NOTE

Pickering Emulsions and Capsules Stabilized by Wool Powder Particles

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Abstract: We prepared emulsions and capsules that were stabilized by wool powder particles. These powder particles were adsorbed on oil-water interfaces, and they formed both oil-in-water and water-in-oil emulsions. These emulsions were observed in ternary systems containing silicone oil, n-dodecane, fluoroc acid, oleic acid, or linoleic acid as the oil phase.

Key words: emulsion, capsule, wool powder

1 INTRODUCTION

Some proteins are used as stabilizers for food emulsions and foams such as whipped cream, ice cream, and milk beverages. These macromolecules are adsorbed on oil-water interfaces and form emulsions and foams. Most protein-stabilized emulsions are oil-in-water (O/W) type, because water-soluble proteins such as casein, β-lactoglobulin and albumin are fairly hydrophilic in amphiphilic molecules. Some agents such as phospholipids have been added to prepare water-in-oil (W/O) emulsions. On the other hand, both W/O and O/W emulsions are stabilized by solid particles when the particles have intermediate hydrophobicity. Many emulsions stabilized by elastic solid particles have been reported and are referred to as "Pickering emulsions". We, therefore, specifically studied wool powder particles that are primarily composed of the protein keratin. The wettability of the wool powder particles can be balanced, because keratin molecules contain both hydrophilic and lipophilic amino acids. In this paper, we describe emulsification behaviors of wool powder/oil/water ternary systems and preparation methods of capsules covered by wool powder particles.

2 EXPERIMENTAL PROCEDURES

2.1 Materials

Wool powder was prepared according to a previously published procedure. The powder was composed of plate-shaped particles that were 59 μm in diameter. Composition analyses showed that the main component of the powder was keratin. Silicone oil KF-96L (Shin-Etsu Chemical Co.; CH₃₃(CH₂)₇O-[Si(CH₃)₃O]₇Si(CH₃)₃; molecular weight = 900), n-dodecane (Kanto Chemical Co.; CH₃(CH₂)₁₀CH₃), fluoroc oil (Ausimont K.K.; CF₄(CHF)CF₂O CF₃; molecular weight = 1500), oleic acid (Wako Chemical Co.; CH₃(CH₂)₇CH=CH(CH₂)₇COOH), linoleic acid (Wako Chemical Co.; CH₃(CH₂)₉CH=CH(CH₂)₇COOH), and the thickener Poiz C-60H (Kao Co.; O-(2-hydroxy-3-(trimethylammonio)propyl)hydroxy cellulose chloride) were used as received.

2.2 Preparation

Ternary mixtures of wool powder, oil, and water (a total of 10 g) were prepared according to the following procedure. The wool powder was dispersed in an oil phase using an AHG-160D homogenizer (AS ONE Co.) at 2000 rpm for 15 min. After adding appropriate amounts of water, the mixture was again stirred using the homogenizer at 2000 rpm for 5 min at 298 K. The capsules were stabilized by wool powder particles and were prepared according to the following procedure. The wool powder (2.1 g) was dispersed in silicone oil (67.9 g) using the homogenizer at 2000 rpm for 15 min. After adding 3 g of 5% thickener aqueous solution, the mixture was gently shaken manually for 30 s. Capsules were obtained from the emulsion by filtration.

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2.3 Measurements
The mixed states of the wool powder/oil/water ternary systems were examined with a BHT optical microscope (Olympus Co.). Electric resistance was measured using a Seven Go SG3 conductivity meter (Mettler-Toledo) to identify the continuous phase of the emulsions. Electrical resistance is a convenient parameter for identifying mixed states because this physical property reflects the continuous phase of the mixtures: the mixtures are conductive if the continuous phase is water and insulating if the continuous phase is oil.

3 RESULTS AND DISCUSSION
Figure 1 shows a mixed state diagram of the wool powder/silicone oil/water ternary systems. The powder/oil ratio is 1:99 (wt/wt), and $\phi_w$ denotes the weight composition of water in the ternary systems. Addition of water induces phase inversions from the dispersed state, in which the wool powder particles are dispersed in an oil phase, to the water-in-oil (W/O) and oil-in-water (O/W) emulsion states. The details of these mixed states are described as follows:

(i) **Dispersed state (O + W):** When $\phi_w = 10\%$, the mixture was in the dispersed state consisting of an oil phase containing dispersed wool powder and a separate water phase. Figure 2a is a microscopic image of the mixture when $\phi_w = 10\%$. The powder particles formed aggregates with a diameter of about 10 μm.

(ii) **W/O emulsion state (O + W/O):** When $20\% \leq \phi_w \leq 30\%$, the mixture was in the W/O emulsion state. Figure 2b is a microscopic image of the mixture when $\phi_w = 30\%$. The water droplets on which the wool powder particles were adsorbed were dispersed in an oil phase. The size of these water droplets was about 100 μm. Some particles were dispersed in the oil or water phases.

(iii) **O/W emulsion state (W + O):** When $40\% \leq \phi_w \leq 90\%$, the mixture was in the O/W emulsion state. Figure 2c shows a microscopic image of the mixture when $\phi_w = 50\%$. The oil droplets on which the wool powder particles were adsorbed were dispersed in the water phase. The size of these oil droplets was also about 100 μm. The formation of such emulsions is not unique to wool powder/silicone oil/water ternary systems. We found that W/O and O/W emulsions were stabilized by wool powder particles in ternary systems containing n-dodecane, fluoric oil, oleic acid, or linoleic acid as the oil phase.

The abovementioned emulsion states retained their...
shape for over a month at 298 K because the rigidity of the oil-water interfaces due to the adsorption of solid particles was effective in preventing coalescence of the emulsion droplets. Examination of the microscopic images and electric conductivities of the emulsion states had indicated that they would retain their shape for 30 days after preparation. We observed that the wool powder particles formed O/W emulsions when the water phase contained 5% of sodium chloride. Further, these emulsion droplets were retained for over a month. However, the emulsion collapsed immediately after filtration. The inner water phase was drained by breaks on the surface layer of the emulsion droplets. We found that the addition of a thickener improved the stability of the capsules. Capsules comprising wool powder/silicone oil/5% thickener aqueous solution in a ratio of 2.1:67.9:30.0 (wt/wt/wt) retained their shapes after filtration. However, the capsules collapsed several hours after filtration because of the evaporation of the water phase. Figure 3 shows microscopic images of the capsules. Most capsules were elongated and potato-like in shape, 1 mm in diameter, and covered with wool powder particles.

As we had expected, the wool powder particles stabilized the emulsions by conferring rigidity to the oil-water interfaces. The wool powder particles stabilized not only the O/W emulsions but also the W/O emulsions. This is a rarely observed phenomenon in protein-stabilized emulsions. Wool powder particles can stabilize W/O emulsions because keratin molecules contain both hydrophilic and lipophilic amino acids, as mentioned in the introduction. The addition of a thickener was effective in obtaining stable keratin capsules. The elongated potato-like shape of the capsules was retained after filtration from the oil phase; this stability results from the mechanical strength of the viscous water inside the capsule. The viscous core of the capsules supports the particle shell and gives the shell sufficient stiffness to allow the capsules to be separated from the dispersion medium. The formation of nonspherical Pickering emulsions or capsules such as these elongated potato-like capsules is significant. When particles are adsorbed on an oil-water interface at a sufficiently high concentration, the interface loses mobility and displays solid-like characteristics. This phenomenon is referred to as "interfacial jamming." Jamming can arrest interfacial tension-driven morphological coarsening in oil-water systems and, therefore, stabilize morphologies with unusual interfacial shapes.

In this study, we prepared W/O emulsions, O/W emulsions, and capsules stabilized by wool powder particles. These emulsions retained their shape for over a month. These emulsions and capsules can be applied toward the development of novel delivery vehicles for the controlled release of drugs, cosmetics, and food supplements.

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