned above, there were no significant differences in ER effect for PEG-4k suspensions by changing particle size and shape.

3.2 Concentration and Electric Field Dependence

Flow curves of PEG-4k suspensions with various concentrations under the 2.0 kV/mm dc electric field are shown in Fig. 3. The plateau (yield stress) appeared at 2.0 wt% and more. In this study, we took the stress value at plateau region of flow curve as σ_y . For PEG 20 wt% suspension, the σ_y value is estimated to be ~ 95 Pa. This dynamic yield stress is smaller than the static yield stress (~ 120 Pa).²⁾ This difference was also shown in yield stress es for the sphere PEG-4k suspension.

Moreover, we made log-log plots of dynamic σ_y against electric field intensity (E) for crushed PEG-4k suspensions and the results are shown in Fig. 4. The slope of the plot was about 1.4. These results correspond to the result of Sim et al. (1.5),¹²⁾ but differ from the previous study, in which the slope is 2.0.²⁾

Marshall's "polarization model"¹³⁾ analyzed the dielectric attractive force between aligned particles and indicated that the σ_y was proportional to $E^{2.0}$. So this model considered the strength of chain structures before flowing. On the other hand, an alternative yield stress model¹⁴⁾ considering nonlinear conductivity effect was constructed to explain the results that dynamic σ_y was proportional to $E^{1.5}$.¹²⁾ In our study, PEG suspensions showed nonlinear conductivity. So it is thought that the alternative yield stress model can be applied for our dynamic measurements.

Fig. 3. Flow curves of crushed PEG-4k suspensions with various concentrations at 2.0 kV/mm, 298 K.

Fig. 2. Flow curves of crushed and sphere PEG-4k 5.0 wt% suspensions under dc electric field.

Fig. 4. Electric field strength dependence of the dynamic yield stress for crushed PEG-4k 20 wt% suspension at 298 K.

In our static measurements²⁾, PEG suspensions flow suddenly by increasing shear stress. This indicates that it takes a long time to re-create chain structures. In this case, not only the strength of chain structures, but also the fluid properties of silicon oil influence dynamic σ_y and the electric field dependence of dynamic σ_y is weaker than that of static σ_y , which is only influenced by the strength of chain structures. However, this effect cannot explain the phenomenon that dynamic σ_y of PEG-4k (20 wt%) suspension (*e.g.* 44 Pa at 1.0 kV/mm) is higher than static σ_y (*e.g.* 18 Pa at same condition) under the low electric field.

In our static studies, many particles aggregated on the lower negative electrode and could be observed by naked eyes before the suspension flow. On the other hand, aggregated particles disappeared in dynamic studies.

To observe the behavior of PEG suspensions under dc electric fields, PEG suspensions were clipped between two clear electrodes and observed by a microscope under electric fields. When the electric fields are applied or turned up, particles pumped fast between electrodes for 10-30 seconds. It can be thought that in dynamic studies, this pumped motion occurs, aggregated particles disappear, and more particles contribute to the ER effect than static studies.

As mentioned above, PEG suspensions show ER effect by different mechanism between static and dynamic measurements.

3.3 Molecular Weight Dependence

Figure 5 shows shear rate dependence of shear stress for 20 wt% crushed PEG suspensions with various molecular weights under a dc electric field (1.0 kV/mm). Fig. 6 shows the yield stress against ρ/M_v (corresponding to the number of hydroxyl end groups per volume). In this figure, we took the stress value at $\sim 10 \text{ s}^{-1}$ as σ_y . As the molecular weight increased, the σ_y became weak. The σ_y of PEG-2M suspension almost disappeared. From these results, the factor affecting the intensity of ER effect for PEG suspension is not main chains of PEG molecules, but end groups of them.

This trend corresponds to static yield stress in the previous study⁴⁾. By measuring ER for PEG-4k/PEG-2M = 2/8 blend ($M_n \sim 20,000$) created by freeze-drying, we found that the σ_y of blend particle suspension under the 2.0 kV/mm dc electric field was similar to that of neat PEG-20k suspension and ER effect of PEG suspension did not change by molecular weight distribution.

From Table 1, the glass transition temperatures of PEGs showed a little molecular weight dependence. Lengálová et al.¹⁵⁾ studied the relationship between dielectric and

electrorheological properties for suspensions of silica coated with polyaniline. In ref. 15, the longer relaxation time (the higher T_g) is, the stronger ER effect becomes. This result is opposite to this study. It is hard to think that T_g and local dynamics of PEG affect the σ_y .

3.4 Temperature Dependence and Transient Behavior

Figure 7 shows the flow curves for crushed PEG-4k suspension (PEG 20 wt%) with various temperatures. The dynamic σ_y showed maximum value at $\sim 300 \text{ K}$ and decreased above the temperature. In our previous studies,^{2,4,5)} static σ_y

Fig. 5. Flow curves of PEG 20 wt% suspensions with various molecular weights at 1.0 kV/mm, 298 K.

Fig. 6. Molecular weight dependence of the yield stress (shear stress at 10 s^{-1}) for PEG (20 wt%) suspensions with various temperature at 1.0 kV/mm, 298 K.

increased monotonically in the temperature range from 293 to 313 K. At low shear rate region in Fig. 7, the slope of stress curve at 313 K is sharper than that at 293 K. By extrapolating to lower shear rate region, it can be considered that shear stress at 313 K becomes higher than the stress at 293 K. In static measurements, the shear rate before flowing was almost 0 and much less than Fig. 7. Therefore, temperature dependences of σ_y are different between static and dynamic studies. From these results, it can be seen that ER effect becomes stronger as temperature increases before flowing, and the strongest at ~ 300 K after flowing.

Next, we applied shear stress (5.0 Pa) to the crushed PEG-4k suspension and measured viscosity. In this measurement, a dc electric field (1.0 kV/mm) is applied at t (time) = 0 s and removed at $t = 60$ s. Figure 8 shows time dependencies of the viscosity for crushed PEG-4k (2.0 wt%) suspension. It took about 30 seconds to reach the constant viscosity on the application or removal of electric fields. The response time did not show the temperature dependence. In addition, this value was almost the same for sphere PEG-4k suspension. Thus, when the temperature increases, viscosity of dispersion medium decreases and the strength of chain structures increases. It can be thought that the dynamic σ_y showed peak at near room temperature by these two opposite effects. For PEG suspensions, a relatively long time to form chain structures causes differences in absolute value of σ_y and electric field strength dependencies between ER effects before and after flowing.

Fig. 7. Temperature dependencies of shear stress for PEG 20 wt% suspensions with various molecular weights at 1.0 kV/mm, 298 K.

4. CONCLUSIONS

For PEG particle suspension, the particle size and shape dependencies disappear in ER effect. The yield stresses (σ_y) of PEG suspensions under dc electric fields increase with decreasing molecular weight and increasing particle concentration. And significant differences in absolute value of yield stress, electric field strength dependence, and so on appear in ER data for PEG suspensions obtained by changing shear stress and shear rate. In particular, static σ_y is proportional to $E^{2.0}$ and dynamic σ_y is proportional to $E^{1.4}$.

The rate of viscosity change by applying or removing an electric field in the measurement of transient behavior of PEG-4k suspension does not show the temperature dependence. Even if low viscosity oil is used as the dispersion medium, the response time to reach the constant viscosity on the application or removal of electric fields is long (~ 30 seconds in this study).

The long time to create chain structures causes sudden flowing by increasing shear stress gradually and different values between static and dynamic yield stress. In addition, dynamic and static σ_y of PEG-4k suspension show different temperature dependencies.

For PEG suspension, dynamic σ_y is relatively low (~ 100 Pa at 2.0 kV/mm, 298 K, PEG 20 wt%). However, we could increase static σ_y by mixing other compounds.²⁾ As mentioned above, PEG particle suspension is expected to applying renewable safety devices to flow when excess stress is applied.

Fig. 8. Viscosity changes of PEG-4k 2.0 wt% suspension at various temperatures. 1.0 kV/mm dc electric field was applied at $t = 0$ and removed at $t = 60$ s. Shear stress was 5.0 Pa.

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