Rheological Properties and Thermal Conductivity of Suspension of Metal Powder

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Abstract

Effects of flocculated structure formed by metal powder in poly(ethylene glycol) on thermal conductivity and rheological properties were investigated. The suspension of metal powder shows a remarkable shear thinning and pseudoplastic flow and this tendency becomes pronounced with increasing the concentration of metal powder. Frequency dependences of $G'$ and $G''$ were also investigated, and they showed the characteristic ones of concentrated suspensions having the flocculated structure. The thermal conductivity of metal powder is larger than that of disperse medium, therefore the thermal conductivity of the system increases with increasing the concentration of metal powder. When the metal powder is uniformly dispersed, the thermal conductivity of the system is comparatively high. However, it decreases as the flocculated structure of metal powder is constructed because the path of thermal conduction is broken or shrunk.

Key-words: Metal powder, Suspension, Flocculated structure, Thermal conductivity

1. Introduction

In concentrated suspensions, the flocculated structure formed by dispersed particles depends on the size and volume fraction of particles, interparticle force, interparticle interactions and surface characteristics. Generally, the flocculated structure of disperse system can be investigated by rheological measurements such as steady flow behavior, dynamic viscoelastic properties, stress relaxation, etc. Recently, we examined the flocculated structure from a viewpoint of thermal conductivity using a modified concentric viscometer for the suspensions of carbon black in a disperse medium, such as linseed oil and mineral oil. Since the thermal conductivity of carbon black particle is smaller than that of the disperse media, the thermal conductivity of suspensions decreases with increasing the concentration of carbon black. Formation of structural network results in an enlargement of the channel of thermal conduction. Therefore the thermal conductivity of the disperse system increases as the network structure is formed. In this study, we investigated the relation between the flocculated structure and thermal conductivity for
the suspension of metal powder in poly(ethylene glycol) (PEG) where the thermal conductivity of dispersed particle is larger than that of the disperse medium. We discussed about the mechanism of thermal conductance in the flocculated system under shear flow and after stopping the steady shear. Furthermore the measurements of steady shear viscosity, dynamic viscoelastic properties and stress overshoot were also performed.

2. Experimental

2.1 Apparatus

A measurement system consists of a modified concentric cylinder viscometer and a thermal measurement unit (Rheocatch JRC-VM 1000, Nippon Denshi Co., Ltd. was used for simultaneous measurements of rheological and thermal properties\(^2\)). The thermal measurement unit consists of an electrically heater wire and a thermister. The length, diameter, and electrical resistance of thermister are 10 mm, 2 mm, and 5 \(\Omega\) respectively. The heater and thermister, 1.2 cm apart, were inserted between the outer and inner cylinders. The temperature difference, \(\theta\), between them was measured as a function of heating time, \(t\). The temperature difference \(\theta\) is directly proportional to the logarithm of the heating time at the initial stage of heating. The slope \(K\) is defined as \(K = \frac{\theta}{J \ln t}\). The relation between \(K\) and thermal conductivity, \(\lambda\), can be represented by Fourier's equation, \(\lambda = \frac{(Q/4 \pi)}{(4014 \ln t)}\), namely, \(K\) is inversely proportional to the thermal conductivity, \(\lambda\).

Rheometrics Fluid Spectrometer (RFS II) was used for the measurements of dynamic viscoelasticity and stress overshoot.

2.2 Sample

Magnetic metal powder was used as disperse particle and PEG (average molecular weight ranging from 200 to 600) and ethylene glycol (EG) were used as disperse medium. The characteristics of samples are shown in Table 1. The metal powder has a rodlike shape with the length about 0.3 \(\mu\)m and the axial ratio about 11. The density and apparent viscosity of PEG increase with increasing molecular weight. The thermal conductivity of the metal powder is larger than that of the disperse media. The metal powder was dispersed in the disperse medium at the concentration of 20 wt% using a ball mill for 24 hours and the suspension was reduced to various concentrations ranging from 1 to 15 wt% using a homogenizing disperser. The suspensions of metal powder in PEG is stable and sedimentation has not been observed for 48 hours except very dilute

| Table 1. Characteristics of samples |
|-----------------|----------------------|-----------------|----------------|
| Particle | Density \((\text{kg/m}^3) \times 10^{-3}\) | Thermal conductivity \(\times 10^{-4} \text{(J/m} \cdot \text{h} \cdot \text{C})\) | Apparent viscosity \(\times 10^{-3} \text{(Pa} \cdot \text{s)}\) |
| Medium | | | |
| PEG (M 600) | 4.56 | 0.26 | |
| PEG (M 400) | 1.26 | 6.23 | 1.16 |
| PEG (M 200) | 1.13 | 6.68 | 0.90 |
| EG | 1.09 | 7.08 | 0.54 |
| PEG : Poly(ethylene glycol) ; EG : Ethylene glycol |

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3. Results and Discussion

3.1 Rheological Measurements

Figure 1 shows the relation between the apparent viscosity and rate of shear for suspensions of metal powder in PEG with molecular weight of 600 (PEG M 600) at various concentrations. Flow curves at higher concentration show a typical steady flow behavior for suspension, namely the apparent viscosity decreases with increasing rate of shear. The curve shifts upwards with increasing the concentration of the metal powder. It is thought that the flocculated structure formed by dispersed particles is broken up as the shear is applied and the particles are dispersed more uniformly.

![Figure 1: Relation between apparent viscosity and rate of shear for suspensions of metal powder in PEG M600 at various concentrations.](image)

Concentration (wt%): 20 (●), 15 (○), 10 (△), 5 (□), 0 (○).

Figure 2 shows the dependence of the yield value on the concentration of metal powder in PEG M 400. The yield value increases with increasing concentration of particles exponentially with the exponent of about 4.5. The degree of flocculation in suspension can be deduced from the value of yield stress. It thought that the flocculated structure becomes denser with increasing concentration of disperse particles.

![Figure 2: Dependence of yield value on concentration for suspensions of metal powder in PEG M400.](image)

In order to investigate the structure recovery, we observed the stress overshoot for the suspension of metal powder after various rest periods. Figure 3 shows a schematic diagram of measurement procedure. At first, the shear flow of 5 sec\(^{-1}\) was applied for 10 min and stopped. After stopping the shear flow, the system left to stand for the time of \(t_s\) and shear flow with same rate of shear was applied again.

Figure 4 shows the plots of square root of stress difference, \((\Delta \sigma)^{1/2}\) against square
root of elapsed time, $t_s^{1/2}$ for 20 wt% suspensions of metal powder in PEG M600 and M400. The value of $(\Delta \sigma)^{1/2}$ is calculated by subtracting the equilibrium value of stress from the peak value of the stress. With increasing standing time, the flocculated structure becomes denser and stronger force is necessary to break the structure. Consequently, $(\Delta \sigma)^{1/2}$ increases with increasing $t_s^{1/2}$. Cartwright\(^4\) pointed out that $(\Delta \sigma)^{1/2}$ is proportional to the $t_s^{1/2}$. However, the linear relation between $(\Delta \sigma)^{1/2}$ and $t_s^{1/2}$ can not be observed in this study. The flocculated structure and the process of structure recovery

![Fig. 3. Experimental mode for the measurement of stress growth](image)

![Fig. 4. Plots of $(\Delta \sigma)^{1/2}$ against $t_s^{1/2}$ for 20% suspensions of metal powder in PEG M600 (○) and PEG M400 (□)](image)

![Fig. 5. Dependence of dynamic viscosity $\eta'$ (a) and modules $G'$ (b) on angular frequency measured at 1% strain amplitude for suspensions of metal powder in PEG M600 at various concentrations](image)

Concentration (wt%): 20 (○), 15 (△), 10 (□), 5 (□)
for acicular metal powder seem to be different from those for ordinary particles.

The dynamic measurement was performed at the strain amplitude of 1% for suspensions of metal powder in PEG M600 at various concentrations. The dependences of dynamic viscosity ($\eta'$) and modules ($G'$) on angular frequency are shown in Figures 5 (a) and (b), respectively. The value of $\eta'$ decreases with increasing angular frequency and this tendency becomes more pronounced with increasing concentration. On the other hand, the dependence of $G'$ on frequency $\omega$ is very small and the curve shifts to upwards with increasing concentration. It is thought that the relaxation time of the flocculated structure is very long and the structural density increases with increasing concentration.

3.2 Thermal Properties of the Suspension

The slope $K$ for the suspensions in the flow field is normalized by the slope of disperse medium, $K_o$ at the corresponding rate of shear to avoid the effect of forced convection on thermal conduction of the system. Figure 6 shows the dependence of $K/K_o$ on rate of shear for suspensions of metal powder in PEG M400 at various concentrations. The value of $K/K_o$ decreases with increasing concentration of metal powder, namely, the thermal conductivity of the suspension increases with increasing the concentration. In the lower concentration region, $K/K_o$ is almost constant irrespective of rate of shear. However, $K/K_o$ decreases with increasing rate of shear at higher shear rate region for the concentrated suspension such as 20 and 15wt%. The inflection point of the curves shifts to lower rate of shear with increasing concentration. Since the shape of the particles is cylindrical, the effect of orientation of metal powder becomes pronounced in higher shear rate region for concentrated suspension. The thermal conductivity of the system may increase as the particles are oriented because the thermal conductivity of the
particles is larger than that of disperse media.

The flocculated structure in disperse system is broken under shear flow, but the broken structure is reconstructed again after cessation of the shear flow. Figure 7 shows the time dependence of slope $K$ after cessation of shear at various rates of shear for 20 wt% suspension of metal powder in PEG M400. Immediately after cessation of shear flow, $K$ is very small, but it increases gradually. The initial value of $K$ is defined as $K_{\text{min}}$. Immediately after stopping the shear flow, the dispersing state is taken as the same one in the flow field, then the particles seem to be uniformly dispersed. Since metal particles are a good thermal conductor, the thermal conductivity of the disperse system increases with dispersing more uniformly. However, as the flocculated structure is formed, the path of thermal conduction may shrink. Consequently, the thermal conductivity of disperse system decreases with elapsed time. Moreover, the time dependence of $K$ becomes more pronounced with increasing the shear rate of preshearing.

Figure 8 shows the dependence of $K$ on the rest time after cessation of shear of 58.2 sec$^{-1}$ for suspensions of metal powder in PEG M400 at various concentrations. At each concentration, initially, the value of $K$ is very small, but increases to an equilibrium. The dependence of $K$ on time becomes pronounced with increasing concentration. However, $K$ attains to the equilibrium more quickly with decreasing concentration. From these results, in the concentrated suspension, the structural density seems to be very high, but long time is required to reconstruct the structural networks.

Figure 9 shows the dependence of $K$ on time for 20 wt% suspensions of metal powder in PEG M400 and EG. The value of $K$ for the disperse system in EG is smaller than that in PEG. Smith pointed out that the higher the viscosity was, the lower the thermal conductivity for Newtonian liquid. Then, the thermal conductivity of PEG is lower than that of EG, because they are Newtonian liquid. However in EG, $K$ reaches to a higher equilibrium state faster than that in PEG. It is thought that the particles in the lower viscous medium form the flocculated structure faster than that in higher viscous medium.

Figure 10 shows the relation between $K_{\text{min}}$ and the rate of shear applied for 20
wt% suspension of metal powder in PEG M400. With increasing the rate of shear, the value of $K_{\text{min}}$ decreases extremely. This result can be explained by the dispersing condition immediately after the cessation of shear flow, namely the dispersing condition depends upon the rate of shear and influences the thermal conductivity of the system.

Figure 11 shows the dependence of $K$ on concentration for suspensions of metal powder in various disperse media. The curve shifts to upwards with increasing the viscosity. 

**Fig. 9.** Time dependence of $K$ for 20% suspensions of metal powder in polyethylene glycol with molecular weight of 400 (●) and ethylene glycol (○)

**Fig. 10.** Relation between $K_{\text{min}}$ and rate of shear prior to stop the shear flow for 20 wt.% suspension of metal powder in PEG M400

**Fig. 11.** Dependence of $K$ on concentration for suspensions of metal powder in various media (PEG M600 (●), PEG M400 (△), PEG M200 (×), EG (○))
of disperse mediums. In other words the thermal conductivity of disperse system decreases with increasing viscosity of disperse medium. In all systems, $K$ decreases with increasing concentration of metal powder. The relation between the thermal conductivity of disperse system and concentration of disperse particles can be represented by Hamilton’s equation,

$$\frac{\lambda}{\lambda_1} = \frac{(n-1)\lambda_1 + \lambda_s - (n-1)\Phi(\lambda_1 - \lambda_s)}{(n-1)\lambda_1 + \lambda_s + \Phi(\lambda_1 - \lambda_s)}$$

where $\lambda$ is thermal conductivity of disperse system, $\lambda_1$ is thermal conductivity of disperse medium, $\lambda_s$ is thermal conductivity of disperse particle, $n$ is shape factor and $\Phi$ is volume fraction of particles. The value of $\Phi$ can be calculated from concentration of disperse particles by weight,

$$\Phi = \frac{C\rho_1}{C\rho_1 + (1-C)\rho_s}$$

where the $C$ is weight concentration, $\rho_1$ is density of disperse medium, $\rho_s$ is density of disperse particle.

**Figure 12** shows the dependence of the relative thermal conductivity on the concentration of metal powder in the disperse system in PEG M400. The theoretical curve calculated by Hamilton’s equation using shape factor of 10 is also shown. The experimental values are smaller than the calculated ones. It is assumed that, in Hamilton’s equation, all the particles have a same shape and size and the particles do not associate with each other. However, in the disperse system studied here, the metal particles form a flocculated structure. In order to apply Hamilton theory, the shape and the volume fraction of flocs formed by the metal particles have to be taken into account instead of those of primary particles.

**Figure 13** shows a schematic representation for suspension of metal powder in PEG. When the shear flow is applied, the disperse particles are oriented in the flow field or dispersed homogeneously depending on the rate of shear as shown in Figure 13 (b). Since the thermal conductivity of disperse particles is larger than that of disperse...
medium, the channel of thermal conduction expands whole the system, then the thermal conductivity of the system becomes higher. However, after stopping the shear flow, the dispersed particles form the flocculated structure gradually as shown in Figure 13 (a), and the path of thermal conduction may be broken and/or shrunk. Consequently the thermal conductivity of system becomes lower.

4. Conclusions

1. The thermal conductivity of the suspension of metal powder in PEG depends on the concentration and dispersing condition of particles as follows:
   i) Since the thermal conductivity of metal powder is higher than that of disperse medium, the thermal conductivity increases with increasing concentration.
   ii) The thermal conductivity decreases as the flocculated structure is constructed.
2. Orientation of particles in a flow field results in the increase of the thermal conductivity of system.
3. The process of formation of flocculated structure can be investigated quantitatively from the time dependence of thermal conductivity after cessation of shear flow.

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References