Fabrication of Hollow Chloroprene Rubber Particles by Solvent Evaporation Method

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Abstract: Hollow particles are gas-filled spherical particles with single or multiple voids; they have advantageous properties such as low effective concentration and high specific surface area. In this study, we developed a simple method for fabricating hollow particles made of widely used chloroprene rubber. Hollow particles with voids less than 10 μm in particle size were obtained by stably maintaining microbubbles or aqueous microdroplets inside a solvent droplet with dissolved chloroprene rubber.

Keywords: Hollow Particle, Solvent Evaporation Method, Chloroprene Rubber, Soft Material, Microbubble

1. Introduction
A hollow particle with a gaseous core affords many advantageous features such as lightweightness, heat insulation, sound isolation, and buffering. Owing to these properties, hollow particles are widely used as building materials and vehicle parts. Furthermore, hollow particles have also been reported to possess unique properties that control light scattering and dielectric property [1, 2].

In recent years, many studies have focused on the fabrication of hollow particles from hard materials such as metal, polymer, and ceramics [3, 4]. The hollow particles are used to give various properties to base material composites, and the composites are used to such as heat insulation or sound insulating material. However, the composite tends to lose the flexibility of its base material by the addition of hollow particles with a hard shell, but this problem can be overcome by adding flexible hollow particles. Unfortunately, there are only a few reports on hollow particle fabrication using soft materials such as elastomer. Hollow particles are typically fabricated by decomposing the core material inside the shell by dissolution, evaporation, or thermolysis after fabricating hollow particles with a liquid or solid core. However, the particle shells often get damaged during this core decomposition process. Recently, the bubble template method was put forth to overcome the above-mentioned problem. This method directly produces hollow particles without a core decomposition process [5, 6]. For example, hollow poly-lactic acid particles were obtained by stably preserving microbubbles inside a solvent droplet, which was subsequently evaporated [7].

The solvent evaporation method can be applied to the fabrication of hollow particles with a solvent-soluble shell material such as elastomer. In this study, we use the above-mentioned solvent evaporation method to fabricate hollow particles with a chloroprene rubber (CR) shell that has advantageous properties such as resistance to heat, weather, and ozone. Hollow particles were obtained by stably preserving microbubbles or aqueous microdroplets inside a solvent droplet with dissolved CR. The resulting hollow particles contained many voids less than 10 μm in particle size.

In this paper, we report the fabrication of hollow CR particles, and put forth a method for controlling the particle size and the formation of hollow structures inside the particle.

2. Experiment
2.1 Materials and experimental apparatus
CR (A-90, Denka Co., Ltd., Japan) which is soluble in organic solvents was the shell material. Toluene and methylene chloride (Wako Pure Chemical Industries, Ltd., Japan) were used as the solvent. The continuous phase was 1 wt% polyvinyl alcohol (PVA) aqueous solution made from anionic polyvinyl alcohol (Gohsenol T-330, Nippon Gohsei Co., Ltd., Japan). A stirrer (RHS-1DN, AS-ONE Co., Ltd., Japan) and homogenizer (AHD-160D, AS-ONE Co., Ltd., Japan) were used for dispersing the CR solution as droplets in the PVA aqueous solution. A pressure bottle was used for pressurizing the droplets and PVA aqueous solution. An optical microscope (VHX2000, KEYENCE Co., Ltd., Japan), a scanning electron microscope (SU6600, Hitachi High-tech Co., Ltd., Japan), and a transmission electron microscope (JSM-1210, JEOL Co., Ltd., Japan) were used to analyze the fabricated particles.

2.2 Fabrication method
The solvent evaporation method involving the following four steps (default process) was used to fabricate hollow CR particles, and Fig.1 shows the summary diagram of the fabrication method. Step (1): CR solution which consisted of 0.2 ml of 10 wt% CR toluene solution and methylene chloride of 5.0 ml was prepared as shell material of the hollow particles, and 100 ml of 1 wt% PVA aqueous solution was prepared as dispersion medium. Then, the CR solution was dispersed as droplets in the PVA aqueous solution by 500 rpm agitation for 3 min. Step (2): the PVA aqueous solution with the dispersed CR solution droplets was enclosed in a bottle, and then it was pressurized using oxygen at 0.5 MPa, which is high pressure required for the reproducible void-nucleus generation. Step (3): after pressurization for 30 min, the pressure of the bottle was decreased to atmospheric pressure, and then, microbubbles or microdroplets were generated in the droplets. Step (4): the solvent was evaporated at a rate of about 0.12 g/h while holding the CR solution droplets with the microbubbles or
microdroplets in the PVA aqueous solution. Thus, hollow CR particles were obtained.

![Fig.1 Fabrication of hollow CR particles](image)

3. Results and Discussion

3.1 Fabricated hollow CR particles

Fig. 2 shows an optical microscope image of a CR solution droplet with microbubbles or microdroplets in the PVA aqueous solution after a few minutes of decompression. Fig. 3 shows the change in the shape of the CR solution droplet during the solvent evaporation process, and Fig. 4 shows a cross section SEM image of a hollow CR particle. CR solution droplets with 200–300 μm diameters were fabricated by agitating the CR solution in the PVA aqueous solution. The microbubbles or microdroplets were generated inside the CR solution droplets, as shown in Fig. 2 by pressurizing and decompressing the PVA aqueous solution in which the droplets were dispersed.

Those microbubbles or microdroplets inside the CR solution droplet float because those densities are lower than that of methylene chloride. However, the surface tension between PVA solution and CR solution prevents the release of microbubbles or microdroplets from the CR solution droplet, therefore, generated microbubbles or microdroplets gathered at the top-center of the CR solution droplet as shown in Fig. 2.

Furthermore, the solubility of toluene in water is 0.067 g/100 ml (23.5 °C), and that of methylene chloride is 1.3 g/100 ml (20 °C). Although these are low, toluene and methylene chloride evaporate into the atmosphere through the water phase, and as a result, the diameter of the droplet shrinks slowly, as shown in Fig. 3. Therefore, the CR particles were fabricated by holding the droplets, including microbubbles or microdroplets, in the PVA aqueous solution for two days. The microbubbles or microdroplets remained stable in the CR solution droplets even while the toluene and methylene chloride were evaporating. As a result, hollow CR particles that have many voids less than 100 μm in size were obtained, as shown in Fig. 4, and the average diameter of the CR particles was 66.8 μm. Those voids were ranging from 0.6 μm to 13.8 μm as shown in Fig. 5 and the average equivalent diameter of voids in CR particles was 2.1 μm.

The possible causes for the generation of microbubbles or microdroplets could be as follows: (1) Oxygen dissolved in the CR droplets because of pressurization using oxygen gas poured into the decompression bottle. (2) Supersaturated microbubbles were generated inside the CR solution droplets during pressurization and decompression. (3) The tension between PV A solution and CR solution prevents the release of microbubbles or microdroplets from the CR solution droplet. Further, it was found that the number of microbubbles or microdroplets inside a CR solution droplet increases with decreasing the diameter of the CR solution droplet. As shown in Table 1, the average diameter of hollow CR particles was decreasing by increasing agitating speed, however, it was found that the number of microbubbles or microdroplets in the CR droplets increased by decreasing the diameter of CR solution droplet size. As shown in Table 1, the average equivalent diameter of voids in CR particles was 2.1 μm.

![Fig.2 Optical microscope image of CR solution droplet](image)

![Fig.3 Shape change of CR solution droplet during solvent evaporation](image)
solution droplet float because those densities are lower in which the droplets were dispersed. Fig.2 by pressurizing and decompressing the PVA aqueous solution. The microbubbles or microdroplets were fabricated by agitating the CR solution in the PVA aqueous solution. CR solution droplets with 200–300 μm diameters were shown a cross section SEM image of a hollow CR particle. Fig.3 shows the change in the shape of the CR solution droplet during the solvent evaporation process, and Fig.4 shows a cross section SEM image of a hollow CR particle. Microbubbles or microdroplets in the PVA aqueous solution. Thus, hollow CR particles were obtained.

3.1 Fabricated hollow CR particles
Those microbubbles or microdroplets inside the CR droplets because of pressurization using oxygen gas at 0.5 MPa, and then, supersaturated oxygen microbubbles were generated inside the CR solution droplets during decompression to atmospheric pressure. (2) Supersaturated water was generated as microdroplets owing to the shrinkage of the CR solution droplets due to solvent evaporation from the droplets.

Hollow CR particles were fabricated by solvent evaporation from CR droplets if the droplets contained microbubbles or by further drying of the CR particles in atmosphere after solvent evaporation if the droplets contained microdroplets.

3.2 Influence of agitation speed
We also changed the agitation speed in the fabrication step (1) to 5000 rpm or 20000 rpm by using a homogenizer. Fig.6 (a) shows an optical microscope image of CR solution droplets dispersed at 5000 rpm, and Fig.6 (b) shows a cross section SEM image of the resultant hollow CR particle. Fig.7 (a) shows an optical microscope image of CR solution droplets dispersed at 20000 rpm, and Fig.7 (b) shows a TEM image of the resultant hollow CR particles. CR solution droplets with 13–53 μm diameters were obtained by dispersing the CR solution at 5000 rpm, and hollow CR particles with an average diameter of 8.7 μm were obtained after the solvent in the droplets was evaporated. Furthermore, 2–18 μm droplets were obtained by dispersing the CR solution droplets at 20000 rpm, and hollow CR particles of which average diameter and pore size were 2.2 μm and 1.1 μm respectively were obtained.

In this case, the surface area of obtained CR particles was about 2.4 m²/g, which was calculated from size distribution data on the assumption that all generated CR particles were spherical shape. Generally, the size of the dispersed droplet in emulsion decreases with the increase of agitating speed by the enhanced shear force acting on the interface between aqueous phase and solvent phase, and these CR particles were generated by the drying-out of CR solution droplet. Therefore the decrease in CR solution droplet size with increasing the agitating speed caused the decrease in CR particle size. As shown in Table 1, the average diameter of hollow CR particles was decreasing by increasing agitating speed, however, it was found that the number of microbubbles or microdroplets inside a CR solution droplet decreased with decreasing diameter of the CR solution droplet. Further, it was found that the number of voids in the hollow CR particles decreased with decreasing diameter of CR particles. Because the diameter of microbubbles or microdroplets in the CR droplets shown in Fig.2 and Fig.7 (a) were almost similar, there is a possibility that the diameter of microbubbles or microdroplets may not depend on the diameter of CR solution droplet. Accordingly, it is thought that the number of hollow CR particles having a single void can be increased by decreasing the diameter of the CR solution droplets.

Table 1 Result of the diameter of hollow CR particle by changing the agitating speed

<table>
<thead>
<tr>
<th>Agitating speed [rpm]</th>
<th>Average diameter [μm]</th>
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<tbody>
<tr>
<td>500 rpm</td>
<td>66.8 μm</td>
</tr>
<tr>
<td>5000 rpm</td>
<td>8.7 μm</td>
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<tr>
<td>20000 rpm</td>
<td>2.2 μm</td>
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3.3 Influence of CR concentration in solvent
The hollow CR particles of less than 10 μm were obtained by the fabrication method mentioned in the previous section. On the other hand, the CR solution droplets not including microbubble or microdroplet were also generated.
in fabrication step (3), and quite a lot of solid CR particles were obtained after the solvent evaporation. Almost all CR particles fabricated in the default condition and those at 5000 rpm had hollow structures. However, the ratio of hollow particles fabricated at 20000 rpm decreased drastically to 4.3% because the total nuclei of the microbubbles or microdroplets in one CR solution droplet decreases with the decreasing in the droplet size. Therefore, we tried to fabricate the hollow CR particles using the CR solution with higher CR concentration than default process for increasing the nuclei of microbubbles or microdroplets in the droplet.

Fig. 8 shows an optical microscope image of droplets of CR solution at 20000 rpm in the case of the tenfold CR concentration than the default process. Fig. 8 clearly indicates that CR droplets have more microbubbles or microdroplets than those in the case in default CR concentration at 20000 rpm as shown in Fig. 7. The TEM image of those CR particles as shown in Fig. 9 also indicates some CR particles have hollow spherical structures. The ratio of hollow particles to all particle measured by optical microscope images was 30.0% and increased with the increase of CR concentration as shown in Table 2. When microbubbles or microdroplets were generated by the rapid pressure decrease, they are often generated from impurities in the liquid (heterogeneous nucleation). Thus, the probability of bubble or droplet generation is thought to be increased with the increase of dissolved CR molecules in the solution which acted like impurities.

<table>
<thead>
<tr>
<th>CR toluene solution [ml]</th>
<th>Hollow CR particle [%]</th>
</tr>
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<tbody>
<tr>
<td>0.2 ml</td>
<td>4.3 %</td>
</tr>
<tr>
<td>2.0 ml</td>
<td>30.0 %</td>
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### 4. Conclusion

In this study, hollow <10 μm CR particles were prepared by the solvent evaporation from droplets of CR solution after these droplets were pressurized and decompressed. Furthermore, we found that the diameter of hollow CR particle was decreasing by increasing agitation speed, and the ratio of hollow CR particle was rising by increasing CR concentration in solution. The resulting hollow CR particles are a soft material because the CR has flexibility, and they are expected to find applications in building materials, vehicle parts such as heat insulators, and buffer materials.

### References


