

Bimodal colloid gels of highly size-asymmetric particlesJooyoung Lee,¹ Seong Jae Lee,² Kyung Hyun Ahn,^{1,*} and Seung Jong Lee¹¹*School of Chemical and Biological Engineering, Institute of Chemical Process, Seoul National University, Seoul, 151-744 Korea*²*Department of Polymer Engineering, The University of Suwon, Gyeonggi, 445-743 Korea*

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We report a type of colloidal gel, induced by a minute incremental addition of mutually attractive small particles (size ~ 12 nm) to a suspension of highly charged large particles (size ~ 500 nm). The gel's morphological behavior does not follow the typical power-law scaling for fractal clusters. Its unique scaling behavior has two distinct power-law indices, based on particle volume fraction. We show the unique scaling behavior arises when nonfractal networks of large particles are bridged by small-particle clusters, which occurs between a lower and upper critical boundary of small particle volume fraction.

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I. INTRODUCTION

Coating fluids, which contain highly size-asymmetric particles, are widely used in many applications, including Li-ion batteries, multilayer ceramic capacitors, and electrical conductors [1–3]. To obtain a desired performance in the final product, particles of different size and surface potential are often used together, which can bring about unexpected results such as aggregation of particles and changing rheological behavior.

These types of complex behavior have been investigated in various model systems of highly size-asymmetric particles, and can be classified based on the relationships of surface potentials between large and small particles. When the two particles are large and small hard spheres, the depletion effect arises because of the size mismatch between the constituent particles, resulting in an attractive interaction between the large particles [4–7]. In a model system of positively and negatively charged particles, the attractive interaction between the small and large particles induces bridging between two or more large particles to form bigger aggregates [8,9]. When the large particles are negligibly charged, they are stabilized by the addition of well-stabilized small particles [10,11]. However, the systems used in the previous studies used well-stabilized small particles, which are quite different from the materials used in industry.

Slurries used in industry include polymers to induce interparticle repulsion and colloidal stability. The polymers adsorb onto the surface of the particles, and are used because the particles are typically suspended in organic solvent, where stabilization by electrostatic double layer is not effective. Unfortunately, polymers do not thoroughly adsorb onto small particles with sizes of a few nanometers. Consequently, under this condition the nanoparticles are not well dispersed, while large particles are stabilized. To understand the behavior of binary particle systems used in industry, therefore, we need to devise a new type of model system composed of attractive nanoparticles.

In this work, we designed a model system consisting of two different kinds of particles with highly asymmetric sizes. Their surface potentials were tuned by varying the solution

pH, which caused the large particles to be electrostatically stabilized and the small particles to be attractive to each other. We found that the rheological behavior of the charged particle suspension was dramatically changed by a very small increase in the amount of small particles. Yielding was observed at low shear rate with shear thinning, and a plateau elastic modulus appeared with the addition of small particles. Moreover, the bimodal gels that formed under this condition showed behavior quite different from typical colloidal gels: the elastic moduli cannot be described by a simple power-law scaling but rather have two regions of vastly different exponents. We report the existence of gels having two regions of distinct morphological characteristics, from which it is concluded that the network structure formed by the small-particle clusters determines the rheological behavior of the whole bimodal gel system.

II. MATERIALS AND METHODS

We used highly size-asymmetric particles of charge-stabilized spherical polystyrene (PS) with a diameter $d = 500$ nm and alumina coated silica (Ludox CL, Sigma Aldrich) with a diameter $d = 12$ nm. The PS particles were synthesized by emulsifier-free emulsion polymerization [12]. 20 wt% of PS stock solution and 30 wt% Ludox CL stock solution were mixed with deionized water to obtain various volume fractions. The pH of the suspension was adjusted to 7.5 ± 0.3 , which is the isoelectric point (IEP) of alumina-coated silica, using NH_4OH . Under this condition, the ζ potential of silica was nearly zero, while the ζ potential of PS was -40 mV, indicating a highly charged state. All the suspensions were mixed with a magnetic stirrer at 100 rpm for 30 min, followed by sonication for 30 min to break large aggregates, if any.

The rheological properties of the suspension were measured using a stress controlled type rheometer, (AR-G2, TA Instruments) at 25°C with a cone and plate fixture. To obtain reproducible results, all measurements were performed after preshearing at 500 s^{-1} for 1 min and equilibration for 300 s, enough to reach a quasisteady state, where G' remained nearly constant over time. This procedure resulted in reproducibility of the elastic moduli to within 10%. Gel transition was determined by rheological method [13]. The onset of gelation was identified by the transition from liquidlike to solidlike behavior with the plateau elastic modulus. Microstructure was observed by cryogenic scanning electron microscopy

*ahnnet@snu.ac.kr

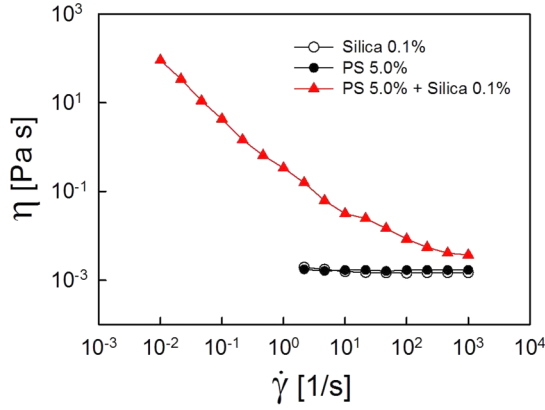


FIG. 1. (Color online) Effect of adding small particles (silica) to a suspension of large particles (PS). Steady shear viscosity as a function of shear stress for a suspension of 0.1 vol% silica (open circles), 5.0 vol% PS (closed circles), and a mixture of 5.0 vol% PS and 0.1 vol% silica (closed triangles).

(cryo-SEM, S-4700, Hitachi), in which a cross section was prepared and imaged after the suspension was first quenched with liquid nitrogen. Structural analysis of the suspension at a few nanometers scale was supplemented by synchrotron small angle x-ray scattering (SAXS, Pohang Light Source II, Korea). The incident x-ray wavelength (λ) was 0.7953 Å. For SAXS samples with thickness of 1 mm were placed in a cell with parallel mica windows.

III. RESULTS AND DISCUSSION

Suspensions composed of each type of particle, and a mixture of both particles, were prepared separately. We measured the steady shear viscosity of each suspension and show the results in Fig. 1. Colloidal dispersions with a single species of particles such as 5.0 vol% PS suspension and 0.1 vol% silica suspension show Newtonian behavior, with a constant viscosity close to 10^{-3} Pa s. When 0.1 vol% of small particles are added to the 5.0 vol% PS suspension, however, the flow curve exhibits shear thinning. The viscosity decreases several orders of magnitude, indicating that the addition of small particles induces the formation of a colloidal network and a transition from liquidlike to solidlike behavior [14].

Because the small particles are mutually attractive, they form a gel above a critical threshold. The critical gel point could be clearly determined from the rheological behavior of the suspension. As shown in Fig. 2(a), when the volume fraction of small particles is too low ($\phi < 3 \times 10^{-3}$), the suspension shows a Newtonian behavior. When the volume fraction of small particles exceeds a critical threshold ($\phi > 3 \times 10^{-3}$), the suspension shows gel-like behavior, exhibiting a constant G' independent of frequency, as in the right-hand side of Fig. 2(a). From this measurement, the critical gel point of small particles is determined as $\phi_c = 3 \times 10^{-3}$.

The onset of bimodal gelation could be also clearly determined from the rheological behavior of the suspension. As shown in the left plot of Fig. 2(b), when the volume fraction of added small particles was too low ($\phi_{\text{small}} < 10^{-4}$), the bimodal suspension exhibits a Newtonian behavior, indicating no

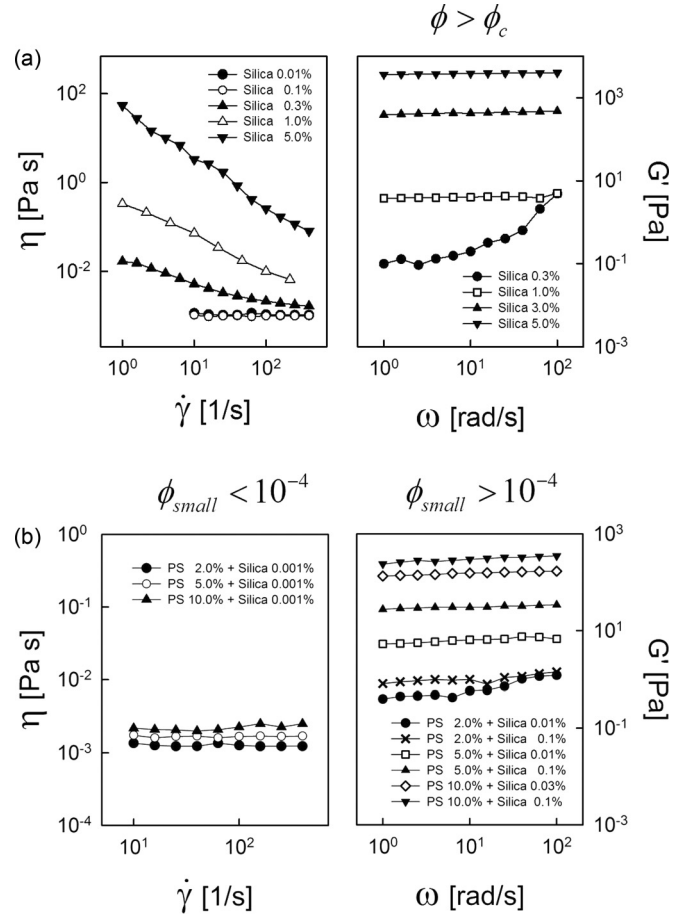


FIG. 2. The rheological properties for (a) the suspension of small particles (silica) and (b) the bimodal suspensions (PS+silica).

spanning network is being formed. After the amount of added small particles exceeds a critical threshold $\phi_{\text{small}} > 10^{-4}$, the bimodal suspension shows gel-like behavior, showing a constant G' independent of frequency, as in the right side of Fig. 2(b). The amount of small particles required for the onset of gelation is much lower than the critical gel point of small particles ($\phi_c = 3 \times 10^{-3}$).

To compare the mechanical properties of bimodal gels formed by the addition of small particles, with colloidal gels consisting only of small particles, we explored the scaling behavior of elastic modulus G' on total volume fraction of the particles. Because G' is nearly independent of the frequency, we could identify a plateau modulus G'_p for the colloidal gels. The elastic modulus of gels of monodisperse small particles followed a scaling behavior $G'_p = A\phi^v$ with an exponent of 4.6 ± 0.1 , in good agreement with the scaling observed for a variety of previously reported colloidal gels, in which the power-law exponent v often has values between 3 and 5 [15–17].

In contrast, the bimodal gels that resulted from the addition of small particles were not described by a single power-law relationship, but rather had two regions of vastly different exponents. This is clearly observed in Fig. 3 where small particles were added to fixed concentration PS suspensions of 2.0 vol%, 5.0 vol%, and 10.0 vol respectively. At high

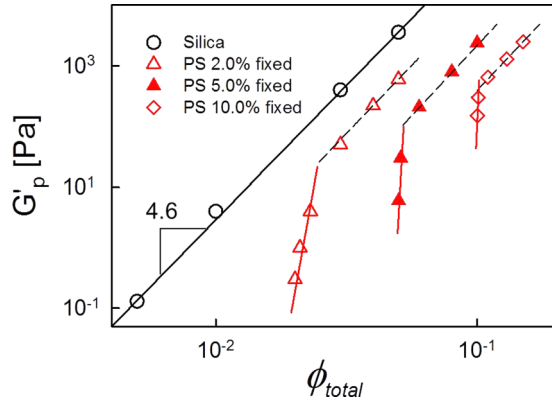


FIG. 3. (Color online) Power-law scaling of plateau modulus with volume fraction of total particles for the silica suspension (open circles) and the bimodal suspensions of fixed PS concentration at 2.0 vol% (open triangles), 5.0 vol% (closed triangles), and 10.0 vol% (open diamonds). Solid lines and dashed lines are the results of fits to power-law equations, $G'_p = A\phi^\nu$. For bimodal suspensions, fitting was performed separately for the data in the high- and low-exponent regions.

concentration of small particles, the exponents of the bimodal gels are the same as those of monodisperse colloidal gels, 4.6 ± 0.1 . Each data set of bimodal gels with PS loading of 2.0 vol%, 5.0 vol%, and 10.0 vol% has the same exponent in this region. On the other hand, at low concentration of small particles, the bimodal gel shows a significant difference from the typical colloidal gels, with a power-law exponent much larger than 3–5. Because various models based on fractal aggregates predict exponents between 3 and 5, the results of this study suggest that the microstructure of the bimodal gels at low concentration of small particles is significantly unlike a fractal structure. Such a distinct exponent demonstrates that the elastic moduli of bimodal gels cannot be scaled onto a single master curve. This conclusion deviates from previous reports on colloidal gels whose elastic moduli scale onto a single curve with respect to the volume fraction of the particles [15].

Interestingly, for all the sets of bimodal gels, the volume fraction of small particles was almost same, $\phi_{\text{small}} \sim 3 \times 10^{-3}$ at the transition point of the two distinct curves, and that the volume fraction is identical to the gel point of monodisperse small-particle suspensions. This result presents a different point of view than previous research on binary colloids, in which the relative contents of two different particles have been considered to be the main parameter that determines mechanical behavior [7]. In our system, the transition of mechanical behavior is determined solely by the small particles' ability to form gels.

Using Cryo-SEM and SAXS, we explored the structure of the bimodal gels and the origin of their rheological behavior. We choose two representative samples, one each from the high-exponent region (low small-particle loading) and low-exponent region (high small-particle loading), corresponding to PS 5.0 vol% + silica 0.1 vol% and PS 5.0 vol% + silica 1.0 vol% samples.

First, the microstructures of the small particles were analyzed by SAXS to understand their morphology at a few nanometers scale. In the SAXS experiments, although both

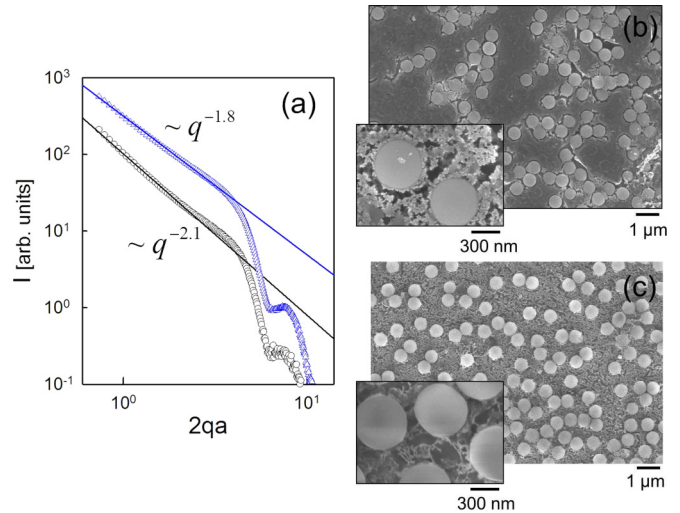


FIG. 4. (Color online) Microstructure of two representative samples, one each from a high-exponent region (low small-particle loading) and a low-exponent region (high small-particle loading). (a) SAXS data of PS 5.0 vol% + silica 1.0 vol% (open triangles) and PS 5.0 vol% + silica 0.1 vol% (open circles) in which solid lines are fitted to the equation $I = q^{-D_f}$, (b) cryo-SEM image of PS 5.0 vol% + silica 1.0 vol%, (c) cryo-SEM image of PS 5.0 vol% + silica 0.1 vol%.

large and small particles exist in the fluid we can only observe the structure formed by the small particles, as the operating q range is $q > 0.06 \text{ nm}^{-1}$. As shown in Fig. 4(a), they exhibit a power-law behavior whose exponent gives an estimate of the fractal dimension, with values of 2.1 and 1.8 for PS 5.0 vol% + silica 0.1 vol% and PS 5.0 vol% + silica 1.0 vol% samples, respectively. A similar decrease of fractal exponent in a scattering experiment was observed with increasing particle concentration in a previous study [18]. Therefore, from the microstructure of the two representative samples at high- and low-exponent regions, we confirmed that the small particles form aggregates with a fractal structure regardless of their concentrations.

Although the small particles in the two samples had similar fractal clusters, we found distinctly different morphology between the two samples at micrometer scale in cryo-SEM images. At high small-particle loading ($\phi_{\text{small}} > \phi_{\text{small, gel}}$), the large particles formed a network structure, as in Fig. 4(b). This resembles the fractal structure of typical colloidal gels, which have been reported previously [19]. At low small-particle loading ($\phi_{\text{small}} < \phi_{\text{small, gel}}$), on the other hand, the large particles did not form a fractal-like structure and were just interspersed throughout the fluid [Fig. 4(c)].

The inset image of Fig. 4(b) shows that the clusters of small particles fully cover the surfaces of the large particles, which implies that the large particles are a part of the space-filling network formed by small particles. Therefore, the microstructure of high small-particle loading exhibits fractal networks composed of both small and large particles, leading to the power-law exponent between 3–5.

At low small-particle loading, although the large particles seem to be well dispersed, a closer examination, as shown in the inset of Fig. 4(c), reveals that the small particles are

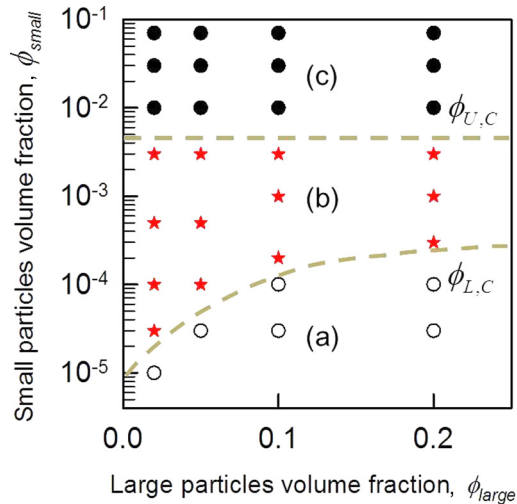


FIG. 5. (Color online) Phase diagram of bimodal suspensions of repulsive large particles and attractive small particles ($d_{\text{large}} = 500$ nm and $d_{\text{small}} = 12$ nm). Open circles represent a fluid consisting of discrete clusters of large and small particles, closed stars represent a bimodal gel in which small-particle clusters bridge large particles, and closed circles represent a bimodal gel in which both small and large particles form fractal structures. The lower and upper dashed lines illustrate the experimentally observed critical boundary of phase behavior as a function of small particle volume fraction, $\phi_{L,C}$ and $\phi_{U,C}$.

bridging these large particles in the medium. This bridging allows the interspersed large particles to form a spanning network and exhibit gel behavior. The small particles form fractal clusters as seen in Fig. 4(a), and the discrete fractal clusters of small particles simply bridge the large particles: the large particles do not form a fractal structure, which explains why the rheological behavior of the samples with low small-particle loading does not follow the typical power-law behavior of previously reported colloidal gels.

As the particles are dispersed in aqueous medium, the balance between the electrical double-layer force and the van der Waals force determine the particle interaction. The interaction between the same species of particles is clear—the electrical double-layer repulsion dominates between highly charged large particles and the van der Waals attraction dominates between neutral small particles. As in Figs. 4(b) and 4(c), the attractive interaction plays a dominant role between large and small particles. According to a model that calculates the electrical double-layer repulsion between dissimilar particles [20], the electrostatic repulsion does not arise between large and small particles, even though the Debye length of large particles changes. In addition, the behavior of bimodal gels in this study is observed at very low volume fraction of small particles, thus it is distinguishable to depletion gels, which are observed at higher volume fraction in the region

of $\phi_{\text{small}} \geq 0.07$ for $\phi_{\text{large}} = 0.2$ at various size ratios [21]. Thus the van der Waals attraction is the only force that drives the gel formation.

We distinguished two types of bimodal gels and plotted the phase diagram in Fig. 5, which is divided into three regions: Fig. 5(a), a fluid consisting of discrete clusters of small and large particles below the critical value of small-particle volume fraction, $\phi_{\text{small}} < \phi_{L,C}$; Fig. 5(b), a bimodal gel, in which small-particle clusters bridge large particles at intermediate small-particle volume fraction, $\phi_{L,C} < \phi_{\text{small}} < \phi_{U,C}$; Fig. 5(c), a bimodal gel above the upper critical value of small-particle volume fraction, $\phi_{\text{small}} > \phi_{U,C}$, in which both small and large particles form fractal structures.

Below a lower critical concentration of small particles, $\phi_{\text{small}} < \phi_{L,C}$, the amount of small particles is too low to connect the large particles to form a spanning network. Each remain in the fluid state, with discrete clusters of large and small particles. At intermediate small-particle volume fraction, $\phi_{L,C} < \phi_{\text{small}} < \phi_{U,C}$, the large particles form a nonfractal network with the small particles, altering the rheological behavior from liquidlike to gel-like. The bimodal gels formed in this region have much larger power-law exponent than the 3–5 that is typical for fractal gels. The lower critical concentration is the minimum volume fraction of small particles required to connect the large particles to form a gel, and it increases with the volume fraction of large particles.

Above the upper critical concentration of small particles, $\phi_{\text{small}} > \phi_{U,C}$, the transition to bimodal gel structure occurs, where the power-law exponent is reduced to a value between 3 and 5. While the $\phi_{L,C}$ increases with the volume fraction of large particles, the $\phi_{U,C}$ is independent of it and remains equal to the gel point of small particles. Therefore, the region of high-exponent bimodal gels in the phase diagram decreases with the increase in the volume fraction of large particles. We expect that it would be difficult to form high-exponent bimodal gels at high concentration of large particles.

IV. CONCLUDING REMARKS

This study reports a type of colloidal gel, induced by a minute incremental addition of small particles, not described by the typical power-law scaling for fractal clusters. We suggest that this gel results from the formation of nonfractal networks of large particles, which are bridged by small-particle clusters in the range of $\phi_{L,C} < \phi_{\text{small}} < \phi_{U,C}$. We expect that the discovery of this regime of colloidal gels in the phase diagram advances our understanding of the complex behavior of size-asymmetric colloids.

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