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Application of Scaling Theories to Estimate Particle Aggregation in a Colloidal Suspension

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Abstract – Average aggregate size in particulate suspensions is estimated with scaling theories based on fractal concept and elasticity of colloidal gel. The scaling theories are used to determine structure parameters of the aggregates, i.e., fractal dimension and power-law exponent for aggregate size reduction with shear stress using scaling behavior of elastic modulus and shear yield stress as a function of particle concentration. The structure parameters are utilized to predict aggregate size which varies with shear stress through rheological modeling. Experimentally rheological measurement is conducted for aqueous suspension of zinc oxide particles with average diameter of 110 nm. The predicted aggregate size is about 1135 nm at 1 s^{-1} and 739 nm at 1000 s^{-1} on the average over the particle concentrations. It has been found that the predicted aggregate size near 0.1 s^{-1} agrees with that the measured one by a dynamic light scattering analyzer operated un-sheared.

Key words: Colloidal aggregate, Fractal dimension, Yield stress, Elastic modulus, Aggregate size

1. Introduction

Particle aggregation occurs in colloidal suspensions when the net attractive force acts among the particles at proximity. The particle aggregation means a state of particle arrangement where the particles are placed closely each other forming an assembly. The microscopic particle arrangement is interrelated with macroscopic properties or behavior of the particulate suspensions. A typical example of the macroscopic properties is rheological properties. The particle arrangement is one of the important factors to affect the rheological properties of the suspensions. Especially, the particle aggregation often gives a noticeable influence on the rheological properties. It can occur between individual particles or between particle and aggregate, or between aggregates. As the particle concentration increases in aggregated suspensions, it is much likely that the aggregates link to adjacent aggregates and grow to form network structure such as colloidal gel. Onset of this network structure usually gives rise to an apparent change in the rheological behavior and properties. On the converse, the particle arrangement is also affected by macroscopic condition such as external flow field. Under shear flow, isolated or aggregated particles tend to align along the force direction and size of aggregates reduces when the shear force exceeds the interparticle attractive force. It is, therefore, expected that rheological properties of the suspension can be used to quantitate the particle aggregation. There have been many studies on the relations between the rheological properties and the structure of particulate aggregates [1-10]. The aggregate structure can be described in terms of fractal concept based on self-similar nature of aggregate structure [11,12]. The parameters of the fractal aggregate can also be related with the rheological properties. The relations between the structure parameters and the rheological properties are often expressed by scaling theories. Many scaling theories on colloidal aggregates have been suggested. The scaling theories usually assume mass-radius relation in which mass of an aggregate containing a certain number of particles scales with the aggregate size powered by an exponent. The power-law exponent is the fractal dimension which exhibits compactness of the aggregate.

When the aggregates are under shear force, the aggregate size reduces with the shear. This is expressed by a scaling relation that the aggregate size scales with the inverse of shear rate powered by an exponent. This exponent indicates the degree of size reduction with shear force and has been reported by previous investigators [6,13,14].

These microstructural parameters are also necessary for developing rheological model for shear viscosity of the suspensions with aggregation. The rheological model is obtained by combining concentration dependence and shear dependence of the suspension viscosity. This combination requires the structure parameters to take the particle aggregation into account. This modeling procedure allows us to estimate average aggregate size as a function of shear rate. Although there have been many studies on scaling analysis regarding particle aggregation, the study on estimation of aggregate size from rheological properties is hardly found.

Recently, our research group [15] has presented a scheme for predicting aggregate size from the rheological properties of the colloidal suspension and scaling theories. It was based on the scaling theory by Shih et al. [2] to determine the fractal dimensions of

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aggregate and its backbone from behavior of elastic modulus. This theory assumed there exist two extreme regimes of aggregation, i.e., strong-link and weak-link regime. In the strong-link regime, the overall elasticity of the colloidal suspension is due to the intrafloc link. Meanwhile, the weak-link regime refers to the state that the overall elasticity is governed by weaker interfloc link. Their theory also enables us to directly deduce the fractal dimension of backbone chain. It was pointed out that the backbone fractal dimension showed unrealistic values for some colloidal suspensions [5]. To overcome this problem, Wu and Morbidelli [5] suggested a scaling theory which generalized Shih et al.'s theory by taking consideration of intermediate regime between the strong-link and the weak-link regime.

The present study employed Wu and Morbidelli's theory to ultimately predict aggregate size using rheological properties of the colloidal suspension. The rheological properties were measured to determine the structure parameters such as fractal dimension and power-law index for size reduction of aggregate under shear flow. These parameters were used to estimate average aggregate size through rheological modeling for the shear viscosity of aggregated suspension. Experimentally steady shear and oscillatory shear measurement were carried out for aqueous suspension of zinc oxide particles with the average size of 110 nm. The volume concentration of the particle ranges from 6 to 8% where the elastic behavior becomes noticeable due to colloidal gelation. It was observed that the zinc oxide suspension showed a different behavior from that of carbon black suspension in the previous work [15] in the elasticity with the particle concentration. Finally, the rheological estimates of the aggregate size were compared with those measured by a dynamic light scattering analysis.

2. Experimental Procedure

2-1. Sample preparation

For rheological measurement, we prepared aqueous suspensions of zinc oxide (ZnO) particles through mechanical dispersion. The zinc oxide particles manufactured by Sukgyung AT Co. (grade: SG-ZNO01) in Korea were used. The manufacturer's specification for the particle size is 110 ± 30 nm. The photographic images of the particles are shown in Fig. 1. The particles were dispersed in deionized water. The particle density was taken as 5.61 g/cm^3 from a literature [16] to calculate particle volume concentration, which ranged from 6 to 8%.

For the mechanical dispersion zinc oxide particles were wetted by a small amount of deionized water on a glass plate. One gram of the zinc oxide particles was wetted with 10-20 mL of the water for about 5 minutes with spatula. Together with the wetted particles remaining water was then poured into a polyethylene bottle. This inhomogeneous mixture was treated by a mechanical homogenizer (Model HG-150, WiseTIS Corporation). This operation was performed for 3 minutes at 3000 RPM at a time. Then a homogenized state of the mixture is

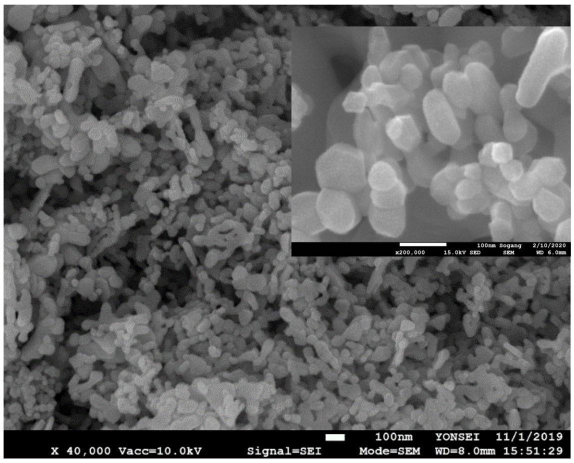

Fig. 1. Photographic images of zinc oxide (ZnO) particles with two magnifications by Field Emission-Scanning Electron Microscope (FE-SEM, Model: JSM-7100F, Maker: JEOL). The scale bar (white color) in each image indicates 100 nm.

obtained after three times repetition. The mixture was milled using a paint shaker device (PK2003T, PK Lab). For milling operation, 3 mm steel balls were packed in the bottle of the mixture. Simple water jacket was implemented on the bottle to prevent temperature increase while milling operation. The paint shaker was operated for 30 min. at 280 W and 60 Hz. The maximum temperature checked was 32 ^{o}C. Through this milling operation we finally obtained an aqueous suspension of the zinc oxide particles.

2-2. Measurement

For rheological measurement, we used a plate-plate type rheometer (MCR 102, Anton Paar Co.). The diameter of plate is 50 mm and gap between plates is 1 mm. The temperature was set at 25 ^{o}C (±0.1 ^{o}C) for measurement. Both steady and oscillatory shear measurements were performed. For the steady shear measurement, shear rate range was set to 1-1000 s^{-1}. Test sample was pre-sheared at 10 s^{-1} for 1 min. Then shear stress was measured over the whole range of the shear rates for 1 min. Oscillatory shear measurement was conducted to measure elastic and viscous moduli. Frequency sweep test was performed in the range of 1-10 rad/s at 0.01% strain. The moduli were measured in the strain range of 0.01-1% at angular frequency of 10 rad/s. We also conducted optical measurement using a dynamic light scattering (DLS) analyzer (Litesizer 500, Anton Paar Co.). The DLS measurement was performed for test samples at the particle volume fraction of 0.06 and 0.08. The samples were measured three times each after dilution.

3. Results and Discussion

Rheological response due to colloidal aggregation is manifested when the aggregates grow to form network structure, i.e., colloidal gel at which suspension tend to be more elastic. This elasticity is reflected on elastic modulus and yield stress. Behavior of these properties with the particle concentration ϕ is quite useful in determining structure parameters of colloidal aggregates.

We consider scaling behavior of elastic modulus with ϕ first. Shih et al.'s theory [2] has been well used to estimate structural parameters such as fractal dimensions of aggregate and backbone chain in an aggregate using the elasticity of colloidal gel. As mentioned in Introduction, elasticity of colloidal gel is determined by the relative magnitude of interfloc and intrafloc link. When the intrafloc link is stronger than interfloc link, the elasticity K of overall colloidal gel is equivalent to K_{intra} which is the elasticity from the intrafloc link, i.e., $K \approx K_{intra}$. This is called strong-link regime. Likewise, when the interfloc link dominates, the elasticity K is governed by K_{inter}, the elasticity of the interfloc link, i.e., $K \approx K_{inter}$, and this case corresponds to weak-link regime. Since this classification oversimplifies colloidal suspensions, it has limitation in accounting for the various behavior of aggregation. Wu and Morbidelli [5] generalized Shih et al.'s theory by considering intermediate regime where both the intrafloc and the interfloc links contribute to the overall elasticity. In the generalized theory, the overall elasticity K is expressed by

$$\frac{1}{K} = \frac{1}{K_{inter}} + \frac{1}{K_{intra}}. \tag{1}$$

This generalization finally leads to

$$G'_{lim} \propto \phi^{\frac{\beta}{d-d_f}},\ \gamma_{lim} \propto \phi^{\frac{2-\beta}{d-d_f}}, \tag{2}$$

where $\beta = d - 2 + (x+2)(1-\alpha)$. (3)

Here, G'_{lim} is the elastic modulus at plateau and γ_{lim} is the linear limit of the strain at the plateau. The symbol d denotes the Euclidean dimension and is 3 in three-dimensional space. The symbol d_f is the fractal dimension of aggregate and x is the fractal dimension of backbone chain of an aggregate. And α reflects contribution of each regime and lies between 0 and 1. It is 0 for strong-link regime and 1 for weak-link regime. This theory includes the strong-link and weak-link regimes as well as intermediate regime.

Rheological measurement was conducted to obtain the behavior of elastic modulus with the particle concentration. Fig. 2 shows the elastic modulus and the viscous modulus as a function of strain at various ϕ. The elastic modulus at each ϕ exhibits the plateau zone at small strains beyond which it starts to decrease with the strain. It is apparent that the plateau elastic moduli increase with ϕ. The elastic moduli also change smoothly near the linear limits. The G'_{lim} and γ_{lim} were chosen as the point beyond which the elastic modulus begins to drop over 2% from the previous point and then continuously decreases. These G'_{lim} and γ_{lim} are plotted as a function of ϕ in Fig. 3. It is clearly seen that G'_{lim} increases with ϕ whereas γ_{lim} decreases with γ_{lim} in log-log plot. Thus, the scaling relations can be written as $G'_{lim} \propto \phi^{4.876}$, $\gamma_{lim} \propto \phi^{-2.131}$ as indicated by the dotted lines in Fig. 3. This scaling behavior belongs to the strong-link regime. From Eqs. (2) and (3), we obtain that $d_f = 2.271$ and β = 3.553. The value of d_f indicates that this aggregation is close to reaction-limited cluster aggregation (RLCA) in which aggregation takes place slower and aggregates are more compact than in diffusion-limited cluster aggregation (DLCA). The fractal dimension of the backbone chain x is conceptually based on the aggregate model by Shih *et al.* and has not been directly measured. They calculated x for two-dimensional case of cluster aggregation system using similarity to electrical conduction problem and showed that x is theoretically 1.0-1.3. In actual colloidal suspensions, x was calculated as 1.0-1.4 from the experimental data. However, some cases showed unrealistic x values which were negative or far less than unity. Employing Shih *et al.*'s theory to the zinc oxide suspension in the present study, x is 0.553. This result belongs to the cases where Shih *et al.*'s theory is not suitable. In Wu and Morbidelli's theory, the conceptual fractal dimension of backbone is assumed to be 1.0-1.4 and a new parameter α is introduced indicating how close the aggregation is to each regime. Assuming that x is 1.0-1.4, α is 0.149-0.249, roughly 0.2 on the average. This result means that overall elasticity of the gel is due to interfloc link by 80% and intrafloc link by 20%.

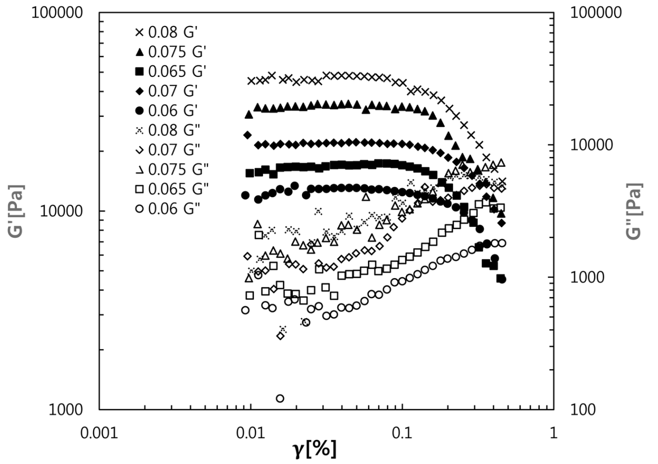

Fig. 2. Elastic modulus G' vs. shear strain γ at various ϕ. Angular frequency (ω) is 10 rad/s.

While G'_{lim} increases with ϕ, behavior of γ_{lim} with ϕ is relatively diverse. The γ_{lim} can increase or decrease with ϕ. The ϕ dependence

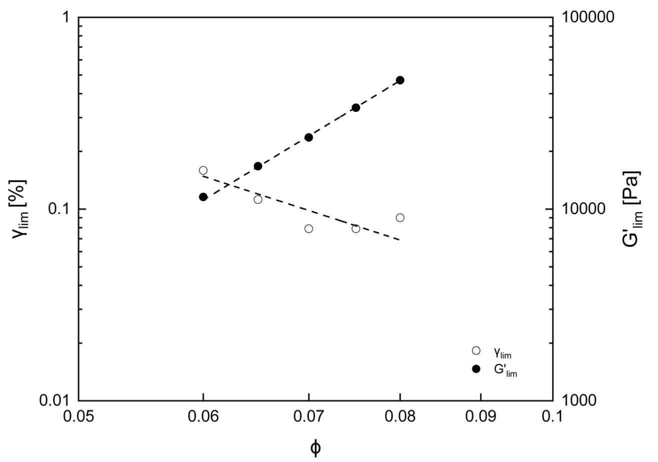

Fig. 3. Linear limits of elastic modulus G'_{lim} and strain γ_{lim} as a function of ϕ. The dotted lines are regression results. $G'_{lim} \propto \phi^{4.876}$ ($R^2 = 0.999$), $\gamma_{lim} \propto \phi^{-2.131}$ ($R^2 = 0.764$).

of γ_{lim} plays major role in determining aggregation type as well as fractal dimensions. More attention is paid to the behavior of γ_{lim}. In Fig. 3, it is observed that γ_{lim} seems slightly scattered. Scattered data pattern of γ_{lim} is easily found in the previous experimental results [17]. This scattering is inherently attributed to the sensitive behavior of γ_{lim}. Another reason for the scattering might be crossover behavior [2] from strong-link regime to weak-link regime since it can be seen that γ_{lim} decrease with ϕ at ϕ=0.06-0.07 and turn to be flattened at ϕ=0.07-0.08.

Next, we consider the shear yield stress behavior which reflects elasticity of colloidal gel. Fig. 4(a) and 4(b), respectively, show shear stress and shear viscosity vs. shear rate data for the zinc oxide suspension. It is observed that the suspension shows shear-thinning behavior and yield stress. To determine the yield stress, we employ Casson [18] and Herschel-Bulkley models [19].

$$\tau^{1/2} = \tau_y^{1/2} + (\eta_\infty \dot{\gamma})^{1/2}, \quad (4)$$

$$\tau = \tau_y + K'(\dot{\gamma})^n, \quad (5)$$

where τ is the shear stress at the shear rate $\dot{\gamma}$, τ_y is the yield stress. The symbols η_∞, K' and n are respectively the suspension viscosity at the limit of infinite shear rate, the consistency index, and the flow index. Fig. 5(a) and 5(b) show the regression results for Casson model and Hershel-Bulkley model, respectively. Correlation coefficients R^2 between the regression and the data are 0.904-0.985 for Casson model and 0.992-0.997 for Hershel-Bulkley model. Hershel-Bulkley model gives better fit than Casson model does. Over the range of the shear rates, the model fits the shear stress-shear rate data well. However, at $\dot{\gamma}$=1 s^{-1}, the model shows deviation from the measured data in log-log plot in Fig. 5(b). Variation of the shear stress near zero shear limit is too steep to get reasonable regression, as seen in the linear scale plot of Fig. 5(a). In particular, the regressed yield stress shows negative value at ϕ=0.08. Thus, the yield stress data for ϕ=0.06-0.075 are taken for scaling analysis. The yield stress data are plotted against ϕ in Fig. 6. The yield stress shows power-law behavior with ϕ. It is expressed by $\tau_y \propto \phi^{4.139}$.

This scaling relation is connected to aggregate size variation with shear force. It is well-known that the aggregate size inversely scales with shear stress [13,14]. When a suspension contains aggregates of equal size without free single particles of radii a, the radius of

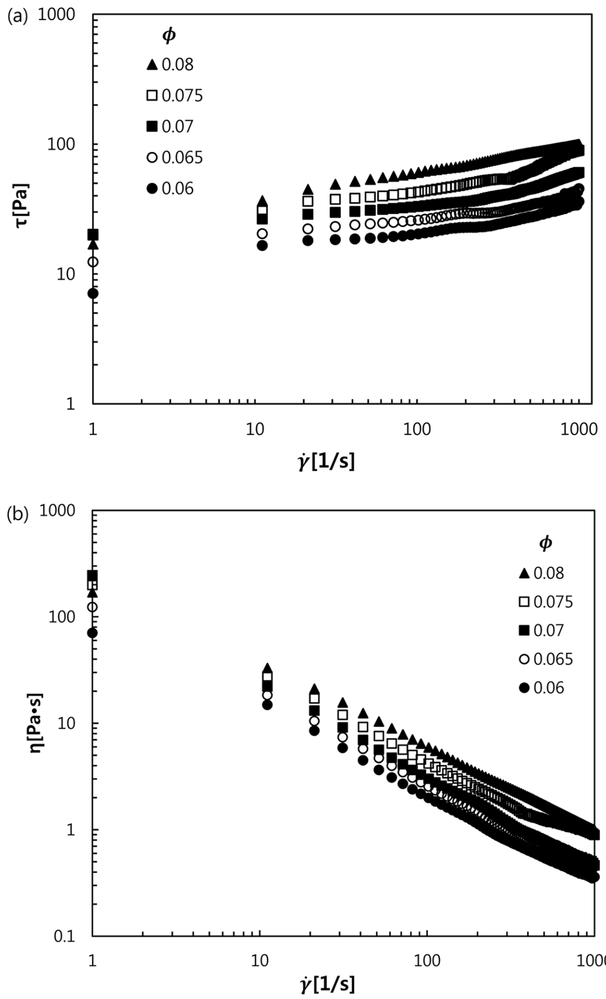

Fig. 4. (a) Shear stress τ-shear rate $\dot{\gamma}$ and (b) Shear viscosity η - shear rate $\dot{\gamma}$ data.

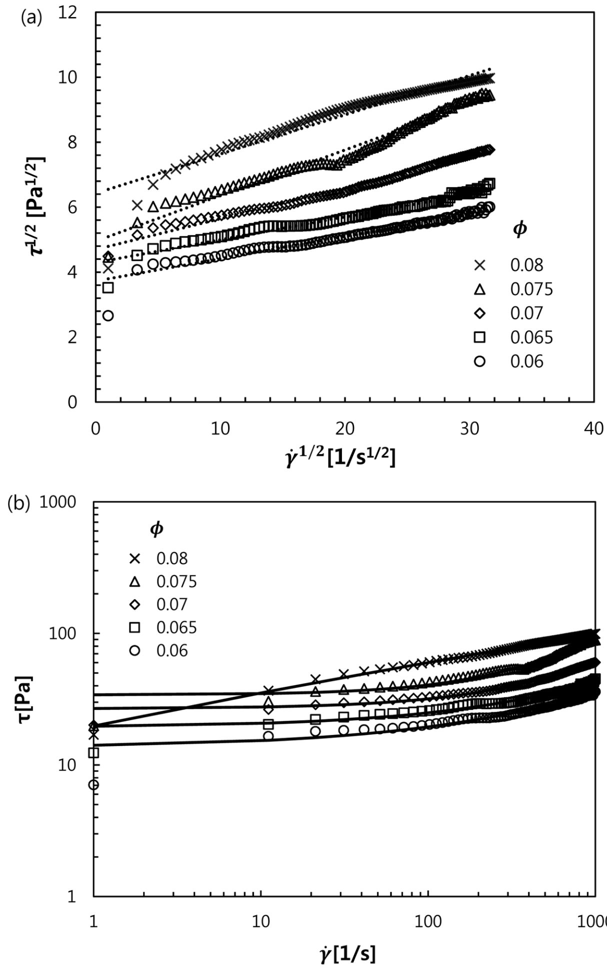

Fig. 5. (a) Regression by Casson model (b) Regression by Herschel–Bulkley model between shear stress τ and shear rate $\dot{\gamma}$. The dotted and sold lines indicate the regression results for each model.

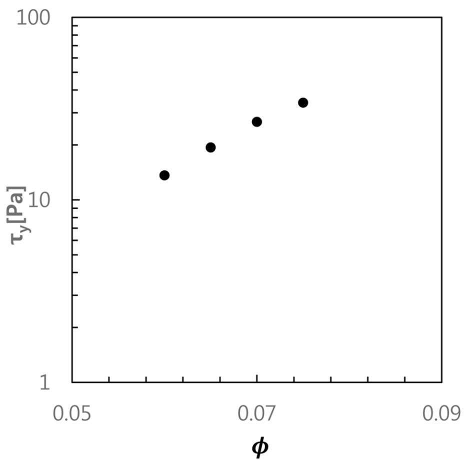

Fig. 6. Shear yield stress τ_y as a function of ϕ. The yield stress can be expressed by $\tau_y \approx 2.0 \times 10^6\phi^{4.139}$ (R^2=0.998).

gyration R_g for an aggregate under shear flow is given by

$$\frac{R_g}{\alpha} \propto (\eta_\infty\dot{\gamma})^{-m}, \tag{6}$$

where η_0 is the fluid viscosity and $\dot{\gamma}$ is the shear rate [1,14]. The exponent m exhibits shear dependence of aggregate size and it is connected to the yield stress behavior through a scaling theory. The scaling theory for the yield stress is based on mass-radius relation for an aggregate, which states that mass and number of primary particles of an aggregate scale as $(R_g/a)^{d_f}$ [11,20]. Since the yield stress can be considered as the state in which the entire suspension behaves like single aggregate, scaling relation behavior of the yield stress with particle concentration [1] is given by

$$\tau_y \propto \phi^{\frac{1}{m(d-d_f)}}. \tag{7}$$

When d_f is 2.271, the parameter m becomes 0.332. The parameter m has been reported in previous work [6,13,14]. Potanin's calculation [14] showed that m ranges about 0.24-0.50 depending on whether attraction force between particles includes non-central interaction or not. In other previous work, the value of m was around 0.35-0.37 [6,13]. The parameter m for aggregates of zinc oxide in the present study is close to those by the previous investigators.

To estimate average size of aggregate, we make use of shear dependence of aggregate size. Converting Eq. (6) for the aggregate size with a proportionality constant C,

$$\frac{R_g}{a} = C\left(\frac{\eta\dot{\gamma}}{\sigma_m}\right)^{-m}. \tag{8}$$

Note that the product of the fluid viscosity and the shear rate, i.e., $\eta\dot{\gamma}$ represents the shear stress acting on an aggregate which takes multiparticle effect due to presence of other aggregates into account [21]. This shear stress term is scaled by a material constant term σ_m resulting from the attractive dispersion force F_d between particles, i.e., $\sigma_m = F_d/(\pi a^2)$. Because information on the dispersion force is lack, we approximate the term with the extrapolated yield stress at maximum packing of particles [22].

Now we need to determine the constant C in Eq. (8). It is convenient to utilize a formula for predicting the viscosity of the suspension as a function of ϕ. Quemada's formula [23] is suitable for suspension viscosity with aggregation. Assuming the suspension contains equal-sized aggregates without free isolated particles, the formula can be written in terms of the volume fraction of aggregates ϕ_{ag}.

$$\frac{\eta}{\eta_0} = \left(1 - \frac{\phi_{ag}}{\phi_m}\right)^{-2}, \tag{9}$$

where ϕ_m is the maximum random packing fraction of particles, i.e., 0.63 [24]. The ϕ_{ag} can be written in terms of R_g/a. Using boundary conditions that ϕ_{ag} becomes 1 and d_f approaches to 3 at $\phi = \phi_m$, one can obtain a formula to predict the shear viscosity of aggregated suspension as a function of ϕ as well as $\dot{\gamma}$, i.e., $\eta = \eta(\phi, \dot{\gamma})$.

The constant C was chosen so that the predicted viscosity should fit the experimentally measured data. Fig. 7 shows the fitting results at ϕ of 0.06 and 0.08. It is seen that the predictions are in good agreement with the measured data when C is $(1/6)^m$.

With the constant C determined, one can estimate aggregate size using Eq. (8). Fig. 8 shows the variation of the ratio of estimated aggregate radius to the particle radius R_g/a with the shear rate in log-log scale. The size ratio decreases as the shear rate increases. The size ratio is 9.3-12.6 at 1 s^{-1}, 5.8-7.8 at 1000 s^{-1}. The estimated aggregate diameter, i.e., $2R_g$ ranges from 1023-1386 nm at 1 s^{-1} to 638-858 nm at 1000 s^{-1}. Since we assumed that aggregates are of equal size, it is appropriate to take the average of the aggregate size. Then the average aggregate diameter is 1135±154 nm at 1 s^{-1} and 739±93 nm at 1000 s^{-1}.

For comparison, we conducted optical measurement for the aggregate size using a dynamic light scattering (DLS) analyzer. The measurement was performed for ϕ=0.06 and 0.08. The suspension

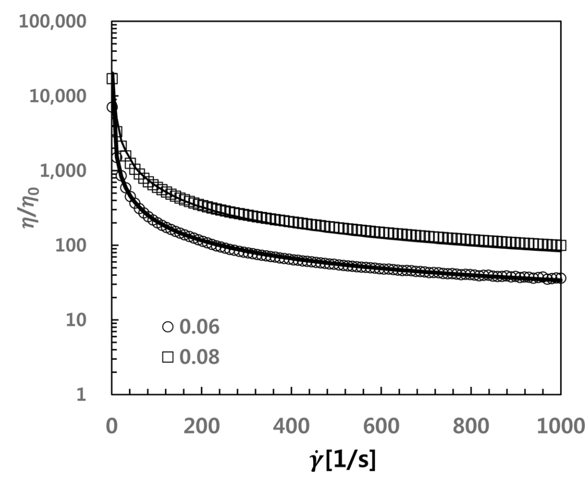

Fig. 7. Relative viscosity η/η_0 vs. shear rate $\dot{\gamma}$ at ϕ=0.06 and 0.08. The solid lines correspond to the predicted viscosity by Eq. (15) when C is $(1/6)^m$. The data marks are from the experimental measurement.

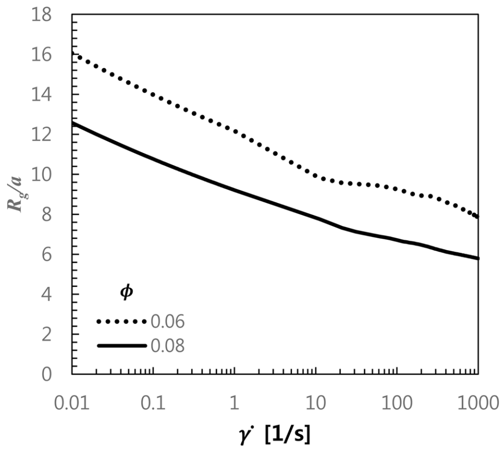

Fig. 8. Variation of R_g/a with shear rate $\dot{\gamma}$.

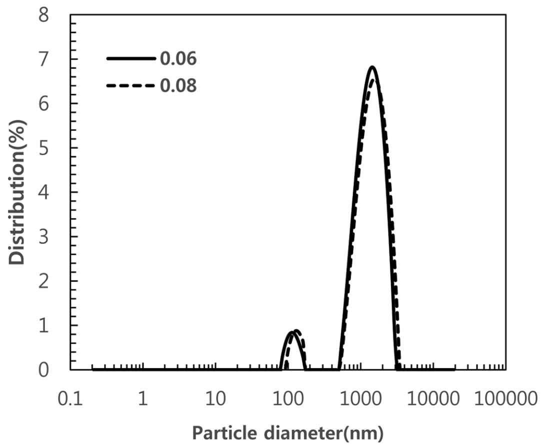

Fig. 9. Aggregate size distribution by dynamic light scattering (DLS) analyzer.

was diluted for DLS measurement. Fig. 9 presents the aggregate size distribution by the DLS analyzer. The aggregate size in this figure is hydrodynamic radius of the aggregate R_h. There are two peaks, i.e., a small peak around 80-200 nm and a large peak at 500-3000 nm. It is interpreted that the small peak is for isolated particles and small flocs and the large one is for the aggregates. From the large peak data, the average diameter $2R_h$ is 1319 nm for ϕ=0.06 and 1434 nm for ϕ=0.08. According to Chen *et al.* [25], R_h is equivalent to 0.97 times R_g for RLCA. Using this relation, the average diameter $2R_g$ is 1360 and 1479 nm, each. Since the DLS analyzer operates at un-sheared state, it is expected to be close to the rheological prediction of the aggregate size near zero shear rate. It is shown that the aggregate size by the DLS analysis agrees with the rheological estimate around 0.1 s^{-1} which ranges 1188-1540 nm. This range corresponds to 10.8-14.0 in the size ratio R_g/a. A similar agreement is found in a previous study [15]. The study has also shown that the rheological estimate at low shear rate for the aggregate of carbon black particles of 23 nm in average agrees with the measured result by small-angle X-ray scattering analysis. In overall it is seen that the optical measurement results agree with the rheological estimates of the aggregate size at low shear rates.

4. Conclusions

A scheme for rheological estimation of aggregate size was modified by using a scaling theory by Wu and Morbidelli in which overall elasticity of colloidal gel was constituted by contribution of both interfloc and intrafloc link in colloidal gel. This theory based on Shih *et al.*'s theory enables us to overcome the limit of Shih *et al.*'s theory and to determine fractal dimension of aggregates from the elastic modulus behavior. Shear yield stress which scales as ϕ was also utilized to determine the shear dependence of aggregate size.

Rheological measurement was performed for aqueous colloidal suspensions of submicron-sized zinc oxide particles, 110 nm. The range of ϕ was chosen to be from 6.0 to 8.0 % where the elastic behavior is observed. From the behavior of the elastic modulus, fractal dimension of aggregates d_f was estimated as 2.271. Power-law behavior of yield stress with the particle concentration renders us to determine shear dependence of aggregate size, which is expressed by the power-law exponent m in Eq. (6). The exponent m was determined as 0.332. With these two parameters scaling theories were utilized to predict average size of aggregates. We have found that the predicted aggregate size decreases with the shear rates, ranging from is 1135±154 nm at 1 s^{-1} and 739±93 nm at 1000 s^{-1} on the average. This prediction is compared with DLS data. The DLS data shows that aggregate size is 1360 nm for ϕ=0.06 and 1479 nm for ϕ=0.08. The aggregate size by DLS data reasonably agrees with the average rheological estimate near 0.1 s^{-1}, which is nearly static.

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Nomenclature

a	: radius of individual particles
C	: proportionality constant
d_f	: fractal dimension of the aggregate
F_d	: attractive dispersion force between particles
G'	: elastic modulus
G'_{lim}	: elastic modulus at linear limit of plateau zone
G''	: viscous modulus
K	: elasticity of overall colloidal gel
K_{inter}, K_{intra}	: elasticity of interfloc/intrafloc link in overall colloidal gel
K'	: consistency index of Hershel-Bulkley model
m	: power-law exponent for shear dependence of aggregate size
N	: number of particles in an aggregate
R_g	: radius of gyration for an aggregate
x	: fractal dimension of backbone chain in an aggregate

Greek letters

α : parameter indicating intermediate regime between strong-link(0) and weak-link(1) regime
$\dot{\gamma}$: shear rate
γ : shear strain
γ_{lim} : shear strain at the linear limit of plateau zone
η : shear viscosity of colloidal suspension
η_0 : shear viscosity of suspending fluid
η_∞ : infinite shear viscosity of colloidal suspension
σ_m : material constant related with attractive dispersion force between particles
τ : shear stress
τ_y : shear yield stress
ϕ : volume fraction of suspended particles in the colloidal suspension
ϕ_{ag} : volume fraction of aggregates
ϕ_m : volume fraction of the particles at the maximum random packing (=0.63)

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