

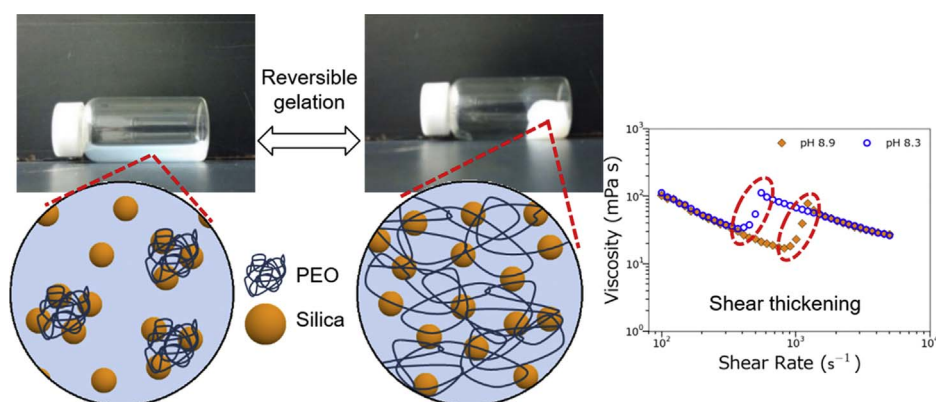


Research Paper

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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GRAPHICAL ABSTRACT



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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.

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

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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.

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 HO-[CH₂CH₂O]_n-H. In this study, PEO with the average molecular weight of 1.0 × 10⁶ 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 Eqs. (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,

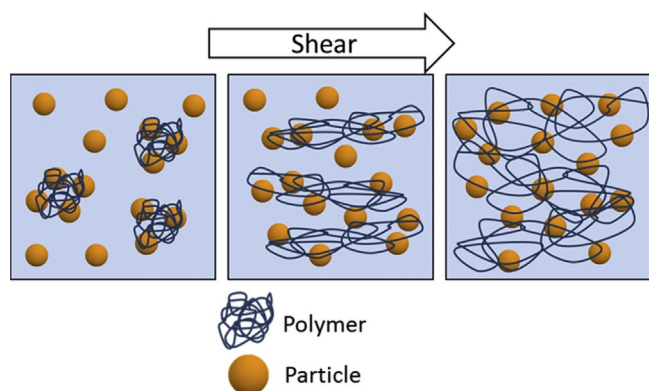


Fig. 1. Schematic illustration of the mechanism of gelation and shear thickening.

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