W/O 에멀젼에서 폴리머를 이용한 hollow 형태의 실리카 입자 제조

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Preparation of Hollow Silica Particles in W/O Emulsions with Polymers

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1.Introduction

In recent years, there has been intense interest about the fabrication of micrometer- and nanometer-sized hollow particles. These hollow particles often exhibit properties that are substantially different from general particles (for example, their low density, large specific surface area, stability and surface permeability), thus making them attractive from both a scientific and a technological viewpoint. Applications for such particles are cosmetics, including capsule agents for drug delivery system (DDS), catalysis, coatings, composite materials, dyes, inks, artificial cells, fillers and protecting sensitive agents such as enzymes and proteins.[1-8]

The application and commercialization of hollow spherical structures have, however, been limited mainly because of the disadvantages associated with the techniques used for their production. Relatively harsh conditions are employed in some methods, making them unsuitable for the encapsulation of sensitive materials, and encapsulation of materials after their formation is often difficult. Other disadvantages are the lack of control over size, geometry, wall thickness, and wall uniformity of the hollow spheres produced. But, the preparation method of hollow silica particles proposed in this study is so simple that it can be used in various industrial fields.

In this study, an attempt was made to synthesize hollow silica particles by water-in-oil emulsion technique, a more advantageous process in respect of high yield, short processing time, and relatively simple system. Also the conditions of hollow silica particle formation in W/O emulsions were examined. The viscosity of water droplets was varied because it influenced the formation of hollow particles. In order to investigate the effects of viscosity, polyethylene glycol or polyvinylpyrrolidone was added into water droplets. The morphology, size, and wall thickness of samples were investigated using field emission scanning electron microscopy.

2. Experimental Section

Materials

Tetraethyl orthosilicate (TEOS, 98 %) as a silica source, hydroxypropyl cellulose (HPC, average Mw ca. 370,000) as a stabilizer of emulsion structure, and Tween 20 as a high HLB (hydrophilic-lipophilic balance) surfactant to from a stable water phase were purchased from Aldrich Chemical Company. Sorbitan monooleate (Span 80) as a low HLB surfactant to disperse oil phase and polyvinylpyrrolidone (PVP, average Mw. 40000) were purchased from Sigma Chemical Company. 1-Octanol as anoil phase and polyethylene glycol (PEG, average Mw. 18000-25000) as a water stabilizer were purchased from Junsei Chemical Company. Also, ammonium hydroxide (NH_4OH 25 %) as a catalyst and ethanol (95 %) as a washing reagent were purchased from Acros and Teamin Chemical Company (Korea). All chemicals were used as received without further purification. The water used in this study was deionized and doubly-distilled by Milli-Q Plus system (Millipore, France), having 18.2 ㏁ electrical resistivity.

Characterization

An Ostwald viscometer was used to measure the viscosities of water phase with polyethylene glycol or polyvinylpyrrolidone. Field emission scanning electron microscopy (FE-SEM, JEOL Co. model JSM-6700F, Japan) was used to investigate the morphology and size distribution of silica particles prepared by W/O emulsion method. The samples were coated with platinum by sputtering for 10 minutes at 15kV, a working distance 15 ㎜ at 3000 magnification.

Preparation of W/O emulsion

In order to make hollow silica particles, two types of polymers (HPC and PEG) were used.

First, external oil phase was prepared by dissolving HPC in octanol (45 g), then held at 80 ℃for 4 hr. Then oil phase was kept at 40 ℃. After 30 minutes, a low HLB surfactant (3 wt% Span 80) was added into oil phase. HPC and Span 80 which were added into the external oil phase increased the stability of the W/O emulsion structure.

Second, when preparing water phase with PEG or PVP, each step reaction time is very important. The PEG (2 - 10 wt%) as a viscosity of controller and a high HLB surfactant (5 wt% Tween 20) were dissolved in water phase. After stirring with the use of magnetic stirrer for 20 minutes, NH_4OH as a catalyst was added to the water phase.

Third, water phase was added to an external oil phase. The weight ratio of water phase to oil phase in emulsion was kept as 1:9. To disperse water phase into oil phase, the agitation using the magnetic stirrer for 1hr at 40 ℃ was performed. All the experimental compositions in emulsion are shown in table 1.

Fabrication of hollow silica particles

The reagent of TEOS was added into the W/O emulsion formed with various amounts of polymers. TEOS is soluble in the continuous phase of W/O emulsion, but it becomes water-soluble after its hydrolysis. The Rw (H_2O/TEOS) molar ratio was 4 in all experiments. Samples with 60 ml approximate volume were prepared in the experimental beakers with flat bottom and kept for 14 hr with soft agitation using small magnet stirrers. After reaction was completed, the samples were centrifugation at 2500 rpm for 15 minutes to obtain hollow silica particles. In order to remove polymers, octanol and surfactants (Tween 20 and Span 80), the particles obtained by centrifugation were washed with ethanol. After this procedure was repeated three times, the hollow silica particles were collected. Then, particles were dried in an incubator at 40 ℃ for 1day. During this drying process, the water inside particles would be eliminated.

3. Results & Discussion

In figure 1, SEM images exhibited the morphology of silica particles formed at various PEG concentrations. As shown in figure 1A, the sample prepared under conditions of PEG=2 wt% didn't have the hollow silica particles and the size distribution was more or less broad. Though hollow particles were not obtained in the samples, the density of the aggregation between primary particles ranging from 30 nm to 40 nm in a particle is lower than other samples prepared by emulsion method without PEG polymer. When PEG concentration was increased in water phase of emulsion from 2 wt% up to 6 wt%, the hollow silica particles was obtained as shown in figure 1B. Through magnified SEM image of the hollow silica particle, the shell thickness ranging from 200 nm to 500 nm was observed.

And in order to confirm the viscosity effect of polymer in the inner phase for the formation of hollow silica particles, the polymer used in the inner phase was replaced from PEG to PVP and the spherical silica particles were prepared. To have the same viscosity of PEG and PVP in the water phase, the viscosity of water phase was measured by Ostwald viscometer. Through the measurements, the viscosity of 2 wt% PEG was the equal to 3.5 wt% PVP and 6 wt% PEG is the same as 10 wt% PVP.

As shown in figure 2A, the sample prepared under conditions of 3.5 wt% of PVP did not have the hollow silica particles. When PVP concentration was changed from 3.5 wt% up to 10 wt%, the hollow silica particles were obtained as shown in figure 2B. Using PVP polymer, on the whole, the particle size was larger and the size distribution was broader than other samples prepared by using PEG polymer. Here, it can be suggested that the increase of viscosity in the water phase had an important role on the formation of hollow silica particles. But in spite of the same viscosity of internal phase, there was a little difference in the size and the size distribution among the samples. It was shown that the other property of PEG affects the formation of hollow particles.

4. References

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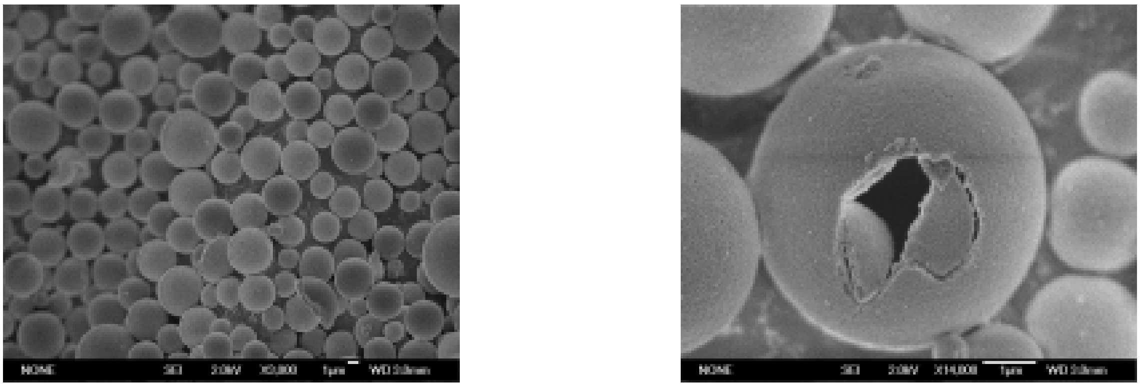
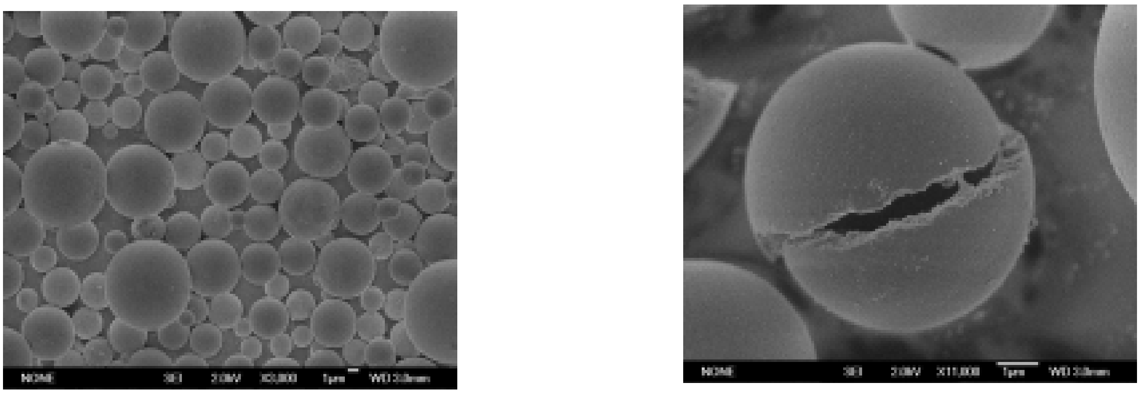
Table 1. Chemical compositions of emulsions used for the formation of silica particles.

sample	Internal phase (Water phase)				External phase (oil phase)		H_2O / TEOS molar ratio (Rw)
	Tween 20	NH_4OH	PEG	PVP	HPC	Span 80	
Fig. 1A	5 wt%	2 wt%	2 wt%		1.4 wt%	5 wt%	4
Fig. 1B	5 wt%	2 wt%	6 wt%		1.4 wt%	5 wt%	4
Fig. 2A	5 wt%	2 wt%		3.5 wt%	1.4 wt%	5 wt%	4
Fig. 2B	5 wt%	2 wt%		10 wt%	1.4 wt%	5 wt%	4



(A) (B)

Figure 1. SEM images of particles produced from W/O emulsions containing PEG in inner phase; (A) concentration of PEG is 2 wt%, (B) concentration of PEG is 6 wt%.



(A) (B)

Figure 2. SEM images of particles produced from W/O emulsions containing PVP in inner phase; (A) concentration of PVP is 3.5 wt%, (B) concentration of PVP is 10 wt%.