doi:10.1246/cl.2011.818

Drying Process of Emulsions Stabilized by Solid Particles

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We observed the drying process of Pickering emulsions with a microscope. In the case of water-in-oil (w/o) emulsions stabilized by common surfactants, the emulsion droplets shrunk while maintaining their spherical shapes. On the other hand, in the case of w/o emulsions stabilized by solid particles, wrinkles occurred and expanded on the droplet surfaces. The colorant dissolved in the water phase remained in a wide area after drying.

Solid particles exhibiting suitable wettability are adsorbed to fluid–fluid interfaces, and they stabilize emulsions and foams which are called Pickering emulsions/foams.[1–8] Recently, some researchers have reported Pickering emulsions as drug delivery systems and stimulus-responsive materials.[9–11] When we prepare emulsion-type formulations for external medications or cosmetics, we should design them while considering their collapse processes due to external forces or drying.[12,13] In this study, we focus on the collapse of Pickering emulsions in drying processes. There are some reports on this topic, because the extremely rigid interfaces of these emulsions can cause characteristic transient states.[14–20] The wrinkling or buckling of droplets occurs with reduction of the volume of the droplets. In this study, we prepared water-in-oil (w/o) emulsions consisting of solid particles, e.g., spherical silicone resin powder, hydrophobic silica, and hydrophobic mica, and oil and water, and observed the drying process with a microscope.[28] The lifetime and change of Feret diameter of emulsion droplets were evaluated to understand their drying behavior quantitatively.

Spherical silicone resin particles were adsorbed at the oil–water interfaces and stabilized w/o emulsions, which had an average diameter of 62 µm. These emulsions maintained their dispersed states for more than one month in a glass tube. However, the droplet shape drastically changed when the emulsion was applied on a glass slide; a number of wrinkles occurred and expanded gradually as shown in Figure 1a. In several tens of minutes after application, the droplet surfaces were wrinkled like a dry raisin. Interestingly, after about 60 min, the emulsion droplets suddenly disappeared and the red marks of Rhodamine 6G in the water phase remained where the emulsion droplets existed. The contrast of the red mark was weaker than that for the emulsion droplets, because light absorption characteristics of the dye molecules depend on media around them.[21] In the case of the emulsions stabilized by hydrophobic silica or hydrophobic mica, the formation of wrinkles and the disappearance of the emulsion droplets were also observed as shown in Figure 1b. The drying process of w/o emulsions stabilized by isostearyl glyceryl ether GE-IS and glyceryl undecyl dimethicone SI-U were very different from that of the Pickering emulsions. When the emulsions stabilized by GE-IS were applied on a glass slide, the spherical droplets with an average diameter of about 26 µm shrunk gradually while their spherical shape was maintained as shown in Figure 1c. The formation of wrinkles was not observed in these systems. The droplet size decreased more rapidly than did that of the Pickering emulsions.

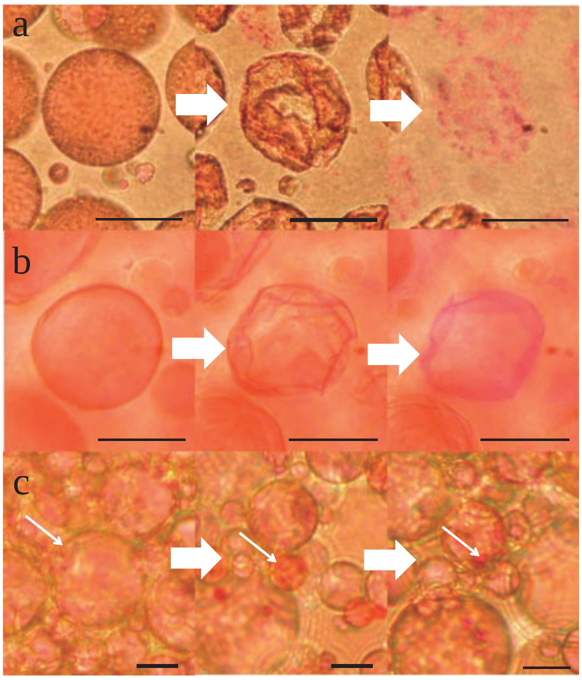

Figure 1. Microscopic images of w/o emulsions: (a) spherical silicone resin particle:*n*-dodecane:water 8:72:20, (b) hydrophobic silica:dodecane:water 5:45:50, and (c) GE-IS:dodecane:water 0.4:39.6:60. The images are water droplets at 0 min (left), 10 min (middle), and *T* (right) after application. Scale bars: (a) and (b) 50 µm, (c) 10 µm.

The lifetimes *T* of the emulsion droplets were evaluated for each emulsion system. Here, *T* is defined as the period from the application to disappearance of the droplets. The lifetimes of the emulsions stabilized by spherical silicone resin particles, hydrophobic silica, and hydrophobic mica were 59, 31, and more than 60 min, respectively, while those of the emulsions stabilized by GE-IS and SI-U were 18 and 20 min, respectively. These results indicated that Pickering emulsions were more stable than the emulsions stabilized by common surfactants and maintained their emulsion states for longer periods of time than common emulsions. The change of the Feret diameters D_t of the emulsion droplets was also evaluated (Figure 2). The diameters D_t of the emulsions stabilized by GE-IS or SI-U were halved at 10–20 min after application. On the other hand, although some wrinkles

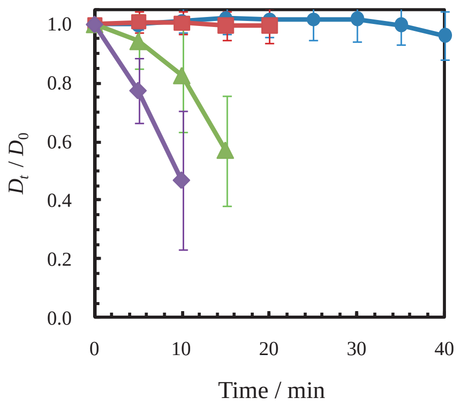

Figure 2. Changes of the relative diameter D_t/D_0 of the emulsion droplets. ●: Spherical silicone resin particles; ■, Hydrophobic silica; ▲, GE-IS; ◆, SI-U.

formed on the emulsion surfaces, the D_t values of the Pickering emulsions remained about the same for more than 30 min. In the case of hydrophobic mica, the D_t values of the droplets could not be measured because their outlines were unclear.

The relative areas of colorant S_t/S_0 for each emulsion system were evaluated: here, S_0 and S_t are the areas of the water droplets just after application on a glass slide and the droplets at their lifetime T. We assumed that the droplets are spheres and evaluated these areas from the Feret diameter D_t: S_t, $S_0 = \pi D_t^2$, πD_0^2. The relative areas S_t/S_0 of the emulsions stabilized by spherical silicone resin powder and hydrophobic silica were 0.85 and 0.82, respectively. On the other hand, those of the emulsions stabilized by GE-IS or SI-U were both 0.03. These results showed that the colorant dissolved in the water phase remained in a wide area after drying in the case of Pickering emulsions while it was concentrated at one point in the case of common emulsions.

In this section, we discuss the mechanism of the characteristic behaviors of Pickering emulsions. In the systems of the emulsions stabilized by common surfactants, surfactant molecules are in equilibrium between three states, i.e., the micelle and dissolved and adsorbed states.[22,23] In such a situation, if the surface area of the emulsion droplets decreases due to drying, the surfactant molecules in the adsorbed state can be desorbed from the oil–water interfaces and form micelles. Then, the spherical form of emulsion droplets is maintained also in the drying process. On the other hand, in the case of Pickering emulsions, the solid particles are not desorbed from the oil–water interfaces because the particle size is several tens of thousands of times larger than that of normal surfactant molecules.[2] Therefore, even if the surface area of the emulsion droplets decreases after drying, the solid particles are adsorbed at oil–water interfaces, and some wrinkles are formed at the interfaces to maintain the interfacial area. Hirose et al. discussed the adsorption dynamics of colloidal particles at liquid–liquid interfaces and showed that the adsorption rate of solid particles decreases with an increase in the particle size.[24] On the basis of the curvature elasticity model, Quilliet et al. showed that the amount of buckling of hollow spheres depends on the relative volume variation and a dimensional parameter that takes into account both the relative spontaneous curvature and the relative thickness of the shell.[25,26] In addition, a drying process of liquid marbles, which are water droplets covered with hydrophobic powder particles, has been reported. Tosun et al. showed that liquid marbles, i.e., water droplets covered with solid particles, shrunk isotropically at the beginning of evaporation, thereby causing their skins to thicken. Further evaporation caused the skin of the liquid marbles to buckle, giving disordered shapes.[27]

We observed the drying processes of Pickering emulsions and found that some wrinkles were formed on the droplet surfaces. The colorant dissolved in the water phase remained in a wide area. These results showed that the formulation made of Pickering w/o emulsions is desirable to achieve uniform distribution of ingredients on a wide area after drying. These findings should be useful in designing Pickering emulsion for foods, cosmetics, and pharmaceuticals.

This work was supported by a Grant-in-Aid for Young Scientists (Start-up) No. 19810001 from the Ministry of Education, Culture, Sports, Science and Technology, Japan and the Cosmetology Research Foundation. The authors gratefully acknowledge the donation of the silicone powder from Takemoto Oil & Fat Co.

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28 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.