Thermal Properties of Hexadecane Encapsulated in Poly(divinylbenzene) Particles

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ABSTRACT: The thermal properties of n-hexadecane (HD) encapsulated in crosslinked capsule particles containing a water and/or air domain were studied from the viewpoint of heat-storage applications. The capsule particles were prepared by the microsuspension polymerization of divinylbenzene at 70°C with the self-assembling of phase-separated polymer method that we developed. In the differential scanning calorimetric thermograms, pure HD had a single solidification temperature (T_s) peak at 15°C, whereas the encapsulated HD containing a water domain had two peaks at 6 and 1°C. That is, the encapsulated HD containing the water domain required a longer time and lower temperature to complete the solidification than pure HD, which was negative for heat-storage applications. However, once the particles were dried and the water domain was replaced with air, the problem with the partially lowered T_s improved. The air domain was also found in the encapsulated HD core after solidification because of the shrinkage of HD. The presence of the air domain did not affect the thermal stability of the encapsulated HD. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3257–3266, 2009

Key words: differential scanning calorimetry (DSC); microencapsulation; thermal properties

INTRODUCTION

Polymer particles with hollow structures are attractive because of numerous industrial applications, such as microcapsules, hiding or opacifying agents in coatings, and molding compositions.[1–6] We succeeded in preparing approximately 5-μm monodisperse crosslinked polymer particles with a single hollow center by the seeded polymerization of divinylbenzene (DVB)/toluene-swollen polystyrene (PS) particles[7,8] prepared by the dynamic swelling method.[9,10] The formation of the hollow structure is named the *self-assembling of phase-separated polymer* (SaPSeP) method, and a mechanism was proposed.[11] Initially, PS dissolved in the DVB/toluene droplets homogeneously. As the polymerization proceeded, polydivinylbenzene (PDVB) chains precipitated in the droplets because of crosslinking. They were trapped near the interface because of surface coagulation and gradually piled at the inner interface, which resulted in a crosslinked PDVB shell. PS dissolved in toluene and DVB were repelled gradually to the inside. After the completion of polymerization, toluene and dissolved PS were entrapped by the PDVB shell, then toluene in the hollow evaporated by drying, and PS clung to the inner wall of the shell uniformly. On the basis of this mechanism, hollow polymer particles were also prepared by the microsuspension polymerization of DVB/toluene droplets containing dissolved PS and benzoyl peroxide (BPO), although they were polydisperse.[12] The PS dissolved in the DVB/toluene droplets worked as an accelerator for the phase separation of PDVB formed during the polymerization.[13] The phase separation in the early stage was the first required point for the formation of the hollow structure because, at low conversion, PDVB could move and adsorb at the interface of the droplets because of low viscosity. The second required point was the preferential adsorption of PDVB at the interface of the droplets over PS previously dissolved therein to form a PDVB shell. The microsuspension polymerization of DVB droplets containing n-hexadecane (HD) yielded HD-encapsulated particles, where HD as a nonsolvent worked as PS in the SaPSeP method.[14] The 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 and adsorbed there to form the polymer shell. That is, the SaPSeP method was applicable not only to the preparation of hollow particles but also to the encapsulation of HD.

Heat-storage materials can absorb and release latent heat when the temperatures of the materials overpass the temperature of phase change. Phase-transition temperatures close to the application temperatures are considered optimal for most thermal energy storage systems.[15–17] Paraffin waxes are useful as one group of numerous heat-storage materials that melt and solidify at a wide range of temperatures; this makes them attractive for many applications. They are generally cheap and have moderate thermal energy storage but low thermal conductivity. Therefore, they require large surface areas in applications. The encapsulation of these materials is associated with many advantages; for example, they provide a large heat-transfer area and control the volume change of the storage materials as phase change occurs.[15] Microencapsulated heat-storage materials have been widely used in many fields, such as the heating and air conditioning of buildings,[15,18] solar and nuclear heat storage,[19] thermal adaptable fibers,[17,20,21] and climate environmental control for vegetation and seeds in agriculture.[22] Yamagishi et al.[23] studied the melting and solidification processes of microencapsulated n-tetradecane and n-dodecane with a gelatin shell prepared by complex coacervation. The microcapsule diameters were in the range 5–1000 μm. Zhang et al.[24,25] reported the preparation of phase-change microcapsules and nanocapsules containing n-octadecane with a melamine–formaldehyde shell and the crystallization of microencapsulated n-alkanes in a urea–melamine–formaldehyde shell prepared by *in situ* polycondensation. The supercooling of the encapsulated n-alkanes was clearly observed in both cases. The preparation of polyurea microcapsules with encapsulated HD by interfacial polycondensation used for thermal energy storage was also reported by Zou et al.[26] It was shown that the heat of melting (H_m) of encapsulated HD was much decreased from that of pure HD.

Recently, we reported the preparation of PDVB capsule particles with encapsulated HD, a paraffin wax, as heat-storage materials by microsuspension polymerization with the SaPSeP method of micrometer-sized, comparatively monodisperse DVB/HD droplets prepared by the Shirasu Porous Glass (SPG) membrane emulsification method.[27,28] The H_m, which corresponded to the heat of solidification (H_s), of the pure HD used was approximately 230 J/g, and its melting temperature (T_m), which corresponded to its solidification temperature (T_s), was approximately 15°C. The H_s value of HD encapsulated in the PDVB particles was much lower than that of the pure HD. Moreover, the T_s value of the encapsulated HD was also approximately 10°C lower than that of the pure HD, whereas T_m still remained at 15°C.[29] These phenomena are, of course,

negative with regard to application as heat-storage materials. However, the problem with the reduction in H_s of the encapsulated HD is improved by the copolymerization of acrylic monomers, such as butyl acrylate.[30] This seems to be based on the fact that the copolymerization of polar monomers enhances the phase separation of copolymer chains in HD, which eventually results in the complete isolation of the HD core from the polymer shell. Furthermore, it was also found that PDVB particles of different shell thicknesses resulted in different particle shapes.[14] In the case of a thicker shell (DVB/HD = 2/2 w/w), a single water domain was observed in the HD core encapsulated in spherical PDVB capsule particles. On the other hand, in the thinner shell (DVB/HD = 2/3 w/w), nonspherical (dimple) capsule particles, in which such a water domain was not contained in the HD core, were prepared. The formation of the water domain in the HD core inside spherical PDVB particles and its influence on the thermal properties of the encapsulated HD were clarified.[31] To our knowledge, there has been no report describing the formation and influence of water domains in encapsulated paraffin.

In this study, to clearly understand the influence on the thermal properties of encapsulated HD of the water domain, we examined the thermal properties of encapsulated HD in crosslinked capsule particles containing a water and/or air domain from the viewpoint of heat-storage applications.

EXPERIMENTAL

Materials

DVB (Nippon Steel Chemical, Tokyo, Japan; purity = 96%) was washed with 1N NaOH and distilled water to remove inhibitors before use. Poly(vinyl alcohol) (Gohsenol GH-17; degree of polymerization = 1700; 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 microsuspension polymerization

The organic phase of 2/2 w/w DVB/HD consisted of DVB (3.3 g), HD (3.3 g), and BPO (0.1 g, 4 wt % of the monomer), whereas that of 2/3 w/w DVB/HD consisted of DVB (2.6 g), HD (4.0 g), and BPO (0.1 g, 4 wt % of the monomer). Emulsification was carried out with the SPG membrane emulsification technique (SPG Technology, Miyazaki, Japan) with a microporous glass membrane with pore sizes of 1.1

and 3.9 μm. A homogeneous solution of the organic phase was dispersed as droplets in the aqueous phase [0.5 g of poly(vinyl alcohol) in 50 g of water]. The resulting emulsions were transferred to glass ampules, degassed with several N_2/vacuum cycles, and sealed off. The polymerizations were carried out at 70°C for 24 h with the ampules shaken horizontally at a rate of 80 cycles/min (3-cm strokes). The prepared particles were observed with an optical microscope (ECLIPSE 80i, Nikon Corp., Tokyo, Japan).

Evaporation behavior of water from the PDVB/HD capsule particles

The evaporation behavior of water from the two kinds of PDVB/HD aqueous dispersions was studied by measurement of weight loss with thermogravimetry (TG/DTA 220U, Seiko Instruments, Chiba, Japan). The measurement of the weight loss was carried out for approximately 35 mg of each dispersion in an aluminum pan at 30°C under a nitrogen atmosphere. The solid content of each sample was above 50 wt % for clear observation. The instantaneous evaporation rate of water was determined by differentiation of the weight-loss curve.

Measurement of the thermal properties and thermal stability of HD encapsulated in the crosslinked capsule particles

The H_s, T_s, H_m, and T_m values of HD encapsulated in the capsule particles in both the aqueous dispersed (solid content ≈ 10%) and dry states were measured in an aluminum pan with differential scanning calorimetry (DSC; DSC 6200, Seiko Instruments) under a N_2 flow at a scanning rate of 5°C/min. Dry samples were prepared as follows. The same amount (ca. 0.5 g) of aqueous dispersed sample (solid content ≈ 10%) in each aluminum cup was dried at 70°C in an oven for different drying times.

The stability of capsule particles and the thermal properties of encapsulated HD were examined by the cycling of the wet particles through 100 accelerated melting/freezing cycles in an aluminum pan under a N_2 flow at a scanning rate of 5°C/min.

RESULTS AND DISCUSSION

Formation and influence of the water domain in encapsulated HD

Figure 1 shows optical micrographs at room temperature of PDVB particles with encapsulated HD produced by the microsuspension polymerization at 70°C of DVB/HD droplets prepared by the SPG membrane method. Generally, the size distribution of monomer droplets prepared by mechanical stir-
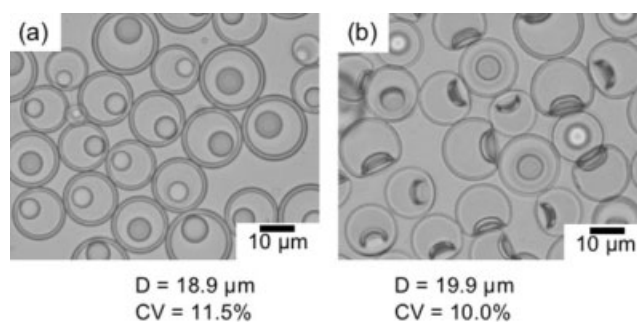

Figure 1 Optical micrographs of PDVB/HD particles in an aqueous dispersed state produced by the microsuspension polymerization with the SaPSeP method of DVB/HD droplets prepared with the SPG emulsification method (pore size = 3.9 μm): (a) 2/2 and (b) 2/3 w/w DVB/HD.

ring is very broad. However, with the SPG emulsification technique, fairly uniform droplets can be obtained. The coefficient of variation (CV) is usually approximately 10%.[32,33] With the suspension polymerization of such monomer droplets, the capsule particles were comparatively monodisperse. The particle diameter (D) and CV of PDVB/HD (DVB/HD = 2/2 w/w) were 18.9 μm and 11.5%, respectively, whereas those of PDVB/HD (DVB/HD = 2/3 w/w) were 19.9 μm and 10.0%, respectively. At a ratio of DVB/HD of 2/2 (w/w) [Fig. 1(a)], spherical capsule particles with smooth outer surfaces were obtained. No porous structure was observed in the shell with transmission electron microscopy of an ultrathin cross section sample.[30] Poly(styrene-divinyl benzene) (P(S-DVB)) particles with high mechanical strengths and smooth surfaces with no porous structures were also prepared by suspension polymerization by Tanaka et al.[34] Cho et al.[35] also reported the preparation of monodisperse PDVB macrobeads without the porous structure. In addition, a single domain was observed in the encapsulated HD core. The single domain was not observed in the capsule particles just after polymerization at 70°C. This suggests that any domain had not formed yet or very fine domains, which were not visible with the optical microscope, formed because of the shrinkage of the DVB/HD core phase with the polymerization after the crosslinked shell formation on the basis of the different densities of DVB and PDVB (0.91 and 1.04 g/cm^3, respectively).[36] The calculated shrinkage volume was 5.6%. During cooling from 70 to 25°C, a single domain appeared in each particle, and the domain size increased with decreasing temperature. The occupied volume of the domain was 7–9% of the particles. Cooling after the polymerization increased the density of HD, which led to the formation of space inside the capsule particles. The calculated volume shrinkage of HD at 20°C was 2.6% on the basis of the densities of HD at 20 and 70°C,
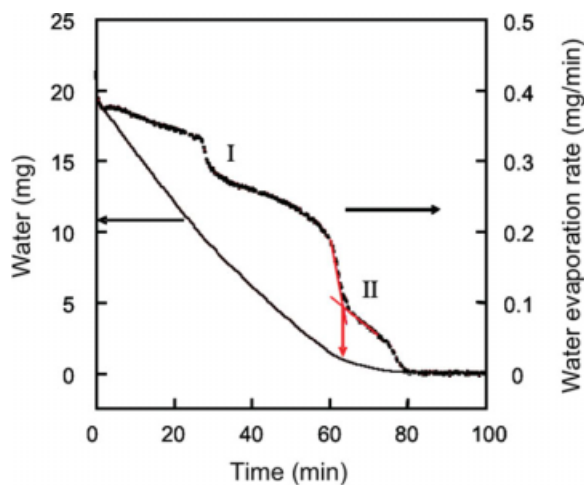
Figure 2 Weight-loss curve based on the evaporation of water at 30°C from aqueous dispersions of PDVB/HD (DVB/HD = 2/2 w/w) particles and an evaporation rate curve obtained by the differentiation of the weight-loss curve. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

which were 0.773 and 0.738 g/cm³, respectively.[37] Then, the calculated total volume shrinkage was 8.2% of the particles. Because this space reduced the internal pressure of the core, it seemed that water penetrated into the core from the aqueous medium without shape transformation of the spherical particles, which resulted in a water domain in the HD core when the shell strength was sufficient to withstand the external pressure.[31]

On the other hand, in the case of DVB/HD = 2/3 (w/w) [Fig. 1(b)], nonspherical (dimple) particles were formed. As discussed in previous articles,[30,31] it seemed that this shape deformation occurred as a result of the shrinkage of the monomer phase during the polymerization after crosslinked shell formation on the basis of the different densities of DVB and PDVB. Because the shell strength was insufficient to withstand the outer pressure, part of the shell buckled before water penetration. Therefore, water domains were not observed. Further particle deformation was not clearly observed during spontaneous cooling from 70°C to room temperature. Even when the temperature was raised again to 70°C, the nonspherical shape did not change.

To confirm the existence of a water domain, the evaporation behaviors of water from the capsule particles both with a water domain and without any water and air domains were studied by thermogravimetry/differential thermal analysis. Figures 2 and 3 show weight-loss curves based on the evaporation of water at 30°C from aqueous dispersions and their differential ones, respectively, for 2/2 and 2/3 weight ratios of PDVB/HD particles. In their final drying stages, the rate of weight loss from the

aqueous dispersions of PDVB/HD (DVB/HD = 2/2 w/w) was slower than that of the particles of DVB/HD = 2/3 (w/w). This seemed to be based on the slow evaporation rate of water from the insides of the capsule particles.[38] In the case of PDVB/HD (DVB/HD = 2/2 w/w; Fig. 2), the water evaporation rate decreased in step I, which corresponded to the evaporation of water in aqueous medium, whereas the decrease in step II corresponded to the evaporation of water inside particles.[38] The evaporation rate of water from the inside of capsule particles was much slower than that of free water because the water in the particles had to diffuse through the hydrophobic polymer shell. On the other hand, the particles without any water domain showed only one step (step I) because of the evaporation of the aqueous medium, as shown in Figure 3.[38] These results could support our assumption that the water domain was formed inside the PDVB/HD (DVB/HD = 2/2 w/w) particles.

The thermal properties of the encapsulated HD were measured with DSC. Figure 4 shows the DSC thermogram of an aqueous dispersion of PDVB/HD (DVB/HD = 2/2 w/w) particles. The solidification peak of water was observed in the cooling curve at approximately −20°C, whereas melting peak was observed in the heating curve at approximately 0°C. These peaks in the temperature descending and ascending processes should correspond to the heat-evolving peak of water in both media and to the water domain inside capsule particles. However, because the volume of the water domain was extremely low in comparison with the aqueous medium, the heat evolving of the water domain had to be neglected. Therefore, with the water solidification
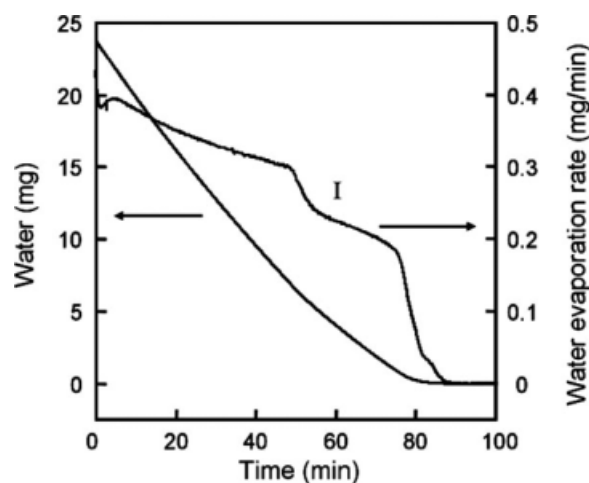

Figure 3 Weight-loss curve based on the evaporation of water at 30°C from aqueous dispersions of PDVB/HD (DVB/HD = 2/3 w/w) particles and an evaporation rate curve obtained by the differentiation of the weight-loss curve.
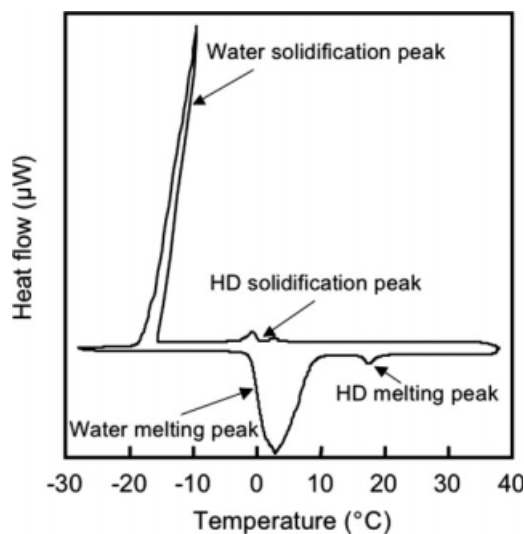
Figure 4 DSC thermogram of an aqueous dispersion of PDVB/HD (DVB/HD = 2/2 w/w) particles recorded at a scanning rate of 5°C/min.

curve, it was difficult to examine the existence of the water domain. Moreover, the water solidification peak increased in the temperature descending process, which may have been because of the increase in sample temperature due to a large amount of heat evolving of solidification of the whole aqueous medium. To clearly study the influence of the water domain on the thermal properties of encapsulated HD, we focused on the solidification peak. DSC thermograms of HD encapsulated in PDVB particles with different DVB/HD weight ratios are shown in Figure 5. In both cases, the T_s value of the encapsulated HD decreased from that of pure HD, whereas T_m still remained at 15°C. The reason for the decrease in T_s may have been based on a compartmentalization effect; that is, impurities located in the capsule particle could not induce the nucleation of HD encapsulated in the other particles.[30] In bulk systems, it is known that there is an impurity that works as a trigger for the nucleation, which results in heterogeneous nucleation.[23,39] In emulsion, the numbers of impurities that usually cause heterogeneous nucleation as in the bulk phase are distributed among a large number of isolated droplets. Therefore, the probability for heterogeneous nucleation for all droplets is drastically reduced, which results in a decrease in T_s. In the case of a DVB/HD ratio of 2/3 w/w, a sharp single peak of the encapsulated HD due to solidification was observed with $H_s = 162$ J/g of HD and $T_s = 6°C$. On the other hand, for DVB/HD = 2/2 w/w, the peak was bimodal with $H_{s1} = 38$ J/g of HD and $T_{s1} = 6°C$ for the first peak and $H_{s2} = 123$ J/g of HD and $T_{s2} = 1°C$ for the second peak. This lower temperature side peak (H_{s2} and T_{s2}) was due to the influence of the water domain in

the HD core.[31] This result suggests that the encapsulated HD containing the water domain required a longer time and lower temperature to complete the solidification. This phenomenon is disadvantageous with regards to heat-storage application. The total H_s ($H_{s1} + H_{s2} = 161$ J/g HD) was almost the same as that with DVB/HD = 2/3 w/w (162 J/g HD); however, it was lower than that of pure HD. On the basis of the formation mechanism of hollow polymer particles,[11] the polymer molecules formed in the monomer droplet separated and adsorbed at the inner interface, which resulted in a crosslinked shell encapsulating HD. The interfacial interaction of the polymer shell at the inner interface and encapsulated HD may have disturbed the solidification of encapsulated HD contacting the inner shell, which led to the decrease in H_s. To clarify this assumption, copolymerizations of DVB and acrylic monomers were carried out.[30] An increase in hydrophilicity of poly(divinylbenzene-n-buthyl acrylate) (P(DVB–BA)) chains with increasing n-buthyl acrylate (BA) content should have enhanced the phase separation between the copolymer chains and HD, which would eventually result in the complete isolation of the HD core from the polymer shell. This HD core seemed to be more smoothly solidified than the incompletely isolated HD located in the inner interface of the polymer shell, which resulted in the increasing of H_s with the BA content. This was more obvious in the case of poly(divinylbenzene-ethyl acrylate) (P(DVB–EA)) capsule particles because of the higher hydrophilicity of ethyl acrylate (EA) than of
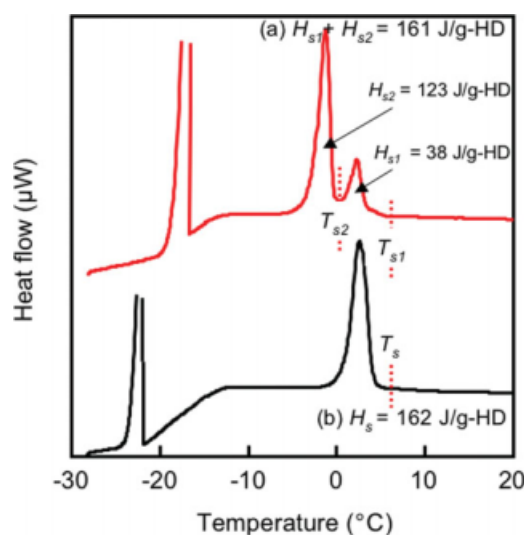

Figure 5 DSC thermograms of encapsulated HD in PDVB particles in an aqueous dispersion produced by the microsuspension polymerization of DVB/HD droplets prepared by the SPG emulsification method (pore size = 1.1 μm): (a) 2/2; (b) 2/3 w/w DVB/HD. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
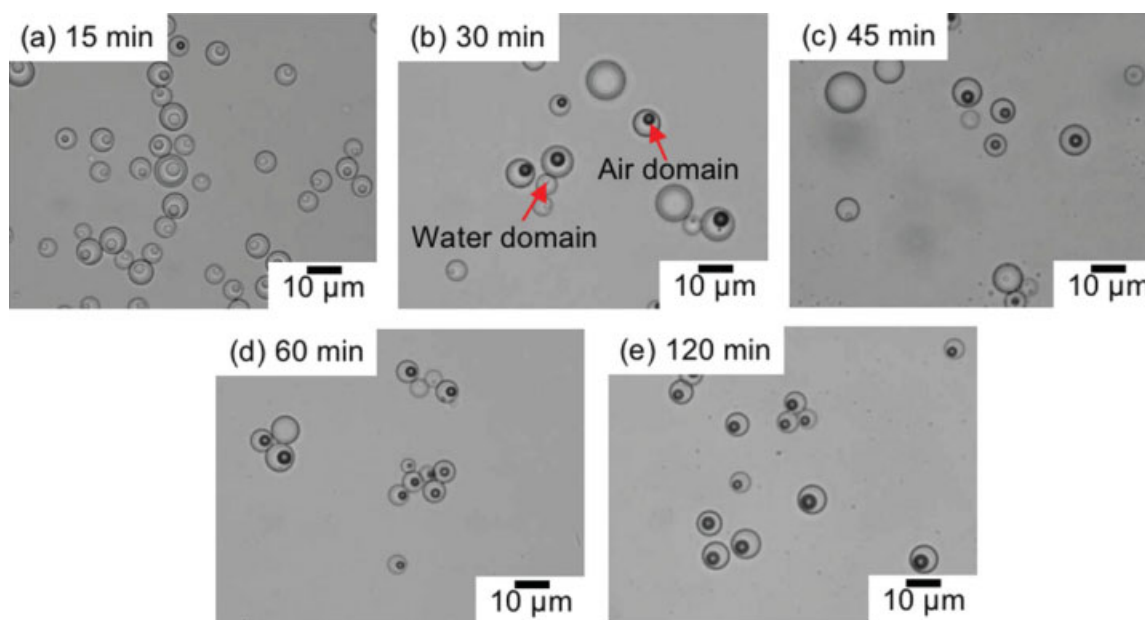
Figure 6 Optical micrographs of PDVB/HD (DVB/HD = 2/2 w/w) particles (SPG pore size = 1.1 µm) redispersed in water at room temperature after being dried at 70°C for different time periods: (a) 15, (b) 30, (c) 45, (d) 60, and (e) 120 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

BA. However, the influence of the incorporation of acrylic monomers to the shell was not observed on the T_s of encapsulated HD.

Thermal properties of the encapsulated HD with the water and air domains

To clearly understand the influence of the water domain formed in the HD core on the thermal properties, incompletely and completely dried particles were prepared by changes in the drying time of the dispersion samples. Samples dried at 70°C for 15–30 min were still in the wet state, whereas those dried for 45 min or more were in the dry state (no aqueous medium was observed). Figure 6 shows optical micrographs taken just after redispersion in water (to prevent penetration of water into the particles) of the incompletely and completely dried PDVB/HD (DVB/HD = 2/2 w/w) particles. Almost all capsule particles dried for 15 and 30 min still contained a water domain in the HD core. The percentage of capsule particles in which the water domain was replaced with an air domain increased with drying time (the interface of the air domain was observed as a black ring). After 120 min of drying, all water domains were replaced with air domains, which indicated that the formation of air domains was due to the evaporation of water from the HD core.

Figure 7 shows optical micrographs taken just after redispersion in water of the nonspherical PDVB/HD (DVB/HD = 2/3 w/w) capsule particles at 70°C

for dried 60 and 120 min. No air domains were observed, although the capsule particles were dried for 120 min. This also supported the previous idea that the evaporation of the water domain in the HD core resulted in the formation of the air domain.

Figure 8 shows DSC thermograms of the encapsulated HD in the spherical PDVB (DVB/HD = 2/2 w/w) particles in water (original dispersion) and in different dry states. The wet samples dried for 15 and 30 min [Fig. 6(a,b)] exhibited bimodal peaks similar to those of the original particles in the aqueous dispersed state. After 45 min of drying, at which point a considerable percentage of the water domains were replaced with air domains [Fig. 6(c)], the lower temperature side peak (T_{s2} = 1°C) decreased, which resulted in a reversal of the peak sizes of T_{s1} and T_{s2}, although the peak was still
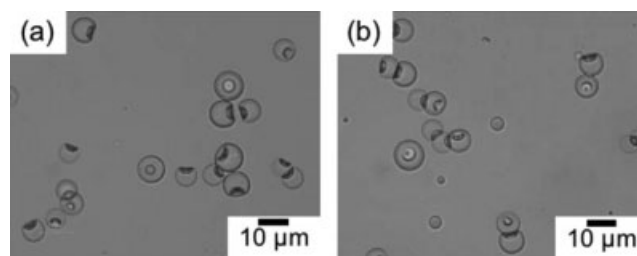

Figure 7 Optical micrographs of nonspherical PDVB/HD (DVB/HD = 2/3 w/w) particles (SPG pore size = 1.1 µm) redispersed in water at room temperature after different drying times at 70°C: (a) 60 and (b) 120 min.
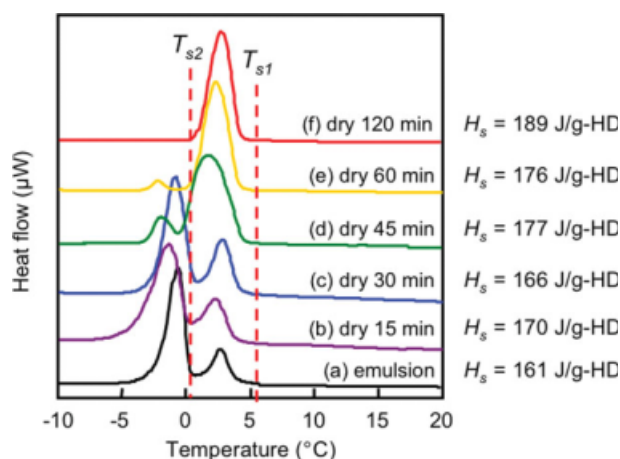
Figure 8 DSC thermograms of encapsulated HD in PDVB/HD (DVB/HD = 2/2 w/w) particles in (a) an aqueous dispersed state and (b–g) in dry states for different drying times: (b) 15, (c) 30, (d) 45, (e) 60, and (f) 120 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

bimodal. The lower temperature side peak gradually disappeared with increasing drying time. In the cases of the samples dried for 120 min, the lower temperature side peak disappeared, and the DSC thermograms showed a sharp single peak. These results indicate that the lower temperature side peak was due to the influence of the water domain in the HD core.[31] On the other hand, the presence of water or air domains did not have a negative influence on

H_s of the encapsulated HD. The total H_s of the dried particles did not decrease from that of the original capsule particles in the aqueous dispersion (161 J/g of HD).

Influence of the water and air domains in the encapsulated HD in the redispersed particles

The dried particles were redispersed in water for a few minutes to examine whether a water domain would be formed again in the HD core. Larger capsule particles were produced with an SPG membrane with a 3.9-μm pore size to facilitate visual observation. In the case of PDVB/HD (DVB/HD = 2/2 w/w; 20.4 μm) particles dried at 70°C for 45 min, several small water domains were observed in the HD core just after redispersion in water (Fig. 9). This suggests that the water domain was not completely removed during the drying and/or water had already repenetrated into the HD core inside the capsule particles. During the redispersion period, several small domains gradually coagulated, which resulted in a single large water domain in each HD core. Because the incompletely dried particles still contained water in the shell, water may have penetrated the shell from the aqueous medium into the core, which led to the several small water domains and eventually a single domain in the HD core.

In contrast, for particles dried at 70°C for 120 min (Fig. 10), in which the water domain was replaced with an air domain, the penetration of water into the
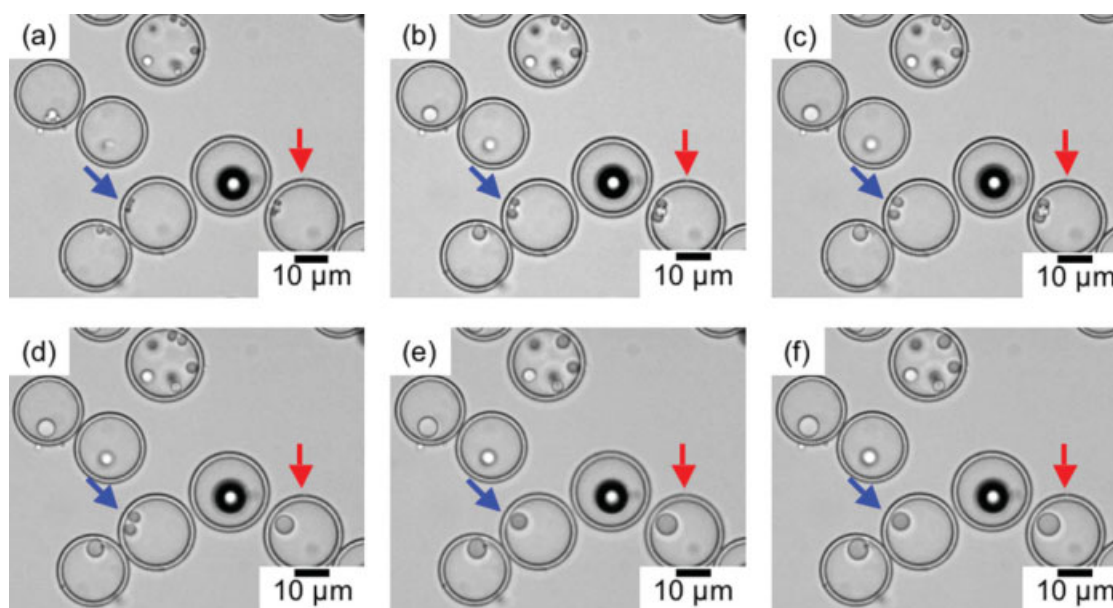

Figure 9 Optical micrographs of incompletely dried PDVB/HD particles (70°C, 45 min) produced by the microsuspension polymerization of DVB/HD (2/2 w/w) droplets prepared by the SPG emulsification method (pore size = 3.9 μm) and redispersed in water for a few minutes at room temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
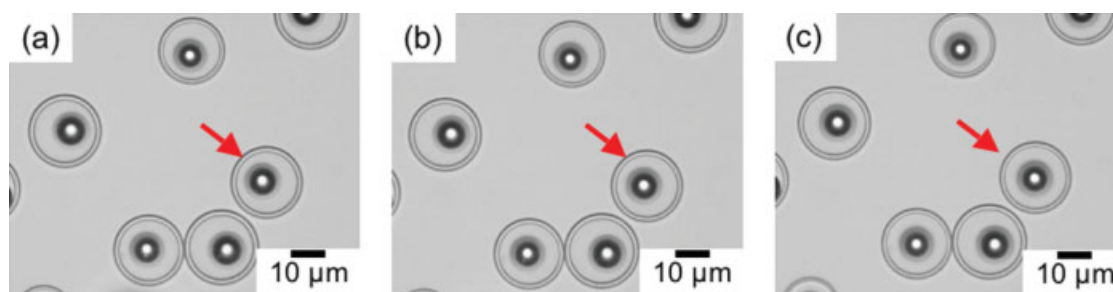
Figure 10 Optical micrographs of completely dried PDVB/HD particles (70°C, 120 min) produced by the microsuspension polymerization of DVB/HD (2/2 w/w) droplets prepared by the SPG emulsification method (pore size = 3.9 μm) and redispersed in water for a few minutes at room temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

HD core was not observed, even after redispersion in water for 48 h. As described next, when the particles were dried completely, water did not diffuse into the core anymore.

Figure 11 shows DSC thermograms of the encapsulated HD in the PDVB/HD particles (DVB/HD = 2/2 w/w) redispersed in water after being dried for different times. The results are consistent with the previous findings; that is, the incompletely dried particles (drying times = 30 and 45 min) had a bimodal peak. In the case of the particles dried for 45 min, the lower temperature side peak was larger in the redispersed state [Fig. 11(b)] than in the dry state [Fig. 8(d)], possibly because of water penetration from the aqueous medium during the DSC measurement. On the other hand, the lower temperature side peak was not clearly observed for the completely dried particles [120 min; Fig. 11(d)], in which no
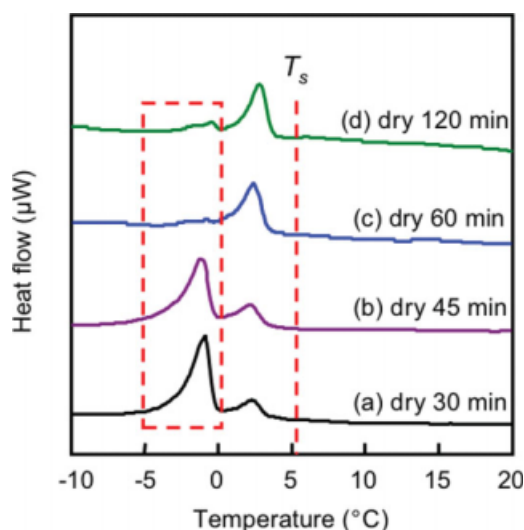
water domain reappeared in the HD core despite there being sufficient time for the penetration of water during the DSC measurement. This indicated that, once an air domain appeared in place of the water domain, water penetration could not occur. This seemed to be due to the cancellation of the pressure difference between the inside and outside of the particles by the replacement of the water domain with the air domain.

We concluded that complete removal of the water domain in the HD core of the particles led to the disappearance of the lower temperature side peak. Thus, the encapsulated HDs without a water domain but with an air domain needed a shorter time and higher temperature to complete solidification than the ones with a water domain. This improvement is an advantage for its application.

In addition, the existence of the air domain in the HD core had no significant influence on the thermal properties of the encapsulated HD.

Thermal stability of the encapsulated HD with an air domain

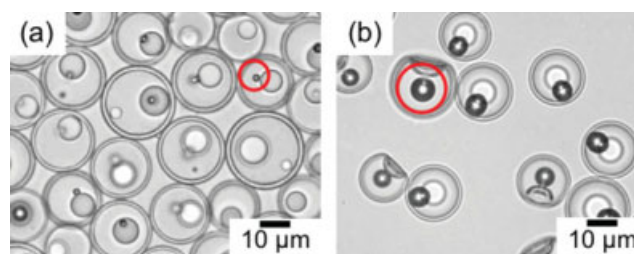An air domain was also found in the HD core inside the particles after DSC measurement with aqueous

Figure 11 DSC thermograms of encapsulated HD in PDVB/HD (DVB/HD = 2/2 w/w) particles (SPG pore size = 1.1 μm) redispersed in water at room temperature after being dried at 70°C for different time periods: (a) 30, (b) 45, (c) 60, and (d) 120 min. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

Figure 12 Optical micrographs taken after the DSC measurements from −30 to 40°C for four scans of PDVB/HD particles produced by the microsuspension polymerization of DVB/HD droplets prepared by the SPG emulsification method (pore size = 3.9 μm): (a) 2/2 and (b) 2/3 w/w DVB/HD. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
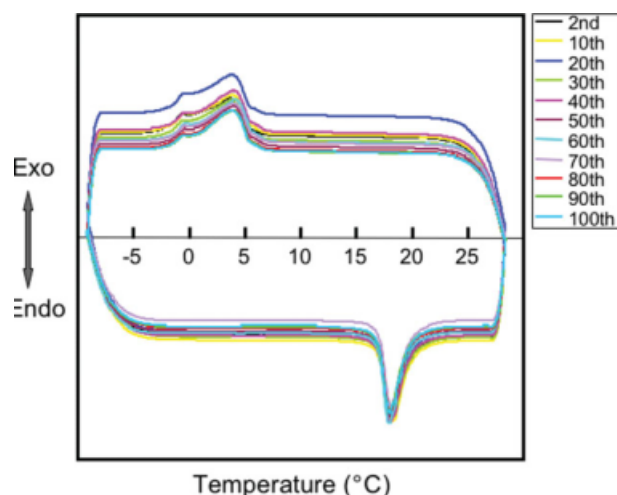
Figure 13 DSC thermograms for various melting/freezing cycles of encapsulated HD in PDVB (DVB/HD = 2/2 w/w) particles (SPG pore size = 3.9 μm) in an aqueous dispersed state measured at a scanning rate of 5°C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

dispersed state samples (Fig. 12). In the case of PDVB/HD (DVB/HD = 2/2 w/w), a small air domain formed in the HD core after the solidification process of the encapsulated HD, whereas a large air domain was observed in the case of 2/3 DVB/HD (w/w; red circle in Fig. 12). This difference may have been due to the presence/absence of a water domain in the HD core. During solidification, the shrinkage of the encapsulated HD led to the formation of an air domain. To study the effect of the air domain formed in the HD core on the thermal stability with long-term thermal cycling of the encapsulated HD, 100 accelerated melting/freezing cycles without the flow of capsule particles in the aqueous dispersion were continuously measured with DSC.

Figure 13 shows the DSC thermograms of various thermal cycles of the encapsulated HD in PDVB particles with a DVB/HD ratio of 2/2 w/w. Both the melting and freezing curves of the encapsulated HD did not change significantly throughout 100 cycles. Although the air domain of the particles having a DVB/HD ratio of 2/3 w/w was larger than that of the other ones, a similar result was obtained (data are not shown). Therefore, we concluded that the presence of the air domain did not affect the stability of the encapsulated HD in either case.

CONCLUSIONS

The thermal properties of HD encapsulated in micrometer-sized, monodisperse PDVB capsule particles produced by microsuspension polymerization with the SaPSeP method was influenced by a single water domain formed in the HD core. This water

domain led to the partial decrease of T_s ($\rightarrow T_{s2}$) of the encapsulated HD in the capsule particles, which would retard its solidification for heat-storage applications. However, this influence gradually decreased with an increase in the drying time because of the replacement of the water domain with an air domain. The appearance of the air domain prevented the repenetration of water from the aqueous medium into the core of redispersed particles in water. The air domain in the HD core did not affect the thermal properties and stability of the encapsulated HD.

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