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Phase Inversion of Pickering Foam and Dry Water Stabilized by Microbowls

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Microbowls, which are hollow particles with holes on their surfaces, stabilize air-in-water-type foams and water-in-air-type powders in particle/air/water ternary systems. We found a particle-dispersed state between the foam state and the powder state. Interestingly, the mixture in this new state displayed remarkable dilatational behavior, preventing the formation of foams and water droplets.

Anisotropic particles are attractive as building blocks in self-assembling processes because their anisotropic shape induces well-ordered structures.[1] Some anisotropic particles are adsorbed at fluid–fluid interfaces when the particles possess suitable wettability to both fluids.[2–7] In the case of Janus particles, which have both hydrophobic and hydrophilic parts on the same particle, the hydrophobic part is oriented toward the oil phase at the interface while the hydrophilic part is oriented toward the water phase.[2,3] Our previous studies predict that disk-shaped and rod-shaped particles are also adsorbed at the fluid–fluid interfaces in oriented states.[4–7] In this paper, we focus on microbowls composed of a spherical surface, a flat surface, and a hemispherical hollow, as shown in Figure 1. These particles have recently attracted attention because they are useful as optical, magnetic, or catalytic materials due to their anisotropic nature.[8–10] Noda et al. established a preparation method of microbowls made of silicone resin.[8] We expect that the anisotropic shape changes the surface activity and self-assembling behavior of microbowls. In the present study, we investigate the mixed state of ternary systems composed of microbowls, air, and water to demonstrate the effects of the anisotropic shape.[17] We expect that such hydrophobic particles would be adsorbed at the air–water interface and stabilize air-in-water-type foams (called "Pickering foams") and water-in-air-type powders (called "dry water").[11–13]

Figure 2 shows a mixed state diagram of the microbowls/air/water ternary systems. The mixed states were classified into three regions and were ruled by the composition ratio of water ϕ_W. For $\phi_W = 0.05$–0.45, the systems were in the water-in-air powder state (W/A), in which solid particles covered water droplets (Figure 2-I and Figure 3a). In this state, the mixture was in powder form, while the grain size of the water droplets was of the order of several tens of micrometers. We observed the separation of excess water at the bottom at $0.40 < \phi_W < 0.45$. The water-in-air powder state was kept undisturbed for at least one month. For $\phi_W = 0.45$–0.75, the systems were in the dispersed state, in which self-assembled structures such as dry water and Pickering foams were not observed. The systems composed of two separated phases: the white water phase in which the solid particles were dispersed and the transparent water phase ($W_P + W$, Figure 2-II). Interestingly, the particle dispersions displayed a remarkable dilatational behavior: a

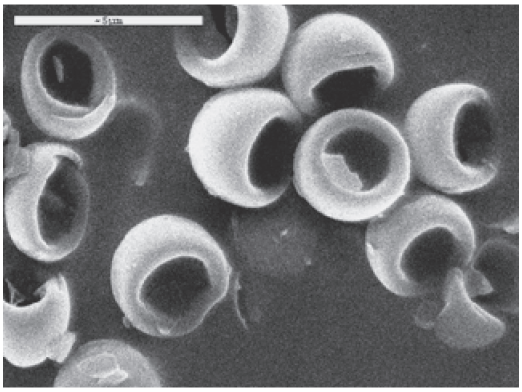

Figure 1. A SEM image of the microbowls.

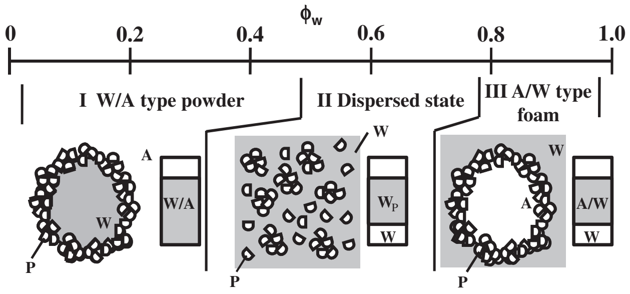

Figure 2. The state diagram of the microbowls/air/water ternary systems.

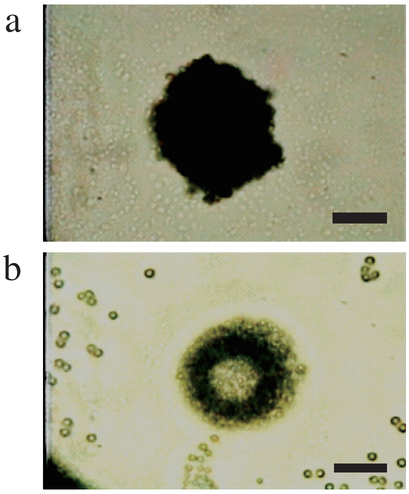

Figure 3. Optical microscopic photographs of the microbowls/air/water system. (a) $\phi_W = 0.2$, water-in-air powder state; (b) $\phi_W = 0.6$, air-in-water foam state. In these photographs, the length of bars is 20 µm.

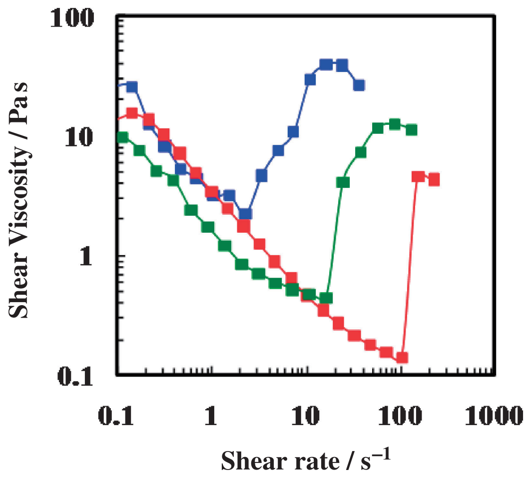

Figure 4. The shear–stress curve of the bowl-shaped particle/air/water system in the dispersed state: red, $\phi_{\mathrm{W}} = 0.475$; green, $\phi_{\mathrm{W}} = 0.485$; blue, $\phi_{\mathrm{W}} = 0.5$.

rheological flow characterized by increase in viscosity at increasing shear rates, as shown in Figure 4. When $\phi_{\mathrm{w}} =$ 0.475, 0.485, and 0.5, the shear viscosity of the mixtures increased discontinuously at shear rates of 3, 15, and 100 s^{-1} as per shear–stress curves. We did not observe this state for systems containing spherical particles. For $\phi_{\mathrm{W}} = 0.75$–0.95, the system was in the air-in-water foam state (A/W + W), in which the solid particles were adsorbed at the air/water interfaces (Figure 2-III and Figure 3b). The size of foam bubbles was several tens of micrometers. Flocculation and creaming of the foam and separation of the excess water phase at the bottom were also observed. The air-in-water foam state was also kept undisturbed for at least one month.

As mentioned above, the addition of water induced a phase inversion from the water-in-air powder state ("dry water") to the air-in-water foam state ("Pickering foam") through the dispersed state with the dilatational property. Such inversion occurred when the hydrophilicity and lipophilicity of the solid particles balanced with the air/water binary phases.[12] If these characteristics were not balanced, the increase in the water phase would have induced a state in which the water phase separated out by coalescence.

To our knowledge, this is the first report of an intermediate state between the water-in-air powder state and the air-in-water foam state. We now discuss the reasons for the dispersed state to arise in these systems. We propose that the dilatational property of the mixture prevents the formation of dry water or Pickering foam. In our previous study, we observed a similar phenomenon induced by the rheological properties of the mixtures.[5] The separated state (in which a silicone oil phase was separated from a milky white phase composed of powder and fluorinated oil) was formed in a ternary system consisting of plate-shaped organic crystalline particles and two oils.[5] In this state, emulsions did not form because the network aggregates of the powder particles prevented the formation of spherical emulsions. In the present systems containing microbowls, the discontinuous increase in the viscosity might prevent the formation of water droplets or spherical foams. We propose that the dilatational behavior is caused by the large cluster formation of the microbowls under shear flow. In general, hydrophobic interaction between particles induces the formation of large clusters in the dispersed medium, which change the dilatational flow behavior of the dispersions.[14–16] Computer simulations predicted that shear thickening would be observed under specific conditions, usually along with a change in the microstructure from ordered layers to a state with large clusters.[15] This cluster formation is determined in colloidal silica dispersions by small-angle neutron scattering analysis of turbidity and flow.[16]

The present results contribute to our understanding of the self-assembling behavior of surface-active particles. The microbowls should be suitable as an ingredient in some composite materials; the air-in-water type foams and water-in-air type powder might be useful in the preparation of cosmetic products while the dilatational dispersions might be useful as shock absorbers in braking devices.

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