「접착 및 계면」
논문(original article)
제4권 (제1호), 2003

Preparation of Nanocapsules Containing Phase Change Materials by Miniemulsion Polymerization

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ABSTRACT

Polystyrene nanocapsules containing octadecane as a core material were prepared by miniemulsion polymerization. The morphology and size of the nanocapsules were measured with varying the surfactant concentration, content of initiator, core/shell ratio and content of comonomer. The morphologies of the prepared nanoparticles were examined by a scanning electron microscope, a transmission electron microscope and the core material was confirmed by a differential scanning calorimeter. The particles below 70 nm in diameter were formed at a high surfactant concentration. The size of the nanoparticles was not significantly affected by the initiator content. With increasing the core/shell ratio and polar comonomer content, the particle size and its distribution were increased.

KEYWORDS : NANOCAPSULE, MINIEMULSION, PHASE CHANGE MATERIAL, PARTICLE SIZE

Introduction

The control of the morphology of small particles has been an important field in polymer science, especially in latex particles because of having potential applications such as drug delivery system (DDS), paper coatings, inorganic encapsulation, cosmetics, *etc.*[1-4] Technology has developed such that a variety of structured latex particles are available including core-shell, microdomain, and interpenetrating network particles. These advanced technologies have been based on a deepening understanding the thermodynamic and the kinetic aspects of emulsion polymerization. This ability to control a particle morphology has enhanced significantly the range of physical properties available in a variety of application areas such as organic and inorganic encapsulations.

Nanocapsules are generally considered as spherical, hollow structures with an average diameter smaller than 1 μm.[5,6] Recently 20 nm size hollow particles have been made by using a cationic surfactant through microemulsion polymerization.[7] To keep a stable dispersion, the capsule surface is stabilized by surface charges or by adsorption of an amphiphile. The potential value of nanocapsules has been discussed for a variety of pharmaceutical

• 2002년 12월 12일 접수(received), 2003년 1월 20일 채택(accepted)
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applications, such as a medium for controlled release of calcitonin,[8] for peroral administrations of insulin,[9] or as a part of blood substitutes.[10] J. M. Kurner and colleagues prepared the inert phosphorescent nanospheres as markers for optical assays with using a coprecipitation phenomenon, which is very simple method.[11] Hollow latex particles can play a role as synthetic pigments, which contribute to the opacity of coatings by scattering light and improve the gloss of paper coatings.[12,13]

The storage of thermal energy as latent heat represents an attractive option to thermal energy storage and thermal energy insulator. A phase change material(PCM) is able theoretically to change state at a constant temperature and therefore store large quantities of energy. PCM is generally used after encapsulating with urea, urethane, or melamine through in-situ polymerization for preventing leak and reducing contamination. Sizes of PCM capsules available commercially are generally in the range of 1~100 μm.

Small capsules, especially nanocapsules, would pass readily through walls and reduce light scattering, giving great advantages in medical applications, electrical/electronic and optic industries. Achieved technologies thus will be useful for DDS (drug delivery system), high-resolution electronic inks, etc. The method for the synthesis of nanocapsules described below is based on the principle of miniemulsion using the differences of interfacial tension (solubility) and the phase-separation process during polymerization to obtain nano capsule morphology.

Miniemulsions are stable, submicron (50~500 nm) sized dispersions prepared by highly shearing a system including monomer, water, surfactant and co-surfactant (highly water-insoluble) which is suppressing Ostwald ripening of droplets.[14,15] To obtain the small droplets later changed into nanocapsules by miniemulsion polymerization, it is so important to make a stable starting situation, small primary droplet with a narrow droplet size distribution, by using high shearing tools. The encapsulation process initially involves nucleating a droplet, well-mixed hydrocarbon-monomer-initiator mixture, being phase-separated during the polymerization. The phase- separated polymer is considered the polymerization loci for making nanocapsules.

In this study, a miniemulsion polymerization was investigated to prepare nanocapsules containing PCM. By the encapsulation process, it is possible to prepare latex particles having highly hydrophobes of PCMs with a facile control of a particle diameter and morphology. The changes in particle sizes are mainly investigated with varying the surfactant concentration, initiator content, core/shell ratio and comonomer content.

Experimental

Materials

All chemicals and solvents used were of analytical grade and used without further purification. The monomers, styrene and acrylonitrile (AN), were purchased from Junsei and Acros, respectively. The phase change material (octadecane, m.p. : 30°C) was obtained from Aldrich. Sodium dodecyl sulfate (SDS)(Fluka) and 2,2′-azobisisobutyronitrile (AIBN)(Junsei) were used as a surfactant and an initiator, respectively. Distilled water was of Milli-Q quality (Millipore, USA- Bedford, MD).

Preparation

The nanoparticles were prepared by

miniemulsion polymerization. A 3-neck round bottom flask equipped with a mechanical stirrer, thermometer, reflux condenser, temperature controller, oil bath and nitrogen inlet, was used as a polymerization reactor. The PCM was stored in a convection oven at 35°C until use. The monomers and PCM were mixed and cooled at room temperature to prevent unexpected polymerization, and then an initiator was dissolved in the mixture. The resulting mixture was added to a solution of different contents of a surfactant in water. After the mixture was stirred for 1 h with a magnetic bar, miniemulsification was carried out by a homogenizer (Ultra turax T25, IKA Labotechnik, Germany) at an rpm of about 13000 for 2 min. Prepared miniemulsion was poured into the reactor in an oil bath and stirred with a half-moon blade-type impeller at 170 rpm. The reaction temperature was increased to 70°C for 25 min, and kept for 3 h. To complete the polymerization, the temperature was finally raised to 80°C for 10 min, and kept for 1 h. The latex particle was separated

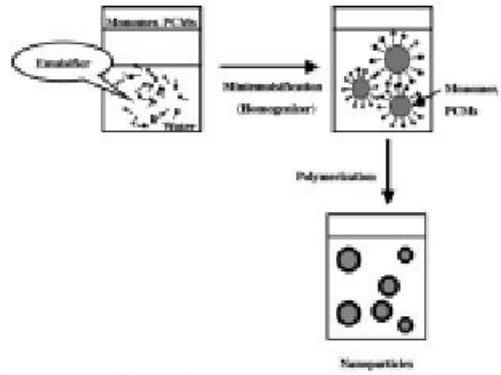


Figure 1. Schematic process of encapsulation.

by centrifugation at 5000 rpm for 15 min after being diluted with ethanol. The particle was dried under vacuum at room temperature overnight. A schematic description of he preparation method is given in Figure 1, and a recipe for preparing the nanocapsule is described in Table 1.

Characterization

The sizes of the particles were examined using scanning electron microscopy (JEOL, JSM-6700F). A droplet of the diluted ethanol solution was dried on a

Table 1. Recipe for Nanocapsules Containing PCM

Sample	Styrene(g)	Acrylonitrile(g)	Octadecane(g)	AIBN (wt%)[a)]	SDS (mM)[b)]
NC-1	15		5	0.73	3.5
NC-2	15		5	0.73	7
NC-3	15		5	0.73	17.5
NC-4	15		5	0.73	35
NC-5	15		5	0.37	17.5
NC-6	15		5	0.53	17.5
NC-7	15		5	1.46	17.5
NC-8	12.5		7.5	0.73	17.5
NC-9	10		10	0.73	17.5
NC-10	7.5		12.5	0.73	17.5
NC-11	5		15	0.73	17.5
NC-12	14.25	0.75	5	0.73	17.5
NC-13	12.75	2.25	5	0.73	17.5
NC-14	11.25	3.75	5	0.73	17.5

a) based on monomer content, b) based on water content, c) water content is 50 g

carbon mount and sputter-coated with platinum. All samples were observed at an accelerating voltage of 5.0 kV. The particle diameter was calculated by measuring that of at least 100 particles on each photograph. The number average diameter (Dn) is calculated from the following equation.[16]

$$D_n = \Sigma N_i D_i / \Sigma N_i$$

where Ni and Di are the number and diameter of particle "i", respectively.

Transmission electron microscopy (Carl ZEISS, EM912) was used to confirm whether nanocapsules were successfully prepared or not. Samples were prepared by allowing a droplet in diluted ethanol solution to dry on a carbon-coated grid. All samples were investigated at an accelerating voltage of 50 kV.

Melting behaviors of encapsulated PCMs were measured by a differential scanning calorimeter (TA instrument, DSC 2910) over a temperature range -20°C to 150°C, at a heating rate of 10°C/min under N_2 flow.

Results and Discussion

The effect of surfactant concentration

Miniemulsion polymerization was performed with varying a surfactant concentration using styrene as a monomer for a shell material and octadecane as a core material. The nanocapsule was successfully prepared by dispersion with high shearing force followed by polymerization. A well-defined spherical structure of the particle was observed from TEMs as shown in Figure 2. Dark regions due to PCM are shown in the center area. The particle morphologies will be discussed in more detail in the following section.

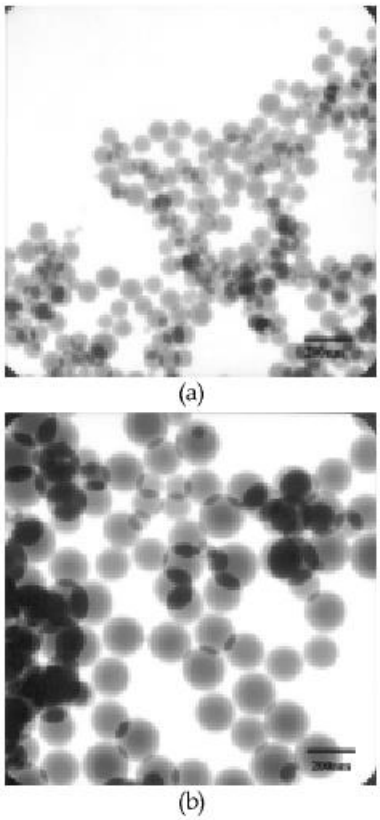


Figure 2. TEM photographs of nanocapsules. (a) NC-1, (b) NC-3

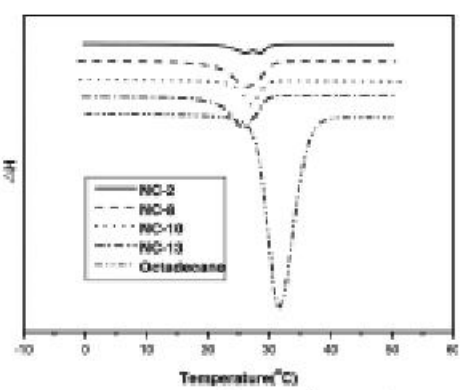


Figure 3. DSC curves for verifying that nanocapsules contain octadecane.

Figure 3 shows DSC curves for encapsulated PCM nanocapsules prepared in this study, verifying that the nanocapsules contain PCM that melts at around 30°C.

To obtain nanosized latex particles by

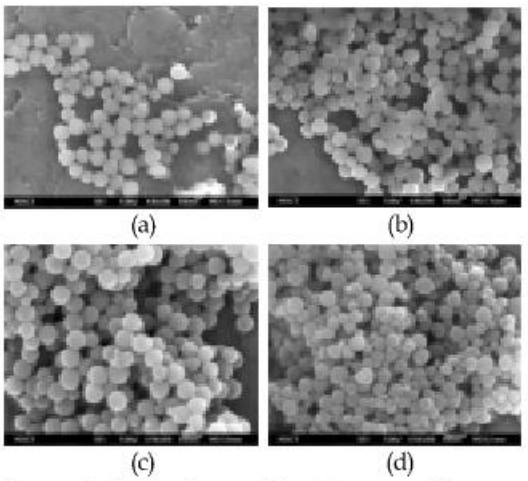


Figure 4. SEM micrographs of nanoparticles prepared with varying SDS concentrations. (a) NC-1, (b) NC-2, (c) NC-3, (d) NC-4.

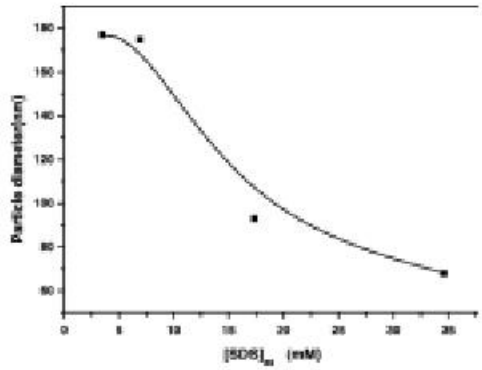


Figure 5. Particle size as a function of SDS concentration.

miniemulsion polymerization, high concentration of surfactants may be needed to reduce an interfacial tension and enhance the emulsion stability of small mixture droplets. Therefore, a series of miniemulsions were prepared in order to examine the effects of the surfactant concentration. The changes of morphologies and particle sizes (i.e., diameters) of nanocapsules are shown in Figure 4 and Figure 5. The particle sizes in Figure 5 were measured from SEMs in Figure 4. With an increase in the concentration of $[SDS]_{aq}$ (simply the total moles of SDS in the miniemulsion divided by unit volume (L) of water) from 3.5 mM to 35 mM, the average sizes of the particles were reduced from 175 nm to 70 nm. These results suggest that there is a strong dependence of the particle sizes on the surfactant concentration. With decreasing SDS concentration, the interfacial tension at the droplet/water interface increases due to a lower occupation by surfactant molecules. Comparing NC-1 with NC-4, it is observed that the dispersity of particle size for NC-4 is bigger than that for NC-1. The increase in the surfactant concentration would lead often to bimodal distributions for those monomer mixtures. In Figure 4(d), it is shown that there are some smaller particles (10~50 nm) than average particle size (70 nm). It is thought that when this miniemulsion was polymerized, particle formation did not occur predominantly by monomer droplet nucleation. This is because the residual concentration of the surfactant in the water phase increases at higher surfactant concentration and presumably led to another mechanism of nucleation (homogeneous nucleation). Actually, in miniemulsion polymerization, nucleation could take place not only in the monomer droplets, but also in the micelles and in the aqueous phase (homogeneous nucleation).

The effect of initiator concentration

Another important factor in miniemulsion polymerization is the concentration of initiator that not only has a large influence on the interfacial properties of the system, but also controls the dynamics of polymerization and phase separation. Oil-soluble initiator, for example, AIBN is partitioned preferentially into a styrene monomer droplet in the polymerization system of this study and generates the free radical in a confined space. AIBN

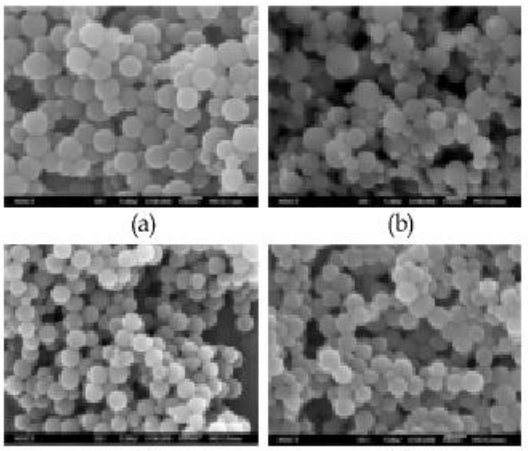


Figure 6. SEM micrographs of nanoparticles prepared with varying initiator contents. (a) NC-5, (b) NC-6, (c) NC-3, (d) NC-7

was used as an oil-soluble initiator in this study. The AIBN content was varied from 0.37 to 1.46 wt% based on the monomer content (see (a) NC-5, (b) NC-6, (c) NC-3 and (d) NC-7 in Figure 6). Particle sizes are slightly decreased from 103 to 80 nm with increasing the initiator content as shown in Figure 7.

From comparing Figure 5 with Figure 7, it is seemed that the concentration of surfactant is more effective for changing the particle size than that of initiator.

The effect of core/shell ratio

The effect of core/shell ratios in the styrene/octadecane system on the morphologies of the nanosized encapsules was investigated. Figure 8 shows scanning electron micrographs for the nanocapsules prepared with varying the core/shell ratios, revealing a significant change in the morphology of the nanoparticle. Keeping the surfactant concentration at 17.5 mM and the initiator content at 0.73 wt%, particles of about 90 nm were obtained as shown in Figure 8 and Figure 4(c) when the content of octadecane was less than

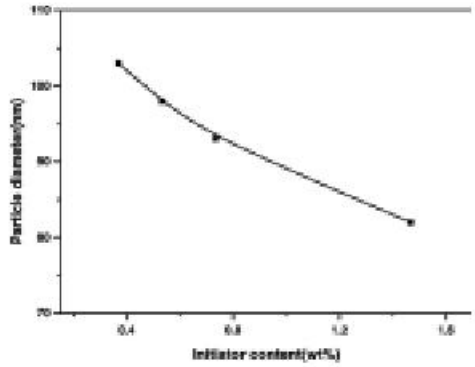


Figure 7. Particle size as a function of initiator content.

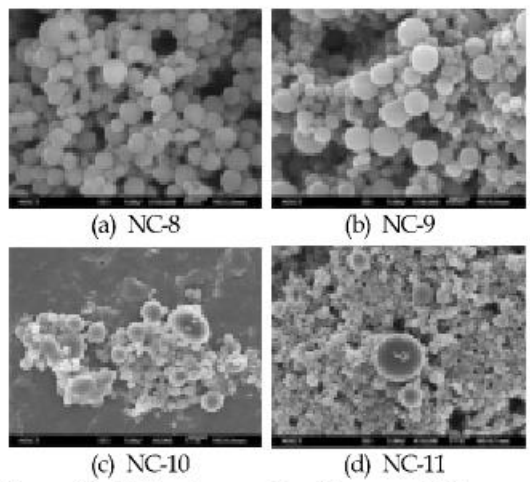
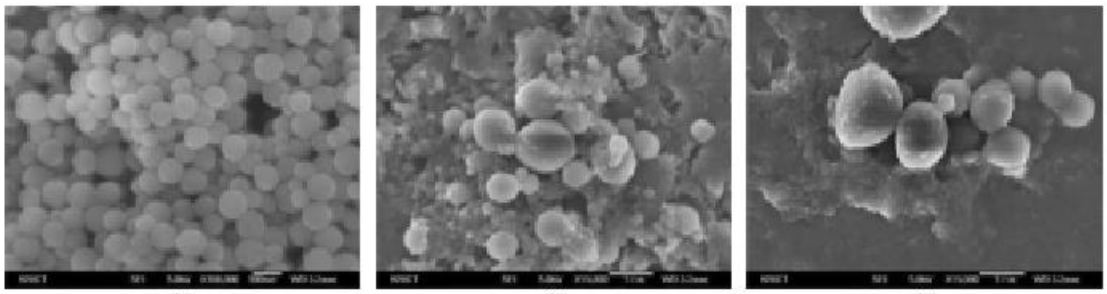


Figure 8. SEM micrographs of nanoparticles prepared with varying core/shell ratios. (a) NC-8, (b) NC-9, (c) NC-10, (d) NC-11

50%. With increasing the core/shell ratio, the particle size distribution becomes broader. For the nanocapsules prepared with more than 50% PCM content in PCM/styrene, it was difficult to prepare discrete spherical nanocapsules. On comparison of NC-8 and NC-9, the size of the nanocapsules increased with increasing the PCM content (see parts (a) and (b) of Figure 8). When the octadecane content was 75%, it was very difficult to obtain the spherical nanocapsule. The increase of the core content leads to a fragile shell, that is, its extension to form an



(a) (b) (c)

Figure 9. SEM micrographs of nanoparticles prepared with varying comonomer contents. (a) NC-12, (b) NC-13, (c) NC-14

oil-filled capsule, resulting in an obstacle in obtaining the particle powder by centrifugation.

The effect of comonomer

A promising way to improve the perfection of the capsules is the addition of a comonomer to the shell phase. In terms of thermodynamics, Torza and Mason pioneered the study of the interfacial behavior of systems containing various types of three mutually immiscible liquids.[17] They proposed that two immiscible liquid drops, designated as phase-1 and phase-3, suspended in a third immiscible liquid, phase-2, are brought into contact, resulting equilibrium configuration is readily predicted from the interfacial tensions σ_{ij} and spreading coefficients, $S_i = \sigma_{jk} - (\sigma_{ij} + \sigma_{ik})$. In terms of the convention $\sigma_{12} > \sigma_{23}$ ($S_1 < 0$), pahse-1 is completely engulfed by phase-3 when $S_2 < 0$ and $S_3 > 0$; no engulfing occurs when $S_2 > 0$ and $S_3 < 0$; and S_1, S_2, $S_3 < 0$ leads to partial engulfing and formation of 2-phase drops with three interfaces the shapes of which can be calculated. For simplicity it was assumed that the final equilibrium state is determined solely by the three interfacial tensions, σ_{12}, σ_{13}, σ_{23}.

Torza and Mason's theory can be applied to our study especially for this section. To make more stable nanocapsule, namely, complete engulfing phase, we can speculate that spreading coefficient, a key factor in determining the particle morphology, is closely related to interfacial tension. Let the phase-1 be the octadecane, the phase-2 be water and the phase-3 be the styrene polymer. We already know that styrene and octadecane are highly hydrophobic. Therefore, if styrene polymer is modified with a more hydrophilic moiety, σ_{12} is always greater than other interfacial tension, σ_{13}, σ_{23}, and thermodynamically favorable nanocapsule morphology is obtained. Styrene-AN copolymer is more probable as a shell polymer compared with polystyrene because it permits the preparation of core/shell particle with thinner wall.[18] The efficiency of the encapsulation of the octadecane in the presence of AN is closely related to the lowering of the interfacial tensions and spreading coefficient in this miniemulsion system. Figure 9 shows that with increasing AN concentration, particle morphology is significantly changed. At the 5 wt% of the AN in the shell phase, the morphology shows uniform spherical particles, but over 15% of AN, the size and its distribution are considerably large due to the increased affinity of shell phase to water phase. Very large particles of about 1 μm in diameter were

observed at 25% AN concentration.

Conclusions

In this paper, the synthesis of nanocapsules containing PCM (octadecane) as a core material was successfully performed using miniemulsion polymerization. The nanocapsules were prepared from the mixtures of styrene monomer and PCM with varying the concentrations of surfactant and initiator, core/shell ratio and comonomer content. In the case of varying the surfactant, the capsule size was decreased to below 70 nm when SDS concentration was increased. With increasing an initiator concentration, the particle size was slightly reduced from about 100 nm to 80 nm. It was difficult to obtain discrete spherical morphologies for the nanocapsules with PCM content more than 50%. With an addition of polar monomer, AN into styrene shell phase, large particles of about 1 μm in diameter was obtained by miniemulsion polymerization.

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