Rheological Behavior of Concentrated Monodispersed Colloidal Suspensions

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(Received : July 10, 2018)

The effect of suspending medium on the rheological behavior of monodispersed colloidal suspensions was examined to identify the characteristic rheological behavior of concentrated colloidal suspensions. Colloidal suspensions of monodispersed silica particles form colloidal crystals and exhibit shear-thinning flows. With the change of the suspending medium from an aqueous medium to a polyethylene-glycol di-acrylate monomer, both the viscosity of the suspensions and the degree of shear-thinning decreased, and the suspensions exhibited shear-thickening behavior under high shear rates. Additionally, increasing the particle size, critical shear-rate and critical shear-stress at the onset of shear-thickening decreased.

Finally, the research found that shear-thickening becomes more noticeable as the increase in the ethylene-glycol chain lengths of the monomer and the particle size.

Key Words: Rheology / Silica / Suspension / Shear-thinning / Shear-thickening

1. INTRODUCTION

Colloidal suspensions have come to be used in manufacturing processes for a wide range of functional materials and assembly components, such as electrode slurry for lithium (Li) ion batteries and catalyst inks for fuel cells. Unlike a solution, the viscosity of these colloidal suspensions increases in accordance with the volume of colloidal particles in the suspension. However, once the particle concentration reaches a certain concentrated level, the interaction between the particles becomes intense and the micro-structure of the suspension changes. For example, the Newtonian flow exhibited with a dilute suspension may change to a non-Newtonian flow, such as a shear-thinning flow in which the viscosity decreases as the shear rate increases (a phenomenon known as pseudoplastic)1-3). However, if the concentration increases further, these suspensions are known to exhibit characteristic rheological behavior such as shear-thickening behavior in which the viscosity increases as the shear rate increases (a phenomenon known as dilatancy)4-8). The characteristic rheological behavior of concentrated colloidal suspensions, such as shear-thinning flow and shear-thickening behavior, has a major impact on the productivity, quality, and performance of materials and parts used in Li ion batteries and fuel cells, thereby necessitating appropriate rheological control.

Therefore, with the objective of identifying rheological control guidelines for concentrated colloidal suspensions, the rheological behavior and micro-structures of these types of suspensions is being researched using monodispersed colloidal particles with an extremely high degree of size uniformity. This research is examining concentrated suspensions of monodispersed colloidal particles, and has found that the colloidal particles form three-dimensional ordered arrays (i.e., colloidal crystals) in aqueous media suspensions9-11). This research also examined the formation of colloidal crystals in monomers as well as in an aqueous medium, and succeeded in creating polymer-immobilized colloidal crystal films through polymerization processes involving monomer suspensions12, 13). This paper describes the rheological behavior that occurs when concentrated monodispersed colloidal particles are suspended in an aqueous medium or a monomer, while considering the formation of colloidal crystals in the suspension with the monodispersed colloidal particles. The following sections also discuss the micro-structures and rheological behavior dominant mechanism of these suspensions.

2. EXPERIMENTAL

Colloidal suspensions were prepared by suspending monodispersed silica particles in aqueous media or acrylic
monomers at high concentrations. The rheological behavior of these suspensions was then measured. The suspensions were prepared by adding Seahostar KEP10 (particle size: 100 nm), KEP20 (200 nm), KEP50 (500 nm), and KEP100 (1 μm) silica particles produced by Nippon Shokubai Co., Ltd. into the suspending media without additional processing. The following two monomers produced by Shin Nakamura Chemical Co., Ltd. were used: NK Ester A-200 and NK Ester A-600 (polyethylene glycol di-acrylate with ethylene glycol (EG) chain lengths of 4 and 14, respectively) (Fig. 1), and these monomers indicated Newtonian flow. The aqueous media and monomer suspensions were prepared with concentrations between 20 and 60 wt% (11 ~43 vol%). The rheological behavior was examined by placing a cone-plate or parallel-plate on a MCR 301 rheometer manufactured by Anton Paar, and measuring the shear rate dependence of steady flow viscosity (shear rate: 0.01 to 1000 s\(^{-1}\)), as well as the strain \(\gamma\) dependence (frequency: 6.28 rad\(\cdot\)s\(^{-1}\), strain: 0.01 to 1000 %) and frequency dependence (frequency: 0.1 to 100 rad\(\cdot\)s\(^{-1}\), strain: 10 %) of storage modulus \(G'\) and loss modulus \(G''\). In both cases, the measurement temperature was set to 25 °C. The reflection spectra were also measured by spectrophotometer to confirm the formation of colloidal crystals.

### 3. RESULTS AND DISCUSSION

#### 3.1 Colloidal Crystal Formation

Figure 2 shows the reflection spectra of the KEP10 (particle size: 100 nm) monodispersed silica particle suspensions with aqueous media. The figure illustrates the reflection peak of each colloidal suspension of 20~60 wt\% (11~43 vol\%). The peak positions are shifted toward the short-wavelength range as the particle concentration increases. This result suggests that the reflection peaks follow the concept of Bragg diffraction of ordered structures, and that the particles formed three-dimensional ordered arrays of colloidal crystals in each of the suspensions\(^6\)-\(^12\). In other words, the reflection peaks are shifted toward the short-wavelength range since the spacing between the lattice planes becomes smaller as the particle concentration increases. After confirming that the colloidal particles form colloidal crystals in the suspension, the rheological behavior was then measured.

#### 3.2 Rheological Behavior of Colloidal Suspensions with Aqueous Media

Figure 3 shows the relationship between the shear rate \(\dot{\gamma}\) and the steady shear flow viscosity \(\eta\) of the KEP10 colloidal suspensions with aqueous media. In all cases, the suspensions exhibited shear-thinning flows in which the viscosity decreases as the shear rate increases. The viscosity also increased in accordance with the concentration. Since this shear-thinning flow suggests that the three-dimensional microstructure of the colloidal crystals formed in the aqueous media was fractured to the smaller structure by shear, and that these three-dimensional structures were formed more densely as the particle concentration increased\(^{14\text{-}16}\).

Figure 4 shows the relationship between the strain \(\gamma\) and the storage modulus \(G'\) and loss modulus \(G''\) of the KEP10 aqueous suspensions. In all cases, \(G'\) and \(G''\) remained linear and unchanged at a strain of approximately 1 % or less. In contrast, \(G'\) and \(G''\) became non-linear as the strain increased: with \(G'\) decreasing steadily while \(G''\) increased briefly and then decreased with the increase in strain amplitude. In the linear region, \(G'\) was greater than \(G''\) at all concentrations, indicating a gel-like elastic response, which was probably due to the three-dimensional networks derived from the colloidal crystal structures. Subsequently, these three-dimensional networks likely fractured in the nonlinear region as the strain increased, conforming to the shear rate dependence of viscosity results shown in Fig. 3. Although both \(G'\) and \(G''\) increased in accordance with the particle concentration, this may reflect the formation of more densely packed three-dimensional networks as the particle concentration increased, as shown by the results in Fig. 3.

Figure 5 shows the relationship between the frequency \(\omega\) and the storage modulus \(G'\) and loss modulus \(G''\) of the KEP10 aqueous suspensions. Neither \(G'\) nor \(G''\) demonstrated a particular dependence on frequency at any concentration. In

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\begin{align*}
A-200: & \quad CH_2=CH-CO-O(CH_2-CH_2O)_4OC-CH=CH_2 \\
A-600: & \quad CH_2=CH-CO-O(CH_2-CH_2O)_{14}OC-CH=CH_2
\end{align*}
\]

Fig. 1 Acrylate monomers.
addition, $G'$ was greater than $G''$ at all frequencies. This is evidence for the formation of three-dimensional networks with an elastomer- or gel-like elastic response in the colloidal suspensions. These three-dimensional networks were probably derived from the colloidal crystal structures, and the results conform to the shear rate dependence of viscosity shown in Fig. 3, as well as the strain dependence of the storage modulus and loss modulus shown in Fig. 4.

The relationship between the shear rate $\dot{\gamma}$ and the steady shear flow viscosity $\eta$ was then measured in the same way using the aqueous suspensions fabricated using the KEP20 (200 nm), KEP50 (500 nm), and KEP100 (1 μm) silica particles (Fig. 6). Although the steady shear flow viscosities were different, each particle suspensions exhibited shear-thinning flows that are probably derived from the formation of colloidal crystals. In addition, the viscosity and degree of shear-thinning of these suspensions increased in accordance with the increase in particle concentration. Furthermore, the viscosity decreased as the particle size increased when compared across the same concentration levels. This phenomenon suggests that the three-dimensional networks become weaker as the number of particles in the same concentration decreases in accordance with the increase in particle size, i.e., as the number of particles that form the colloidal crystal structure decreases. These results were also supported when the relationships between strain $\gamma$, frequency $\omega$ and storage modulus $G'$, loss modulus $G''$ were measured using each aqueous suspension.

### 3.3 Rheological Behavior of Colloidal Suspensions in Monomers

Figure 7 shows the relationship between the shear rate $\dot{\gamma}$ and the steady shear flow viscosity $\eta$ for colloidal suspensions of KEP10 particles with the A-200 monomer. In the same way as the suspensions with aqueous media, all the monomer suspensions exhibited shear-thinning flow. This shear-thinning flow suggests that the three-dimensional micro-structure was formed with the A-200 monomer. The reflection spectra measurement confirmed the formation of colloidal crystals in each of the colloidal suspensions (Fig. 8). However, shear-thinning was less than the aqueous suspensions, and the low-concentration (20 and 30 wt%) monomer suspensions also exhibited Newtonian flow at low shear rates. In contrast, the shear-thickening phenomenon, in which the viscosity increases as the shear rate increases, occurred at a high particle concentration of 60 wt%. Therefore, it should be possible to identify the shear-thickening mechanism by analyzing the suspensions.

Figure 9 shows the relationship between strain $\gamma$ and the storage modulus $G'$ and loss modulus $G''$ of the KEP10 suspensions with the A-200 monomer. In all cases, $G'$ and $G''$ remained linear and unchanged at a strain of approximately 1 % or less. In contrast, $G'$ and $G''$ became non-linear as the
strain increased, with both $G'$ and $G''$ decreasing. However, unlike the aqueous suspensions, $G'$ was greater than $G''$ at concentrations of 40 wt% or more. Although these suspensions exhibited an elastic response derived from the three-dimensional networks, $G'$ was smaller than $G''$ in the case of the 20 and 30 wt% concentrations and these suspensions demonstrated partially fluid characteristics.

Figure 10 shows the relationship between the frequency $\omega$ and the storage modulus $G'$ and loss modulus $G''$ of the KEP10 suspensions with the A-200 monomer. At high concentrations (50 and 60 wt%), $G'$ and $G''$ were virtually independent on the frequency, suggesting the formation of three-dimensional networks with an elastic response. However, at low concentrations, $G'$ and $G''$ decreased as the frequency decreased, indicating a mainly viscous response that is typical of a fluid. This probably means that the formation of three-dimensional network structures in the monomer was insufficient to indicate an elastic response, which confirms with the strain dependency results for storage modulus and loss modulus in Fig. 9.

Figure 11 shows the relationship between the shear rate $\dot{\gamma}$ and the steady shear flow viscosity $\eta$ was then measured in the same way using the A-200 monomer suspensions prepared using the KEP10(100 nm), KEP20 (200 nm), KEP50 (500 nm), or KEP100 (1 µm) silica particles. Although the steady shear flow viscosity was different, each colloidal particle suspension exhibited shear-thinning flows. In addition, the viscosity and degree of shear-thinning of these suspensions increased in accordance with the increase in particle concentration. Furthermore, the degree of shear-thickening increased as the particle size increased when compared across the same concentration levels (Fig. 11). Finally, shear-thickening behavior occurred with all particle sizes at a particle concentration of 60 wt% (43 vol%).

3.4 Comparison Using Different Suspending Media

To investigate the differences in rheological behavior due to the suspending medium, the same measurement analysis was carried out using the A-600 monomer, which has an EG chain length of 14 compared to the 4 EG chain length of the A-200 monomer.

Figure 12 compares the relationship between the shear rate $\dot{\gamma}$ and the steady shear flow viscosity $\eta$ of each colloidal suspension prepared using 60 wt% (43 vol%) of KEP100 silica particles in an aqueous medium and in the A-200 and A-600 monomers. All the suspensions exhibited shear-thinning flow, and the degree of shear-thinning was as follows: aqueous medium > A-200 > A-600. In other words, the degree of shear-thinning decreased as the EG chain lengths increased. In contrast, the order of the shear rate indicating shear-thickening behavior was as follows: aqueous medium < A-200 < A-600. In other words, the critical shear rate at the onset of shear-thickening decreased as the EG chain lengths increased. This result suggests that shear-thickening
behavior depends on the characteristics of the suspending medium. The same comparison was carried out using different sized particles. For these dispersions as well, the degree of shear-thinning was as follows: aqueous medium > A-200 > A-600. Similarly, the degree of shear-thickening was as follows: aqueous medium < A-200 < A-600. It was also found that shear-thickening behavior was more noticeable at lower shear rates as the particle size increased.

These results described above show that rheological behavior changes depending on the suspending medium. However, the influence of the viscosity of the suspending medium itself must be removed to identify the cause of this effect. Compared to the viscosity of the aqueous medium (1 mPa·s), the viscosities of the A-200 and A-600 monomers are 19.6 and 100.4 mPa·s, respectively. Figure 13 plots the relative viscosity $\eta_r$, which was calculated by dividing the viscosity in Fig. 12 by the viscosity of the suspending medium. From the standpoint of relative viscosity, the viscosity in the shear-thinning region was as follows: aqueous medium > A-200 > A-600. This supports the idea that three-dimensional network structure formation by the colloidal crystals was insufficient.

### 3.5 Dominant Mechanism for Rheological Behavior of Concentrated Colloidal Suspensions

This section discusses the differences in rheological behavior depending on differences in the suspending medium for concentrated colloidal suspensions where monodispersed particles can form colloidal crystals in the fluids. The reduction in viscosity was greater with the monomers than with the aqueous medium at low shear rates for the following reason. Since the dielectric constant of a monomer is lower than water, the surface charge of the silica particle becomes smaller despite the increase in electric double layer thickness. As a result, colloidal crystal formation is inhibited because the electrostatic repulsion between the particles decreases and the three-dimensional micro-structure forms insufficiency (amorphous). In contrast, shear-thickening behavior occurred in the monomer mediums and not in the aqueous medium due to the following reason. Because little electrostatic repulsion occurs in a monomer (i.e., because a monomer resembles a hard-sphere particle with no interaction between particles and the viscosity of the dispersion medium is high), the structure is more likely to re-forming and stabilize by lubrication and friction between the colloidal particles that occur at high shear rates. Consequently, the micro-structure with the colloidal particles re-forms due to the shear flows, thereby increasing the viscosity. This shear-thickening mechanism is consistent with the idea reported Brady et al. and Wagner et al. in which particle diffusion induced by shear flow dominates the formation of the particle re-forming structure: This mechanism has been reported by Brady et al. and Wagner et al.

The following section discusses this diffusion-dominant mechanism. The viscosity behavior of concentrated colloidal suspensions is determined by the ratio between diffusive and shear flows of the particles governed by Brownian motion. This ratio can be explained using so-called diffusion-dominant models expressed by the Péclet number $Pe$. $Pe$ is the ratio of diffusive and shear particle flows. The diffusive
to the viscosity of the suspension. In concentrated colloidal suspensions, as solvent is considered the suspension viscosity of the solvent. However in case of concentrated colloidal suspensions, the solvent viscosity is substituted by the viscosity of the suspension. In this research examined the effect of suspending media on the rheological behavior of colloidal suspensions containing uniform size monodispersed particles to identify the characteristic rheological behavior of concentrated colloidal suspensions. The research found that colloidal suspensions of monodispersed silica particles form colloidal crystals and exhibit shear-thinning flows. It also found that, when the suspending medium is changed from an aqueous medium to a monomer, both the viscosity and degree of shear-thinning decrease and the suspensions exhibit shear-thickening under high shear rates. Additionally, increasing the particle size, critical shear-rate and critical shear-stress at the onset of shear-thickening decreased. Finally, the research found that the viscosity and degree of shear-thinning decrease and shear-thickening becomes more noticeable as the ethylene glycol chain lengths of the monomer increase.

\[
\begin{align*}
D &= kT/6\pi\alpha a^2 \quad (1) \\
Pe &= \alpha^2 \gamma / D \quad (2) \\
&= 6\pi\alpha^2 \eta \gamma / kT \quad (3) \\
&= 6\pi\alpha^2 \sigma / kT \quad (4)
\end{align*}
\]

\(D\): particle radius \(k\): boltzmann constant \(\eta\): solvent viscosity \(\gamma\): shear rate \(\sigma\): shear stress

Brady, and Wagner \textit{et al.} consider that shear-thickening also follows this diffusion-dominant model. In this case, when the particle sizes are the same, the shear rate at which shear-thickening occurs is principally determined by the shear stress, regardless of the viscosity of the solvent \cite{17-22}. Figure 14 plots the relationship between shear stress \(\sigma\) and steady shear flow viscosity \(\eta\) shown in Fig. 12 based on the relationship between the shear rate \(\dot{\gamma}\) and the steady shear flow viscosity \(\eta\). Shear-thickening occurred at virtually the same stress, even with different suspending media. Therefore, shear stress was the principal cause of shear-thickening, regardless of the viscosity of the solvent. This also supports the idea that rheological behavior can be explained using the diffusion-dominant model described above, which is controlled by \(Pe\) (i.e., the ratio between diffusive and shear flows of particles).

Figure 15 and Fig. 16 shows the relationship between viscosity \(\eta\) and the shear rate \(\dot{\gamma}\) and shear stress \(\sigma\) of 60 wt% (43 vol%) of KEP10, KEP20, KEP50, and KEP100 silica particles suspended in the A-600 monomer. The shear rate and shear stress that cause shear-thickening decreased as the particle size increased. When the rheological behavior of monodispersed silica colloidal suspensions can be explained using the diffusion-dominant model, which is controlled by \(Pe\), these behaviors support the model.

4. SUMMARY

This research examined the effect of suspending media on the rheological behavior of colloidal suspensions containing uniform size monodispersed particles to identify the characteristic rheological behavior of concentrated colloidal suspensions. The research found that colloidal suspensions of monodispersed silica particles form colloidal crystals and exhibit shear-thinning flows. It also found that, when the suspending medium is changed from an aqueous medium to a monomer, both the viscosity and degree of shear-thinning decrease and the suspensions exhibit shear-thickening under high shear rates. Additionally, increasing the particle size, critical shear-rate and critical shear-stress at the onset of shear-thickening decreased. Finally, the research found that the viscosity and degree of shear-thinning decrease and shear-thickening becomes more noticeable as the ethylene glycol chain lengths of the monomer increase.
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