Colloid Polym Sci (2008) 286:753–759
DOI 10.1007/s00396-007-1831-5

ORIGINAL CONTRIBUTION

Influence of water domain formed in hexadecane core inside cross-linked capsule particle on thermal properties for heat storage application

Preeyaporn Chaiyasat · Yumiko Ogino ·
Toyoko Suzuki · Masayoshi Okubo

Received: 9 October 2007 / Revised: 10 December 2007 / Accepted: 15 December 2007 / Published online: 14 January 2008

Abstract The influence of a water domain formed in *n*-hexadecane (HD) core in cross-linked polymer capsule particles on the thermal properties of encapsulated HD was studied from the view point of heat storage application. The capsule particles were prepared by micro-suspension polymerization of divinylbenzene at 70 °C utilizing the Self-assembling of Phase-Separated Polymer (SaPSeP) method that the authors proposed. The water domain was not observed for particles taken just after the polymerization and kept at 70 °C, but it was gradually formed with an increase of the size during cooling process from 70 °C to room temperature. In differential scanning calorimetric thermograms, pure HD had a single peak because of solidification (T_s) at 15 °C, and the encapsulated HD containing the water domain had two peaks of T_{s1} and T_{s2}, at 6 and 1 °C, respectively. That is, the encapsulated HD containing the water domain required longer time and lower temperature to complete the solidification than the pure HD, which is negative for its application. However, the lower temperature-side peak at T_{s2} gradually disappeared with an increase of capsule particle diameter, which seems to be based on the decrease of total interfacial area between the water domains and encapsulated HD in the capsule particles.

Keywords Micro-suspension polymerization · Capsule particles · Hexadecane · Heat storage material · Hollow particle

Introduction

Polymer particles with hollow structures have been made attractive for many industrial applications, such as microcapsules, hinding, or opacifying agents in coating and molding compositions [1–6]. We have succeeded in preparing about 5-μm-sized, monodisperse, cross-linked polymer particles with a single hollow at the center by seed polymerization of highly divinylbenzene (DVB)/toluene-swollen polystyrene (PS) particles [7, 8] prepared by the dynamic swelling method [9, 10]. The formation mechanism of the hollow polymer particles was proposed [11]. On the basis of this mechanism, hollow polymer particles were also prepared by micro-suspension polymerization of DVB/toluene droplets dissolving PS and benzoyl peroxide (BPO), although they were polydisperse [12]. The PS dissolved in the DVB/toluene droplets worked as the accelerator for the phase separation of polyDVB (PDVB) formed therein during the polymerization [13]. The formation of this hollow structure was named the Self-assembling of Phase-Separated Polymer (SaPSeP) method. Micro-suspension polymerization of DVB droplets including *n*-hexadecane (HD) yielded HD-capsulated particles where HD as nonsolvent worked like as PS in the SaPSeP method [14]. HD accelerated phase separation of PDVB in the droplets even in an early stage of the polymerization, and the phase-separated PDVB moved toward the interface of the droplets. The time at which phase separation began depended on both

---

Part CCCIII of the series “Studies on suspension and emulsion”.

P. Chaiyasat · Y. Ogino · T. Suzuki · M. Okubo (✉)
Department of Chemical Science and Engineering,
Graduate School of Engineering, Kobe University,
Kobe 657-8501, Japan
e-mail: okubo@kobe-u.ac.jp

Table 1 Recipes for the production of PDVB capsule particles with encapsulated HD by micro-suspension polymerization (N_2, 70 °C, 24 h, 80 cycles/min (3-cm strokes)) of comparatively monodisperse DVB/HD droplets prepared by SPG membrane method (SPG membranes (pore sizes: 1.1, 1.9, 3.1, 3.9, and 4.9 μm))

Ingredient	DVB/HD (*w*/*w*)	
	2/2	2/3
DVB (g)	3.3	2.6
HD (g)	3.3	4.0
BPO (g)	0.1	0.1
PVA (g)	0.5	0.5
Water (g)	50	50

DVB Divinylbenzene, *PDVB* poly(DVB), *HD* *n*-hexadecane, *BPO* benzoyl peroxide, *PVA* poly(vinyl alcohol)

the HD content and the polymerization rate of DVB. That is, the SaPSeP method is applicable not only to the preparation of hollow particles but also to the encapsulation of HD.

HD, which is a paraffin wax, is useful as one of numerous numbers of heat storage materials that melt and solidify at a wide range of temperatures, making them attractive for many applications. Paraffin waxes are generally cheap and have moderate thermal energy storage but low thermal conductivity, therefore, it requires large surface areas for the application. The encapsulation of these materials have many advantages that provide large heat transfer area and control the volume change of the storage materials as phase change occurs [15–16].

Recently, we have studied the preparation of PDVB capsule particles with encapsulated HD as heat storage materials by micro-suspension polymerization utilizing the SaPSeP method of micron-sized, comparatively monodisperse DVB/HD droplets prepared by Shirasu porous glass (SPG) membrane method [17, 18]. The heat of melting (H_m), which corresponds to the heat of solidification (H_s), of pure HD used in our experiment was about 230 J/g, and its melting temperature (T_m), which corresponds to solidification temperature (T_s), was about 15 °C. It was found that H_s of HD encapsulated by PDVB shell was much lower than that of pure HD. Moreover, T_s of the encapsulated HD was also about 10 °C lower than that of the pure HD, while T_m still remained at 15 °C [19]. These phenomena are, of course, negative to apply it for heat storage materials. However, the problem in the decrease of H_s of the encapsulated HD was improved by the copolymerization of acrylic monomer such as butyl acrylate [20]. This seems to be based on that the copolymerization of polar monomer enhances the phase separation of copolymer chains in HD, eventually resulting in the complete isolation of the HD core from the polymer shell. Moreover, it was also found that PDVB particles of different shell thicknesses resulted in the different particle shapes [14]. In the case of thicker shell (DVB/HD=2/2, *w*/*w*), a single water domain was observed in HD core encapsulated by PDVB shell of spherical capsule particles, whereas in the thinner shell (DVB/HD=2/3, *w*/*w*), nonspherical capsule particles, in which such a water domain was not contained in HD core, were prepared. The differential scanning calorimeter (DSC) thermogram of spherical capsule particles containing water domain had bimodal solidification curve consisting of lower and higher temperature-side peaks, whereas the other ones showed single peak without lower temperature-side peak [19, 20]. Therefore, for heat storage application, it is important to clarify the reason why the water domain forms.

In this article, the formation and influence of the water domain existing in the HD core in the cross-linked capsule particle on the thermal properties of the encapsulated HD will be studied from the view point of heat storage application.

Experimental section

Materials

DVB (Nippon Steel Chemical, Tokyo, Japan; purity, 96%) was washed with 1 N NaOH and distilled water to remove polymerization inhibitors before use. Poly(vinyl alcohol) (PVA) (Gohsenol GH-17: degree of polymerization, 1,700; degree of saponification, 88%) was supplied by Nippon Synthetic Chemical, Osaka, Japan. Reagent-grade BPO was purified by recrystallization. Deionized water was distilled with a Pyrex distillator. HD (Nacalai Tesque, Kyoto, Japan; guaranteed reagent grade) was used as received.

SPG membrane emulsification and micro-suspension polymerization

A homogeneous solution of DVB, HD, and BPO was dispersed as droplets in PVA aqueous solution with SPG membrane (SPG Technology, Japan). Micro-suspension polymerization of the monomer dispersions was carried out at 70 °C for 24 h under nitrogen atmosphere in sealed glass tubes under the conditions listed in Table 1. The tubes

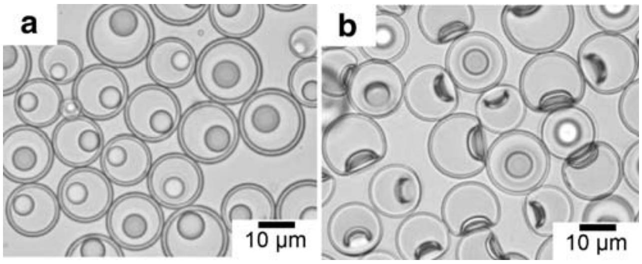

Fig. 1 Optical micrographs of PDVB/HD particles prepared by micro-suspension polymerization utilizing the SaPSeP method of DVB/HD droplets prepared with SPG emulsification method under the conditions listed in Table 1. DVB/HD (*w*/*w*): **a** 2/2; **b** 2/3

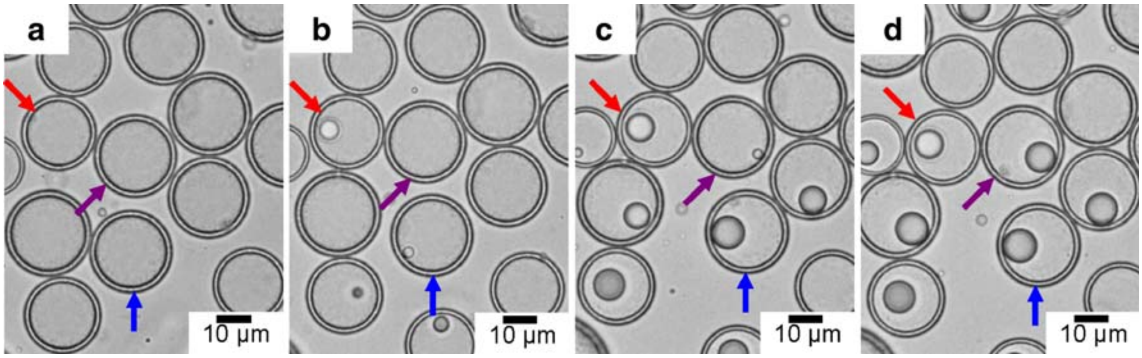

Fig. 2 Optical micrographs during spontaneous cooling process of PDVB/HD particles prepared by micro-suspension polymerizations of DVB/HD (2/2, *w*/*w*) droplets prepared by SPG emulsification method under condition listed in Table 1. Temperatures (°C): **a** 70; **b** 55; **c** 40; **d** 25

were horizontally shaken at 80 cycles/min (3-cm strokes). Prepared particles were observed with an optical microscope (ECLIPSE 80i, Nikon Corporation, Tokyo, Japan).

Measurement of thermal properties

H_s, T_s, H_m, and T_m of encapsulated HD in capsule particles at emulsion (solid content: ca 10%) and dry states were measured on an aluminum pan with a DSC (DSC 6200, Seiko Instruments Inc., Chiba, Japan) under a N_2 flow at a scanning rate of 5 °C/min.

Observation of solidification process of encapsulated HD

Solidification process of HD encapsulated by PDVB shell was observed with an optical microscope (MICROPHOT-FXA, Nikon Corporation, Tokyo, Japan) equipped with a high-speed camera (FASTCAM Viewer, Photron, Tokyo, Japan) and a temperature control system (FP 900 Thermosystem, Mettler Toledo, Switzerland).

Results and discussion

Figure 1 shows optical micrographs (at room temperature) of PDVB particles with encapsulated HD produced by micro-suspension polymerization (at 70 °C) of DVB/HD droplets prepared by SPG membrane method under the conditions listed in Table 1. The particles were comparatively monodisperse. At the ratio of DVB/HD=2/2 (*w*/*w*; Fig. 1a), spherical capsule particles with smooth outer surface were obtained. In addition, a single domain was observed in the HD core encapsulated by PDVB shell, which will be discussed later. On the other hand, in the case of DVB/HD=2/3 (*w*/*w*; Fig. 1b), nonspherical particles with smooth outer surface were formed. As discussed in the previous article [20, 21], because the shell strength was not enough, a part of the shell buckled because of external pressure.

To understand the formation mechanism of the single domain in the HD core inside the capsule particle (PDVB/HD=2/2, *w*/*w*), a spontaneous cooling process of the capsule particles from the polymerization temperature (70 °C) to room temperature, where the sample produced at 70 °C was kept at room temperature, was observed with an optical microscope. Figure 2 shows the result. The single domain was not observed in the capsule particles taken just after the polymerization and kept at 70 °C. This suggests that any water domain has not formed yet or very fine domains, which are not visible with optical microscope, have formed because of the shrinkage of DVB/HD core phase with the polymerization after the cross-linked shell formation based on the different densities of DVB and PDVB (0.91 and 1.04 g/cm^3, respectively) [22]. During

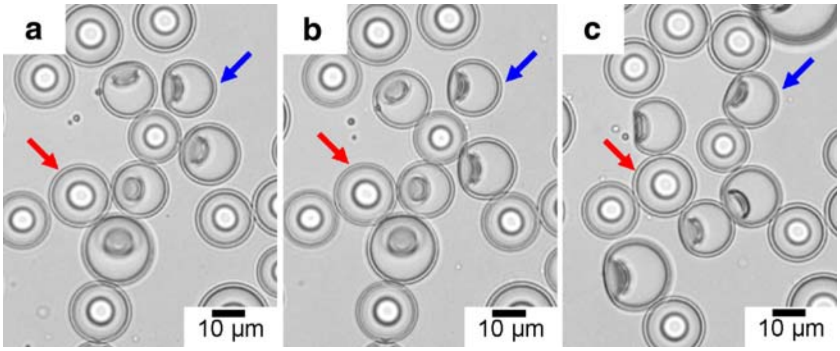

Fig. 3 Optical micrographs during spontaneous cooling process of PDVB/HD particles prepared by micro-suspension polymerizations of DVB/HD (2/3, *w*/*w*) droplets prepared by SPG emulsification method under condition listed in Table 1. Temperatures (°C): **a** 70; **b** 50; **c** 25

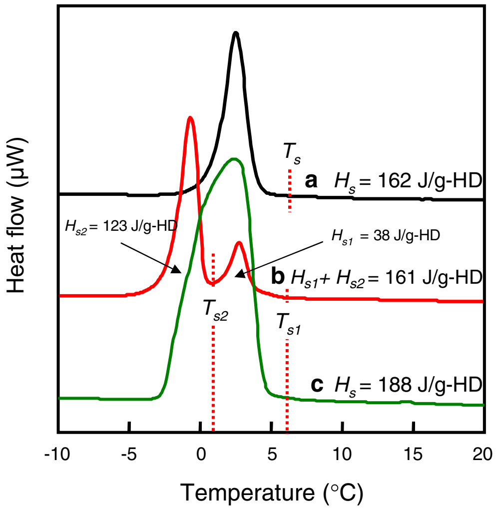

Fig. 4 DSC thermograms of HD encapsulated by PDVB shell at different weight ratios of DVB/HD produced by micro-suspension polymerization of DVB/HD droplets prepared by SPG (pore size 1.1 μm) emulsification method under the conditions listed in Table 1. Measured states: (*a*, *b*) emulsion; (*c*) dry. DVB/HD (*w*/*w*): (*a*) 2/3; (*b*, *c*) 2/2

cooling from 70 to 25 °C, the single domain appeared in each particle and the domain size increased with descending the temperature. The occupied volume of the domain was 11–16% of HD. Even if the temperature was increased again from room temperature to 70 °C, the single domain did not disappear. Cooling after the polymerization increases the density of HD, leading to the formation of space inside the capsule particles. The volume shrinkage of HD at 20 °C is calculated to be 4.6% based on the densities of HD at 20 and 70 °C, which are 0.773 and 0.739 g/cm^3, respectively [23]. Because this space reduces the internal pressure of the core, it seems that water penetrates into the core from the aqueous medium without shape transformation of the spherical particles, resulting in the water domain in the HD core if shell strength is enough to withstand the external pressure.

On the other hand, in the case of PDVB particles of DVB/HD = 2/3 (*w*/*w*; Fig. 3), even if just after the polymerization, nonspherical particles, which did not contain a water domain, were observed. It seems that this shape deformation was taken place by shrinkage of the monomer phase as previously mentioned during the polymerization. Because the shell strength was not enough to withstand the outer pressure, a part of the shell buckled before the penetration of water. Therefore, water domain was not observed in the particles. Further deformation of particles was not clearly observed during spontaneous cooling from 70 °C to room temperature. Even if the temperature was raised again to 70 °C, the nonspherical shape did not change.

From the view point of heat storage application, the measurement of the thermal properties of both encapsulated HD with and without water domain was carried out to understand whether or not this water domain affects the thermal properties of encapsulated HD. Figure 4 shows DSC thermograms of HD encapsulated by PDVB shell having different weight ratios of DVB/HD, measured using emulsion and dried samples. In all cases, T_m of the encapsulated HD still remained at 15 °C, which is equal to that of pure HD. In the case of DVB/HD ratio of 2/3 (*w*/*w*), a sharp single peak of encapsulated HD because of solidification was observed, and its H_s and T_s values were

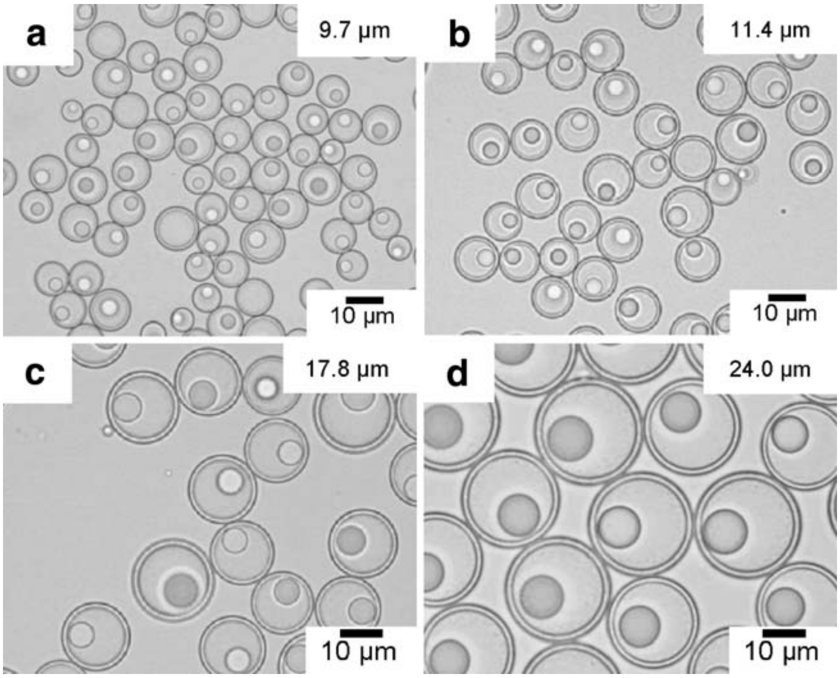

Fig. 5 Optical micrographs of PDVB/HD particles prepared by micro-suspension polymerization utilizing the SaPSeP method of DVB/HD (DVB/HD=2/2, *w*/*w*) droplets prepared with SPG membrane emulsification method under the conditions listed in Table 1. SPG membrane pore size (μm): **a** 1.3; **b** 1.9; **c** 3.1; **d** 4.9

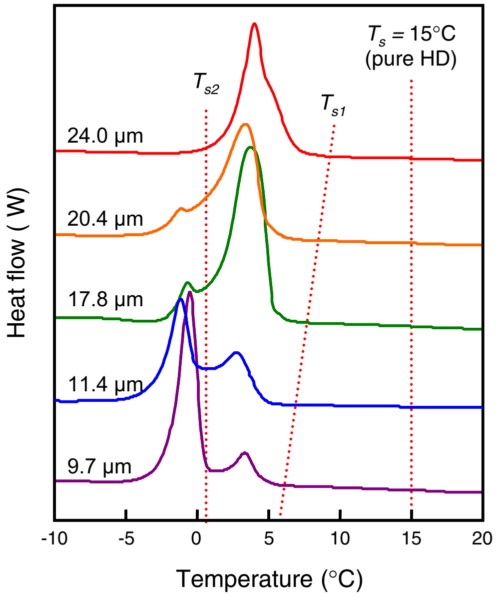

Fig. 6 DSC thermograms of encapsulated HD of PDVB/HD (DVB/HD= 2/2, *w*/*w*) dispersion measured by DSC at a scanning rate of 5 °C/min. *Numbers* on thermograms indicate particle diameters

162 J/g-HD and 6 °C, respectively. On the other hand, in the case of DVB/HD ratio of 2/2 (*w*/*w*), the peak was bimodal. H_{s1} and T_{s1} values at the first peak (higher temperature side) were 38 J/g-HD and 6 °C, respectively. H_{s2} and T_{s2} values at the second peak (lower temperature side) were 123 J/g-HD and 1 °C, respectively. Total H_s ($H_{s1}+H_{s2}$=161 J/g-HD) was almost the same as that (162 J/g-HD) with DVB/HD of 2/3 (*w*/*w*). The encapsulated HD containing the water domain in the spherical capsule particles needed longer time and lower temperature to complete the solidification than the other ones. This phenomenon is negative for its heat storage application.

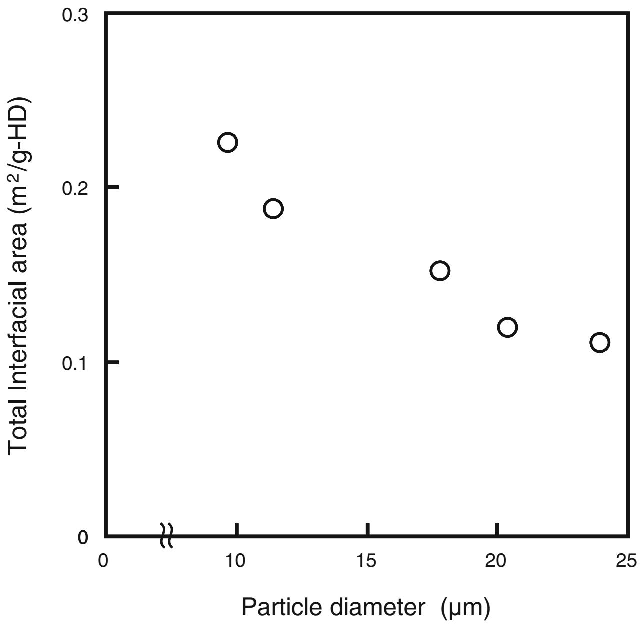

Fig. 7 Relationship between the diameter of PDVB/HD (DVB/HD= 2/2, *w*/*w*) particles and total interfacial area of water domain in encapsulated HD

When the spherical capsule particles with DVB/HD of 2/2 (*w*/*w*) were dried at 70 °C for 2 h, the water domain was replaced by air. A DSC thermogram of the dried particles had a single peak: H_s=188 J/g-HD; T_s=6 °C. These seem that the lower temperature-side peak (H_{s2}, T_{s2}) is because of the influence of the water domain in the HD core. Zhang et al. have reported the observation of multiple peaks on the DSC cooling curves of some encapsulated *n*-alkanes such as *n*-octadecane and *n*-eicosane in urea melamine-formaldehyde capsule particles [24]. They did not refer to the existence of such a water domain in the *n*-alkane core. They suggested that the multiple peaks' behavior on the DSC cooling curves is mainly caused by the difference in the average diameters attributed to the heterogeneous and homogeneous nucleations. Therefore, to clarify our assumption, capsule particles having various particle diameters resulting in different water domain diameters were prepared.

Figure 5 shows optical micrographs of PDVB/HD capsule particles produced by micro-suspension polymerization of DVB/HD (2/2, *w*/*w*) droplets having various diameters prepared with SPG membranes having different pore sizes under the conditions listed in Table 1. Regardless of particle diameter, all particles were spherical and contained a single water domain in encapsulated HD.

The influence of water domain having different diameters was investigated by DSC measurement. Figure 6 shows their DSC thermograms. Lower temperature-side peak (T_{s2}=1 °C) gradually disappeared with an increase of the particle diameter. As the particle diameter increased, water domain size also increased. Therefore, the total interfacial area of the water domains based on the total amount of the encapsulated

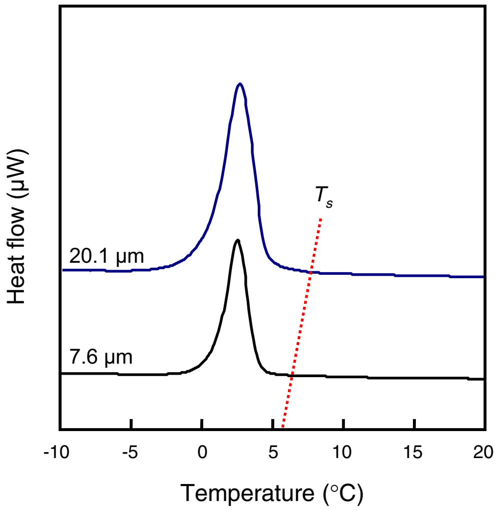

Fig. 8 DSC thermograms of encapsulated HD of PDVB/HD (DVB/HD= 2/3, *w*/*w*) dispersion measured by DSC at a scanning rate of 5 °C/min. *Numbers* on thermograms indicate particle diameters

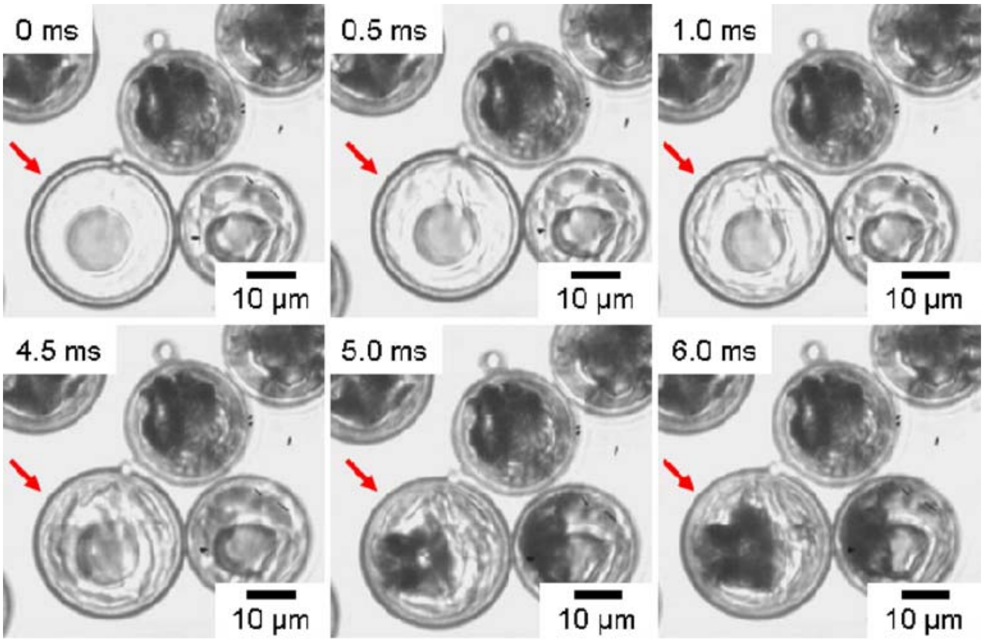

Fig. 9 Optical micrographs (with high-speed camera) of solidification of HD encapsulated by PDVB (DVB/HD=2/2, *w*/*w*) shell during cooling at 5 °C/min

HD decreased with the increase in the particle diameter as shown in Fig. 7. Consequently, the influence of water domain on encapsulated HD properties should also be decreased. This seems to be the reason why the lower temperature-side peak gradually disappeared with the increase of the particle diameter.

In addition, it was also found that the sharp single solidification peak of encapsulated HD was observed in the case of PDVB (DVB/HD=2/3, *w*/*w*) capsule particles without water domain having various particle diameters as shown in Fig. 8. This also supports our assumption that the volume of encapsulated HD or particle diameter should not affect the formation of bimodal peak in our PDVB capsule particles, because this peak was not observed in capsule particles without water domain. Thus, it can be concluded that the lower temperature-side peak is because of the influence of the water domain in the HD core.

Moreover, T_s (T_{s1}) of encapsulated HD increased from 5 to 9 °C with the increase of particle diameter from 9.7 to 24.0 μm, as already discussed in the previous article [18]. The reason of T_s decreasing of HD by encapsulation may be based on a "compartmentalization" effect: Impurities located in capsule particle cannot induce the nucleation of HD encapsulated in the other particles [20]. In a bulk

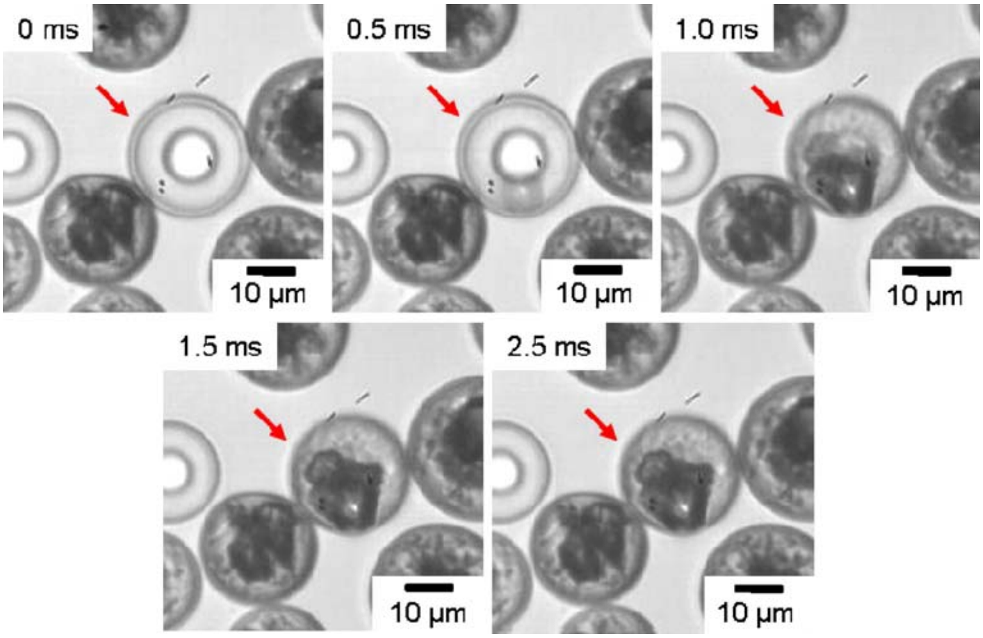

Fig. 10 Optical micrographs (with high-speed camera) of solidification of HD encapsulated by PDVB (DVB/HD=2/3, *w*/*w*) shell during cooling at 5 °C/min

system, it is known that there is an impurity that works as a trigger for the nucleation resulting in heterogeneous nucleation [25]. When particle diameter is increased, the number of impurities in each particle should be increased, leading to the increase of T_s (T_{s1}) to that of pure HD.

As previously discussed, the encapsulated HD containing the water domain in the spherical capsule particles needed longer time and lower temperature to complete the solidification than the other ones. This is, of course, negative for its heat storage application. The observation of solidification of encapsulated HD by optical microscope with high-speed camera obviously supported this result. Figures 9 and 10 show optical micrographs (with high-speed camera) of solidification of HD encapsulated by PDVB shells produced at DVB/HD weight ratios of 2/2 and 2/3, respectively. In Fig. 10, only the particles at which a dented point was located in vertical direction was focused to clearly observe the starting point of solidification of HD in the nonspherical capsule particles. In both cases (Figs. 9 and 10), the solidification of the encapsulated HD started at the interface of the polymer shell and HD and continued until completely solidified. Solidification time of HD encapsulated by PDVB shell with DVB/HD weight ratio of 2/2 (6 ms) was longer than that (2.5 ms) of DVB/HD weight ratio of 2/3. This is consistent with the DSC results that in the former case the lower temperature-side peak of the solidification (H_{s2}, T_{s2}) was observed.

Conclusions

There was an influence of a single water domain formed in HD core in PDVB capsule particles produced by microsuspension polymerization utilizing the SaPSeP method on the thermal properties of the encapsulated HD, which is important for heat storage application. It was found that the water domain in the HD core was not observed for particles taken just after polymerization and kept at 70 °C, but it was gradually formed with the increase of their sizes during cooling process from 70 °C to room temperature. This is because the density of HD increases with the descending of temperature, leading to the formation of space inside the capsule particles. When the shell strength is enough to withstand the external pressure derived from the evacuated space, water penetrated into HD core through the shell without shape transformation of the capsule particles. This water domain led to the decrease of T_s ($\rightarrow T_{s2}$) of encapsulated HD in the capsule particles, which is negative for its application. However, this influence gradually decreased with an increase of the particle diameter, which seems to be because of the decrease of total interfacial area of water domains in encapsulated HD cores.

Acknowledgment This work was partially supported by a Grant-in-Aid for Scientific Research (Grant 17201025) from the Japan Society for the Promotion of Science (JSPS).

References

1. Kowalski A., USP (1984)
2. Okubo M, Ichikawa K, Fujimura M (1991) Colloid Polym Sci 269:1257
3. Okubo M, Okada M, Shiba K (2003) Macromol Symp 195:115
4. Okada M, Okubo M, Motaba T (2004) Colloid Polym Sci 282:193
5. Itou N, Masukawa T, Ozaki I, Hattori M, Kasai K (1999) Colloid Surf A: Physiochem Eng Aspect 153:311
6. McDonald CJ, Bouck KJ, Chaput AB, Stevens CJ (2000) Macromolecules 33:1593
7. Okubo M, Minami H, Yamashita T (1996) Macromol Symp 101:509
8. Okubo M, Minami H (1996) Colloid Polym Sci 274:433
9. Okubo M, Shiozaki M, Tsujihiro M, Tsukuda Y (1991) Colloid Polym Sci 269:222
10. Okubo M, Shiozaki M (1993) Polym Int 30:469
11. Okubo M, Minami H (1997) Colloid Polym Sci 275:992
12. Okubo M, Konishi Y, Minami H (1998) Colloid Polym Sci 276:638
13. Konishi Y, Okubo M, Minami H (2003) Colloid Polym Sci 281:123
14. Okubo M, Konishi Y, Minami H (2003) Progr Colloid Polym Sci 124:54
15. Farid MM, Khudhair AM, Razack SAK, Al-Hallaj S (2004) Energy Convers Manag 45:1597
16. Wei J, Kawaguchi Y, Hirano S, Takeuchi H (2005) Appl Therm Eng 25:2903
17. Nakajima Y, Shimizu M (1988) Journal of the Mineralogical Society of Japan 18:393
18. Ma GH, Nagai M, Omi S (1999) Colloid Surf A: Physiochem Eng Aspect 153:383
19. Ogino Y, Suzuki T, Okubo M (2007) Kobunshi Ronbunshu 64 (3):171
20. Chaiyasat P, Ogino Y, Suzuki T, Minami H, Okubo M (2008) Colloid Polym Sci (in press)
21. Minami H, Kobayashi H, Okubo M (2005) Langmuir 21:5655
22. Brandrup J, Immergut EH, Grulke EA (eds) (1999) Polymer Handbook, 4th ed. Wiley, New York
23. Queimada AJ, Quinones-Cisneros SE, Marrucho IM, Coutinho JAP, Stenby EH (2003) Inter J Thermophysics 24:1221
24. Zhang XX, Fan YF, Tao XM, Yick KL (2005) J Colloid Interface Sci 281:299
25. Coupland JN (2002) Curr Opin Colloid Interface Sci 7:445