Rheological characteristics of non-spherical graphite suspensions

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Abstract

Since the microstructure of functional thin films depends on the dispersion characteristics of dense slurry, it is important to control the agglomerative nature of slurries under processing. The present authors have been discussing the model prediction of agglomerative nature and local rate of agglomeration in dense suspensions. The experiments have been performed under shear flow using the nearly spherical and oblate type graphite particles. In this study, the experiment has been conducted using water and glycerol as dispersion media. Stress control type rheometer was used to measure the slurry rheology. Local agglomeration of graphite particles has been predicted by using Usui's model. The experimental results show that both the shape and slurry processing method affect on the local dispersion condition. The agglomeration formed by oblate type graphite particles seems to be more difficult to break up than that of spherical particles.

Keywords : slurries, viscoelasticity, non-spherical particle, agglomeration

1. Introduction

Suspension containing high volume fraction of solid particles are frequently encountered in slurry transportation and manufacturing processes. Some examples for industrial application of filler-modified fluid are fuel cell, printing ink and dyes. It is important to predict the rheological properties as a function of various parameter concerning solid volume fraction, particle shape, particle size distribution, specific surface area of particle, solid liquid interaction and fluid properties as well.

Many investigators have been conducting the experimental measurements and theoretical prediction in the field of suspension rheology containing mono-dispersed and poly-dispersed particles. Among other, Schmidt and Munstedt (2002) have investigated the influence of pre-shearing on the rheological behavior of concentrated mono-dispersed model suspensions. They have applied steady pre-shearing at low shear stress and solid volume fractions ranging from 0.20 to 0.35. It was found that the features observed in the low frequency range could be attributed to structure formation of a particular network. In the high frequency range, the behavior obeyed the Newtonian fluid. Smith and Van De Ven (1985) have identified the behavior of solid/liquid clusters undergoing simple shear in an immiscible liquid medium. Attention was concentrated on the effects of changing the volume fraction of solids within

the cluster, liquid/liquid interfacial tension and wet-ability of the solid surface. An increasing volume fraction of solids was found to alter both the cluster strength and also the mode of rupture. Decreasing the liquid/liquid interfacial tension resulted in a lower overall cluster strength but increased the likelihood of emulsion formation.

Usui (1999) has developed a rheological model for the prediction of non-Newtonian viscosity of agglomerative suspensions with particles size distribution. Usui et al. (2001b) have proposed the viscosity prediction model of dense slurries prepared by non-spherical solid particles. For this purpose, Simha's cell model was applied for concentrated slurry with wide particles size distribution. Usui's model was able to predict the rheological behavior of suspensions with non-spherical particles. This model will be applied to graphite particle suspension to obtain the information on the agglomeration nature of suspensions.

Graphite particles are used to prepare electrode materials in fuel cell technology or lithium secondary battery making technology. Many kinds of graphite particles with different catalytic characteristics have been tested to increase the efficiency of electrode performance (Kasuh, et al., 1997; Ohsaki et al., 1997; Chung, 2002). However, the information on the dispersion control of electrode materials is not clearly understood. It is known that the shape of graphite particle and method of coating also affect on the performance of electrode. In this study, it is aimed to give the effect of shape and slurry processing method on the local dispersion condition and viscoelastic behavior in dense slurries.

(a) Nearly spherical particles
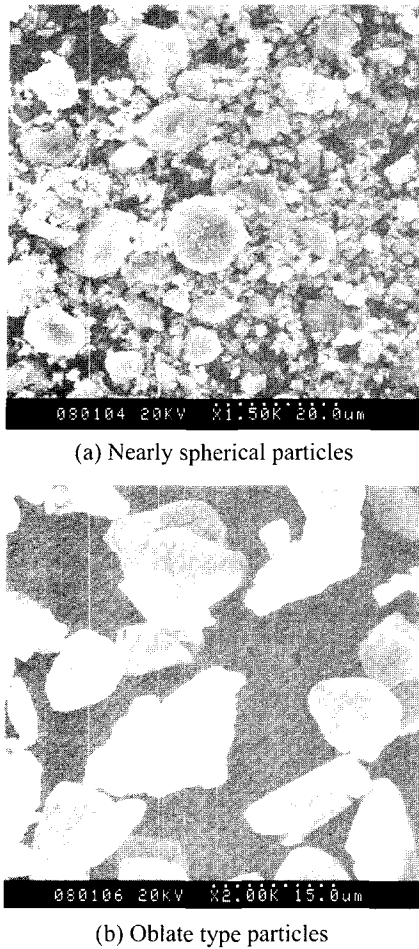

(b) Oblate type particles

Fig. 1. Graphite particles on SEM image analysis.

2. Experiments

Two kinds of graphite particles were used in this study. First one is nearly spherical graphite particle and the other one is oblate-type particles. Both particles on SEM image analysis are shown in Fig. 1. Both particles were suspended in Newtonian fluid with solid volume fraction, $\phi = 0.25$. As a Newtonian dispersion media, water and glycerol ($\eta=1.0$ Pa.s at 25°C) were used. The pH of tested suspensions was kept constant (pH=5.5). Non-spherical characteristics of graphite particles can be evaluated by circularity or sphericity. Two dimensional particle image give us the circularity of non-spherical particle as shown by Eq. (1).

$$\psi = \frac{(diameter\ based\ on\ area\ of\ particle\ image)}{(diameter\ based\ on\ periphery\ of\ particle\ image)} \quad (1)$$

Since we are intending to apply it to three dimensional case, hereafter we call ψ as sphericity, and the volume averaged diameter of non-spherical particles should be devided by ψ to obtain the non-spherical particle diameter. The flow particle image analyzer, FPIA-2000, Sysmex Co. was used to obtain the two dimensional particle images for
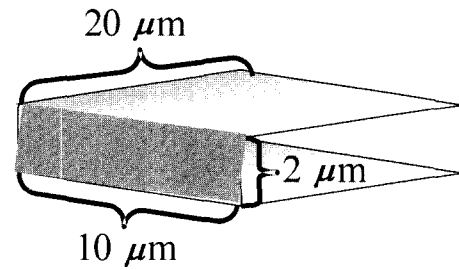

Fig. 2. Typical shape of oblate type graphite particle.

nearly spherical graphite particles. The averaged sphericity for nearly spherical graphite particles was given as $\psi_{av}= 0.92$. On the other hand, it was difficult to obtain the sphericity of oblate type graphite particles shown in Fig. 1-b, because the oblate type particles are three dimensionally winded in the picture. So, we decided to get very rough estimate of sphericity for oblate type particles from SEM image photographs. From the thirty representative pictures of oblate type particles, typical shape of the oblate type particle is drawn in Fig. 2. From this figure, the sphericity of oblate type graphite particle is estimated as $\psi=0.84$.

The suspensions were mixed by means of magnetic stirrer for one hour. After matured one day on the rotating machine to avoid non-uniform agglomeration, the test slurry was mounted on the rheometer. Stress control type rheometer (Rheometric Scientific Co. Ltd., SR-5) was used to measure the slurry rheology characteristics. In case of viscoelastic behavior, the measurement was conducted under the condition of 10% strain by using cone plate system with 4 cm diameter. Apparent viscosity and viscoelastic behavior measurements were performed at 298 K.

The laser diffraction type particle size measurement has been conducted by using Horiba LA-920. The experimental results of the particle size distribution of graphite particles are shown in Fig. 3. In case of nearly spherical graphite particles, shown in Fig. 3-a, this particle size distribution was subdivided into nine discrete ranges. On the other hand, oblate type particle size distribution, shown in Fig. 3-b, was subdivided into ten discrete ranges. The number based particle size distribution of both nearly spherical and oblate type particles used for model calculation is shown in Table 1 and Table 2, where D(I), PD(I), NN are particle size, probability density and the number based particle size distribution, respectively.

3. Experimental results and discussion

3.1. Coating experiments using nearly spherical graphite particles suspended in nafion

To get the information of the effect of shear rate on the dispersion of characteristics of suspension, we have carried out the coating experiments using nearly spherical graphite particles suspended in nafion with the solid volume frac-
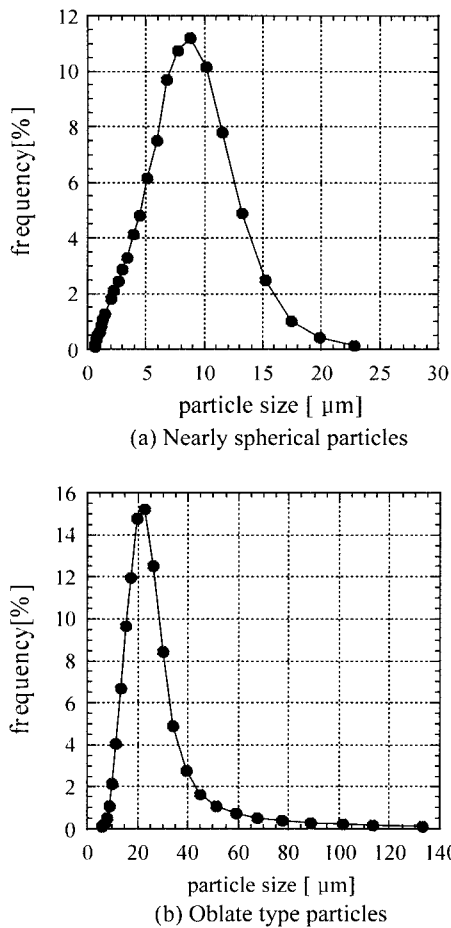
(a) Nearly spherical particles

(b) Oblate type particles

Fig. 3. Particles size distribution of graphite particles.

Table 2. The number based particle size distribution used for the model calculation (oblate type)

D(I)[m]	PD(I)[−]	NN[1/m³]	Ψ(I)[−]
8.50×10⁻⁰⁶	0.0805	3.76×10¹³	8.37×10⁻⁰¹
1.44×10⁻⁰⁵	0.163	1.57×10¹³	8.37×10⁻⁰¹
1.88×10⁻⁰⁵	0.267	1.16×10¹³	8.37×10⁻⁰¹
2.43×10⁻⁰⁵	0.273	5.47×10¹²	8.37×10⁻⁰¹
3.15×10⁻⁰⁵	0.133	1.22×10¹²	8.37×10⁻⁰¹
4.14×10⁻⁰⁵	0.0437	1.77×10¹¹	8.37×10⁻⁰¹
5.45×10⁻⁰⁵	0.0178	3.14×10¹⁰	8.37×10⁻⁰¹
7.17×10⁻⁰⁵	0.009	7.00×10⁰⁹	8.37×10⁻⁰¹
9.41×10⁻⁰⁵	0.005	1.72×10⁰⁹	8.37×10⁻⁰¹
1.24×10⁻⁰⁴	0.0028	4.25×10⁰⁸	8.37×10⁻⁰¹

Larger particle number gives higher fractal dimension

D=1.33   D=1.39

Higher agglomeration gives higher fractal dimension

D=1.48   D=1.55   D=1.57
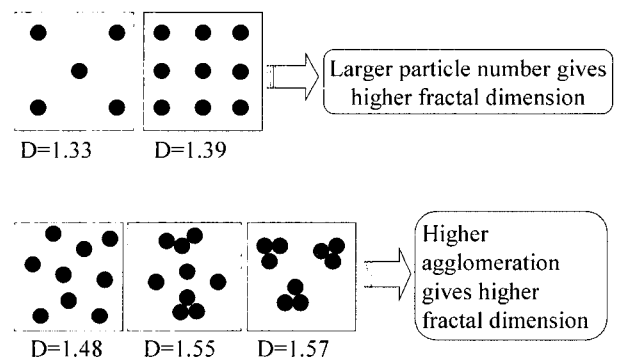
Fig. 4. Model of fractal dimension as a function of size and agglomeration of particles using box-counting method.

Table 1. The number based particle size distribution used for the model calculation (nearly spherical type)

D(I)[m]	PD(I)[−]	NN[1/m³]	Ψ(I)[−]
1.05×10⁻⁰⁶	0.0826	3.41×10¹⁶	9.20×10⁻⁰¹
2.65×10⁻⁰⁶	0.074	1.90×10¹⁵	9.20×10⁻⁰¹
3.68×10⁻⁰⁶	0.0742	7.08×10¹⁴	9.20×10⁻⁰¹
5.25×10⁻⁰⁶	0.1843	6.06×10¹⁴	9.20×10⁻⁰¹
7.23×10⁻⁰⁶	0.2044	2.58×10¹⁴	9.20×10⁻⁰¹
9.42×10⁻⁰⁶	0.2134	1.22×10¹⁴	9.20×10⁻⁰¹
1.22×10⁻⁰⁵	0.1267	3.32×10¹³	9.20×10⁻⁰¹
1.58×10⁻⁰⁵	0.0348	4.20×10¹²	9.20×10⁻⁰¹
2.06×10⁻⁰⁵	0.0053	2.89×10¹¹	9.20×10⁻⁰¹

tion of $\phi=0.28$. Nafion is the well known dispersion medium in the preparation of fuel cell electrode. A controlled coater was used to produce the coated layer with 00 μm thickness with different coating speed, i.e. 2, 3 and 4 cm/sec. After drying the membrane, the replica of cross sectional area was prepared, and the particle images were observed by an optical micro-scope. The fractal dimension

of particle images was calculated by box counting method (Chiaia, et al., 1998). Fractal dimension of known dispersion system is demonstrated in Fig. 4. This diagram indicates that larger particle number gives higher fractal dimension, and higher agglomeration also gives higher fractal dimension. Since the solid concentration of graphite particles was set constant in this experiment, the change in fractal dimension can be attributed to the rate of agglomeration of suspended particles. The fractal dimension measured for graphite-nafion suspension system with different coating speed is shown in Fig. 5. Although large scatter of experimental data exists, there is a general tendency that the well dispersed condition is obtained in the case of higher coating speed. This means that the fuel cell electrode efficiency could be affected by the shearing condition in slurry coating system. Thus, it may be concluded that the prediction of agglomeration characteristics in sheared flow is one of the key factor to improve the performance of fuel cell electrode.

3.2. Apparent viscosity of non-spherical particle suspensions with different dispersing media
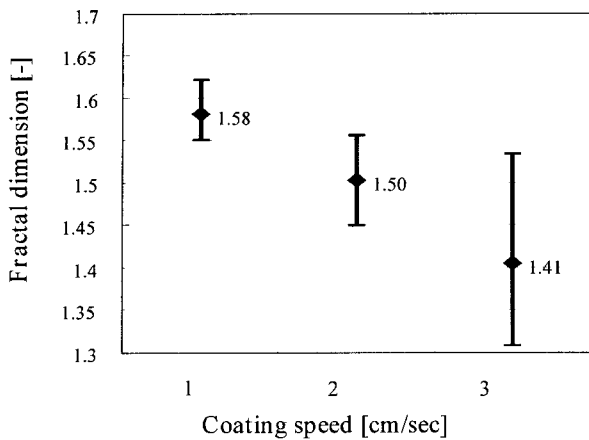
When we prepare the graphite particle suspension in

Fig. 5. Fractal dimension as a function of coating speed on nearly spherical particles - nafion suspension.
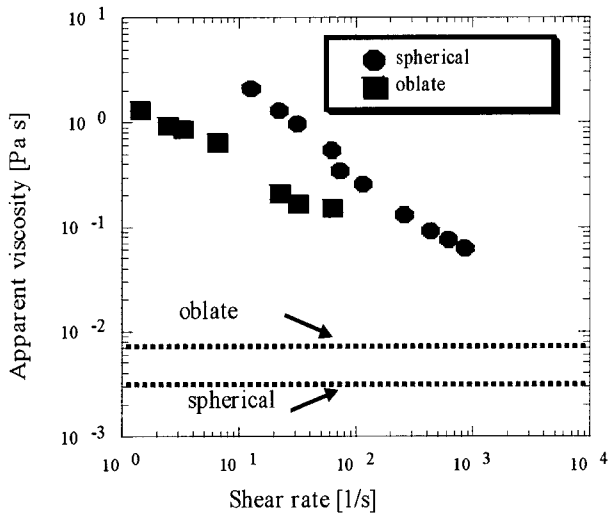

Fig. 6. Apparent viscosity of water suspension as a function of shear rate at 298 K with 0.3%wt of NSF was added as a dispersing agent.

water, dispersion additive is needed because hydrophobic graphite particles agglomerate so strongly in water. Three dispersing agents, naphthalene sulfuric acid formalin condensate (NSF), poly (meth) acrylate (PMA) and polystyrene sulfuric acid (PSS) have been tested. It was found that these three additives had almost the same disperse-ability. Since NSF showed slightly better disperse-ability, we selected NSF as dispersion additive for graphite suspension. Fig. 6 shows the apparent viscosity of both nearly spherical and oblate type graphite suspensions. Experimental results shown in this figure indicate that the apparent viscosity of nearly spherical particle suspension is higher than that observed for the oblate type suspension. Since the sphericity of oblate type graphite particles is smaller than the sphericity of nearly spherical one, we expect that the suspension viscosity of oblate type graphite

particles is higher than that of nearly spherical graphite particle suspension. Usui (2001b) has shown the predicting method of Newtonian viscosity for completely dispersed suspension system of non-spherical particles with particle size distribution. This method was based on Simha's cell model and Usui's algorism to predict the maximum packing volume fraction for non-spherical particle system. Since the non-spherical particles give higher apparent volume fraction as shown in the previous section of this paper, the predicted viscosity level for oblate type graphite suspension is higher than the case of nearly spherical particles as shown by dotted lines in Fig. 6. This is the reverse tendency of experimental results shown in Fig. 6. It is expected that the rotation of graphite particle can be occurred easily causing the alignment of oblate type particles along the shear surface. This may cause the decrease in apparent solid volume fraction for oblate type particles, and finally cause the descend of apparent viscosity. To check this point, glycerol was used as dispersant with different viscosity and different disperse-ability.

Fig. 7 shows the results of apparent viscosity measurements for the graphite particle suspended in glycerol. Again, the horizontal lines indicate the Newtonian viscosity level predicted for completely dispersed condition. The tendency of viscosity increase observed for experimental results is in agreement with the predicted viscosity levels. This experimental evidence shows that the viscosity of non-spherical particle dispersed system depends not only on the disperse-ability but also on the viscosity of medium itself. Since glycerol is a good dispersing medium, the difference between the experimental results and predicted Newtonian viscosity level for completely dispersed system is not significant. The mechanism of viscosity increase in graphite suspensions may be explained as follows.
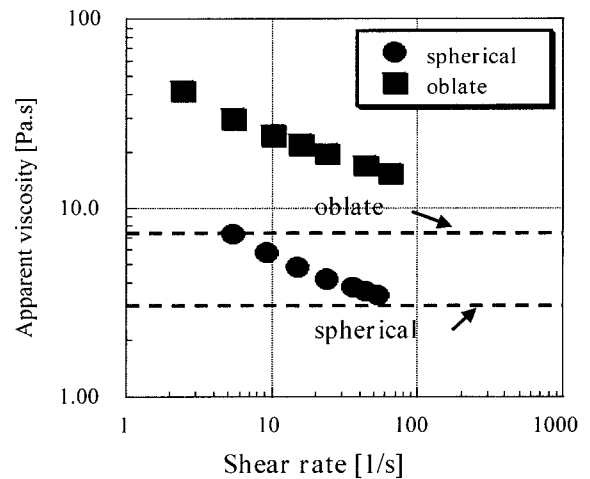

Fig. 7. Apparent viscosity of glycerol suspension as a function of shear rate at 298 K.

In the case of suspensions in glycerol, non-spherical particles do not agglomerate so much, and each particle suspended in simple shear flow would rotate during the shear flow. Oblate type particle suspension causes larger apparent volume fraction because of its lower sphericity, and the suspension viscosity with oblate type particles is higher than the suspension viscosity with nearly spherical particles at the same solid volume fraction. On the other hand, graphite suspensions in water show more strong agglomeration even if we use dispersing additive such as NSF. The oblate type graphite particles agglomerate and they may align along the sheared surface. Since the viscosity of water is very low, the drag force acted by water is not large. This causes the reduction of apparent volume fraction of oblate type graphite suspension, and finally the viscosity of oblate type suspension becomes lower than the viscosity of nearly spherical graphite suspension.

3.3. Viscoelastic behavior of graphite suspensions

For the dynamic measurement on graphite suspensions, glycerol was used as dispersant. The dynamic storage modulus, G', and the loss modulus, G'', plotted against the angular frequency, ω, for graphite suspensions are shown in Fig. 8. Storage modulus, G', indicate the strength of internal structure of agglomeration. Whereas the loss modulus, G'' is related with the dynamic viscosity, η', by $G''= \omega \eta'$. Fig. 8 indicates that the loss modulus G'' both for nearly spherical and oblate type suspensions gives the same tendency, but oblate type suspension shows higher value of loss modulus than that observed for the case of nearly spherical particles. This observation corresponds to the apparent viscosity measurements shown in Fig. 7.

While in the case of storage modulus, G', it seems that there exists very clear difference between nearly spherical and oblate cases. At lower frequency region, oblate type
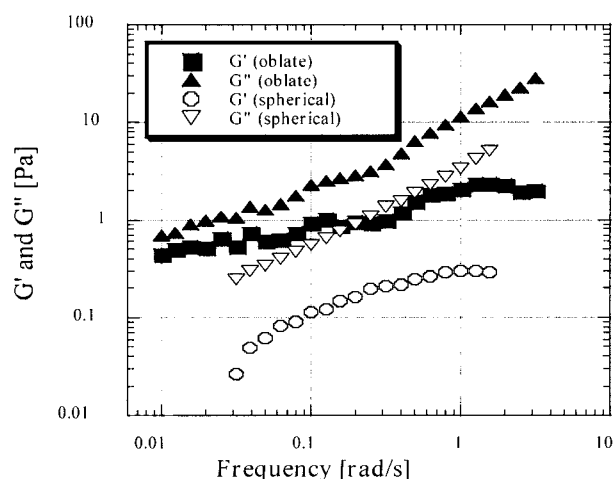

Fig. 8. Dynamic storage modulus, G', and the loss modulus, G'', for graphite suspension in glycerol.

suspension exhibits a flat tendency, while the data of nearly spherical particle suspension fall down. This result indicates that the agglomeration formed by oblate-type particles is more difficult to be broken up than that of nearly spherical case.

3.4. Local agglomeration prediction

Usui (1999) and Usui et al. (2001a) proposed the non-Newtonian viscosity prediction method for agglomerative suspensions with discrete particle size distribution. This model is applicable for non-spherical particle suspension system (Usui et al., 2001b). The basic idea of this model is the combination of Simha's cell model and Usui's non-Newtonian slurry viscosity model. However, Simha's cell model (Simha, 1952) needs the maximum packing volume fraction. Usui et al. (2001b) estimated it by the packing model for non-spherical particles.

The model proposed by Usui (1999) concentrates the effect of the agglomerative nature of suspended particles to the cluster formation by the minimum sized primary particles. The number of primary particles contained in a cluster, n, is chosen as a thixotropy parameter. The shear breakup process was determined by taking the force balance on the two spherical clusters in simple shear flow. Usui proposed a rate equation in which the breakup of the cluster and both Brownian coagulation and shear coagulation processes were taken into account. The rate equation is given by

$$\frac{dn}{dt} = \frac{4\alpha_b k_b T N_0}{3\eta_0} + \frac{4\alpha_s \phi n \dot{\gamma}}{\pi} - \frac{3\pi d_0^3 n}{4 F_0 N_b}\left(\frac{n}{1-\varepsilon}-1\right)\eta\dot{\gamma}^2 \qquad (2)$$

Since the solid concentration is known, the unknown parameters in Eq. (2) are n, F_0 and ε. The dependence of ε on the number of primary particles contained in a cluster is assumed to be given by the following equation (Usui, 1999).

$$\varepsilon = \varepsilon_{max}\{1-n^{-0.4}\} \qquad (3)$$

Where ε_{max} is the void fraction at $n=\infty$. Using the relationship given by Eq. (3), the number of unknown parameters is reduced to two. When a set of apparent viscosity and shear rate data is given experimentally, the number of primary particles contained in a cluster is calculated as follows.

1. Assume the value of n, and estimate the size and number of clusters by Eq. (3). This gives a new particle size distribution.

2. Calculate the maximum packing volume fraction following the method proposed by Usui et al. (2001).

3. Use Simha's cell model (Simha, 1952) to predict the slurry viscosity at a given shear rate.

4. If the predicted viscosity is not the same as the experimentally determined one, the value of n is reassumed until a good convergence is obtained.

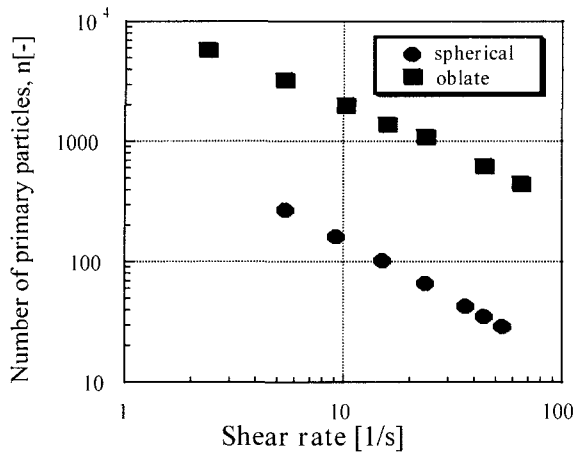The number of primary particles, thus obtained from the

Fig. 9. Number of primary particles contained in cluster of graphite suspension in glycerol as function of shear rate.

Fig. 10. Apparent viscosity of spherical and oblate graphite suspension in glycerol and the comparison with predictions by Usui's non-Newtonian viscosity model.

Fig. 11. Inter-particle bonding energy (F_0) as a function of shear rate.

experimental data of apparent viscosity measurements, is shown in Fig. 9. Graphite particles are very easy to agglomerate, and there exist large clusters in suspension even at higher shear rate range. Since the number of primary particles contained in a cluster at fixed shear rate is obtained from the viscosity data, the inter-particle bonding energy, F_0, can be calculated by using Eq. (2). The averaged values F_0 for both nearly spherical and oblate type graphite particles were determined as 1.45×10^{-13} [J] and 1.98×10^{-9} [J], respectively. The inter-particle bonding energy depends on the diameter and the shape of particles. Based on the experimental results of the particle shape in Fig. 1, it is shown that particle shape of oblate type is more non-spherical than that of nearly spherical case. Minimum sized particle diameter of oblate type particles is larger than the spherical one as shown in Table 1 and Table 2. As the consequence, the inter-particle bonding energy, F_0, for oblate type is higher than that of nearly spherical case.

Once we get the value of the inter-particle bonding energy, the apparent viscosity of graphite suspension can be predicted by using Eq. (2) and Simha's cell model. The predicted viscosity is shown by solid line in Fig. 10. This diagram indicates that the non-Newtonian slurry viscosity of non-spherical particle system can be predicted by the Usui's model. However, the agreement between experiments and theoretical prediction is not satisfactory for the case of oblate type graphite suspension. Two horizontal lines shown in Fig. 10 are the predicted viscosity levels for completely dispersed system. Since the cluster formed by primary particles is completely broken up, the solid line predicted by Usui's model coincides with the horizontal line at higher shear rate region. This means that the effect of agglomeration on suspension viscosity is not evaluated successfully if the viscosity level of completely dispersed system is not properly estimated. The sphericity of oblate type graphite particle was very roughly estimated as shown
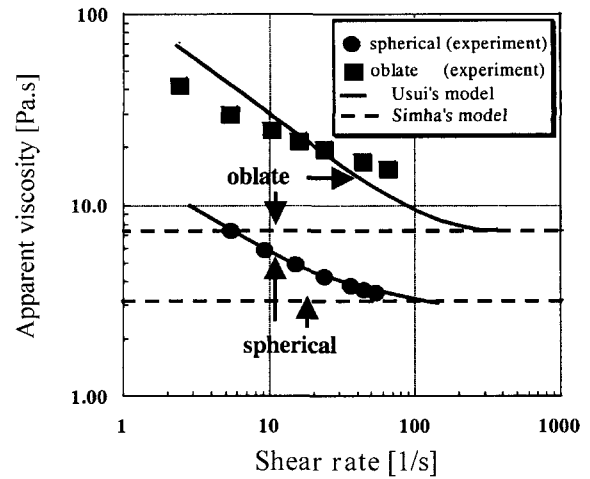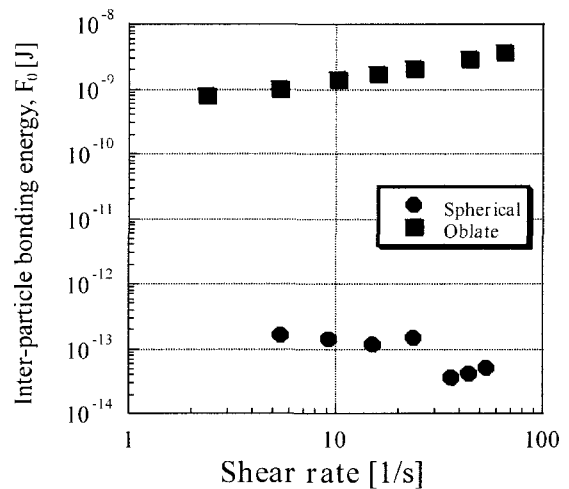
in Fig. 2. With different sphericity value, we can predict the different viscosity level of completely dispersed system. Since the difference of viscosity between the completely dispersed condition and agglomerated suspension system is evaluated by agglomerative nature of suspended particles, improperly estimated Newtonian viscosity level based on the wrong sphericity may cause the significant error of viscosity prediction by the present model. Fig. 11 shows the predicted value of the inter-particle bonding energy based on each set of apparent viscosity and shear rate. Data obtained for nearly spherical graphite particle system show almost constant values except the three data point at higher shear rate region. When the experimentally determined viscosity approach to the viscosity level of completely dispersed system, small experimental error causes very large fluctuation of estimated inter-particle bonding energy. Thus

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the small value of three data points for nearly spherical graphite suspension at shear rate=35~55 s^{-1} is not essential problem. However, the inter-particle bonding energy obtained for oblate type graphite particle suspension shows the tendency of monotonous increase according to the increase of shear rate. This observation suggests indirectly that the estimation of sphericity of oblate type graphite suspension is not appropriately done. If the sphericity of non-spherical graphite particles is precisely obtained, the agreement of predicted apparent viscosity with experimental results may be much improved for oblate type graphite suspension. The precise measurement of non-spherical characteristics is essential for the prediction of non-Newtonian rheological characteristics os suspensions.

4. Concluding remarks

Local agglomeration of graphite particles in dense suspensions has been predicted by using Usui's model. The model can predict the effect of shape and slurry processing on the local dispersion condition. It is expected that this information is useful for manufacturing functional thin films by controlling the dispersion conditions. The oblate type graphite suspensions dispersed in glycerol show higher apparent viscosity than the case of nearly spherical graphite suspension. The reverse tendency is observed for graphite suspensions in water dispersion system. The experimental evidence shows that the viscosity of non-spherical particle dispersed system depends not only on the disperse-ability of dispersing medium but also on the viscosity of dispersing medium itself. The agglomeration formed by oblate-type particles is more difficult to be broken up than that of spherical case.

List of symbols

d_0	= diameter primary particle which create the cluster [m]
F_0	= inter-particle bonding energy [J]
k_B	= Boltzmann constant [J/K]
n	= number of the primary particles contained in a cluster [−]
N_b	= number of chains to be broken-up during the cluster break-up process [−]
N_0	= total number of minimum sized (primary) particles less than critical [−]
t	= time [s]

T	= temperature [K]
α_b	= Brownian coagulation constant (=0.58) [−]
α_S	= shear coagulation constant (=0.60) [−]
γ	= shear rate [s^{-1}]
ε	= void fraction [−]
η	= slurry viscosity [Pa.s]
η_0	= solvent viscosity [Pa.s]
ψ	= sphericity [−]
ρ	= density [kg/m^3]
τ	= shear stress [Pa]
ϕ	= volume fraction of solid particles [−]
$\phi_{p,max}$	= maximum packing volume fraction [−]

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