Synthesis of microcapsule containing oil phase via *in-situ* polymerization

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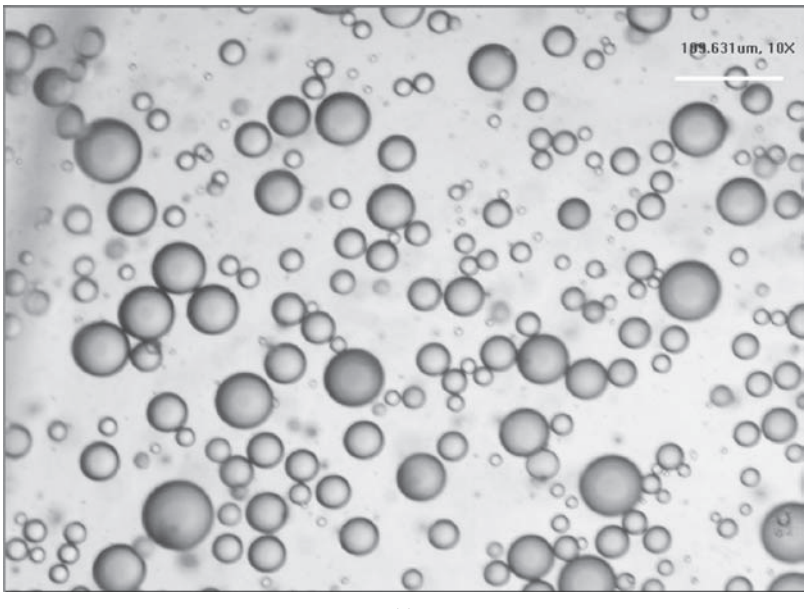
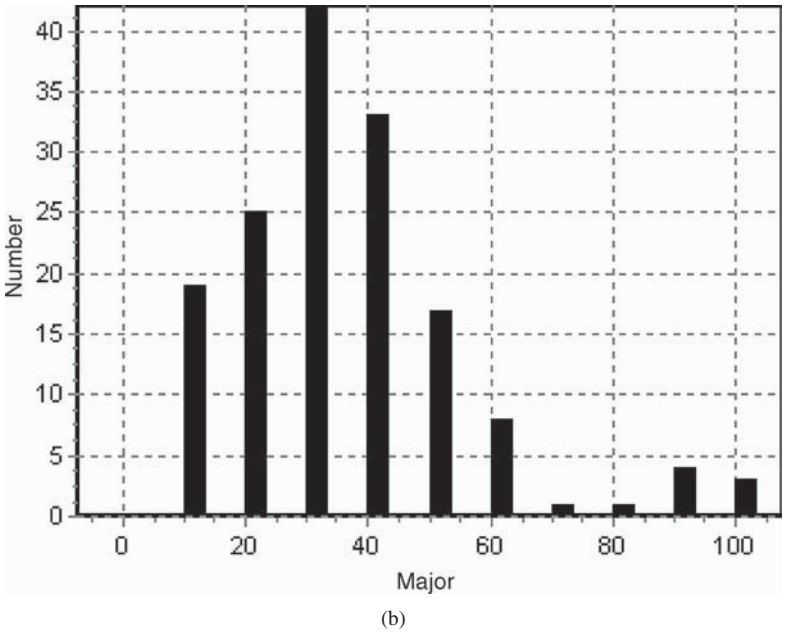
Microcapsules are in general small particles containing either an active agent or a core material surrounded by a coating layer or a shell. Commercial microcapsules typically have a diameter between 3 and 800 μm, and consist of 10–90 wt% core materials. They have been used for various engineering applications including carbonless copying papers, adhesives, cosmetics, insecticides and pharmaceutical materials [1]. Versatile core materials are encapsulated for several reasons, such as improvement of long-time efficiency, stabilization



(a)



(b)

Figure 1 O/W emulsions prepared with PSSA (a) OM image (b) size distribution.

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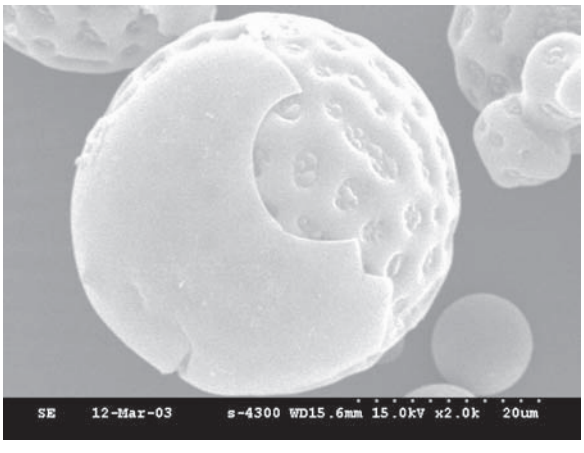
against environmental degradation, easy handling through solidification of liquid core, and maintenance of non-toxicity of degradation products [2]. Recently, the microencapsulation process has been adopted to a number of fields of advanced technology like an electronic paper [3, 4]. Among various chemical methods in the microencapsulation processes, such as interfacial polymerization [5], coacervation [6], and *in-situ* polymerization [7], the *in-situ* polymerization relies on prepolymer formed in a continuous phase. Typical wall materials used are urea formaldehyde [8] and melamine formaldehyde (MF) resins [9, 10]. MF microcapsule with a liquid core and a solid shell has been prepared via *in-situ* polymerization within the droplets of an oil-in-water emulsion using various surfactants.

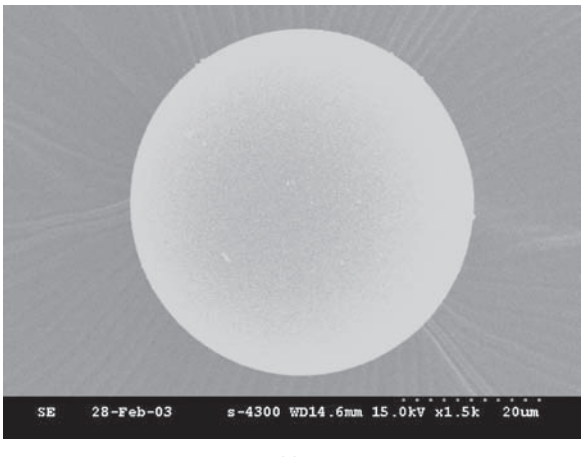
In this letter, we discuss the preparation of microcapsules of high density oil as a core material and MF precondensates as a shell material. Characterizations of the microcapsules synthesized using anionic polymeric surfactant were performed via morphology analysis, mean particle size, size distribution, and shear viscosity. Poly(sodium 4-styrenesulfonate) (PSSA, Aldrich, USA) as an anionic polymeric surfactant, was used for the emulsification process [11]. Because of its good ability of emulsification for higher molecular weights compared with conventional surfactants with low molecular weight, the emulsification state shows improved stability for a long period. A 5-wt% PSSA aqueous solution was dissolved at 90 °C for 3 hr, and then adjusted to be pH 2–5 by 10-wt% aqueous citric acid solution. The oil phase as a core material was prepared by mixing both polytetrachloroethylene (TCE, Junsei Chemical Co., Japan) and oil soluble dye (Oil Blue N, Aldrich, USA) at 30 °C. By adding the oil-soluble dye, we could determine whether the capsules were fabricated well or not using an optical microscope. The oil phase with oil soluble dye was added into the previously prepared 5-wt% PSSA aqueous solution. Consequently, oil-in-water emulsion was prepared with stirring at 400 rpm for 1 hr. We identified stable soluble oil droplets via optical microscope (OM, Olympus BX51, Japan) images and added the prepared shell materials in the emulsion reactor. MF precondensates as shell materials are formed by stirring a mixture of 37% aqueous formaldehyde and melamine at 60 °C for 30 min. The appearance of the MF precondensates changed from opaque to transparent after 30 min. This reaction was performed under a low basic condition with stirring. The microencapsulation process was followed by adding MF precondensates and kept for 3 hr with continuous agitation (250 rpm) at 60 °C. MF resin was crosslinked under an acidic condition. The capsule shell was then formed. The detailed MF reaction mechanism has been previously described [12, 13]. The final capsule slurry was washed by deionized water several times and sieved by using a 400 μm sieve to remove both excess MF precondensates and remnants. The spherical microcapsule was separated and dried in ambient temperature condition.

In the microcapsule fabrication, the emulsification ability of the surfactant has a very important role, based on the fact that the final capsule size and size distribution are determined by the emulsion droplet size established by an emulsification step before and during the encapsulation process. Therefore, we investigated the states of oil-in-water emulsion which were examined by OM images. Agitation at 400 rpm was applied into this oil-in-water emulsion. The size and the state of the emulsion were roughly investigated by OM images (Fig. 1a). The mean droplet size and size distribution were investigated by image analysis software (TDI plus, version 5×, Japan) and the mean droplet size 41 μm was determined (Fig. 1b). After emulsification, the *in-situ* polymerization was performed for 3 hr. By separating the excess MF precondensates using

(a)



(b)



(c)

Figure 2 Wall formation steps: (a) first step (b) intermediate step and (c) final step.

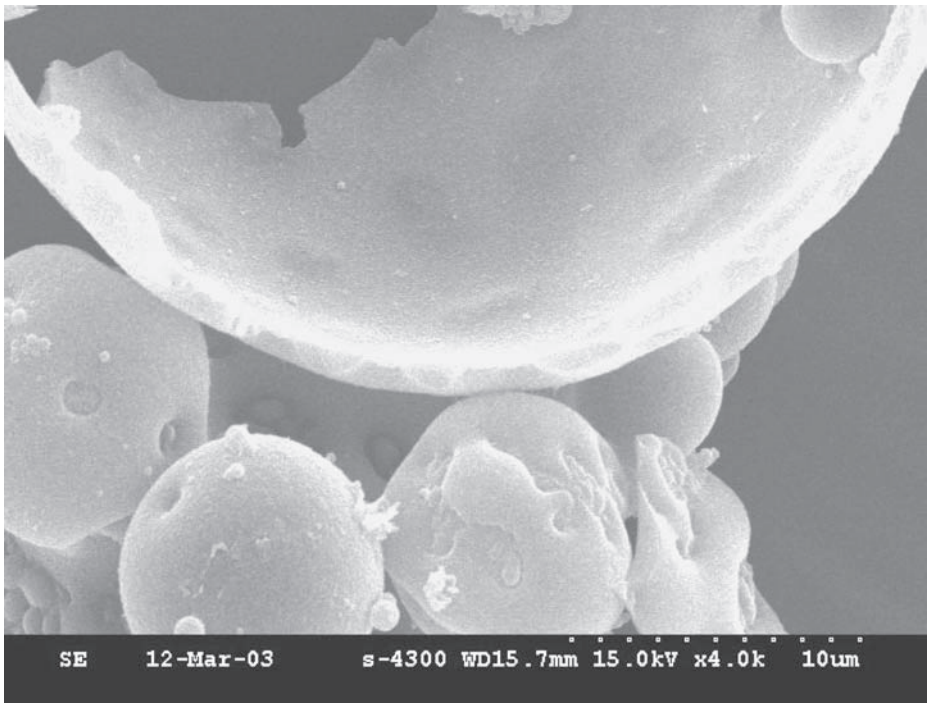


Figure 3 SEM images of microcapsule surface.

400 μm sieve, spherical microcapsules show rather larger sizes than that of oil droplets. The mean size of the microcapsules synthesized was 54 μm. Fig. 2 a–c shows the process of microcapsule wall creation via the scanning electron microscope (SEM, Hitachi S-4300, Japan) images. In this peculiar morphology, microcapsules are identified to possess a surface consisting of rough and smooth parts. In the first step, the rough surface morphology was formed, and then the smooth surface morphology followed as the polymerization proceeded. Those microcapsules with rough surface morphology were produced in intermediate step. The microcapsules seem to possess rigid microcapsule walls as Fig. 3. No aggregates of microcapsule surfaces in microcapsules were observed. From the fractured surface of microcapsule, a wall thickness of microcapsule with 20 μm diameter was estimated to be about 1 μm. In order to investigate the viscosity effects, shear viscosity of the polymeric surfactant was measured by a rotational rheometer (Physica MCR 300, Germany) using a double gap geometry [14]. The shear viscosities of 5-wt% PSSA solution and final capsule slurry were 0.02 and 0.15 Pa·s at a shear rate of 1 s^{-1}, respectively. The slight increase of shear viscosity was observed in the final capsule slurry compared with the surfactant solution. In many microencapsulation processes, large increase of viscosity was observed in the final capsule slurry using typical surfactant compared with a small increase of viscosity in the case of using PSSA as a surfactant [15]. Capsule slurry using PSSA as an emulsifier with small increase of viscosity is thereby separated well.

In summary, microcapsules with a liquid core and a solid shell were prepared via *in-situ* polymerization within the droplets of an oil-in-water emulsion using PSSA. Both particle size and size distribution of microcapsules were measured using an image analyzer. The microcapsules seemed to possess rigid and smooth microcapsule walls. Rare aggregates existed in microcapsule surfaces. Based on shear viscosity of the final capsule slurry, the PSSA as an emulsifier with small increase of viscosity was found to be proper to microencapsulation process.

Acknowledgements

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