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Rheological analysis of particle aggregation in a colloidal suspension of carbon black particles

Noori Kim and Sangkyun Koo*
Department of Chemical Engineering and Materials Science, Sangmyung University, Seoul 03016, Republic of Korea
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We examine scaling theories to estimate microstructural parameters of fractal aggregates in a colloidal suspension. The scaling theories are based on fractal theories and rheological properties of the colloidal suspension. Rheological measurement in oscillatory and steady shear modes is performed for colloidal suspensions of 56 nm carbon black particles in Newtonian ethylene glycol at the particle volume fractions ϕ ranging from 0.005 to 0.05. Elastic modulus G' of the colloidal suspension at $\phi = 0.02$-0.05 in the state of colloidal gel is used to estimate fractal dimension d_f of the aggregates. Steady-shear measurement gives yield stress τ_y as a function of ϕ. Shear dependence of the aggregate radius R is given by a power-law scaling, *i.e.*, $R \propto S^{-m}$, where S is the shear rate. The power-law exponent m is estimated from d_f and a scaling relation between τ_y and ϕ. The estimation gives $d_f = 2.14$ and $m = 0.33$. The parameters d_f and m which can be determined by either direct measurement or theoretical calculation are used to establish a microrheological model for predicting shear viscosity of aggregated suspension as a function of ϕ and S. Both the concentration dependence and the shear dependence of aggregates are combined to obtain an expression for the shear viscosity. Hydrodynamic interaction effect among the aggregates is roughly considered in calculating average shear stress on the aggregate. It is found that this consideration critically contributes to behavior similarity with experimental result. It is shown that the predictions by the model reasonably agree with the experimental result.

Keywords: colloidal aggregate, fractal dimension, elastic modulus, yield stress, intrinsic viscosity, effective-medium approximation

1. Introduction

Understanding of theoretical relation between aggregate structure and physical properties of colloidal suspensions has long been a central issue in colloidal science due to its significance in academic as well as industrial applications. Since introduction of fractal concept due to self-similarity of the aggregate structure, theoretical studies on colloidal aggregation have become more popular. According to the fractal concept, the mass of an aggregate scales as the number of particles in the aggregate and further it scales with the aggregate size in a power-law form. The power-law exponent is defined as the fractal dimension d_f which is also related with aggregation rate and shape of aggregate as well as dimensionality of the aggregate.

The structural parameters of aggregate can be described by scaling laws including the rheological properties due to interactive relation between macroscopic properties and microscopic structure of a colloidal suspension. Numerous studies have been carried out to find the relations between particle aggregation and rheological properties of the colloidal suspension. The studies have been recently summarized by Mewis and Wagner (2012). The particle aggregation is often treated divided into two cases of the particle concentration. One is low particle concentrations at which the interactions among the aggregates are negligible. Intrinsic viscosity due to aggregates is a useful measure to roughly estimate hydrodynamic size of aggregates (Smith and Bruce, 1979). Its scaling with the shear rate gives estimates for a combined structural parameters of fractal dimension and shear dependency of aggregate size (Lee and Koo, 2014).

The other is the state of the colloidal gel at which the aggregates become inter-connected to form a network as the particle concentration increases. In this case, studies on the scaling relations between structural parameters of fractal aggregates and solid-like properties such as elastic modulus and yield stress are noteworthy. Shih *et al.* (1990) have proposed a useful theory to predict the structural parameters of the fractal aggregates using the elastic properties. They distinguished between two regimes for colloidal gels depending on relative magnitude of inter-aggregate (floc) link to intra-aggregate (floc) link. When the inter-aggregate link is stronger, it is called strong-link regime and elastic property of colloidal suspension is governed by intra-aggregate link. In the weak-link regime, intra-aggregate link is stronger and inter-aggregate link determines the elastic property. The elastic property is represented by the elastic modulus at the plateau region and the strain at the upper linear limit of the plateau. Concentration dependence of the plateau elastic modulus and the

*Corresponding author; E-mail: skkoo@smu.ac.kr

linear limit of strain provides a useful scaling relation for fractal dimensions of aggregate and backbone chain of particles in the aggregate.

Yield stress also represents solid-like behavior of gelled colloidal suspension, which is related with interparticle attraction. There have been some investigations on the scaling relations between the yield stress as a function of the particle concentration and the aggregate parameters including a combined parameter of fractal dimension and a power-law exponent representing shear dependence of aggregate size (Buscall *et al.*, 1988; Snabre and Mills, 1996). The power-law exponent m is given by $R \propto S^{-m}$ where R is the radius of gyration for an aggregate and S is the shear rate. It is known that the plateau elastic modulus and the yield stress scale as the particle volume fraction in a power-law form (van der Aerschot and Mewis, 1992; Piau *et al.*, 1999; Potanin, 1992). In this study we measured steady-shear yield stress as well as the elastic modulus. Scaling behavior of the yield stress is compared with that for the plateau elastic modulus.

Since the colloidal suspensions in industrial processes are handled under shear action, the parameter m is significant in predicting variation of aggregate size in the processes. The parameter m can be determined from experimental measurement using optical technique or numerical simulation. Sonntag and Russel (1986) obtained the parameter m using optical measurement for the suspension of aggregated polystyrene particles in glycerol and water under shear. The parameter m was found to be 0.35 for $d_f = 2.1$. Potanin (1993) numerically calculated m for two types of aggregates which are so-called irreversible, rigid aggregate and reversible, soft aggregate, respectively. The value for m was 0.23-0.29 for the rigid aggregate and 0.4-0.5 for the soft aggregate. These values were found to be quite close to 1/3 and 1/2 each predicted by scaling theory. Recent studies on the variation of aggregate structure in shear flow have employed numerical simulation to include calculation of hydrodynamic interaction in multiparticle systems. Eggersdorfer *et al.* (2010) calculated m for colloidal suspension with soft aggregation using a discrete element method. Their value for m was 0.35-0.37. Stokesian dynamics simulations based on calculation of hydrodynamic interaction among particles together with colloidal interaction have been performed to calculate drag force and its distribution on aggregate in shear flow (Seto *et al.*, 2011) or to analyze variation of fractal dimension under shear during aggregation process (Conchuir *et al.*, 2014). Variation of aggregate size and structure in shear flow has drawn attention of many investigators to date. In the present study we examine scaling theories to determine the shear dependence of the aggregate size, *i.e.*, power-law exponent m.

The parameters such as m and d_f are useful not only in quantitative characterization of aggregate but also in rheological modeling of the aggregated suspensions. Once these two parameters are determined by either experimental measurement or theoretical calculation, it allows us to predict shear viscosity of aggregated colloidal suspension as a function of the particle volume fraction and the imposed shear rate. The prediction of the shear viscosity is based on an expression for concentration dependence of suspension viscosity such as Quemada's equation (Quemada, 1977). In aggregated colloidal systems, the particle volume fraction is replaced by the volume fraction of the aggregates in the suspension which can be incorporated with shear dependence of aggregate size. This incorporation is led to an expression for shear viscosity of aggregated colloidal suspensions as a function of the particle volume fraction and the shear rate.

In this study we first consider scaling theories to estimate the structure parameters of d_f and m. The scaling theories relate the structure parameters and the rheological properties of colloidal suspension. Experimental measurement of the rheological properties is carried out for a colloidal suspension comprising of carbon black particles and ethylene glycol. The carbon black is of 56 nm in average diameter. The volume fraction of the particles ranges from 0.005 to 0.05 which covers two concentration zones, *i.e.*, below and above colloidal gelation point. In the state of colloidal gel, plateau elastic modulus and linear limit of strain of the colloidal suspension are measured in oscillatory shear mode. These properties are used to obtain the fractal dimensions of aggregate and backbone chain in the aggregate. From steady-shear measurement, we obtain shear yield stress by extrapolating shear stress-shear rate data. The shear yield stress is utilized to estimate the parameter $m(3-d_f)$. The scaling behavior of the yield stress is compared with that of the plateau elastic modulus. At low particle concentrations below gelation point, we obtain intrinsic viscosity from viscosity-concentration data. Scaling behavior of the intrinsic viscosity with the shear rate gives the parameter $m(3-d_f)$ which is equivalent to that from the yield stress. Comparison is made between two scaling behaviors.

Secondly it is shown that the structural parameters are used to establish a microrheological model for estimating shear viscosity of aggregated suspensions. Aggregate concentration dependence is incorporated with shear dependence of the aggregate to obtain an expression for the suspension viscosity as a function of ϕ and S. For the shear dependence, a self-consistent effective-medium approximation (Patel and Russel, 1988; Potanin, 1992) is employed to calculate average hydrodynamic stress in which hydrodynamic interaction among the aggregates is included. The theoretical predictions of shear viscosity by the model are compared with the experimental results.

2. Experimental Procedure

2.1. Sample preparation

The colloidal suspension in our experiment consists of carbon black particles and ethylene glycol. The carbon black particles manufactured by Saehan Silichem Company in Korea (Grade: Conductex 7054 ultra) are of 56 nm in average diameter. Their specific surface area and density are 42 m^2/g and 1.88 g/cm^3, respectively. Ethylene glycol (Junsei Chemical Co.) with density of 1.10 g/cm^3 is used as suspending medium. It is a Newtonian fluid with viscosity of 15.8 cP at 25°C. The concentration of carbon black ranges from 0.5 to 5.0% in volume.

The colloidal suspension is prepared by mechanical dispersion treatment. We first start with wetting the particles with the suspending fluid. The carbon black particles are wetted by 10-20 mL of the ethylene glycol with spatula for about 5 min. Then the remaining ethylene glycol is mixed with the wetted particles. The mixture is treated by a mechanical homogenizer (Model HG-150, WiseTIS Corporation). This homogenizing treatment is performed for 5 minutes at 3000 RPM. Then a slurry state of the mixture is obtained. The next step is to use a ball mill for dispersion. The mixture is put into a cylindrical polyethylene bottle with 60 mm of diameter and 130 mm of height filled with steel beads of 3 mm diameter. The volumetric amount of the mixture is equally adjusted to that of the steel beads. The bottle is horizontally placed to rotate along with main shaft of ball mill (Model Wisemix BML, Daihan Company). The shaft of the ball mill is set to rotate at the speed of 70 RPM for 5 hours. After the milling we obtain a colloidal suspension of the carbon black particles.

2.2. Measurement

For rheological measurement we use a plate-plate type rheometer MCR 102 made by Anton Paar Company in Austria. The measuring plate is 50 mm in diameter and gap between plates is set to 1 mm. Both oscillatory and steady shear mode measurement are performed at 25°C (± 0.1°C). In oscillatory mode, elastic and viscous moduli are first measured in the strain range of 0.01-10% at angular frequencies of 0.5, 1.0, 5.0, and 10 rad/s. Then the moduli are measured through sweep test which is performed in the range of 0.01-10% at angular frequency of 1 rad/sec. In steady shear mode, shear rate ranges 1-50 s^{-1}. The colloidal suspension is pre-sheared at 10 s^{-1} for 1 min. Then the shear viscosity is measured at the shear rates ranging from 1 s^{-1} to 50 s^{-1}. The range of the shear rate was chosen to focus on behavior at low shear rates where breakup of aggregates is not likely to take place much.

3. Results and Discussion

3.1. Structural parameters of aggregates

Colloidal aggregates are well described by fractal concept. When N colloidal particles with radii a form an aggregate with a radius of gyration R and mass M. Then the aggregate follows mass-radius relation (Jullien and Botet, 1987; Meakin, 1987)

$$N \propto M \propto \left(\frac{R}{a}\right)^{d_f} \tag{1}$$

where d_f is the fractal dimension of the aggregate.

The aggregate is affected by imposed hydrodynamic stress in shear flow. Then the aggregate size can be expressed by a scaling relation as (Buscall *et al*., 1988; Potanin, 1993)

$$\frac{R}{a} \propto S^{-m}, \tag{2}$$

where S is the shear rate. The exponent m indicates shear dependence of aggregate size. The parameters such as d_f and m can be estimated from scaling theories related with rheological properties of the colloidal suspension.

The most commonly used property is the elastic modulus at the state of colloidal gel. The aggregates become inter-connected near the colloidal gelation point where the elastic property of the suspension starts to build up. According to Shih *et al.* (1990), the inter-connected struc-

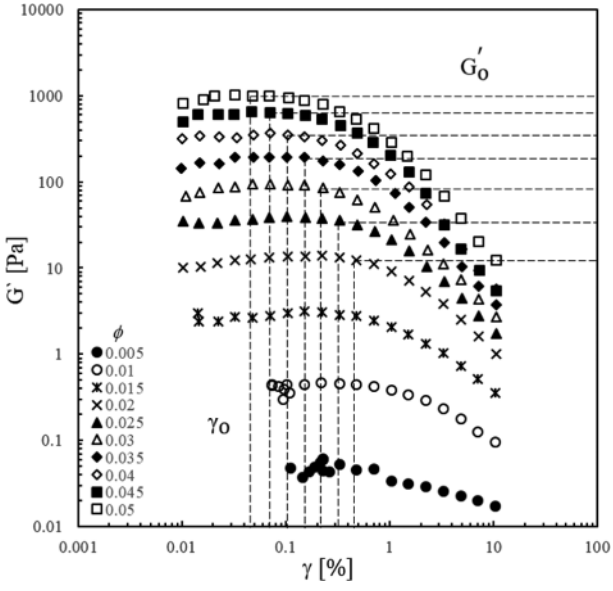

Fig. 1. Elastic modulus G' vs shear strain g at various particle volume fractions ϕ. Dotted lines indicate G_0' and γ_0 at ϕ = 0.02-0.05, determined by behavior of digression from average among serial 4 data points including 3 points at lower adjacent strains and one at the corresponding strain. The limit of G' plateau was taken as the point followed by rapid and continuous increase of digression gap with the strain.

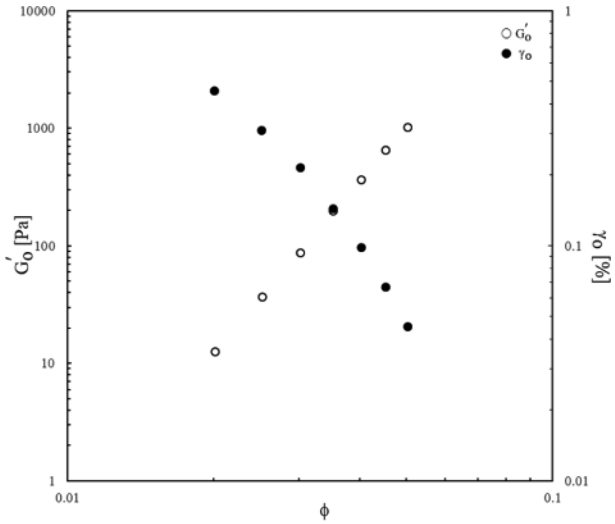

Fig. 2. Plateau elastic modulus G_0' and linear limit of strain γ_0 as a function of particle volume fraction ϕ at ϕ = 0.02-0.05.

ture of the aggregates can be divided into so-called strong-link regime and weak-link regime depending on relative magnitude of inter-aggregate link and intra-aggregate link. In the strong-link regime, the inter-aggregate link is stronger than that of the intra-aggregate link and the elastic property of colloidal suspension is governed by intra-aggregate link. In the weak-link regime, the intra-aggregate link is stronger and the inter-aggregate link determines the elastic property. It has been suggested that a criterion to distinguish two regimes is the behavior of elastic modulus and linear limit of strain with ϕ. In the strong-link regime, as ϕ increases the elastic modulus increases but the linear limit of strain decreases. Meanwhile both the elastic modulus and the linear limit of strain increases with ϕ in the weak-link regime. Their theory is applied to a colloidal suspension of carbon black. Fig. 1 shows the behavior of elastic modulus G' as a function of strain γ at various ϕ. The strain frequency is 1 rad/sec. It is observed that G' plateau becomes stable at $\phi \geq 0.02$. The value of G' plateau is taken as G_0' which corresponds to the elastic modulus in colloidally gelled state. The linear limit of strain γ_0 is chosen as the maximum strain where the G' plateau maintains in Fig. 1. Dotted lines indicate G_0' and γ_0 at ϕ = 0.02-0.05. Logarithmic plot of G_0' and γ_0 with ϕ in Fig. 2 clearly exhibits that this carbon black suspension falls on strong-link regime. In this regime, scaling relations are given by (Shih *et al.*, 1990)

$$G_0' \propto \phi^{\frac{3+x}{3-d_f}}, \tag{3}$$

$$\gamma_0 \propto \phi^{-\frac{1+x}{3-d_f}} \tag{4}$$

where x is the fractal dimension of backbone chain or chemical length exponent. These scaling relations are graphically presented with the experimental data in Fig. 2. Fitting the measured data to Eqs. (3) and (4), we obtain d_f = 2.14 and x = 1.16. The value for d_f indicates that the aggregation type falls on reaction-limited cluster aggregation (RLCA). The slope in the plot of log G_0'-log ϕ is 4.84, that is, $G_0' \propto \phi^{4.84}$. This value is close to the values 4.3-4.7 for a system of RLCA (Buscall *et al.*, 1988) and 4.2-4.6 for a silica-methyl laurate system (van der Aerschot and Mewis, 1992). Regarding x, it is known that the parameter x is 1.1-1.6 (Mewis and Wagner, 2012). We see that our value is within this range.

Yield stress is also considered as indication of solid-like behavior, which is directly related with interparticle attractive force. The yield stress is meant to be obtained from steady shear measurement. When the yield stress is measured under compressive flow, it is termed as compressive yield stress which is known to be larger than shear yield stress. The shear yield stress is also defined in several ways. We take the shear yield stress τ_y extrapolated with Casson's equation (Casson, 1959)

$$\tau^{1/2} = \tau_y^{1/2} + (\eta_\infty S)^{1/2}, \tag{5}$$

where τ is the shear stress at the shear rate S and η_∞ is the suspension viscosity at infinite shear rate. The power-law scaling between τ_y and ϕ is conceptually expected to be equivalent to that between G_0' and ϕ. Some previous studies, however, have reported on discrepancy between behaviors of τ_y and G_0' with ϕ. For example, rheological measurement by Piau *et al.* (1999) has shown that $G_0' \propto \phi^{4.2}$ and $\tau_y \propto \phi^{3.3}$ for the silica-polydimethyl siloxane system when d_f of the aggregate is 1.8. It has been reported that scaling behavior of G_0' with ϕ is analogous to that of compressive yield stress rather than shear yield stress (Buscall *et al.*, 1988) and behavior of compressive yield stress with f is different from that of shear yield stress (Buscall *et al.*, 1987). Hence it seems not proper to identify the ϕ dependence of G_0' and that of τ_y. Then we need a scaling theory for the shear yield stress.

Let us suppose that all the particles in the suspension exist in aggregates with radii R. Each aggregate consists of N particles and suspending fluid inside the aggregate. The volume fraction of aggregates in the suspension ϕ_{ag} is given in a scaling relation

$$\frac{\phi_{ag}}{\phi} = \frac{\frac{4\pi R^3 N_{ag}}{3V}}{\frac{4\pi a^3 N_p}{3V}} = \left(\frac{R}{a}\right)^3 \frac{1}{N} \propto \left(\frac{R}{a}\right)^{3-d_f}. \tag{6}$$

Here, N_{ag} and N_p are the number of aggregates and particles, respectively, in the suspension with volume V. Note that $N_p/N_{ag} = N$ and Eq. (1) is used to obtain Eq. (6). The equation signifies that the aggregate is treated not as a

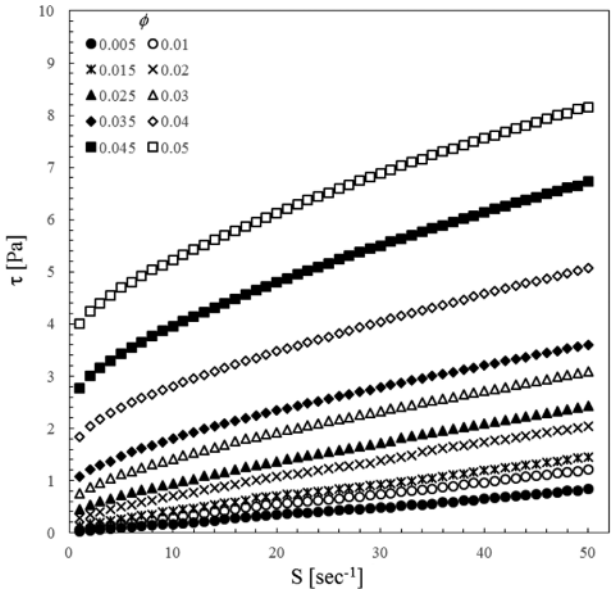

Fig. 3. Shear stress τ-shear rate S data at various particle volume fractions ϕ.

rigid sphere but as a porous sphere with fractal dimensionality. At the yield stress point, the whole suspension can be considered as an aggregate. The scaling relation in Eq. (2) holds even when S is replaced by $\eta_0 S$, where η_0 is the viscosity of suspending fluid. Then, $\eta_0 S$ is taken as τ_y and ϕ_{ag} becomes unity at the yield stress point. From Eqs. (2) and (6) it is straightforward to deduce a scaling relation for the yield stress. It is given by (Snabre and Mills, 1996)

$$\tau_y \propto \phi^{\frac{1}{m(3-d_f)}}. \quad (7)$$

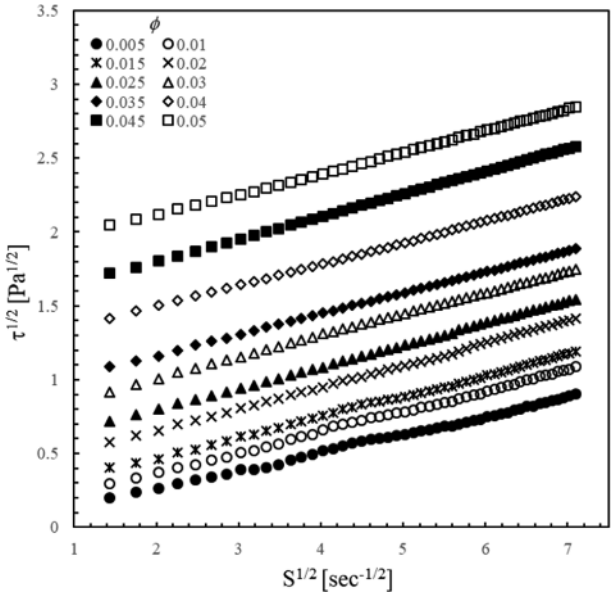

Fig. 4. Casson's plot of shear stress and shear rate.

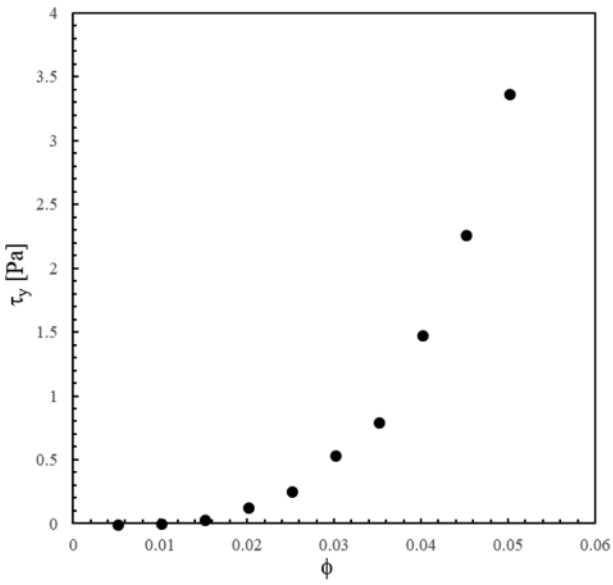

Fig. 5. Yield stress τ_y vs. particle volume fraction ϕ at various ϕ.

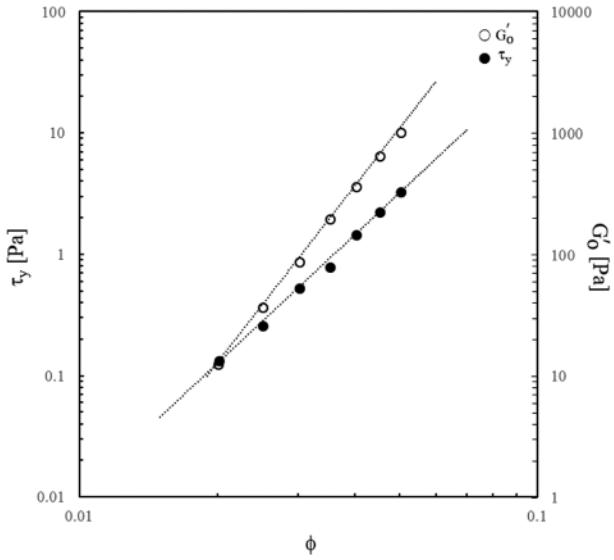

Fig. 6. Particle concentration dependence of yield stress τ_y and plateau elastic modulus G_0' at ϕ = 0.02-0.05.

The yield stress is obtained by extrapolating the shear stress-shear rate data at $\phi = 0.005$-0.05 with Casson's equation as shown in Figs. 3 and 4. The yield stress at each ϕ is presented in Fig. 5. The yield stress begins to increase steeply at $\phi = 0.02$. This behavior is consistent with that of plateau elastic modulus. Hence it is proper to take $\phi \geq 0.02$ for yield stress data. The yield stress and the plateau elastic modulus are logarithmically plotted with ϕ in Fig. 6 to give the pawer-law exponent for each. The exponent from the yield stress is 3.53 while that from the plateau elastic modulus is 4.84. From this exponent 3.53 and the fractal dimension by the plateau elastic modulus, the parameter m is estimated as 0.33. This is close to the

range 0.35-0.37 from previous studies (Sonntag and Russel, 1986; Potanin, 1993; Eggersdorfer *et al*., 2010).

On the other hand, the parameter $m(3\text{-}d_f)$ can obtained from intrinsic viscosity due to aggregates at ϕ below gelation point. When interaction between aggregates is negligible, the intrinsic viscosity $[\eta]$ for an aggregated suspension is given by

$$[\eta] = \frac{2.5}{\phi_{in}} \tag{8}$$

where ϕ_{in} is the particle volume fraction in an aggregate and it is written as

$$\phi_{in} = \frac{\phi}{\phi_{ag}}. \tag{9}$$

The intrinsic viscosity is obtained from the viscosity data at various ϕ and it is written as a function of shear rate. Combining Eqs. (2), (6), and (8), we obtain a power-law relation for the intrinsic viscosity as below

$$[\eta] \propto S^{-m(3-d_f)}. \tag{10}$$

Here, we find that the exponent includes $m(3\text{-}d_f)$ term as in Eq. (7). To estimate the intrinsic viscosity, Krieger-Dougherty's equation (Krieger and Dougherty, 1959) as below is utilized

$$\frac{\eta}{\eta_0} = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m} \tag{11}$$

where η is the suspension viscosity and ϕ_m is the maximum random packing density of particles, 0.63 for randomly packed hard spheres. Figure 7 shows the relative viscosity η/η_0 plotted as a function of ϕ at each shear rate. The slope of each fitting line is the intrinsic viscosity at the corresponding shear rate. It is seen that the slope of each fitting line deflects around ϕ of 0.02. It appears that a structural change occurs near ϕ = 0.02 in the colloidal suspension. Similarly, the yield stress also starts to build up near ϕ = 0.02. It is confirmed that gelation among the aggregates take place near ϕ = 0.02. Because of the assumption for Eq. (8) that interaction among aggregates is negligible, we take the data for ϕ = 0.005-0.015 for the intrinsic viscosity. The slope in this ϕ range gives the intrinsic viscosity as a function of shear rate, as shown in Fig. 8. Logarithmic plot between the intrinsic viscosity and the shear rate gives the value for the exponent in Eq. (10). Therefore, the value for $m(3\text{-}d_f)$ is 0.27 which is very close to 0.28 from the yield stress data. It has been shown that the structure parameter from the shear yield stress above the gelation point is in excellent agreement with that from the intrinsic viscosity below the gelation point. This agreement has been observed in previous studies for colloidal suspensions of inorganic nanoparticles (Kim and Koo, 2018; Lee and Koo, 2014; 2016). It means that the parameters d_f and m maintain constant across the gelation point.

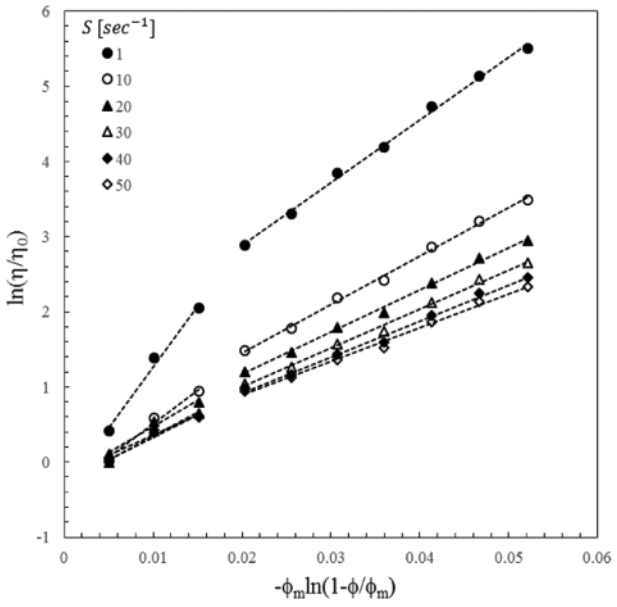

Fig. 7. Plot of $\ln(\eta/\eta_0)$ vs. $-\phi_m \ln(1-\phi/\phi_m)$.

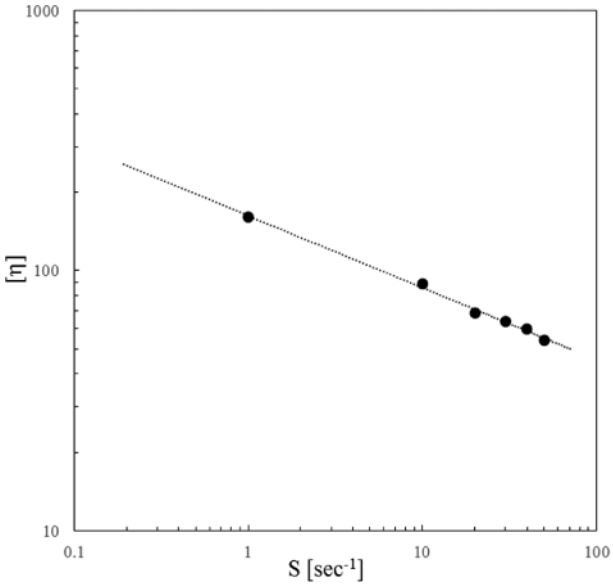

Fig. 8. Fitting plot of intrinsic viscosity $[\eta]$ vs. shear rate S at ϕ = 0.005-0.015.

3.2. Prediction of shear viscosity of aggregated suspension

The parameters d_f and m are significant in predicting shear viscosity of aggregated suspension as a function of ϕ and S. Concentration dependence of the shear viscosity is incorporated with shear dependence of the aggregates. The concentration dependence of suspension viscosity is well described with well-known equations by Quemada (1977) or Krieger and Dougherty (1959). In these equations, the suspension viscosity is expressed as a function

of particle concentration. Since the suspension is modeled as comprising of equal-sized aggregates and suspending fluid, the concentration of particles is replaced by that of aggregates. For example, Quemada's equation is modified to

$$\frac{\eta}{\eta_0} = \left(1 - \frac{\phi_{ag}}{\phi_m}\right)^{-2}. \tag{12}$$

The ϕ_{ag} is related to ϕ and R as in Eq. (6) and the radii of aggregates R can be written in terms of shear stress as in Eq. (2). However, Eqs. (2) and (6) should be given in a closed form. Considering a limit case that ϕ becomes ϕ_m and ϕ_{ag} equals unity as d_f approaches to three, ϕ_{ag} in Eq. (6) can be re-written as

$$\phi_{ag} = \frac{\phi}{\phi_m}\left(\frac{R}{a}\right)^{3-d_f}. \tag{13}$$

Now we consider shear dependence of aggregate. We follow a procedure by Kim and Koo (2018). It is assumed that fractal dimension and spherical shape of aggregates keep constant. The size reduction of the aggregate is dependent on relative magnitude of shear force due to imposed flow to interparticle attractive force. The relative magnitude between two forces is utilized in defining a non-dimensional shear rate S given by Eq. (14) instead of the shear rate S in Eq. (2)

$$\Sigma = \frac{\eta_0 S}{\sigma_m}. \tag{14}$$

Here, σ_m is the material constant directly related with attractive dispersion force F_d between particles, which is given by

$$\sigma_m = \frac{F_d}{\pi a^2}, \; F_d = \frac{Aa}{12h^2}. \tag{15}$$

where A is the Hamaker constant and h is the gap distance between particles. The Hamaker constant A equals $(A_1^{1/2} - A_2^{1/2})^2$ where A_1 and A_2 are the Hamaker constant for the particles and the suspending fluid, respectively. Due to lack of information on A_2 and h in the literature, it is not possible to accurately calculate σ_m. Practically we made use of yield stress data at ϕ_m with proper adjustment for comparison with the experimental results.

The shear rate S in Eq. (2) can be replaced by the non-dimensional shear rate S. Here we employ a simplified effective-medium model (Kim and Koo, 2018; Patel and Russel, 1988; Potanin, 1992) to consider the hydrodynamic stress term in the numerator of Eq. (14). Instead of η_0, we use η to take hydrodynamic interaction effect by surrounding particles (aggregates) into account. In the effective-medium approximation, the suspension is portrayed as consisting of a test aggregate at origin and the surrounding effective-medium with the suspension viscosity η. Hydrodynamic properties at the test aggregate should be consistent with those of the effective medium which reflects hydrodynamic interaction due to presence of many aggregates except the test aggregate. Using the effective-medium approximation, Eq. (2) can be re-written in a closed form as

$$\frac{R}{a} = C\left(\frac{\eta}{\eta_0}\Sigma\right)^{-m}, \tag{16}$$

where C is the numerical constant. The value for C is 2.5^{-m} for rigid aggregates to which imposed stress is fully transmitted. The number powered by $-m$ in C for the soft aggregates is smaller than 2.5, which partially transmit imposed stress.

Substituting Eqs. (13) and (16) into Eq. (12), we finally obtain a formula for the viscosity of aggregate suspension as a function of ϕ and S as below

$$H^2 + 2\kappa H^{m(3-d_f)} - 1 = 0, \; H = \frac{\eta_0}{\eta} \tag{17}$$

where the parameter κ is given by

$$\kappa = \frac{\phi}{2\phi_m^2}\left(\frac{C^*}{\Sigma}\right)^{m(3-d_f)}. \tag{18}$$

Here, we find that the parameter κ contains two independent variables, ϕ and S, for the suspension viscosity. The proportionality constant C^* which equals $C^{1/m}$ is 0.4 for the rigid aggregates. It is expected to be larger than 0.4 for the soft aggregates. In this analysis C^* is properly chosen in this range for comparison with experiment.

This model is compared with two other cases. One is the case that does not consider hydrodynamic interaction effect in shear dependence of the aggregate size, that is, the case without the effective-medium approximation. In this case, Eq. (16) is simplified to

$$\frac{R}{a} = C\Sigma^{-m}. \tag{19}$$

Then Eq. (17) accordingly reduces to

$$H - (1 - 2\kappa)^2 = 0. \tag{20}$$

In Eq. (20) we find that there exists a singularity at $\kappa = 0.5$ where the suspension viscosity becomes infinite. Due to the singularity, it is expected that calculation of the suspension viscosity would be limited to a certain range of ϕ.

The other case is to choose Batchelor's equation (Batchelor and Green, 1972) given below instead of Eq. (12)

$$\frac{\eta_0}{\eta} = 1 + 2.5\phi_{ag} + 6.2\phi_{ag}^2. \tag{21}$$

Likewise, substituting Eqs. (13) and (16) into Eq. (21), we obtain

$$24\phi_m^2\kappa^2 H^2 + 5\phi_m \kappa H^{m(3-d_f)} + 1 - H^{-1} = 0. \tag{22}$$

The shear viscosity predicted by each case, *i.e.*, Eqs. (17), (20), and (22), is compared with the experimental

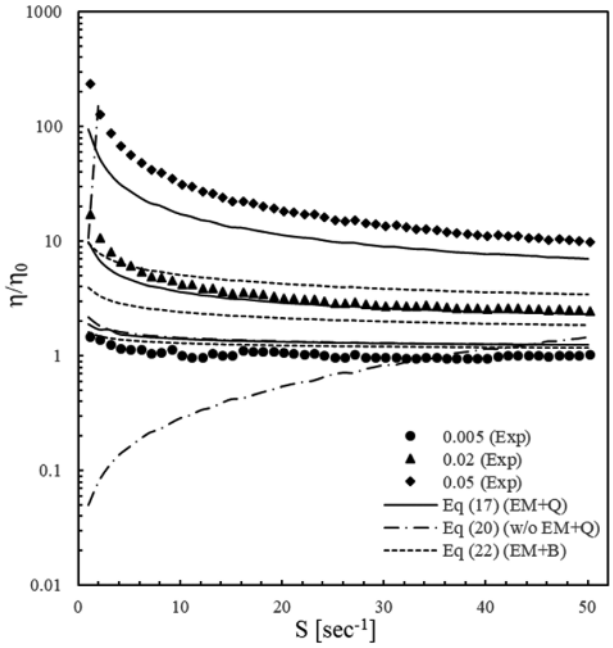

Fig. 9. Relative viscosity η/η_0 vs. shear rate S at $\phi = 0.005$, 0.02, and 0.05. Lower lines for each case correspond to lower ϕ. The letter 'EM' means effective medium and 'Q' and 'B' stand for Quemada's equation and Batchelor's equation, respectively.

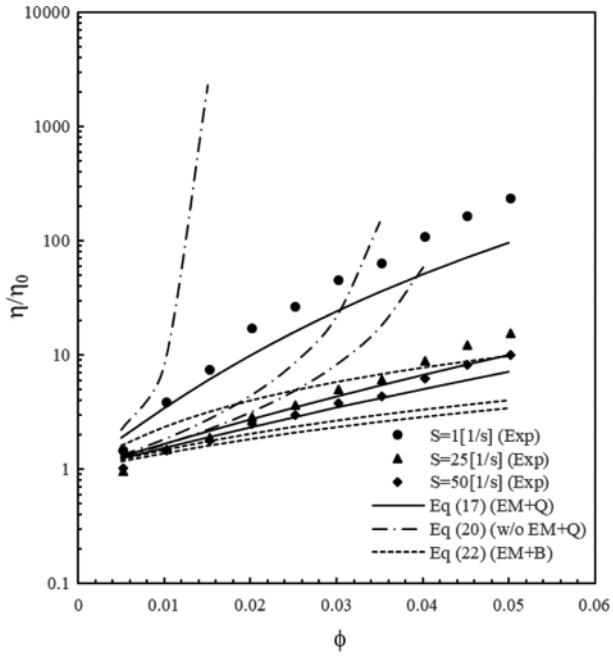

Fig. 10. Relative viscosity η/η_0 vs. particle volume fraction ϕ at S = 1, 25, and 50 s^{-1}. Lower lines for each case correspond to higher S. The letter 'EM' means effective medium and 'Q' and 'B' stand for Quemada's equation and Batchelor's equation, respectively.

data. The comparison is given in Figs. 9 and 10 which show the shear dependence of the relative viscosity at ϕ = 0.005, 0.02, 0.05 and the concentration dependence at S = 10-50 s^{-1}, respectively. In the figures, we find that the inclusion of effective-medium approximation critically contributes to the shear viscosity. In the case without the effective-medium approximation denoted by dashed lines in the figures, *i.e.*, Eq. (20), there is a singularity at $\kappa = 0.5$ where the viscosity becomes infinite. When the constant C is 2.5 or less, κ approaches 0.5 or larger than 0.5 and then the viscosity surges unrealistically high. This nature of Eq. (20) gives unrealistic result. This behavior is shown in Figs. 9 and 10. Another comparison is made between formulas for the concentration dependence of the viscosity. Batchelor's equation (Eq. (21)) is tried for the comparison, which is well used for dilute and semi-dilute suspensions up to about $\phi = 0.1$ for hard-sphere suspensions. The dotted lines in the figures correspond to the case of Batchelor's equation. It is observed that shear thinning behavior of this case is relatively weaker than that of Quemada' equation (Eq. (12)) as well as experimental data in Fig. 9. It is apparent that the prediction by this equation agrees with experimental results at $\phi < 0.02$. However, as ϕ increases, the discrepancy from the experimental data increases. The lack of the agreement at $\phi > 0.02$ is attributed to the fact that the equation is written in terms of ϕ_{ag} larger than ϕ since the aggregate includes suspending fluid inside although the range of ϕ in this study is much less than 0.1. The predictions by the effective-medium model with Quemada equation show the most similar behavior to the experimental results.

4. Conclusion

We investigated scaling theories to estimate the structural parameters for fractal aggregates of the colloidal suspension using the rheological properties. The main structure parameters are the fractal dimension of the aggregates d_f and the power-law exponent m in the scaling relation $R \propto S^{-m}$ where R is the radius of gyration for an aggregate and S is the imposed shear rate. The colloidal suspension in the present study consists of carbon black particles and ethylene glycol. The carbon black particles are of 56 nm in average diameter and their volume fraction ranges ϕ from 0.005 to 0.05. Plateau elastic modulus G_0' and strain γ_0 at the upper limit of the plateau beyond which the elastic modulus starts to decrease were utilized to estimate the fractal dimensions of aggregate and backbone chain inside the aggregate above gelation point $\phi \geq 0.02$. The suspension shows a typical behavior which belongs to a strong-link regime. The exponent m in $G_0' \propto \phi^m$ is 4.84. The estimated fractal dimension is 2.14 for the aggregate and 1.16 for the backbone chain inside the aggregate. It is shown that the shear yield stress data also start to build up near ϕ = 0.02, indicating the gelation point. This behavior is consistent with that for G_0'. The exponent n in $\tau_y \propto \phi^n$ is 3.53 smaller than the exponent m, which gives the value

for the combined parameter $m(3\text{-}d_f)$. The exponent m is found to be 0.33 at $d_f = 2.14$ obtained from G_0' data, which is close to the values 0.35-0.37 in previous studies (Eggersdorfer *et al*., 2010; Potanin, 1993; Sonntag and Russel, 1986). Below gelation point for ϕ = 0.005-0.015, the scaling between intrinsic viscosity and shear rate is used to estimate the $m(3\text{-}d_f)$. The estimated value was 0.27 nearly same as 0.28 from the yield stress data. It was found that the combined parameter $m(3\text{-}d_f)$ keeps constant whether ϕ is in gelled state or not.

The parameters are used to establish a micro-rheological model to predict suspension viscosity as a function of ϕ and S. It is supposed that the colloidal aggregates are spheres of radii R and the fractal dimension of the aggregates is invariant. The model incorporates the concentration dependence and shear dependence of the aggregated suspension. For the concentration dependence Quemada's equation (Eq. (12)) is used with ϕ replaced by ϕ_{ag} the volume fraction of the aggregate in the suspension. An effective-medium approximation is employed to consider hydrodynamic interaction among the aggregates for the shear dependence. For comparison the case where the hydrodynamic interaction is not considered was also treated. The inclusion of the hydrodynamic interaction effect critically contributes to the similarity of behavior to the experimental results. The case without this consideration gives no solution beyond ϕ = 0.02. Another comparison is made with a case using Batchelor's equation (Eq. (21)) instead of Quemada's (Eq. (12)). This case shows large discrepancy as ϕ increases. This behavior is attributed to the fact that the equation is written in terms of ϕ_{ag} which is always larger than ϕ for the aggregated suspensions. In conclusion, it is found that the model based on Quemada's equation combined with the effective-medium approximation shows the best similarity to the experimental data.

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