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**Affirmation of the effect of pH on shake-gel and shear thickening of a mixed suspension of
polyethylene oxide and silica nanoparticles**

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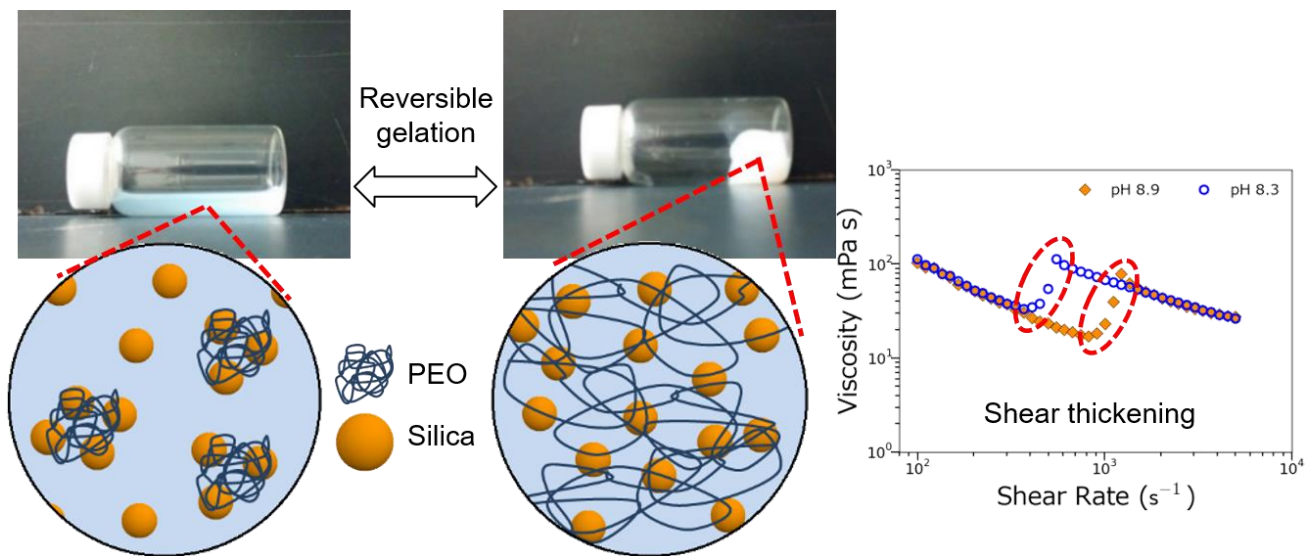
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Abstract

The mixture of silica nanoparticles and polyethylene oxide (PEO) shows unique rheological behaviors, such as reversible gelation and shear thickening, when moderate shear is applied. These behaviors are attributed to the transient bridging network, which is formed via the simultaneous adsorption of a PEO chain onto multiple silica nanoparticles. The adsorption affinity depends on pH and thus, we expect that these behaviors change with pH. Nevertheless, the effect of pH on shake-gel behavior and shear thickening has not yet been systematically examined. In order to improve our understanding, we attempt to study the influence of pH and ionic strength on the relaxation time of the gel and the viscosity of the mixture. Our experimental results demonstrate that shake-gel and shear thickening can be observed in the pH range of 8.0–9.9. Moreover, the relaxation time required for the gel recovery to sol increases and the critical shear rate at which the viscosity begins to rise decreases as the pH decreases. Furthermore, we determined that irreversible shake-gels can be obtained in a narrow range of PEO concentrations at the pH of approximately 8.0. In conclusion, we determined that the relaxation time of gel is longer at low pH, and the critical shear rate decreases with the decrease in interparticle repulsion of silica.

Keywords: gelation, relaxation, shear thickening, bridging network, interparticle repulsion

Graphical abstract



1. Introduction

Colloidal dispersions can be found in our daily life in foods, cosmetics, clays, etc. The dispersion of colloidal particles often shows non-Newtonian fluid properties [1], [2]. Polymers are often added to colloidal dispersions to modify the particle-particle interactions and fluidity of the dispersion [3], [4]. It is desirable to understand and control the non-Newtonian flow characteristic of these colloids.

The mixture of laponite and polyethylene oxide (PEO) demonstrates shake-gel behavior: the phase transition from liquid-like to gel-like states by vigorous shaking [5]–[7]. When the surface of laponite is saturated by the adsorbed PEO, this gelation does not occur. This indicates that the concentration ratio of PEO to laponite is one of the factors controlling the phase transition. The shake-gel of laponite-PEO mixture demonstrates reversibility, provided the concentration ratio of PEO/laponite is within an appropriate range. In other words, within a certain range of concentration ratio, the gel returns to liquid state if it is maintained at rest. The time required to return to liquid state also varies with the concentration ratio of PEO to laponite. It is revealed that the strength of the gel changes with the molar weight of PEO. Similar results have been obtained by the studies with montmorillonite clay and spherical silica [8]. The viscosity and viscoelasticity of the mixture of silica and PEO have been measured [9]–[11]. These measurements have demonstrated that the occurrence of shear thickening and the degree of rise of viscosity are affected by the concentrations of PEO and/or silica and the molar mass of PEO.

Previous studies have demonstrated that the fluidity of the mixture of colloidal particles and polymers is also controlled by the molecule construction of polymer [12], particle size [13], [14], presence of surfactant [15], [16], etc. Some studies have proposed the following measures for the mechanism of gelation and shear thickening [7], [9]. In the mixture of colloidal particles and polymers with relatively large molecular weight, the conformation of dissolved polymers is random coil and flocs can be formed by the adsorption of one polymer onto several particles. Once such a mixture is sheared, the floc is stretched

and subsequently, the stretched flocs collide with one another. During this process, the polymer is subjected to successive adsorption and desorption. The adsorption prevails such that new large flocs are formed. Thus, the flocs grow and the formation of the bridging network spreads out the entire colloidal dispersion. This may cause gelation and shear thickening (Fig. 1). If the shear is ceased, the thermal energy becomes so dominant that desorption is promoted. Subsequently, the suspension returns to liquid state at equilibrium. Fig. 1 indicates the importance of the adsorption and desorption properties of polymers on the particle surface for the shake-gel and shear thickening.

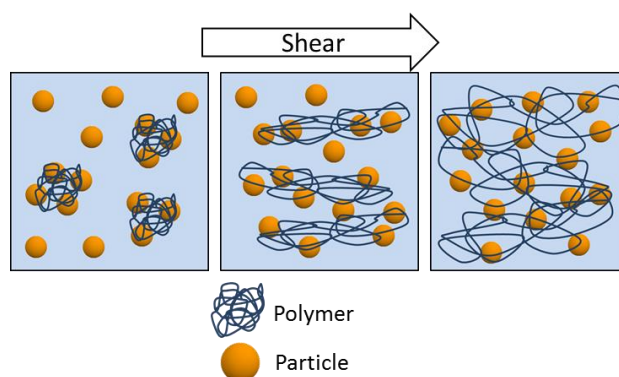


Fig. 1 Schematic illustration of the mechanism of gelation and shear thickening

In addition to the polymer adsorption, the flocculation of colloidal dispersion by polymers is concerned with the range of interparticle repulsion [17]. If the change of fluidity of the colloid-polymer mixture is attributed to the polymer bridging, it is possible that the degree of interparticle repulsion controlled by the surface charge affects the fluidity of the mixture. The adsorption affinity of polymers to particles is also influenced by the dissociation state of ionizable groups on the particle surface. Adsorption mechanisms such as electrostatics and noncovalent bonding are related to the surface charge characteristics. Thus, it is necessary to consider the change of particle surface with the change of pH or ionic strength. The variation of pH and ionic strength affects the interparticle interaction and thus alters the fluidity of the colloidal dispersion. While the effect of pH on the rheological properties of a mixture

with polyelectrolyte was studied [18], the focus was limited to the response of polyelectrolyte to the change in pH, and the reaction on the particle surface was not examined. A study shows that there are relationships between the viscosity of silica suspension and the thickness of the adsorbed polymer (PEO) layer on silica particles estimated from the zeta potential [19]. Another research demonstrates that the yield stress of the mixture of silica and polyvinyl alcohol changes with the electrostatic interaction of particles and has the maximum value at the pH of 7.5 [20]. Thus, other rheological properties of a colloid-polymer mixture may change with the surface charge of particles.

As described above, the SiO₂-PEO mixture demonstrates shake-gel and shear thickening. The surface charge and aggregation of silica depend strongly on the pH and ionic strength. While the PEO is a non-ionic polymer, the adsorption of PEO on silica is also affected by pH [21]. Nevertheless, systematic studies on the effect of pH and ionic strength on the shake-gel and shear thickening of the SiO₂-PEO mixture are lacking. In order to gain insights into the mechanism of shake-gel and shear thickening of a colloid-polymer mixture, we have carried out systematic experiments on the effect of pH on the shake-gel and shear viscosity of the mixture of silica-PEO. In this paper, we report the significant influence of pH and ionic strength on the phase behavior, relaxation time, and viscosity of the mixture of silica and PEO.

2. Experimental

2.1. Materials

The silica suspension used was LUDOX TM-50 obtained from Sigma-Aldrich. The specific surface area of the silica was 139 m²/g. The concentration of silica was 49.9 wt.%. The Na⁺ concentration and pH were measured using a compact Na⁺ meter (B722, Horiba) and a compact pH meter (B212, Horiba), respectively, and they were approximately 80 mM and 9.3, respectively. The particle diameter was 30–34 nm [8]. The hydrodynamic diameter was 32.35 ± 0.22 nm from our result of dynamic light scattering (Zetasizer Nano, Malvern). Colloidal silica particles have silanol groups on their surface. The protonation

of surface silanol groups depends on the pH and ionic strength [22].

PEO is a linear neutral polymer whose molecular formula is $\text{HO}[\text{CH}_2\text{CH}_2\text{O}]_n\text{-H}$. In this study, PEO with the average molecular weight of 1.0×10^6 g/mol was obtained from Alfa Aesar. The z -average radius of gyration, $\langle s^2 \rangle_z^{1/2}$, and the overlap concentration, C^* , of PEO can be calculated using the empirical equations (1) and (2), respectively [8].

$$\langle s^2 \rangle_z^{1/2} = (4.08 \times 10^{-4} \times M_w^{1.16})^{1/2} \quad (1)$$

$$C^* = \frac{3M_w}{4\pi N_A \langle s^2 \rangle_z^{3/2}} \quad (2)$$

where M_w and N_A are the average molecular weight of PEO and Avogadro's number, respectively. In this study, $\langle s^2 \rangle_z^{1/2}$ and C^* were 61 nm and 1.7×10^{-3} g/cm³, respectively. HCl solution and NaOH solution (Wako pure chemicals) were used to adjust the pH, and NaCl (Wako pure chemicals) was used to adjust the ionic strength. Deionized water (Elix, Millipore) was used to prepare the solutions and suspensions.

2.2. Methods

All the experiments were performed at the room temperature of 20 °C. The solution of PEO was prepared by adding PEO to deionized water, and the PEO solution was stirred for three days using a magnetic stirrer (AS-1) in dark. The prepared PEO solution was used within two weeks of preparation. In order to prepare the mixture of silica and PEO, pure water and silica suspension were added to a 30-mL glass vial. Subsequently, HCl or NaOH solution was added to the vial. Finally, the PEO solution was added to the mixture. All the prepared samples had a mass of 5.0 g and silica concentration of 20 wt.%. We also prepared mixture samples with different values of NaCl concentration and pH. Several samples with various ionic strengths were also prepared by adding NaCl solution instead of HCl or NaOH solution. For each sample, the value of PEO mass divided by the total silica surface area, C_p , was

calculated.

In order to observe the behavior of the mixture after shaking, the vial containing silica-PEO was held at the top and shaken for 15 s by flexing the wrist holding the vial 5–6 times per second. Subsequently, we observed the change of the state of the mixed suspension compared with that before shaking. A phase diagram was constructed by performing this process at different values of pH. For samples showing the phase transition from liquid to gel via shaking, the relaxation process from gel to liquid was photographed.

The viscosity of some samples before shaking was measured using a cone-plate type rheometer (Merlin VR, Rheosys) as a function of the shear rate or time. The diameter of the cone was 30 mm and the gap angle was 2° . The shear rate ranged from 100 to 5000 s^{-1} . Both the delay time and integration time were set to 5 s and a measurement was obtained for 400 s. The measurements of viscosity were carried out 1–4 times for each condition. Approximately the same flow curves were obtained.

3. Results and discussion

3.1. Visual observation

The state of the sample immediately after shaking is shown in Fig. 2. The concentration of Na^+ was approximately 12 mM. The samples at a pH less than 6.8 and C_p beyond 0.023 mg/m^2 were flocculated before shaking and fluidity change was not observed after shaking (Fig. 3 (a)). The flocculated suspensions appeared sticky and adhered to the vial wall. The suspension containing only silica was not flocculated even when the pH was decreased to 1.9, where silica has less charge. Silica nanoparticles are stable at low pH probably owing to the existence of a gel-like or hairy layer on the surface [23]. Our experimental results suggest that the silica flocculation was not triggered by the decrease of electrostatic repulsion caused by the decrease in the surface potential, but by the bridging by PEO. The two samples at the pH of 8.9 and $C_p=0.28 \text{ mg/m}^2$ and at the pH of 10.0 and $C_p=0.22 \text{ mg/m}^2$ were too viscous to flow in

the vial even though they were shaken. These samples did not demonstrate a phase transition (Fig. 3 (b)). The samples at the pH of 10.4 and C_p from 0.022 to 0.28 mg/m² generated bubbles by shaking, but did not show a change in fluidity and remained liquid-like (Fig. 3 (e)). For pH in the range of 8.0 to 9.9, some samples showed a decrease in their fluidity (Fig. 3 (d)) or a transition to the gel state (Fig. 3 (c)) after shaking even if they were in the liquid state before shaking. The result indicates that the bridging network can be formed in the pH range of 8.0–9.9. Many of these gels were reversible such that they returned to liquid state if they were maintained at rest for the time of relaxation. These results demonstrate that the formation of reversible shake-gel is possible when both the repulsive force between silica particles and the adsorption affinity of PEO to silica allowing the bridging of silica particles by PEO co-exist. When this condition is satisfied, the network-like structure of PEO molecules connected by silica nanoparticles can expand to the entire mixture and form the gel. At low pH, however, the lack of particle-particle repulsion results in the formation of entangled aggregates composed of particles and polymers. Therefore, we could not expect the formation of an expanded network of PEO nor the appearance of the shake-gel. However, when the pH of the mixture is more than 10, the concentration of deprotonated silanol groups of silica SiO⁻ particles is high. In this case, we suggest that the adsorption of PEO by hydrogen bonds is weakened and thus, the formation of the bridging network is inhibited. Consequently, the gel formation by shaking does not occur.

Figure 4 shows the pH dependency of the relaxation time of gels obtained in the pH range of 8.2 to 9.8 at $C_p=0.107$ mg/m² and the ionic strength of 12 mM. Figure 4 (a), (b), and (c) represent the sample at the pH of 8.2, 9.0, and 9.8, respectively. The images in Fig. 4 represent the sample before shaking, and 5 s, 50 s, and 100 s after shaking from left to right, in that order. A hundred seconds after shaking, the sample

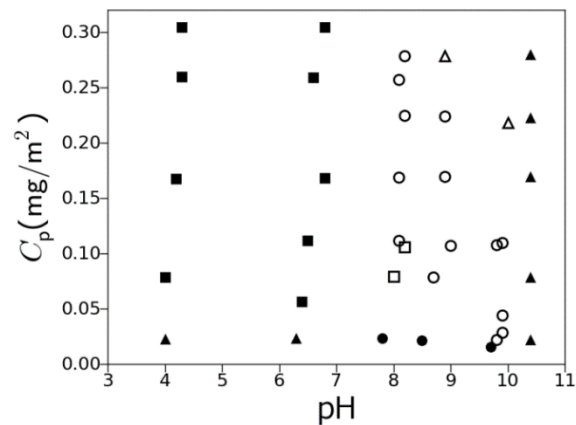


Fig. 2 Phase diagram: fluid (▲); flocculation (■); fluidity decreased (●); gel (no relaxation) (□); gel (relaxation) (○); too viscous (△)

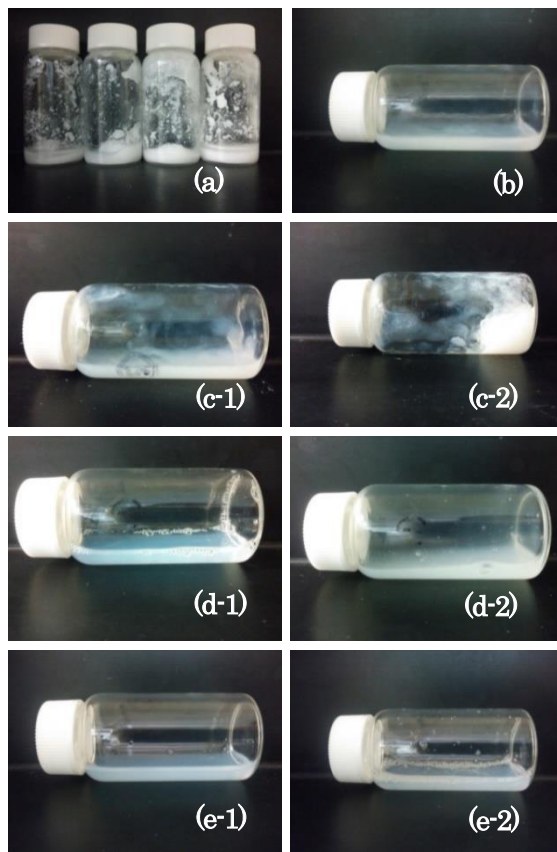


Fig. 3 State of each sample before or after shaking: (a) pH 4.3–6.8 and $C_p=0.26\text{--}0.30$ mg/m², (b) pH 8.9 and $C_p=0.28$ mg/m², (c-1) pH 8.0 and $C_p=0.079$ mg/m² before shaking, (c-2) after shaking, (d-1) pH 9.7 and $C_p=0.015$ mg/m² before shaking, (d-2) 5 s after shaking, (e-1) pH 10.4 and $C_p=0.17$ mg/m² before shaking, (e-2) 5 s after shaking

at the pH of 9.8 almost recovered to liquid state apparently, whereas at the pH of 9.0, the sample was in the process of returning to liquid state. The sample at the pH of 8.2 was still in the gel state 100 s after shaking and the transition to liquid was not observed even after eight months. These results demonstrate that the relaxation time of gel becomes longer and an irreversible gel is formed as the pH decreases from 9.9 to 8.0. Notably, we also observed that new states, i.e., irreversible gels of silica-PEO, were obtained at the pH of approximately 8.0 (Fig. 2 □). According to reference [21], the adsorbed amount of PEO onto silica increases with the decrease in pH. At low pH, silica particles have significant SiOH on their surface such that the adsorption affinity of PEO becomes stronger. As the pH approaches 8.0, many segments of PEO bind to the surface of silica and the formed bridging network can be stiff and irreversible. However, although the adsorption affinity of PEO is strong at a pH less than 6.8, the samples flocculate and do not show symptoms of gelation. This is probably due to the effect of the decrease of interparticle repulsion owing to the reduced surface potential, suggesting that some degree of interparticle repulsion is required for the transition from liquid to gel states.

The dependence of the relaxation time on the ionic strength was examined at the ionic strengths of 13 and 40 mM at the pH of 9.8 and $C_p=0.108$ mg/m². Under these conditions, however, an apparent difference in the relaxation time was not observed. The compression of the electrical double layer did not significantly affect the relaxation time. This result indicates that the number of hydrogen atoms on the surface of silica determines the relaxation time.

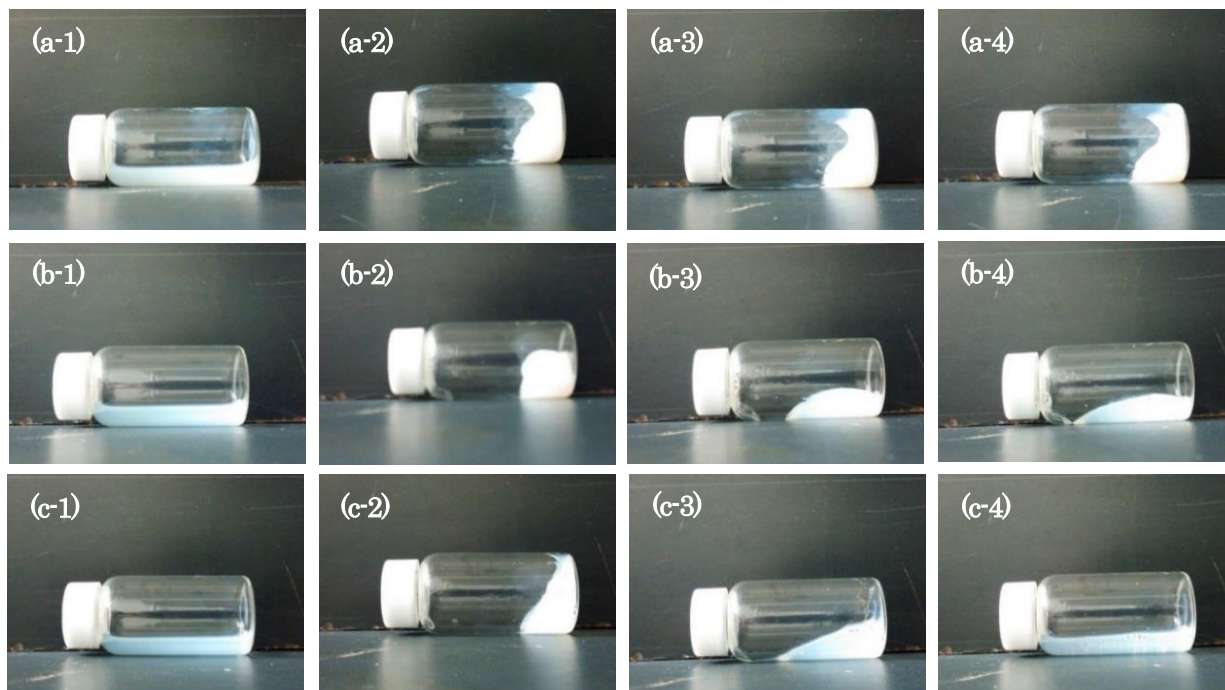


Fig. 4 Dependence of relaxation time of gel on pH at $C_p=0.107$ mg/m². (a) pH 8.2, (b) pH 9.0, (c) pH 9.8.

The images were captured before shaking, and 5 s, 50 s, and 100 s after shaking from left to right, in that order.

3.2. Viscosity

The result of viscosity measurement at the pH of 9.4, low dosage of PEO, $C_p=0.022$ mg/m², under which conditions gelation did not occur, is shown in Fig. 5. In the range of ionic strength of 12 to 40 mM, shear thinning, shear thickening, and shear thinning were observed in regular order as the shear rate increased. Further, the critical shear rate at which the viscosity begins to rise decreased as the ionic strength increased from 12 to 40 mM. The degree of increase in viscosity decreased with the increase in ionic strength. At the ionic strength of 150 mM, shear thickening might occur below the lowest shear rate in this experiment. As the ionic strength increased, the electrical double layer was compressed, and the interparticle repulsion decreased. Thus, in the suspension, the bridging network could be formed at a low shear rate without the extension of PEO [24]. At 280 mM, shear thickening did not occur. Our results

reaffirm that a certain degree of interparticle repulsion is required to induce shear thickening of the silica-PEO mixture. The interparticle attraction becomes dominant owing to the low interparticle repulsion and thus, the bridging network cannot spread out in the sample. Therefore, shear thickening did not occur at 280 mM.

The result of measured viscosity at various values of pH, $C_p=0.022 \text{ mg/m}^2$, and ionic strength of 12 mM is shown in Fig. 6. For pH in the range of 8.0 to 9.9, shear thinning, shear thickening, and shear thickening occurred. The critical shear rates decreased as the pH decreased from 9.4 to 8.3. For pH in the range of 9.4 to 9.9, the critical shear rate did not change significantly but the degree of rise of viscosity was reduced by half. Further, the shear thickening did not occur at the pH of 10.1. These results can be explained by the change of deprotonated silanol groups.

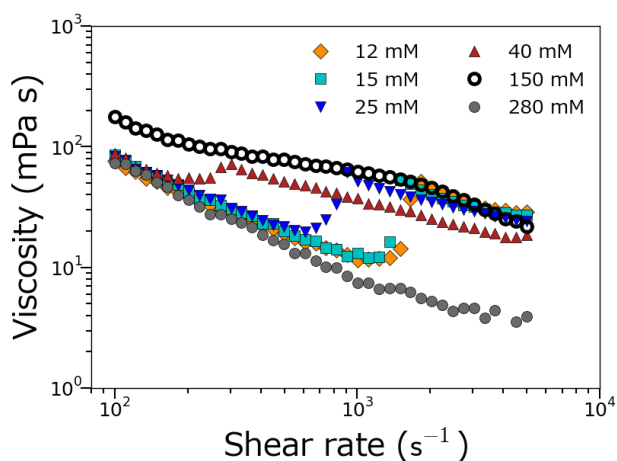


Fig. 5 Relation between viscosity and shear rate at various ionic strengths; $C_p=0.022 \text{ mg/m}^2$; pH=9.4.

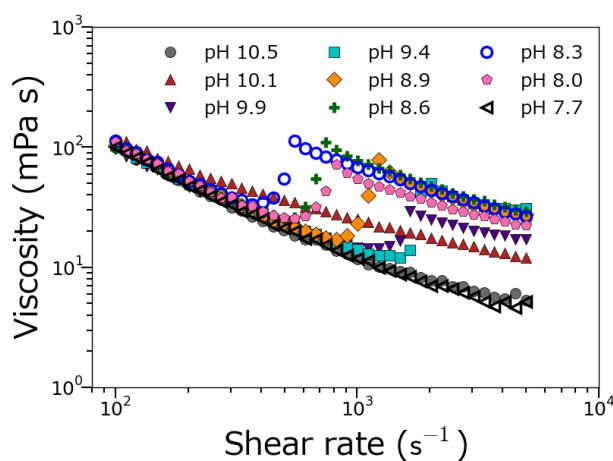


Fig. 6 Relation between viscosity and shear rate at various values of pH; $C_p=0.022$ mg/m²; ionic strength = 12 mM.

In other words, at higher pH, the silanol group of the particle surface is deprotonated and the adsorption affinity of PEO to silica by the hydrogen bonding is weakened. Consequently, the formation of the bridging network is suppressed. When the pH is lowered from 8.3 to 7.7, the degree of rise of viscosity decreases and finally, the shear thickening disappears. This viscosity behavior can be explained by the reduction of the interparticle repulsion as mentioned for the mechanism wherein gelation does not occur at low pH.

The temporal variation of viscosity for various conditions at $C_p=0.021$ mg/m² is shown in Fig. 7. The temporal variation of viscosity was measured at the shear rates of 100, 300, and 1000 s⁻¹. At the pH of 9.5 and Na⁺ ionic strength of 10 mM, the viscosity suddenly begins to increase after 140 s at 1000 s⁻¹ whereas the viscosities are constant at other shear rates (Fig. 7 (a)). At the pH of 8.4, the viscosity begins to increase after 60 s at 300 s⁻¹ (Fig. 7 (b)). When the ionic strength is increased to 33 mM, the rise in viscosity occurs within 20 s at 300 s⁻¹ (see Fig. 7 (c)). Lowering the pH or increasing the ionic strength reduces

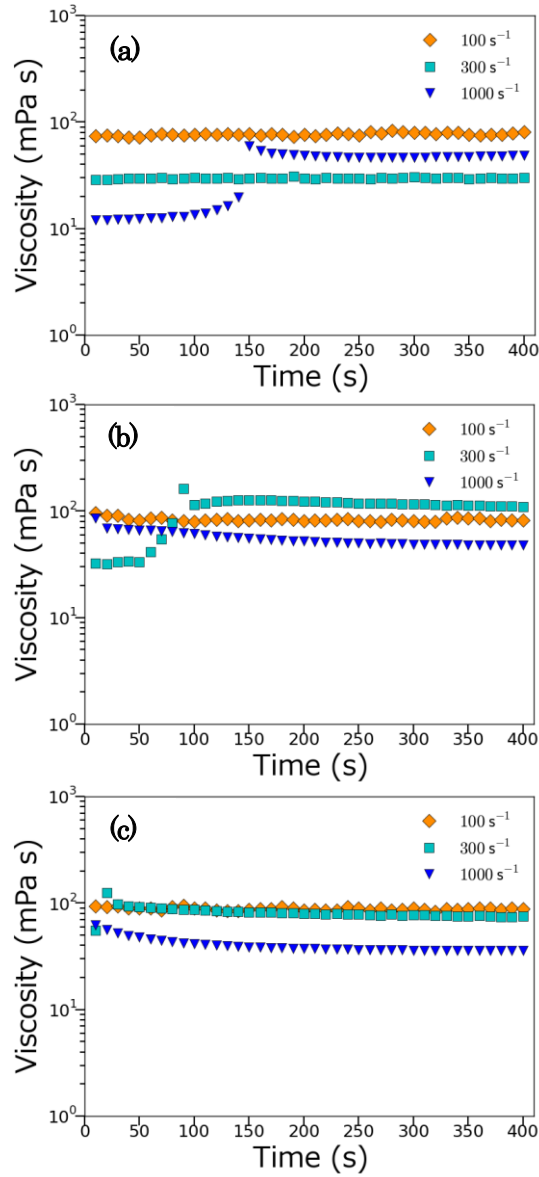


Fig. 7 Viscosity as a function of time at various shear rates, $C_p=0.021$ mg/m². (a) pH is 9.5 and ionic strength is 10 mM, (b) pH is 8.4 and ionic strength is 10 mM, (c) pH is 9.5 and ionic strength is 33 mM.

the critical shear rate as mentioned above. Furthermore, decreasing the interparticle repulsion by decreasing the pH or increasing the ionic strength shortens the time required for the viscosity to rise even at a constant shear rate.

The viscosity of the PEO solution decreases under acidic conditions in the presence of metal ions owing to the degradation of PEO [25]. In order to verify this issue, we measured the viscosity of 20 wt.%

silica suspension and 0.06 wt.% PEO solution separately using a capillary viscometer (μ Visc, CA RheoSense). The viscosity of concentrated PEO solution decreases at high shear rate [26]. In our experiment, the values of viscosities of silica suspension with the pH of 9.3 and PEO solution with the pH of 6.8 were 2.0 and 1.5 mPa s, respectively, indicating that they are Newtonian fluids. A significant change of viscosity was not observed for both silica suspensions at the pH in the range of 3.8 to 10.5 and PEO solution at the pH in the range of 2.9 to 10.5. At high ionic strengths of 33 mM and 322 mM, the viscosity of PEO solution decreased approximately 17 %. The viscosity of the mixed suspension at a low shear rate was approximately 100 mPa s irrespective of pH or ionic strength (Figs. 5 and 6). The viscosity of the silica-PEO mixture is much higher than that of the silica suspension or PEO solution. Therefore, the degradation of PEO with the pH or ionic strength was not significant in this experiment.

Some previous studies mentioned that the gelation and shear thickening are related to the Peclet number [5], [7], [27] defined as

$$Pe = \frac{6\pi\dot{\gamma}a^3\mu}{k_B T} \quad (3)$$

where $\dot{\gamma}$, a , μ , k_B , and T are the shear rate, particle radius, viscosity of the mixture, Boltzmann constant, and absolute temperature, respectively. The calculated Peclet numbers at $C_p=0.022$ mg/m² are shown in Tables 1 and 2, where Pe_{\max} and Pe_{\min} indicate the Peclet numbers calculated at the maximum and minimum viscosities, respectively. The viscosity at the local minimum, namely, at the critical shear rate, all Peclet numbers are in the range of 0.2 to 0.3; $Pe < 1.0$. The bridging network can be formed when the energy generated by shear is smaller than the thermal energy. The adsorption energy of PEO on silica is approximately $1.2 k_B T$ per segment [27]. Hence, it is expected that PEO desorption occurs when $Pe > 1.2$. In Tables 1 and 2, Pe_{\max} values are approximately equal to or larger than 1.2 except for the pH of 9.9 and ionic strength of 40 mM. Shear thinning following shear thickening may occur by the desorption of PEO.

In order to consider the effect of the interparticle potential as a function of the pH or ionic

strength on the critical shear rate at which shear thickening occurs, we calculate the surface charge and potential of silica by using the 1pK basic Stern model [15]. This model has been used to describe the charging behavior of various oxides such as silica. In the 1pK basic Stern model, a set of simultaneous equations for SiOH (and SiO⁻) density, surface potential, surface charge density, etc., is solved. The surface potential is used to calculate the maximum value of ϕ_{Total} , i.e., the interaction potential of silica particles described in equation (4).

$$\Phi_{Total} = \frac{64\pi a \Gamma_0^2 n_\infty k_B T}{\kappa^2} \exp(-\kappa H) - \frac{Aa}{12H} \quad (4)$$

$$\Gamma_0 = \tanh\left(\frac{ze\psi_0}{4k_B T}\right) \quad (5)$$

In equation (4), the first and second terms on the right-hand side express the electrostatic repulsion and attraction between spherical particles, respectively. Further, n_∞ , κ , H , A , z , e , and ψ_0 indicate the number concentration of ions, thickness of electrical double layer, distance between particles, Hamaker constant, valent of ions, elemental electrical charge, and surface potential, respectively. The Hamaker constant is set to 8.3×10^{-21} J [22]. The interaction potential is a function of the distance between particles and this usually has a maximum value at a certain distance called a potential barrier. For silica nanoparticles, the maximum value of the interaction potential generally decreases with the decrease in pH or increase in ionic strength. The critical shear rate is plotted

Table 1 Peclet number at the maximum or minimum viscosity at each pH

pH	8.0	8.3	8.6	8.9	9.4	9.9
Pe_{min}	0.27	0.23	0.24	0.27	0.36	0.35
Pe_{max}	1.13	1.19	1.56	1.84	1.94	0.96

Table 2 Peclet number at the maximum or minimum viscosity at each ionic strength

Ionic strength (mM)	12	15	25	40
$P_{\theta_{\min}}$	0.22	0.21	0.23	0.19
$P_{\theta_{\max}}$	1.79	1.52	1.06	0.41

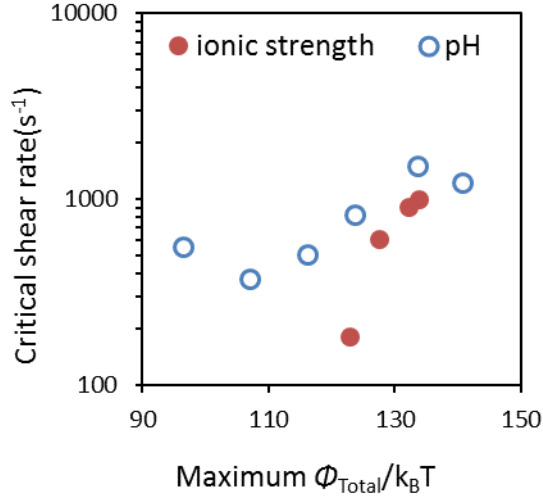


Fig. 8 Relationship between critical shear rate and maximum ϕ_{Total}

against the maximum ϕ_{Total} in Fig. 8. In both experiments, when the ionic strength or pH was changed, good correlation could be observed between the maximum ϕ_{Total} and critical shear rate. At the same ϕ_{Total} , however, the critical shear rate from the series obtained by changing ionic strength was not quantitatively consistent with that obtained by changing pH. The critical shear rate is not determined only by the degree of interparticle repulsion, and thus, other factors should be considered in future studies.

4. Conclusion

The mixed suspension of silica and PEO shows a reversible transition from a liquid-like state to gel-like state by shaking for a certain range of pH. The suspension at low pH is flocculated and sticky. The mixture does not show such a transition at high pH because the silica surface has fewer hydrogen atoms. At low pH, shake-gel does not occur because the interparticle repulsion is too weak or the particle surface

bears too many hydrogen atoms. The relaxation time of gel is longer at lower pH whereas it does not change with the ionic strength under these experimental conditions. The relaxation time is mainly controlled by the amount of hydrogen atoms on the silica surface rather than the degree of interparticle repulsion.

The results of viscosity measurement at the PEO concentration of 0.06 wt.% demonstrate that the shear thickening occurs at a certain pH range of 8.0–9.9 but not at high or low pH and high ionic strength. The critical shear rate at which the viscosity rises decreases from 1500 to 368 s⁻¹ with the increase in ionic strength or decrease in pH. These results suggest that a certain degree of repulsion between silica particles and the adsorption affinity of PEO to silica are required for shear thickening.

A positive correlation can be observed between the critical shear rate and the maximum value of interparticle potential ϕ_{Total} . Therefore, we consider that one of the factors determining the critical shear rate is the interparticle repulsion. For the same maximum ϕ_{Total} , however, the critical shear rates from the experimental series obtained by changing the pH are not quantitatively consistent with those obtained by varying the ionic strength. Thus, other factors controlling the critical shear rate probably exist in addition to the degree of interparticle repulsion.

Acknowledgments

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Conflict of interest

The authors declare that they have no conflict of interest.

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