Concentrated colloidal suspensions of monodispersed silica particles exhibited shear-thickening when a highly viscous suspending media was prepared using ethylene glycol. Although the shear rate at which shear-thickening occurred decreased in accordance with increases in the suspending media viscosity, the shear stress at the onset of shear-thickening behavior occurred was defined regardless of the suspending media viscosity. In addition, based on the dependence of the critical shear stress on the square reciprocal of the particle size, it was found that shear-thickening behavior can be explained by the diffusion-friction-dominant model.

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

1. INTRODUCTION

Concentrated colloid suspensions (also referred to as slurry or paste) are used for electrode slurries in lithium (Li) ion batteries and catalyst inks for fuel cells are known to exhibit characteristic rheological behavior such as shear-thinning flow (a phenomenon known as pseudoplastic) and shear-thickening behavior (a phenomenon known as dilatancy) as the concentration of the colloidal suspension increases. The shear-thinning flow and shear-thickening behavior of concentrated colloidal particle suspensions has a major impact on the productivity, quality, and performance of materials and parts used in Li ion secondary batteries and fuel cells, thereby necessitating the 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 colloidal suspensions is being researched using monodispersed particles with an extremely high degree of size uniformity. This research has already found that concentrated aqueous media suspensions of monodispersed silica particles exhibit shear-thinning flows. It has also found that these suspensions exhibit shear-thickening behaviors when the particles are suspended in an acrylic monomer containing polyethylene glycol chains, and that the degree of shear-thickening depends on the composition of the suspending medium, as well as the size and concentration of the particles\(^1\). And the viscosity behavior of concentrated colloidal suspensions is determined by the ratio between shear flows and diffusion of the particles as shown by Brownian motion. This ratio can be explained using so-called diffusion-dominant models expressed by the Péclet number (Pe).

This paper describes the effects of the suspending medium on shear-thickening behavior and discusses the dominant shear-thickening mechanism by identifying the rheological behavior of colloidal suspensions consisting of concentrated monodispersed silica particles, using various organic solvents as suspending media.

Krieger-Doughty et al. reported that shear-thinning of concentrated colloidal suspensions occurs even with hard-sphere particles when the particle concentration increases. Under these conditions, particle aggregated structures form and shear-thinning occurs when the shear flow exceeds the rate of particle diffusion\(^2\)\. Other reports have also described particles forming three-dimensional ordered arrays of colloidal crystals in liquids when the electrostatic interaction between the particles is strong. These particle three-dimensional aggregated structures then fracture as the shear rate increases, causing viscosity to decrease\(^4,5\). It has also been reported that, when polymers are blended with particles, aggregated structures are formed by interaction between adsorbed polymers or depletion interaction due to non-adsorbed polymers. Aggregated structures then fracture as the shear rate increases, causing viscosity to decrease\(^6,7\). Thus, shear-thinning flow may be regarded as a decrease in viscos-
ity caused by the collapse of aggregated structures.

In contrast, although many researchers have addressed the shear-thickening behavior of concentrated colloidal suspensions, a generally accepted understanding of this phenomenon has yet to be reached. First, although it is known that dilatancy occurs when starch is suspended in a small amount of water or in sandy ground containing small amounts of seawater, this behavior has been identified as large resistance when tightly packed particles are restrained from expanding volumetrically after the application of shear force (i.e., the particles harden and become difficult to move or viscosity increases)\(^8\)\(^9\). On the same subject, reports have described increases in viscosity as the shear rate increases in concentrated colloidal suspensions, and the dominant factors of this behavior. Hoffmann et al. described how a colloidal ordered structure in a suspension changes to a disordered structure as the shear rate rises in a process called the order-disorder transition\(^10\)\(^11\). Brady et al. focused on Stokesian dynamics to explain this behavior based on differences in the magnitude of diffusion caused by Brownian motion and diffusion due to shear, and used this approach to also explain shear-thinning. This research simulated increases in viscosity due to the formation of hydro-cluster structures by lubrication between particles when particles flow close to each other as the shear rate increases\(^12\)\(^13\). Furthermore, results of experiments performed by Wagner et al. inferred hydro-clusters as the cause of shear-thickening behavior\(^14\)\(^15\). However, although a more recent report by Seto et al. also identified diffusion due to shear as the predominant factor, simulations found that friction caused by collision (contact) between particles in a concentrated suspension greatly increased viscosity and led to shear-thickening, even without hydro-cluster structure formation\(^16\)\(^19\). Subsequently, Mari et al. advanced this model and suggested that shear-thickening is determined by shear flow, frictional force due to contact between particles, and repulsion between particles. This hypothesis was verified by experiments carried out by Poon et al.\(^19\).

Consequently, as described above, various hypotheses have been proposed for the mechanism of shear-thickening, and a generally accepted understanding has yet to be reached. For this reason, a series of research efforts has been carried out using concentrated colloidal suspensions of monodispersed particles to identify the mechanism of shear-thickening and other non-Newtonian flows in concentrated colloidal suspensions. This paper describes the dominant mechanism of these phenomena while summarizing the results of this research.

### 2. EXPERIMENTAL

Colloidal suspensions were prepared by suspending monodispersed silica colloidal particles in aqueous media and organic solvents at high concentrations. The rheological behaviors of these suspensions were then measured. The suspensions were prepared by adding Seahostar KEP10 (particle size: 100 nm), KEP20 (200 nm), KEP50 (500 nm), KEP100 (1 μm), and KEP250 (2.5 μm) silica particles produced by Nippon Shokubai Co., Ltd. into the suspending media at a particle concentration of 60 wt% (43 vol%) without additional processing. As shown in Table I, a total of eleven types of organic solvents were used, including alcohols, several types of ethylene glycol, propylene glycol, and two types of polyethylene glycol with different molecular weights (PEG 200, molecular weight: 200, and PEG 400, molecular weight:

| Name of organic solvent | Abbreviation | Viscosity (mPa·s) |
|-------------------------|--------------|------------------|
| Methanol                | MeOH         | 0.54             |
| Ethanol                 | EtOH         | 1.17             |
| Propanol                | PrOH         | 1.94             |
| Butanol                 | BuOH         | 2.95             |
| Ethylene glycol         | EG           | 17.2             |
| Propylene glycol        | PEG          | 48.6             |
| Diethylene glycol       | DEG          | 29.1             |
| Triethylene glycol      | TRIEG        | 39.5             |
| Tetraethylene glycol    | TETEG        | 45.4             |
| Polyethylene glycol (molecular weight: 200) | PEG200 | 51.3 |
| Polyethylene glycol (molecular weight: 400) | PEG400 | 94.7 |

Table II  Blended solvents comprising a mixture of aqueous medium and PEG 400, used as dispersing media.

| The weight ratios of the aqueous medium / PEG 400 | Viscosity (mPa·s) |
|--------------------------------------------------|------------------|
| 0/10                                             | 1.07             |
| 9/1                                              | 1.53             |
| 7/3                                              | 3.92             |
| 5/5                                              | 11.7             |
| 3/7                                              | 36.6             |
| 1/9                                              | 88.2             |
| 0/10                                             | 94.7             |
Although the viscosity of the butanol suspension was higher than methanol, ethanol, and propanol, the viscosity of alcoholic organic solvents was roughly the same. However, since the viscosity of these organic solvents was lower than water, the surface charge 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 becomes disturbed (amorphous). The viscosity of the suspensions prepared using methanol, ethanol, and propanol was roughly the same. Although the viscosity of the butanol suspension was higher at each shear rate, the degree of shear-thinning was approximately identical. Furthermore, the degree of shear-thinning of the ethylene glycol and propylene glycol suspensions decreased, and the colloidal suspensions prepared with these organic solvents exhibited noticeable shear-thickening behavior under high shear rates. These results demonstrate that colloidal suspensions exhibit clear shear-thickening behavior even with non-monomer suspending media such as ethylene glycol or propylene glycol.

Subsequently, the same analysis was carried out using the following ethylene glycol-based organic solvents with different molecular weights: ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TRIEG), tetraethylene glycol (TETEG), and two types of polyethylene glycol (PEG 200 and PEG 400). The results of these organic solvents were also compared with an aqueous suspending medium. Figure 2 shows the relationship between the shear rate $\dot{\gamma}$ and the steady flow viscosity $\eta$ of the colloidal suspensions prepared using the ethylene glycol organic solvents as the suspending media. The results found that, as the molecular weight increased (EG < DEG < TRIEG < TETEG), the viscosity increased, and the degree of shear-thickening was higher and occurred at lower shear rates. Similarly, for the polyethylene glycol suspending media, viscosity also increased in accordance with the molecular weight (PEG 200 < PEG 400), increasing the degree of shear-thickening was higher and lowering the shear rate at which it occurred.

However, since the viscosity of these organic solvents differs widely, the differences in suspending medium viscosity must be removed to identify the effect of the particles on changes in viscosity behavior. Therefore, Fig. 3 shows the relationship between the shear rate $\dot{\gamma}$ and the relative viscosity $\eta$ of the colloidal suspensions prepared using the ethylene glycol organic solvents as the suspending media. The results show that the minimum viscosity value due to shear-thinning...
flow is virtually the same, while the shear-thickening behavior is virtually unchanged.

### 3.2 Basic Shear-thickening Mechanism

Before discussing the shear-thickening mechanism, this section first describes the theory of the characteristic shear-thinning flow of concentrated colloidal suspensions called pseudoplastic. The viscosity behavior of concentrated particle suspensions is determined by the ratio between shear flows and diffusion of the particles as shown by Brownian motion. This ratio can be explained using so-called pure diffusion-vs-flow scenario expressed by the Péclet number \( (Pe) \). In these models, when \( Pe < 1 \) (i.e., diffusion of the particles is dominant), colloidal suspensions are highly viscous and exhibit Newtonian flow. Additionally, when \( Pe > 1 \) (i.e., diffusion caused by shear increases, causing the viscosity to decrease in accordance with the shear), colloidal suspensions exhibit shear-thinning flow, before reverting to Newtonian flow when the viscosity is low.

Furthermore, Brady and Wagner et al., and Melrose et al. demonstrated that particle aggregation structures reform and that viscosity increases due to flows caused by shear even when the shear increases and shear-thickening behavior occurs. In other words, diffusion is the dominant phenomenon. According to this concept, shear-thickening behavior also follows a pure diffusion-vs-flow scenario. In this case, when the particle size is the same, the shear rate at onset of shear-thickening occurs decreases in accordance with increases in the suspending medium viscosity and shear-thickening behavior is principally determined by the shear stress, regardless of the suspending medium viscosity. The initial shear-thinning mechanism was analyzed using a pure diffusion-vs-flow scenario like that adopted in Stokesian dynamics. Additionally, following the hypothesis that hydro-cluster micro-structures are formed by shear described in the shear-thickening behavior research performed by Brady, Wagner, et al., it was found that shear-thickening behavior depends on shear stress.

Furthermore, although Seto, Mari, et al. also identified diffusion due to shear as the predominant factor, this research found that friction caused by collision (contact) between particles in a concentrated suspension greatly increased viscosity and led to shear-thickening, even without hydro-cluster micro-structure formation. Setting aside whether shear-thickening behavior is the result of the formation of hydro-cluster micro-structures, as described by Brady, Wagner et al., or contact friction between particles, as described by Seto, Mari, et al., diffusion due to shear flow is the predominant factor in shear-thickening behavior in both cases. As this phenomenon depends on the critical shear stress \( \sigma^* \) at the onset of shear-thickening can be regarded as constant when the particles are the same.

Figure 4 plots the relationship between shear stress \( \sigma \) and steady shear flow viscosity \( \eta \) actually shown in Fig. 2 based on the relationship between the shear rate \( \dot{\gamma} \) and the steady shear flow viscosity \( \eta \). Although the shear rate at the onset of shear-thickening decreased as the viscosity of the suspending medium increased, the critical shear stress \( \sigma^* \) at the onset of shear-thickening increased remained constant at approximately 80 Pa, regardless of the composition or viscosity of the suspending medium. This result supports the hypothesis that shear-thickening can be explained by the diffusion-only-dominant model described above.

Figure 5 shows the relationship between the shear rate \( \dot{\gamma} \) and the steady flow viscosity \( \eta \) of colloidal suspensions, which were prepared by suspending 60 wt% (43 vol%) of KEP100 silica particles in blended suspending media consisting of an aqueous medium and different ratios of PEG 400. Although all the suspensions exhibited shear-thinning, this was presumed to be caused by the fracture of the particle aggregated structures by shear. In addition, the degree of shear-thinning decreased as the PEG400 ratio increased, and the viscosity increased at high shear rates. Furthermore, shear-thickening occurred when the PEG400 ratio in the aqueous medium was 5/5 or higher and did not occur at all with the aqueous medium. The degree of shear-thickening also became more noticeable at lower shear rates as the PEG400 ratio increased. This result suggests that shear-thickening behavior is caused by a structure induced by the presence of PEG400.

To discard the effects of differences in suspending medium viscosity, the viscosity of each suspending medium was measured and the relationship between the relative viscosity and the shear rate was analyzed by dividing the steady shear viscosity by the steady flow viscosity.
flow viscosity described above with the viscosity of the suspending medium. Figure 5 re-plots the results shown in Fig. 6 based on the relationship between shear rate $\dot{\gamma}$ and relative viscosity $\eta_r$. After discarding the increase in viscosity due to the suspending medium, the decreased viscosity value due to shear-thinning is virtually the same. This value is the viscosity due to the volume fraction of the particles when the aggregated structure is fractured by shear. Therefore, in the same way as shown in Fig. 6, shear-thickening occurred when the PEG400 ratio in the aqueous medium was 5/5 or higher and the degree of shear-thickening also became more noticeable at lower shear rates as the PEG400 ratio increased.

Figure 5 re-plots relationship between shear rate $\dot{\gamma}$ and steady shear viscosity $\eta$ shown in Fig. 7 based on the relationship between shear stress $\sigma$ and steady shear viscosity $\eta$. The results show that the critical shear stress $\sigma^*$ at the onset of shear-thickening remained constant at approximately 80 Pa, regardless of the composition or viscosity of the suspending medium as the PEG400 ratio in the aqueous medium increased (i.e., as the suspending medium viscosity increased). This value is virtually the same as that reported in Fig. 4, which shows that the critical shear stress $\sigma^*$ at the onset of shear-thickening is virtually independent of the viscosity of the suspending medium, providing that the particle size is defined.

### 3.3 Effect of Particle Size on Viscosity Behavior

Figure 8 shows the relationship between the shear rate $\dot{\gamma}$ and the steady shear flow viscosity $\eta$ of PEG400 suspensions containing five types of silica particles with different particle sizes, KEP10 (particle size: 100 nm), KEP20 (200 nm), KEP50 (500 nm), KEP100 (1 μm), and KEP250 (2.5 μm). Viscosity decreased at low shear rates as the particle size increased, and the degree of shear-thinning also decreased. In the case of colloidal suspensions containing monodispersed silica particles, this is caused by the formation of ordered arrays of colloidal crystals due to electrostatic interaction. Since shear-thinning can be regarded as derived from the fracture of these colloidal crystal three-dimensional aggregated structures due to shear, the reduction in the degree of shear-thinning is probably due to the reduction in the number of particles as the particle size increases, which weakens the interaction between particles.

In contrast, although all the colloidal suspensions exhibited shear-thickening, the shear rate at which this occurred decreased as the particle size increased. Section 3.4 analyzes
the root causes of this phenomenon and describes the shear-thickening mechanism.

### 3.4 Advanced Shear-thickening Mechanism (Effect of Particle Size)

Section 3.1 indicated that shear-thickening occurs at the same stress even when the suspending medium differs. Since viscosity behavior can be explained using the diffusion-only-dominant model described above (i.e., a model defined by $\text{Pe}$: the ratio between particle diffusion and flow caused by shear), Fig. 9 plots the relationship between shear stress $\sigma$ and viscosity $\eta$ shown in Fig. 6 based on the relationship between shear rate $\dot{\gamma}$ and steady flow viscosity $\eta$. The results show that the critical shear stress $\sigma^*$ at the onset of shear-thickening decreases as the particle size increases. This section discusses the shear-thickening mechanism based on this relationship between particle size and the shear stress $\sigma^*$ at the onset of shear-thickening.

If determined wholly by the relationship between particle diffusion and shear flow as described by Brady, Wagner, et al., $\sigma^*$ would be proportional to the negative third power of the particle size $a$. However, Fig. 10 shows that $\sigma^*$ is actually proportional to the negative second power of the particle size $a$. This proportional relationship can be explained by the friction model proposed by Seto, Mari, et al. [16-18]

As described above, Brady, Wagner, et al. described that viscosity increased due to hydro-clusters formed by lubrication between particles caused by shear flow. In contrast, despite agreeing with Brady, Wagner, et al. that the diffusion of shear flow is the predominant factor behind shear-thickening, Seto, Mari, et al. stated that friction caused by impacts between particles is the cause, rather than lubrication between particles. This research also described the effects of interaction between particles due to particle proximity when particles colloid. Mari described the following equation to express the critical shear stress $\sigma^*$ at the onset of shear-thickening: $\sigma^* = 5kT/a^2 + 0.01F/a^2$. When diffusion due to shear flow is predominant, the dependent relationship is $1/a^3$. In contrast, when the interaction between particles (electrostatic repulsion) is predominant, the dependent relationship is $1/a^2$. In other words, these results show a case in which the interaction between particles (electrostatic repulsion) is predominant. Therefore, these colloidal suspensions containing monodispersed silica particles are systems that form colloidal crystals by electrostatic interaction, and can be explained by this model.

Similarly, more recently, the research group of Poon et al. has verified that the gradient of the relationship between the shear rate and particle size of concentrated colloidal suspensions containing various particle sizes is proportional to the second rather than the third power [19]. This confirms that the shear-thickening of concentrated particle suspensions can be explained by a diffusion-friction-dominant model due to particle collision, and that the shear stress at the onset of shear-thickening is proportional to the negative second power of particle size. The degree of the effect of electrostatic repulsion and other types of particle interaction should be analyzed in the future by carrying out the same measurement using particles with lower electrostatic repulsion, such as particles with a low surface charge or particles with a thinner electric double layer formed by increasing the concentration of coexistent ions.

A rheological control method for concentrated colloidal suspensions can be described based on these results (Fig. 11). In the case of a concentrated colloidal suspension, viscosity increases at low shear rates due to aggregation structures formed by particles. This decreases as the shear rate (shear stress) decreases, resulting in shear-thinning. If the shear rate (shear stress) is then increased further, viscosity increases due to friction caused by collisions between particles,
resulting in shear-thickening. The occurrence of shear-thinning or shear-thickening is determined by the size of the shear flow with respect to particle diffusion. Therefore, it occurs from lower shear rates (shear stresses) as the particle size increases. Consequently, it should be possible to freely control viscosity behavior through the size and concentration of the particles, and the viscosity of the medium.

4. SUMMARY

This paper identified the rheological behavior and mechanisms of concentrated colloidal suspensions using model monodispersed silica particles with the objective of identifying rheological control guidelines for concentrated suspensions.

The following results were obtained: in concentrated colloidal suspensions containing monodispersed silica particles, aggregation structures (three-dimensional colloidal crystals) formed by the particles fracture due to shear. The resulting increase in shear rate leads to a decrease in viscosity exhibited as shear-thinning. In addition, when the viscosity of the suspending medium increases, increases in the shear rate in high shear rate regions leads to increases in viscosity exhibited as shear-thickening.

This research found that this shear-thickening phenomenon occurs depending on the size of the shear stress (shear rate) due to shear flow. In addition, the shear stress at the onset of shear-thickening is principally determined by the particle size, and increases in proportion to the negative second power of the particle size. This demonstrates that shear-thickening can be explained using a friction model of particle collisions caused by shear flow as described by Seto, Mari, Poon, et al.

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