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Synthesis of Bowl-like Particles by Emulsion Polymerization and Release Behavior of Solvent from the Particles

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Abstract: Bowl-like poly (styrene-co-glycidyl methacrylate) was synthesized by swollen seeded emulsion polymerization. The polymerization was carried out in PS seed emulsion swollen by toluene, whereby the bowl-like particles formed at last. The shape was observed by SEM. These particles became ball-like when swollen by toluene, observed by optical microscope, and the release behavior of solvent from them was examined.

Keywords: Hollow particle, bowl-like particle, seeded emulsion polymerization, release behavior.

Conventionally hollow particles have been produced by the alkali swelling procedure (ASP), dynamic swelling method (DSM), and water in oil in water (w/o/w) emulsion polymerization[1]. And because the hollow particles can preserve in various solvents, they can be used as reservoir and release material[2]. But almost all the work published before was to make hollow spheres. In this paper we tried a novel method, swollen seed emulsion polymerization. The resulted particles have large concavity that they look like bowls. These particles could be swollen and look like spheres. The release behavior of solvent from the particles was examined.

Experiment and Results

Firstly polystyrene (PS) seed latex was synthesized through soap-free emulsion polymerization. Secondly the PS seed particles were swollen by toluene latex prepared by ultrasonic dispersion. Then we added the latex in $K_2S_2O_8$ solution and heated the latex to 74℃, then dropped in the mixture of styrene, glycidyl methacrylate and cross-linker triethylene glycol diacrylate (TEGDA), reacting for 7 h. All the particles collapsed greatly and look like bowls, while some particles have more than one concavity as shown in **Figure 1**, which was viewed by SEM HITACHI S-3500N. When these bowl-like particles were dispersed in toluene, they were swollen again and became ball-like as shown in **Figure 2**, observed by an optical microscope (JIANGNAN XSX-2). It is different from the previous work. When the copolymer chains were long enough, the chains adhered to the swollen seeds, because there was a hydrophilic group (SO_4^-) at

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Figure 1 SEM of bowl-like particle

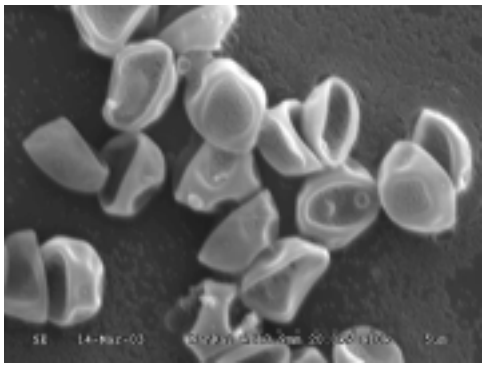


Figure 2 OM photo of swollen particle

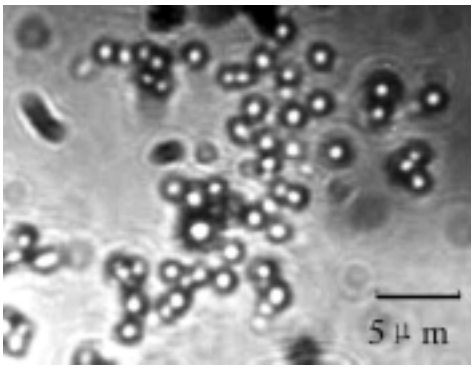
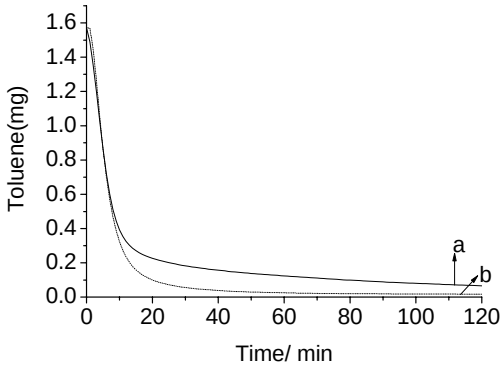


Figure 3 Weight loss curve due to the evaporation of toluene at 20℃ from the (a) bowl-like particles and (b) solid particles



an end of each hydrophobic copolymer chain. Then the polymerization continued at the surface of each core and a thin shell formed. That means the particle had a thin shell and a big hollow core. Because the solvent of PS (toluene in this case) evaporated faster than water as the medium in the drying process, water should penetrate into the shell as the hollow space was evacuated. And the penetration rate of water is much slower than the evaporation rate of the solvent from the hollow[3] because the shell is hydrophobic. These lead to an external pressure and the thin shell buckled.

The release of solvent from the particles was evaluated by measuring the weight loss of solvent with thermogravimetry (NETZSCH TG 209) at 20℃ under flow of nitrogen gas. 4 mg dried particles were placed on an aluminum pan and toluene was injected in. The solid particles were synthesized by seed emulsion polymerization, and the composition of them is the same to that of the bowl-like ones. **Figure 3** shows the weight loss curves due to the evaporation of toluene from the bowl-like (a) and the solid particles (b). The weight decreased at a constant rate and slowed down after certain time. The constant rate of weight loss shows the evaporation of pure toluene outside the particles. The latter weight loss is due to the evaporation of the toluene existing inside

the particles. The weight loss from the bowl-like particles was slower than that from the solid ones as the curves showed.

Conclusion

The bowl-like particles were prepared through swollen seed emulsion polymerization. The particles could be swollen by toluene and became ball-like. These particles may be used as reservoir and release material.

References

1. M. Okubo, H. Minami, Y. Yamamoto, *Colloids and Surfaces A*: *Physiochem. and Engin. Aspects* **1999**, *153*(1-3), 405.
2. B.S. Kim, J.W. Kim, K.D. Suh, *Journal of Appl. Polym. Sci*., **2000**, *76*(1), 38.
3. M. Okubo, H. Minami, K. Morikawa, *Colloid Polym. Sci*., **2003**, *281*(3), 214.

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