Preparation of Novel Particles with Encapsulated Heat Storage Material by Microsuspension Polymerization

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(Degree)
博士（学術）

(Date of Degree)
2008-09-25

(Date of Publication)
2008-10-10

(Resource Type)
doctoral thesis

(Report Number)
甲4400

(URL)
https://hdl.handle.net/20.500.14094/D1004400

Doctoral Dissertation

Preparation of Novel Particles with Encapsulated Heat Storage Material by Microsuspension Polymerization

（マイクロサスペンション重合による熱輸送物質を内包した新規なカプセル粒子の合成）

July 2008

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Kobe University

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Acknowledgement

I wish to express my gratitude to all those who gave me the possibility to complete this Ph. D. thesis.

First of all, I would like to express my heartfelt gratitude and appreciation to my supervisor, Prof. Dr. Masayoshi Okubo, for his kind supervision, valuable guidance and constant encouragement throughout the course of my doctoral study.

I am grateful to Assoc. Prof. Dr. Hideto Minami and Assoc. Prof. Dr. Per B. Zetterlund for their help and thoughtful advices.

I also wish to express my sincere gratitude and thank to Research Associate, Dr. Toyoko Suzuki for her kindly guidance, constant help and useful suggestion throughout this research.

To Ms. Yumiko Ogino, Ms. Yuko Hata, and Ms. Mizuki Ito, SaPSeP team, I am grateful for their help, discussions and useful suggestions.

I am pleased to acknowledge the considerable assistance of Ms. Eriko Takano and Ms. Sachiyo Nishida and thank to all members in Polymer Colloids Lab (CX-6) who made my study here a pleasant and wonderful one.

I also would like to thank Rajamangala University of Technology Thanyaburi, Thailand, for the honour of being awarded scholarship for my doctoral study.

Finally, I am indebted to my family, parents, brothers and sisters-in-law, for their tender love and care. Especially, I would like to give my special thanks to my husband, Mr. Amorn Chaiyasat, for his love, support and endless encouragement which has enabled me to achieve success in my doctoral education.

July 2008

Preeyaporn Chaiyasat

Contents

General Introduction

Synthetic methods leading to particles having voids have been extensively investigated. Hollow particles can serve as synthetic pigments, which contribute to the opacity of architectural coatings by scattering light. In addition, these particles can enhance the gloss of paper coatings [1-3]. The use of the hollow latex in such coatings reduces the need for expensive pigments, such as titanium dioxide (TiO_2), without adding excessive and undesirable weight to the coating [2]. They are also useful in other technologies such as microencapsulation [2, 3]. One of the earliest processes for making hollow latex particles was developed in the research laboratories of The Rohm and Hass Company [4-9]. Their concept involved making a structured particle with a carboxylated core polymer and one or more outer shells. In addition to this approach, a number of alternative processes have also been studied. Okubo et al. found that submicron-sized, monodisperse styrene (S)-butyl acrylate-methacrylic acid terpolymer particles with multihollows were prepared by stepwise alkali/acid treatment after emulsion polymerization [10-12]. Submicron-sized, monodisperse, cross-linked hollow poly(divinylbenzene) (PDVB) and poly(methylmethacrylate-divinylbenzene) particles were prepared by seeded emulsion polymerization [13]. The preparation of micron-sized hollow polymer particles was also reported. Micron-sized monodisperse particles having multihollow structures were produced by extraction of PS with toluene from mincron-sized monodisperse PS/P(S-DVB) composite particles produced by seeded dispersion polymerization [14]. Latex particles with multihollow structure were also prepared by seeded emulsion polymerization [15].

Okubo et al. have succeeded in preparing approximately 5-µm sized, monodisperse, cross-linked polymer particles with one hollow at the center by seeded polymerization of highly DVB/toluene-swollen PS particles [16,17] prepared by the dynamic swelling method

[18,19]. The formation mechanism of these hollow polymer particles was proposed and named the Self-assembling of Phase Separated Polymer (SaPSeP) method [20]. On the basis of this mechanism, hollow polymer particles were also prepared by microsuspension polymerization of DVB/toluene droplets containing dissolved PS and benzoyl peroxide (BPO), although they were polydisperse [21]. Moreover, microsuspension polymerization of DVB droplets containing *n*-hexadecane (HD) as a nonsolvent was also carried out [22]. The HD capsulated particles were prepared under the conditions where phase separation in the droplets occurred in an early stage of polymerization. The encapsulation of hinokitiol abstracted from natural coniferous woods was also reported [23]. That is, the SaPSeP method is applicable not only to the preparation of hollow particles but also to the encapsulation of various chemicals such as agrochemicals, pharmaceuticals and heat storage materials. Polymer microcapsule can be used to either protect the encapsulated materials or to release the active agent.

Heat storage materials

Thermal energy storage plays important roles in conserving available energy and improving its utilization, since many energy resources are intermittent in nature. Solar energy is available only the day, and hence, its application requires an efficient thermal energy storage. Then, the excess heat collected during sunshine hours may be stored for later use during the night [24].

Heat storage materials have received considerable attention in recent years. Originally, heat storage material technology was developed through the National Aeronautics and Space Administration space research program of the late 1970s to the early of 1980s and was used to protect delicate instruments in space from large temperature extremes [25]. To be used for thermal energy storage, they must have a large latent heat and high thermal conductivity. They should have a melting temperature in the practical range of operation, solidification with

minimum supercooling and be chemical stable, low in cost, non-toxic and non-corrosive [24]. They can absorb and release the latent heat when the temperature of the material undergo or overpass the temperature of phase change. The selection of a heat storage material is dependent on the application temperature as well as the extent of latent heat to be exchanged. Phase transition temperatures close to the application temperatures are considered optimal for most thermal energy storage systems [24, 26, 27]. There are numerous numbers of heat storage materials that melt and solidify at a wide range of temperatures, making them attractive for many applications. The two main classes of materials used as thermal energy storage systems are inorganic compounds such as salt hydrate and organic compounds [26, 28]. $Na_2SO_4 \cdot 10H_2O$ and $CaCl_2 \cdot 6H_2O$, with their melting temperature (about 30 °C) slightly above room temperature, are two typical inorganic heat storage materials. Common problems associated with inorganic heat storage materials are supercooling and thermal instability [24, 28]. Organic heat storage materials can be classified as paraffins and non-paraffins compounds. Paraffins provide relatively high latent heat and have significant other characteristics suitable for their application as heat storage materials, being non-toxic, non-corrosive and possessing long-term stability but low thermal conductivity. Therefore, they require large surface area in applications [24, 26].

Microencapsulation of heat storage materials

The field of microencapsulation emerged in 1950s and got rapidly expanded in 1970s, originally directing toward entrapping solids, liquids, or gas into polymeric shells. Microcapsules have been developed, studied, and used in various applications. A wide range of core materials have been encapsulated, including drugs, enzymes, electronic ink, fragrant oils, waxes, etc [29-34]. Microencapsulated heat storage materials have been studied and have attracted more and more attention in recent years. They have been widely used in many fields,

such as heating and air conditions of building [24, 35], solar and nuclear heat storage [36], thermal adaptable fibers [25, 27, 37], and climate environmental control for vegetation and seeds in agriculture [38]. As the conventional solid-liquid heat storage materials, paraffins tend to have the solid-liquid phase change while being used. It is not convenience to use paraffins as heat storage material directly. However, microencapsulation of paraffins is effective to solve the problem. The main advantages of heat storage material encapsulation are providing large heat transfer area, reduction of the materials reactivity towards the outside environment and controlling the changes in volume of the storage materials as phase change occurs [24, 39].

Many methods have been studied to prepare microcapsules with liquid/solid core and polymer shell, for example interfacial polycondensation. This method is one monomer dissolved in dispersed phase reacts with another monomer in continuous phase at the oil-water interface to form polymer shell. The microcapsules of about 1 μm in diameter were prepared using an interfacial polycondensation method with toluene-2, 4-diisocyanate and diethylenetriamine as monomers and *n*-octadecane (OD) as heat storage material [10]. Ni et al. reported the preparation of oil-containing microcapsules using tolylene 2, 4-diisocyanate as an oil-soluble monomer and diethylenetriamine or lysine as a water-soluble monomer by interfacial polycondensation [40]. Poly(hexamethylene)urea microcapsules were formed by carrying out an interfacial polycondensation in an emulsion between hexamethylene-1, 6-diisocyanate and hexamethylene-1, 6-diamine to encapsulate cyclohexane [41]. In situ polymerization is one of common methods of microcapsule preparation. Prak et al. reported the preparation of urea-formaldehyde microcapsules with lemon oil as the core material by in situ interfacial polymerization [31]. Melamine-formaldehyde microcapsules containing various heat storage materials such as eicosane [25], OD [42, 43] were prepared by in situ polymerization. Another method is coacervation which creates the shell of the microcapsule

by precipitation of polymer from the continuous phase of an emulsion to surround the droplets of the dispersed phase [44]. Yamagishi et al. studied the melting and solidification of microencapsulated *n*-tetradecane and *n*-dodecane with gelatin shell prepared by complex coacervation. The microcapsule diameters were in the range of 5-1000 μm [45]. Internal phase separation is also studied for the preparation of microcapsules. Microcapsules with phenolic resin shell and HD core were prepared by internal phase separation within the droplets of an oil-in-water emulsion by Jiang et al. [34]. Poly(methyl methacrylate) microcapsules with various poor solvents were prepared by the controlled phase separation within the droplets of an oil-in-water emulsion [44]. PS microcapsules with HD core were prepared by the controlled internal phase separation of polymer dissolved within the oil droplets of an oil-in-water emulsion [46, 47].

There are numerous numbers of reports on the preparation of microcapsules with a polymer shell and a heat storage material core by a suspension polymerization. This technique generally involves the dispersion of the monomer, mainly as a liquid in small droplets, into an agitated stabilizing aqueous medium. The initiator is dissolved in the monomer- heat storage material mixture [27]. Ma et al. developed a suspension polymerization process to encapsulate a heat storage material. They carried out a microencapsulation method to retain HD inside a shell formed by a mixture of N, N-dimethylaminoethyl methacrylate and styrene as monomers [48]. Microencapsulation of various heat storage materials with a polystyrene shell by suspension polymerization was also carried out by Sanchez et al. [27].

This dissertation focuses on the preparation of micron-sized, monodisperse cross-linked microcapsules encapsulating a heat storage material, HD, utilizing the SaPSeP method by microsuspension polymerization for use in heat storage application. The capsule particles and thermal properties of encapsulated HD were determined from the viewpoint of the application.

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Chapter 1

Preparation of divinylbenzene copolymer particles with encapsulated hexadecane for heat storage application

Introduction

Polymer particles with hollow structures are attractive for many industrial applications such as microcapsules, hinding or opacifying agents in coating and molding compositions [1-6]. We have succeeded in preparing approximately 5-μm sized, monodisperse, cross-linked polymer particles with one hollow at the center by seeded polymerization of highly divinylbenzene (DVB)/toluene-swollen polystyrene (PS) particles [7, 8] prepared by the dynamic swelling method [9, 10]. The formation mechanism of these hollow polymer particles was proposed [11]. On the basis of this mechanism, hollow polymer particles were also prepared by 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 was needed as accelerator for phase separation of polydivinylbenzene (PDVB) formed during the polymerization [13]. The phase separation in the early stage is the first required point for the formation of the hollow structure because at low conversion the PDVB can move and adsorb at the interface of the droplets due to low viscosity. The second required point is the preferential adsorption of PDVB at the interface of the droplets over PS previously dissolved therein. Therefore, the formation of the hollow structure was named the Self-assembling of Phase Separated Polymer (SaPSeP) method. Moreover, microsuspension polymerization of DVB droplets containing *n*-hexadecane (HD), instead of a polymer, as a nonsolvent was also carried out [14]. The HD capsulated particles

were prepared under the conditions where phase separation in the droplets occurred in an early stage of polymerization. The time at which phase separation began depended on both the content of HD and the crosslinking reaction of PDVB. That is, the SaPSeP method is applicable not only to the preparation of hollow particles but also to the encapsulation of chemicals. In actual, we succeeded in encapsulating hinokitiol, which is abstracted from natural coniferous woods, although the rate of radical polymerization obviously decreased compare with that in the absence of it due to high chain transfer reaction to hinokitiol [15].

Energy storage materials play an important role in conserving available energy and improving its utilization. There are numerous numbers of heat storage materials that melt and solidify at a wide range of temperatures, making them attractive for many applications. One group of them is paraffin waxes that are cheap and have moderate thermal energy storage but low thermal conductivity, therefore, it requires large surface areas. 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 [16].

Recently, we reported the encapsulation of HD, one of paraffin waxes used as heat storage materials, in PDVB particle produced by microsuspension polymerization utilizing the SaPSeP method of micron-sized DVB/HD droplets prepared by the Shirasu Porous Glass (SPG) membrane emulsification technique [17, 18]. The heat capacity of pure HD is approximately 230 J/g defined as heat of melting (H_m) and heat of solidification (H_s) while melting (T_m) and solidification (T_s) temperatures are approximately 15 °C. It was found that H_s of HD encapsulated in PDVB particles was much lower than that of pure HD. Moreover, T_s of the encapsulated HD was also lower approximately 10 °C than that of pure HD while T_m still remains at 15 °C [19]. These phenomena are, of course, negative to apply it for heat storage materials.

In this study, in order to clarify the reason and to improve the thermal properties of

encapsulated HD, microsuspension copolymerizations of DVB and acrylic monomers are carried out in droplets containing HD.

Experimental

Materials

DVB (Nippon Steel Chemical, Tokyo, Japan; purity, 96%) was washed with 1N NaOH and distilled water to remove inhibitors before use. Butyl acrylate (BA), ethyl acrylate (EA) and methyl acrylate (MA) (Nacalai Tesque Inc., Kyoto, Japan; extra pure reagent grade) were purified by distillation under reduced pressure. Poly(vinyl alcohol) (PVA) (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 Inc., Kyoto, Japan; guaranteed reagent grade) was used as received.

SPG membrane emulsification and microsuspension polymerization

A homogeneous solution of the organic phase consisting of monomer, HD and BPO initiator was dispersed in PVA aqueous solution with SPG membrane (SPG Technology Co., Ltd., Japan). The resulting emulsions were transferred to glass ampoules, degassed using several N_2/vacuum cycles and sealed off. Microsuspension polymerizations were carried out at 70 °C for 24 h under the conditions listed in Table 1, 2 and 3, respectively, for DVB-BA copolymer [P(DVB-BA)], DVB-EA copolymer [P(DVB-EA)] and DVB-MA copolymer [P(DVB-MA)] particles. The tubes were horizontally shaken at 80 cycles/min (3-cm strokes). Capsule particles were observed with an optical microscope (ECLIPSE 80i, Nikon Corporation, Tokyo, Japan). Particle sizes were measured using image analysis software

(MacScope®, Mitani Co., Ltd., Japan) from optical microscope images based on > 150 particles.

Table 1 Recipes for the preparation of P(DVB-BA) capsule particles with encapsulated HD by microsuspension copolymerization [a)] of (DVB-BA)/HD (2/3, w/w) droplets prepared by SPG emulsification method [b)]

		DVB/BA (w/w)					
Ingredient		100/0	80/20	65/35	50/50	35/65	20/80
DVB	(g)	2.6	2.1	1.7	1.3	0.9	0.5
BA	(g)	0.0	0.5	0.9	1.3	1.7	2.1
HD	(g)	4.0	4.0	4.0	4.0	4.0	4.0
BPO	(g)	0.1	0.1	0.1	0.1	0.1	0.1
PVA	(g)	0.5	0.5	0.5	0.5	0.5	0.5
Water	(g)	50	50	50	50	50	50

[a] N_2, 70 °C, 24 h, 80 cycles/min (3-cm strokes)

[b] SPG membrane (pore size: 1.1 μm)

Abbreviations: DVB, divinylbenzene; BA, butyl acrylate; HD, *n*-hexadecane;

BPO, benzoyl peroxide; PVA, poly(vinyl alcohol)

Measurement of thermal property

H_s, T_s, H_m and T_m values of encapsulated HD were measured in an aluminum pan by differential scanning calorimeter (DSC) (DSC 6200, Seiko Instruments Inc., Chiba, Japan) under a N_2 flow with a scanning rate of 5 °C/min. The measurement was also carried out in the presence of acrylic polymer as follows. Polybutyl acrylate (PBA), Polyethyl acrylate

(PEA) and Polymethyl acrylate (PMA), which were prepared by solution polymerization [20], were separately dissolved with HD in toluene. Toluene was evaporated in a capless bottle and phase separated pure HD top layer was removed as much as possible. Each polymer, inwhich HD dissolved or dispersed, was put in an aluminum pan for DSC measurement.

Table 2 Recipes for the preparation of P(DVB-EA) capsule particles with encapsulated HD by microsuspension copolymerization [a)] of (DVB-EA)/HD (2/3, w/w) droplets prepared by SPG emulsification method [b)]

		DVB/EA (w/w)					
Ingredient		100/0	80/20	70/30	50/50	35/65	20/80
DVB	(g)	2.6	2.1	1.8	1.3	0.9	0.5
EA	(g)	0.0	0.5	0.8	1.3	1.7	2.1
HD	(g)	4.0	4.0	4.0	4.0	4.0	4.0
BPO	(g)	0.1	0.1	0.1	0.1	0.1	0.1
PVA	(g)	0.5	0.5	0.5	0.5	0.5	0.5
Water	(g)	50	50	50	50	50	50

[a] N_2, 70 °C, 24 h, 80 cycles/min (3-cm strokes)

[b] SPG membrane (pore size: 1.1 μm)

Abbreviation: EA, ethyl acrylate

Miscibility of HD in polymer particles

Dried PS [21] and poly(iso-butyl methacrylate) (P*i*-BMA) [22] particles, which were prepared by emulsifier-free emulsion polymerization with potassium persulfate (KPS) as initiator, were separately dispersed and heated in HD for 24 h at 100 °C and 70 °C,

respectively, which are above their glass transition temperatures (T_g). The miscibilities of HD in the polymer particles were estimated by measuring the T_g values of PS and P*i*-BMA using DSC under a N_2 flow with a scanning rate of 5 °C/min after unabsorbed HD was removed.

Table 3 Recipes for the preparation of P(DVB-BA) capsule particles with encapsulated HD by microsuspension copolymerization [a)] of (DVB-BA)/HD (2/3, w/w) droplets prepared by SPG emulsification method [b)]

		DVB/MA (w/w)	
Ingredient		100/0	80/20
DVB	(g)	2.6	2.1
MA	(g)	0.0	0.5
HD	(g)	4.0	4.0
BPO	(g)	0.1	0.1
PVA	(g)	0.5	0.5
Water	(g)	50	50

[a] N_2, 70 °C, 24 h, 80 cycles/min (3-cm strokes)

[b] SPG membrane (pore size: 1.1 μm)

Abbreviation: MA, methyl acrylate

Observation of ultrathin cross sections of particles

Dried capsule particles were dispersed in epoxy matrix, cured at room temperature for 24 h and then microtomed. The ultrathin cross sections were observed with a transmission electron microscope (TEM, JEOL JEM-1230 electron microscope, Japan).

Results and discussion

Preparation of copolymer capsule particles

The prepared capsule particles were observed with an optical microscope. Figure 1 shows optical micrographs of monodisperse, P(DVB-BA) particles with encapsulated HD at various weight ratios of DVB/BA produced by microsuspension copolymerization of (DVB-BA)/HD (2/3, w/w) droplets prepared by the SPG emulsification technique under the conditions listed in Table 1. All particles were nonspherical with smooth outer surface. Because the shell strength was not enough, a part of the shell buckled by shrinkage of HD, which is induced by cooling from the polymerization temperature (70 °C) to room temperature, similarly as discussed in previous articles [23-25]. The densities of HD at 20 °C and 70 °C are 0.773 and 0.739 g/cm^3, respectively [26]. In the case of P(DVB-EA) particles, they were also nonspherical particles, but with rough outer surface (Fig. 2), which is probably due to the adsorption of byproduct particles in an aqueous medium during the polymerization because of higher water solubility of EA. The byproduct particles were observed by dynamic light scattering (FPAR-1000, Otsuka Electronics, Osaka, Japan). The amounts of byproduct particles were measured to be 7.55, 10.84, 10.87, 12.42 and 15.60 wt% of polymer solid for P(DVB-EA) with DVB/EA (w/w) = 80/20, 70/30, 50/50, 35/65 and 20/80, respectively, by centrifugation at 5000 rpm for 30 min.

The particle diameter (D) and coefficient of variation (CV) are shown in Figs. 1 and 2 for P(DVB-BA) and P(DVB-EA) particles, respectively. The particle size distributions seem to be affected by the amount of acrylate used. It may be due to the effect on SPG membrane emulsification process. In this experiment, particle size was controlled by SPG membrane pore size used for monomer droplet preparation. Since hydrophilic SPG membrane was used, hydrophilic components are easily to wet the membrane surface. When acrylate amount was

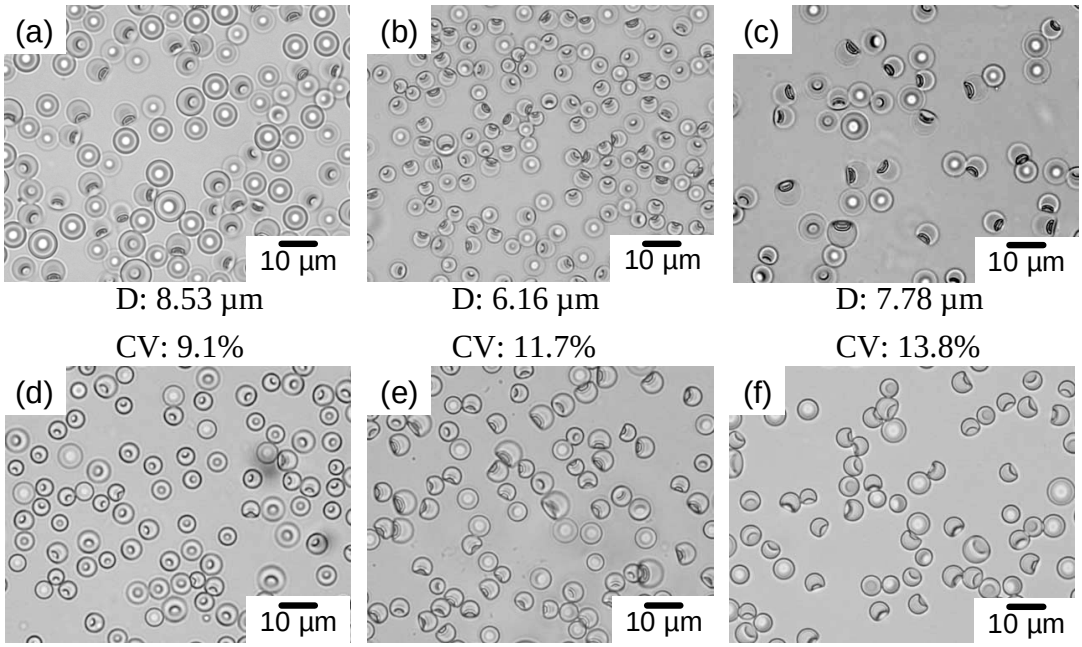

Fig. 1 Optical micrographs of P(DVB-BA) particles, produced by microsuspension copolymerizations utilizing the SaPSeP method of (DVB-BA)/HD (2/3, w/w) droplets prepared by the SPG emulsification technique under the conditions listed in Table 1 at 70 °C. DVB/BA (w/w): (a) 100/0; (b) 80/20; (c) 65/35; (d) 50/50; (e) 35/65; (f) 20/80

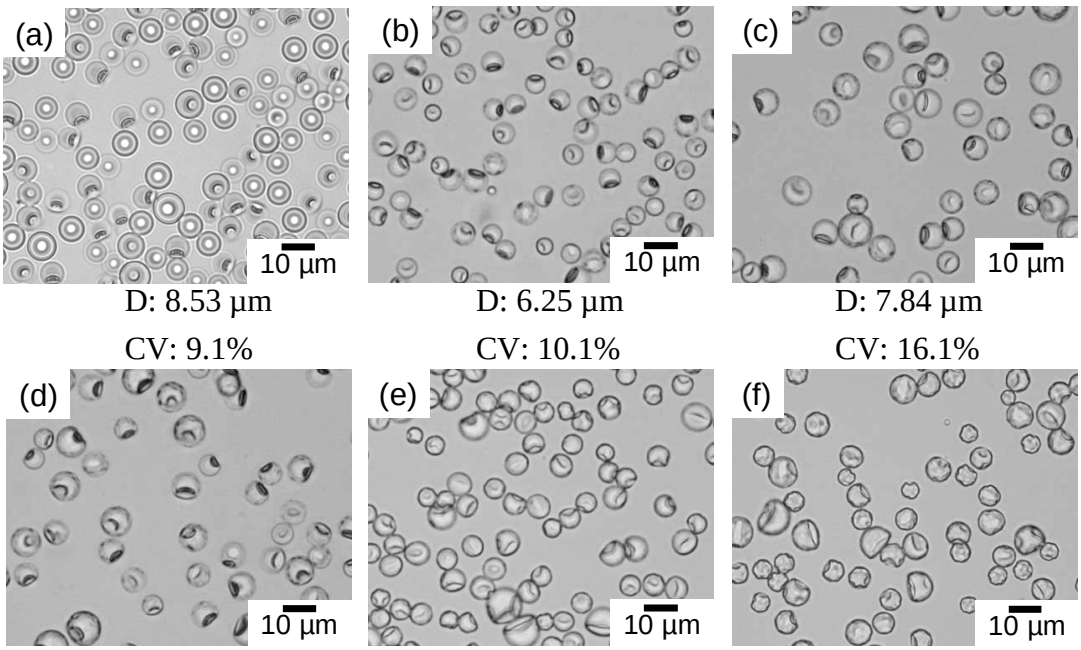

Fig. 2 Optical micrographs of P(DVB-EA) particles, produced by microsuspension copolymerizations utilizing the SaPSeP method of (DVB-EA)/HD (2/3, w/w) droplets prepared by the SPG emulsification technique under the conditions listed in Table 2 at 70 °C. DVB/EA (w/w): (a) 100/0; (b) 80/20; (c) 70/30; (d) 50/50; (e) 35/65; (f) 20/80

increased, hydrophilicity of dispersed oil phase was also increased. This high hydrophilic dispersed phase apts to wet the membrane surface leading to the difficulty of droplet size and size distribution control. Therefore, in some cases, quite polydisperse particles were obtained even though the same SPG membrane (pore size, 1.1μm) was used.

Thermal properties of encapsulated HD

From the viewpoint of heat storage application, thermal properties of encapsulated HD were measured with DSC. Figure 3 shows DSC thermograms of HD encapsulated in P(DVB-BA) particles having the various weight ratios of DVB/BA. In all cases, T_s values of the encapsulated HD were about 5 °C, i.e. approximately 10 °C lower than that of pure HD while T_m values still remained at 15 °C. The reason of T_s decreasing may be based on a compartmentalization effect that is impurities located in capsule particle can not induce the nucleation of HD encapsulated in the other particles. In the bulk system, it is known that there is an impurity that works as a trigger for the nucleation resulting in heterogeneous nucleation [27]. In emulsion, the numbers of impurity that usually cause heterogeneous nucleation as in bulk phase are distributed among a large number of isolated droplets. Therefore, the probability for heterogeneous nucleation for all droplets is drastically reduced. The supercooling was also observed in the case of P(DVB-EA) particles as shown in Fig. 4.

Figure 5 shows the relationships between MA, EA and BA contents in the copolymer particles and H_s values, which were obtained from the area of solidification curves shown in Figs. 3 and 4 for HD encapsulated in P(DVB-BA) and P(DVB-EA) particles, respectively. The H_s value of encapsulated HD in PDVB particles was the lowest, whereas in the cases of the copolymer particles, they always increase with MA, EA and BA contents until reached that of pure HD (approximately 230 J/g). On the basis of the mechanism of hollow polymer particle discussed in the previous article [11], the polymer molecules formed in the monomer

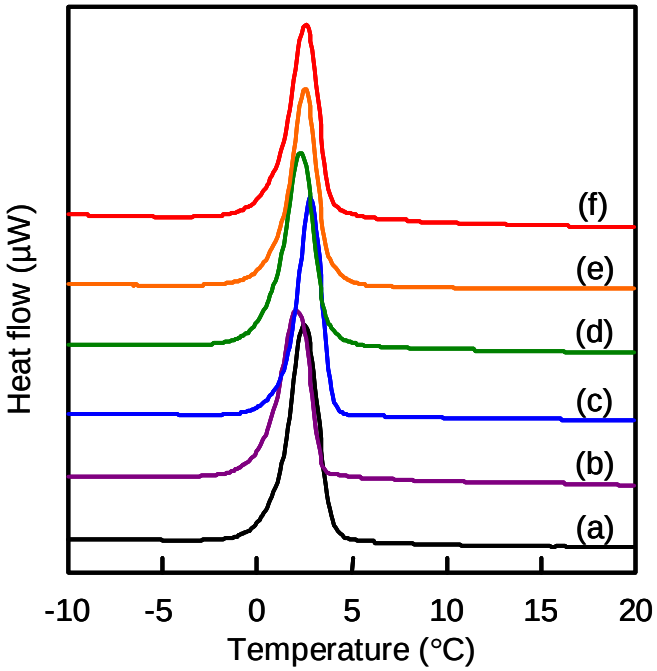

Fig. 3 DSC thermograms of HD encapsulated in P(DVB-BA) particles, produced by microsuspension copolymerizations utilizing the SaPSeP method of (DVB-BA)/HD (2/3, w/w) droplets, measured with a cooling rate at 5 °C/min. DVB/BA (w/w): (a) 100/0; (b) 80/20; (c) 65/35; (d) 50/50; (e) 35/65; (f) 20/80

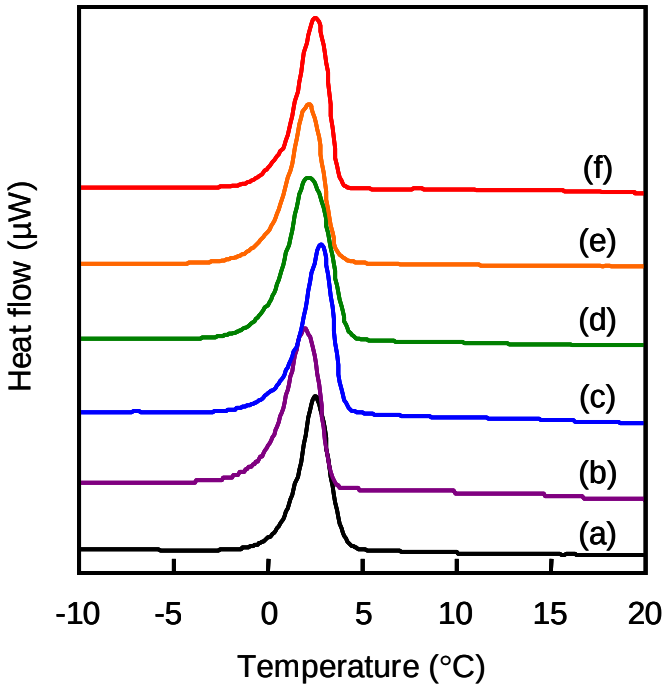

Fig. 4 DSC thermograms of HD encapsulated in P(DVB-EA) particles, produced by microsuspension polymerizations utilizing the SaPSeP method of (DVB-EA)/HD (2/3, w/w) droplets, measured with a cooling rate at 5 °C/min. DVB/EA (w/w): (a) 100/0; (b) 80/20; (c) 70/30; (d) 50/50; (e) 35/65; (f) 20/80

droplet separate and adsorb at the inner interface, resulting in cross-linked shell. An increase in hydrophilicity of P(DVB-BA) chains with increasing of BA content should enhance the phase separation between the copolymer chains and HD, eventually resulting in the complete isolation of the HD core from the polymer shell. This HD core seems to be more smoothly solidified than incompletely isolated HD locating in the inner interface of polymer shell, resulting in the increasing of H_s with the BA content. This is more obvious in the case of P(DVB-EA) capsule particles because of higher hydrophilicity of EA than BA unit. This seems to be the reason why H_s values of HD encapsulated in P(DVB-EA) particles were always higher than those in P(DVB-BA) particles. In the case of P(DVB-MA) capsule particles, the highest H_s value was obtained at the same composition as P(DVB-EA) and P(DVB-BA), but the large amount of byproduced particles in an aqueous medium was observed due to the highest water solubility of MA.

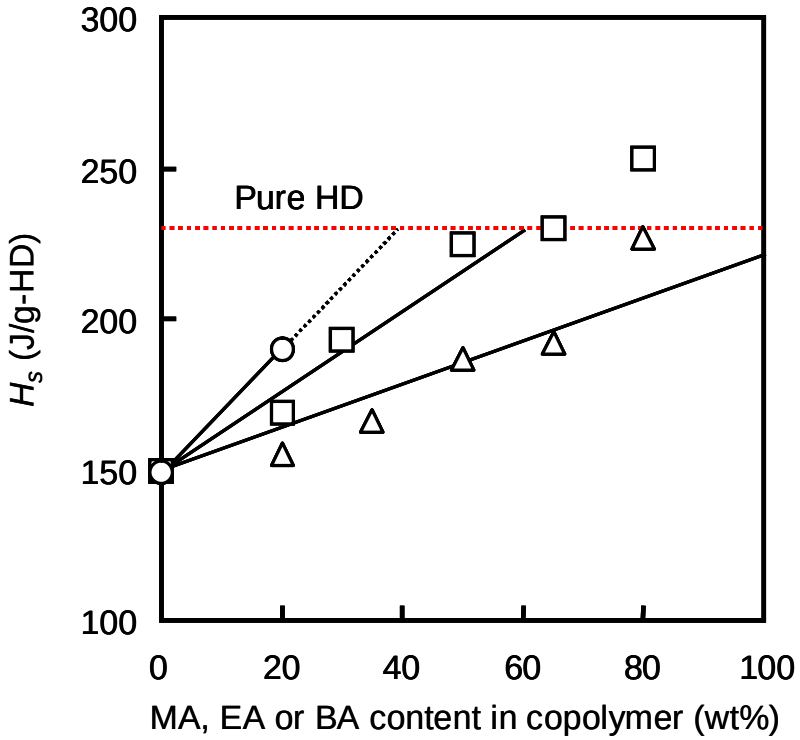

Fig. 5 Relationships between MA (○), EA (□) and BA (△) contents in P(DVB-MA), P(DVB-EA) and P(DVB-BA) capsule particles, respectively, (polymer/HD, 2/3 by weight) and heats of solidification (H_s) of HD encapsulated in the copolymer particles

Polymer shell formation

Figure 6 shows conversion-time curves of DVB and BA in microsuspension copolymerization of (DVB-BA)/HD (2/3, w/w) droplets prepared by the SPG membrane emulsification at DVB/BA of 50/50 (w/w). It was found that DVB was faster polymerized than BA, which well accords with presumption based on the significant difference between copolymerization reactivity ratios of DVB and BA, which (r_1 and r_2) are 1.396 and 0.082, respectively [28]. Therefore, it seems that considering the formation mechanism of the capsule particle using the SaPSeP method [11], cross-linked DVB-rich copolymer shell (outer shell) is formed in the former stage of the copolymerization, and then BA-rich copolymer inner shell is formed in the latter stage. To confirm this assumption, the observation of ultrathin cross sections of particles is carried out.

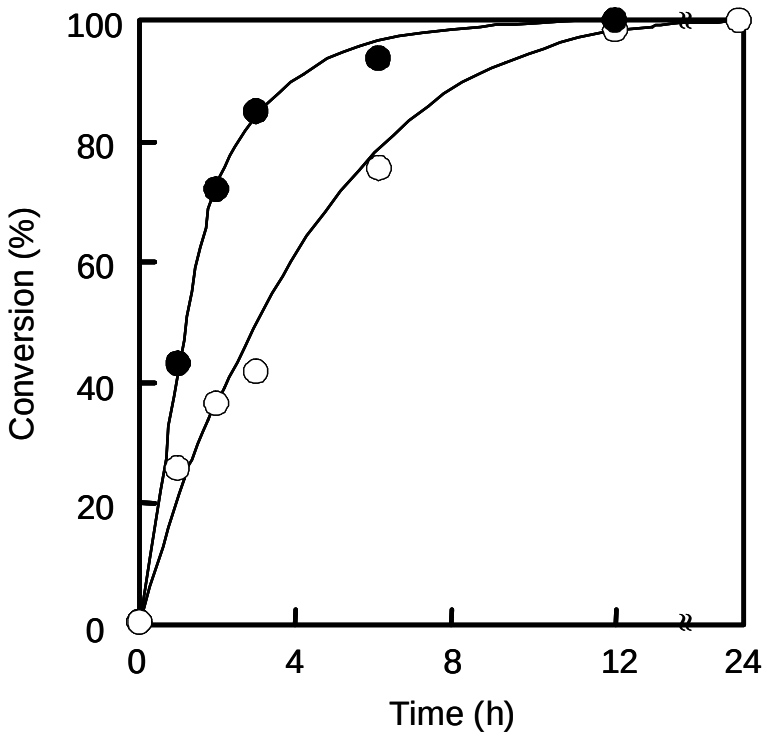

Fig. 6 Conversion-time curves of DVB (●) and BA (○) in microsuspension copolymerization of (DVB-BA)/HD droplets (DVB-BA/HD, 2/3 by weight) at DVB/BA of 50/50 w/w prepared by the SPG membrane under the conditions listed in Table 1

Figure 7 shows transmission electron microscope (TEM) photographs of cross sections of PDVB and P(DVB-BA) (DVB/BA = 20/80, w/w) capsule particles. It was found that a single layer was observed in the shell of PDVB capsule particle, whereas a double-layered structure was formed in the shell of P(DVB-BA) capsule particle. This supports the above assumption that the shell of the latter particles consists of BA-rich inner shell and DVB-rich outer shell. Considering the reactivity ratios in the cases of DVB/EA and DVB/MA, such a two layers shell might be also formed in the P(DVB-EA) and P(DVB-MA) capsule particles. The acrylate-rich inner shell is expected to contribute to an increase in H_s value of the encapsulated HD due to their hydrophilicity, which will be discussed in the following section

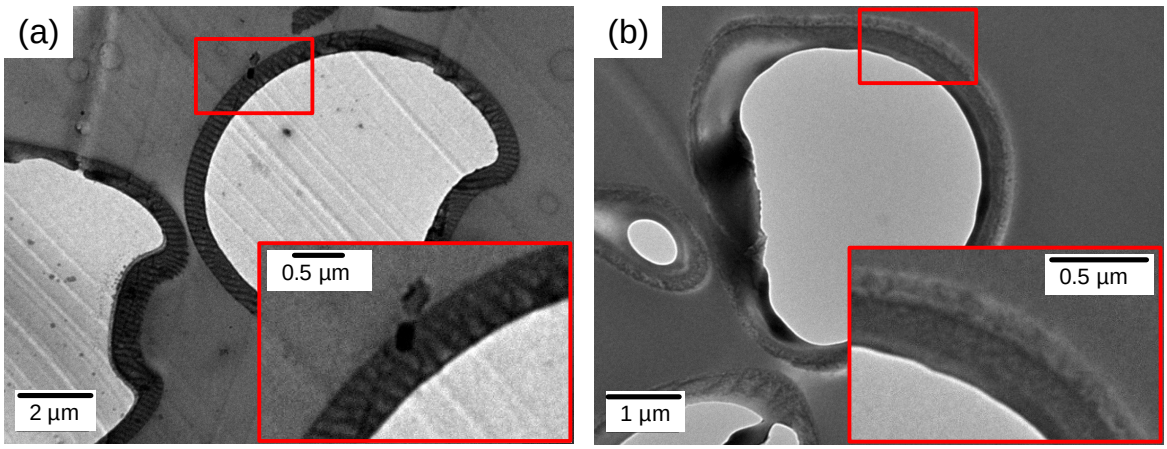

Fig. 7 TEM photographs of cross sections of (a) PDVB and (b) P(DVB-BA) (DVB/BA = 20/80, w/w) particles, produced by microsuspension polymerizations utilizing the SaPSeP method under the conditions listed in Table 1

Miscibility of HD with polymers

Table 4 shows the miscibilities of HD in PS and P*i*-BMA particles used as representatives of PDVB and the DVB-acrylic copolymers, respectively. At the temperatures

above their T_g, the polymer particles absorbed HD leading to the decreasing of the T_g. In the case of PS particle, its T_g was much more decreased than that in the case of P*i*-BMA indicating that HD was more absorbed in PS than P*i*-BMA particles. That is, the miscibility of HD with PS was higher than that with P*i*-BMA. This suggests that the miscibility of HD with DVB-acrylic copolymer is lower than that with PDVB. Corresponding to Fig. 5, the low miscibility of HD in P(DVB-BA) accelerates the phase separation of HD core leading to the increase of H_s with the BA content as previously discussed. This influence must be more effective in the case of P(DVB-EA) particles.

Table 4 Glass transition temperature (T_g) of polymer particles dispersed in HD before and after the heat treatment at 10 °C higher than corresponding T_g

Sample	T_g (°C)		
	before heating	after heating	ΔT_g
PS	89.0	48.5	40.5
P*i*-BMA	60.5	54.0	6.5

Furthermore, the effect of various hydrophilic acrylic polymers on the H_s of HD was studied as shown in Table 5. When toluene was removed by evaporation from homogeneous solutions of polymer/HD/toluene, a mixture of HD with PBA was transparent whereas those with PEA and PMA were turbid. It can be assumed that in the former case, HD dispersed in PBA as monomolecular state or fine domains, which gives high total interfacial area between PBA and HD. In latter cases, large HD domains must be dispersed in each polymer phase.

Therefore, the total interfacial area seems to be in the order of PBA > PEA > PMA. These suggest that the decrease in the total interfacial area increases H_s of HD dispersed in polymer phase.

Moreover, it seems that H_s of HD dispersed in polymer phase also increased with an increase of hydrophilicity of polymer in the order of PMA > PEA > PBA. The H_s value for PMA nearly equaled to that of pure HD. Therefore, not only the total interfacial area but also the hydrophilicity of polymer must affect the H_s of HD contacting the polymer.

Table 5 Heat of solidification (H_s) of incorporated HD in PMA, PEA or PBA, measured by DSC of 5 °C/min cooling rate

	Polymers			
	None	PMA	PEA	PBA
H_s (J/g-HD)	230	220	214	129

Conclusions

Monodispersed DVB copolymer particles with encapsulated HD were prepared by microsuspension copolymerization utilizing the SaPSeP method. The H_s of encapsulated HD in PDVB particles was much decreased from that of pure HD. The problem in the application of the polymer particles with encapsulated HD as heat storage material was improved by the copolymerization of hydrophilic acrylic monomer. This seems to be based on that the copolymerizations of hydrophilic monomer enhance the phase separation of copolymer chains and HD, eventually resulting in the complete isolation of the HD core from the polymer shell.

Acknowledgement

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).

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Chapter 2

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

Introduction

Polymer particles with hollow structures are attractive for many industrial applications such as microcapsules, hiding or opacifying agents in coating and molding compositions [1-6]. We have succeeded in preparing approximately 5-μm-sized, monodisperse, cross-linked polymer particles with a single hollow at the center by seeded 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 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 accelerator for phase separation of polyDVB (PDVB) formed during the polymerization [13]. The formation of this hollow structure was named the Self-assembling of Phase Separated Polymer (SaPSeP) method. Microsuspension polymerization of DVB droplets containing *n*-hexadecane (HD) yielded HD capsulated particles where HD as nonsolvent worked 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 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 in applications. 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 studied the preparation of PDVB capsule particles with encapsulated HD as heat storage materials by microsuspension polymerization utilizing the SaPSeP method of micron-sized, comparatively monodisperse DVB/HD droplets prepared by the Shirasu Porous Glass (SPG) membrane method [17, 18]. The heat of melting (H_m), which corresponds to the heat of solidification (H_s), of the pure HD used was approximately 230 J/g, and its melting temperature (T_m), which corresponds to solidification temperature (T_s), was approximately 15 °C. It was found that H_s of HD encapsulated in PDVB particles was much lower than that of pure HD. Moreover, T_s of the encapsulated HD was also approximately 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 for heat storage materials. However, the problem with 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 the fact that the copolymerization of polar monomers 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 different particle shapes [14]. In the case of a thicker shell (DVB/HD = 2/2, w/w), a single water domain was observed in HD core encapsulated in spherical PDVB capsule particles. On the other hand, in the thinner shell (DVB/HD = 2/3, w/w) nonspherical capsule particles, in which such a water domain was not

contained in the HD core, were prepared. The 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 are studied from the viewpoint of heat storage application.

Experimental

Materials

DVB (Nippon Steel Chemical, Tokyo, Japan; purity, 96%) was washed with 1 N NaOH and distilled water to remove inhibitors before use. Poly(vinyl alcohol) (PVA) (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 Inc., Kyoto, Japan; guaranteed reagent grade) was used as received.

SPG membrane emulsification and microsuspension polymerization

A homogeneous solution of the organic phase consisting of DVB, HD and BPO was dispersed as droplets in PVA aqueous solution with SPG membrane (SPG Technology Co., Ltd, Japan). The resulting emulsions were transferred to glass ampoules, degassed using several N_2/vacuum cycles and sealed off. Microsuspension polymerizations were carried out at 70 °C for 24 h under the conditions listed in Table 1. The tubes were horizontally shaken at

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

Table 1 Recipes for the production of PDVB capsule particles with encapsulated HD by microsuspension polymerization[a)] of comparatively monodisperse DVB/HD droplets prepared by SPG membrane method [b)]

		DVB/HD (w/w)	
Ingredient		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

[a)] N_2, 70 °C, 24 h, 80 cycles/min (3-cm strokes)

[b)] SPG membranes (pore sizes: 1.1, 1.9, 3.1, 3.9 and 4.9 µm)

Abbreviations: DVB, divinylbenzene; PDVB, poly(DVB); HD, *n*-hexadecane; BPO, benzoyl peroxide; PVA, poly(vinyl alcohol)

Measurement of thermal properties

H_s, T_s, H_m and T_m of HD encapsulated in capsule particles at emulsion (solid content: ca 10%) and dry states were measured in an aluminum pan with a differential scanning

calorimeter (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 in 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

Formation mechanism of water domain

Figure 1 shows optical micrographs at room temperature of PDVB particles with encapsulated HD produced by microsuspension polymerization at 70 °C of DVB/HD droplets prepared by the 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 encapsulated HD core, 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 insufficient, 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.

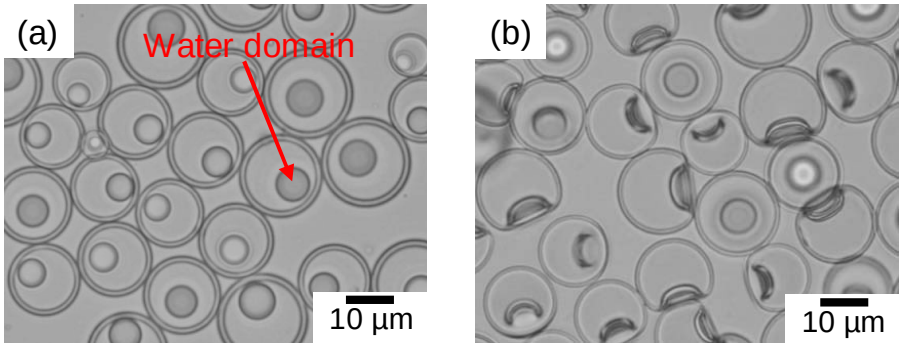

Fig. 1 Optical micrographs of PDVB/HD particles in aqueous dispersed state, produced by microsuspension polymerization utilizing the SaPSeP method of DVB/HD droplets prepared with the SPG emulsification method (pore size, 3.9 µm) under the conditions listed in Table 1. DVB/HD (w/w): (a) 2/2; (b) 2/3

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 due to 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 cooling from 70 °C to 25 °C the single domain appeared in each particle and the domain size increased with decreasing temperature. The occupied volume of the domain was 7-9% of particles. 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 2.6% based on the densities of HD at 20 °C and 70 °C, which are 0.773 and 0.739 g/cm^3, respectively [23]. The calculated total volume shrinkage is 8.25%. 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 the

shell strength is sufficient to withstand the external pressure.

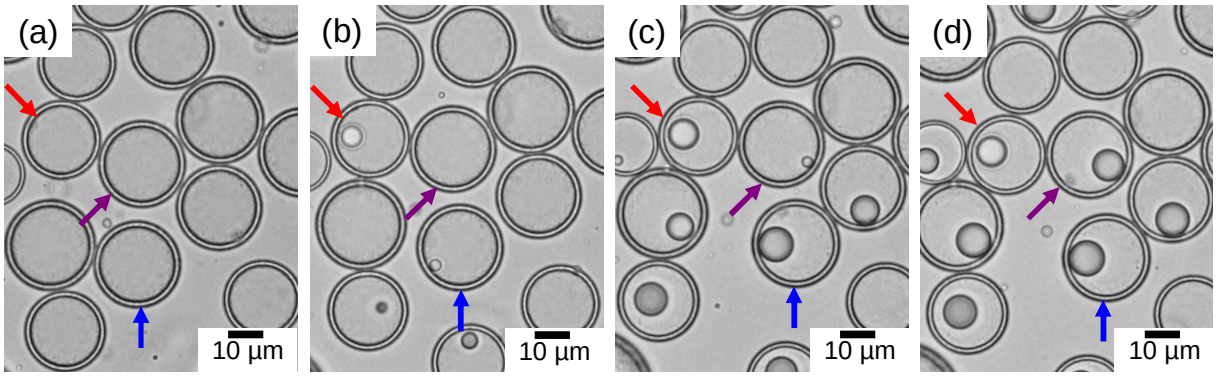

Fig. 2 Optical micrographs during spontaneous cooling process of PDVB/HD particles, produced by microsuspension polymerizations of DVB/HD (2/2, w/w) droplets prepared by the SPG emulsification method under condition listed in Table 1. Temperatures (°C): (a) 70; (b) 55; (c) 40; (d) 25

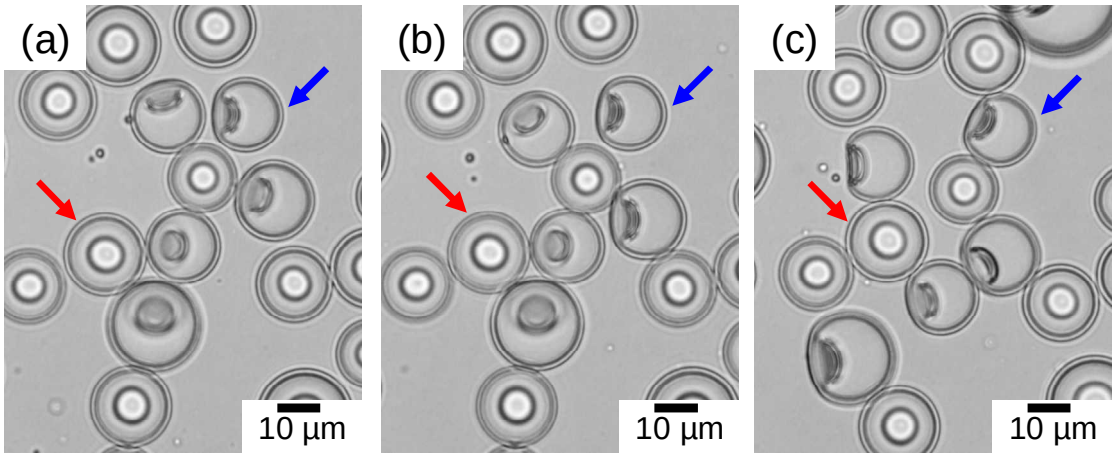

Fig. 3 Optical micrographs during spontaneous cooling process of PDVB/HD particles, produced by microsuspension polymerizations of DVB/HD (2/3, w/w) droplets prepared by the SPG emulsification method under condition listed in Table 1. Temperatures (°C): (a) 70; (b) 50; (c) 25

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 occurred as a result of shrinkage of the monomer phase as previously mentioned during the polymerization. Because the shell strength was insufficient to withstand the outer pressure, a part of the shell buckled before the water penetration. Therefore, water domains were not observed in the particles. Further particles 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.

Influence of water domain in HD core on thermal properties of encapsulated HD

From the viewpoint 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 in PDVB particles having different weight ratios of DVB/HD, measured using aqueous dispersed 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 a DVB/HD ratio of 2/3 (w/w), a sharp single peak of encapsulated HD due to solidification was observed with H_s = 162 J/g-HD and T_s = 6 °C. On the other hand, for DVB/HD = 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. The 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 required longer time and lower temperature to complete the solidification than the other ones. This phenomenon is disadvantageous with regards to heat storage application.

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 with 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 due to the influence of the water domain in the HD core. Zhang et al. 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.

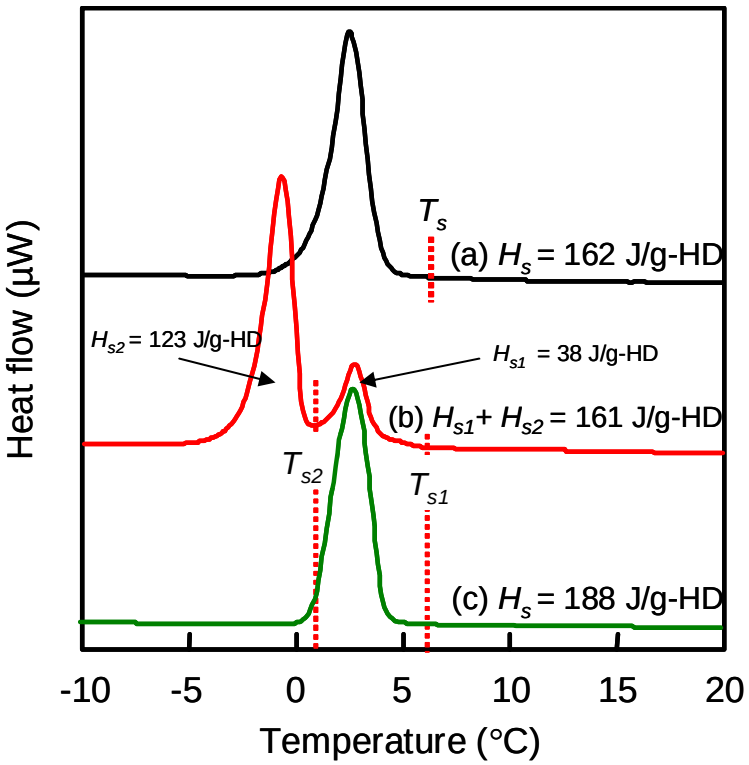

Fig. 4 DSC thermograms of HD encapsulated in PDVB particles in aqueous dispersion, produced by microsuspension polymerization of DVB/HD droplets prepared by the SPG (pore size, 1.1 μm) emulsification method under the conditions listed in Table 1. Measured states: (a, b) emulsion; (c) dry. DVB/HD (w/w): (a) 2/3; (b, c) 2/2

Figure 5 shows optical micrographs of PDVB/HD capsule particles produced by microsuspension polymerization of DVB/HD (2/2, w/w) droplets having various diameters prepared with the 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.

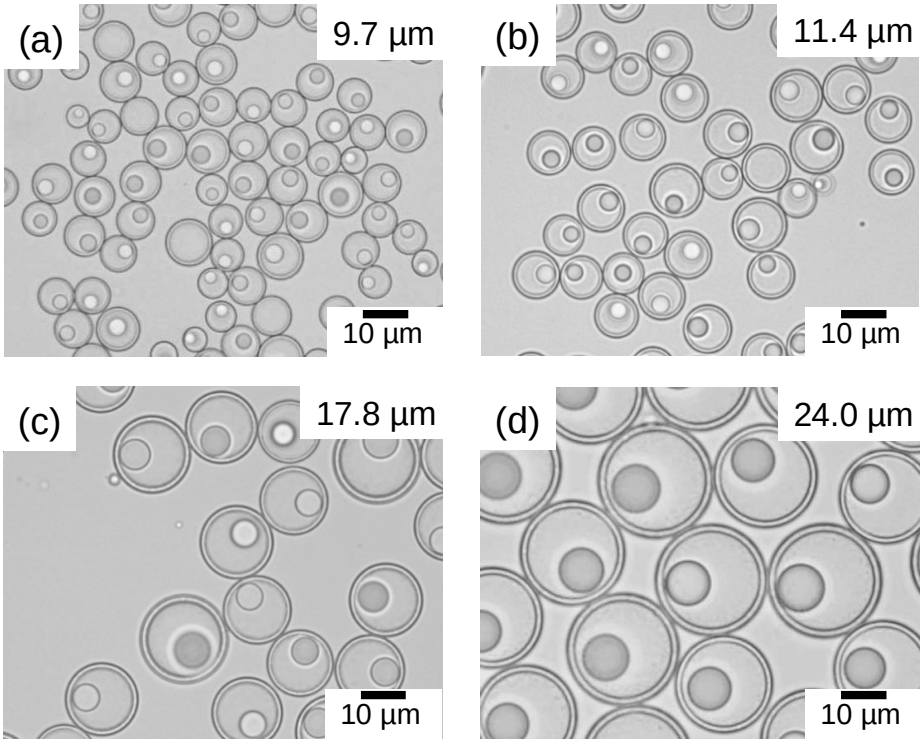

Fig. 5 Optical micrographs of PDVB/HD particles, produced by microsuspension polymerization utilizing the SaPSeP method of DVB/HD (DVB/HD = 2/2, w/w) droplets prepared by the SPG membrane emulsification method under the conditions listed in Table 1. SPG membrane pore size (µm): (a) 1.3; (b) 1.9; (c)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

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 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.

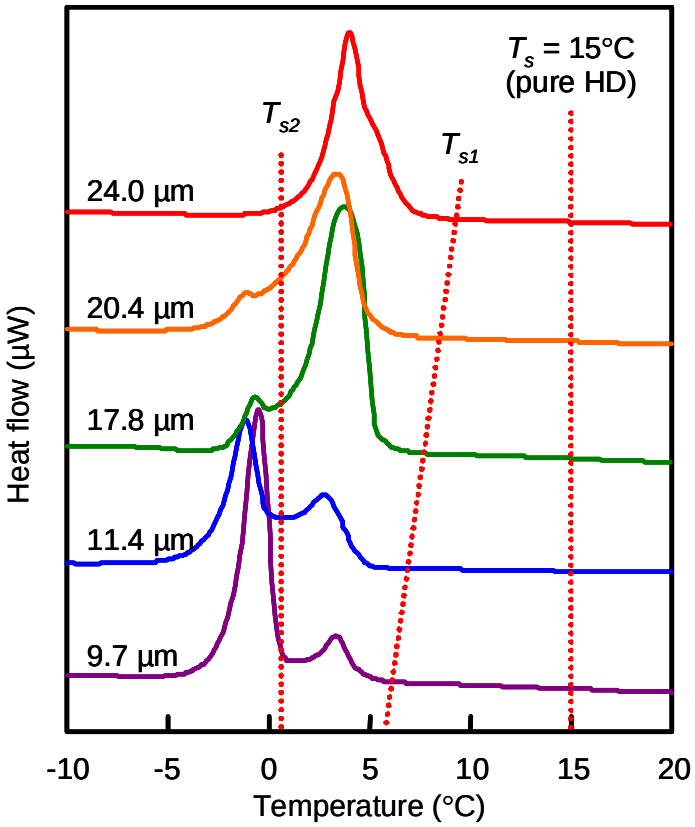

Fig. 6 DSC thermograms of encapsulated HD of PDVB/HD (DVB/HD = 2/2, w/w) dispersion measured with DSC at a scanning rate of 5 °C/min. Numbers on thermograms indicate particle diameters.

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 due to the influence of the water domain in the HD core.

Moreover, T_s (T_{s1}) of encapsulated HD increased from 5 °C 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 with encapsulation may be based on a "compartmentalization" effect: impurities located in capsule particle can not induce the nucleation of HD encapsulated in the other particles [20]. In a bulk 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.

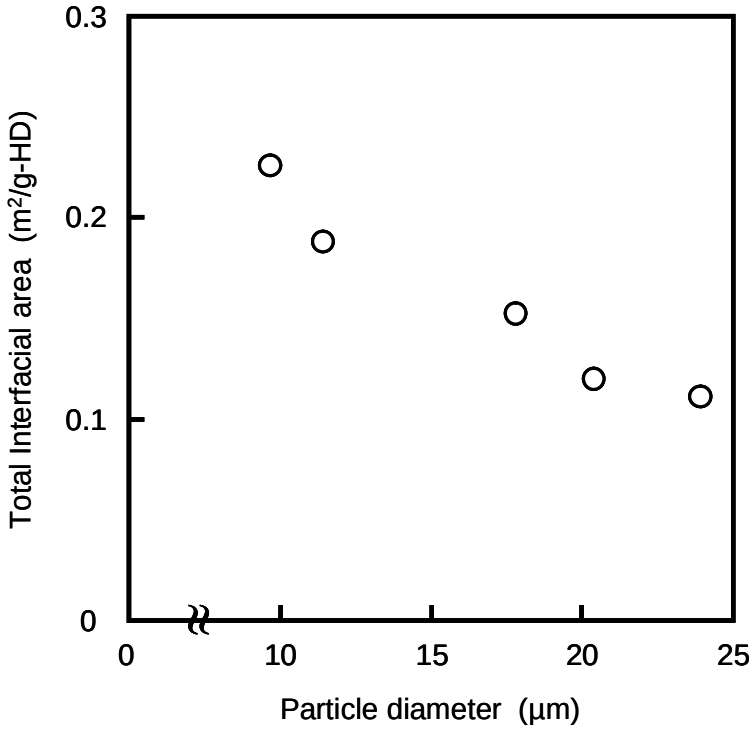

Fig. 7 Relationship between the diameter of PDVB/HD (DVB/HD = 2/2, w/w) particles and total interfacial area of water domain in encapsulated HD

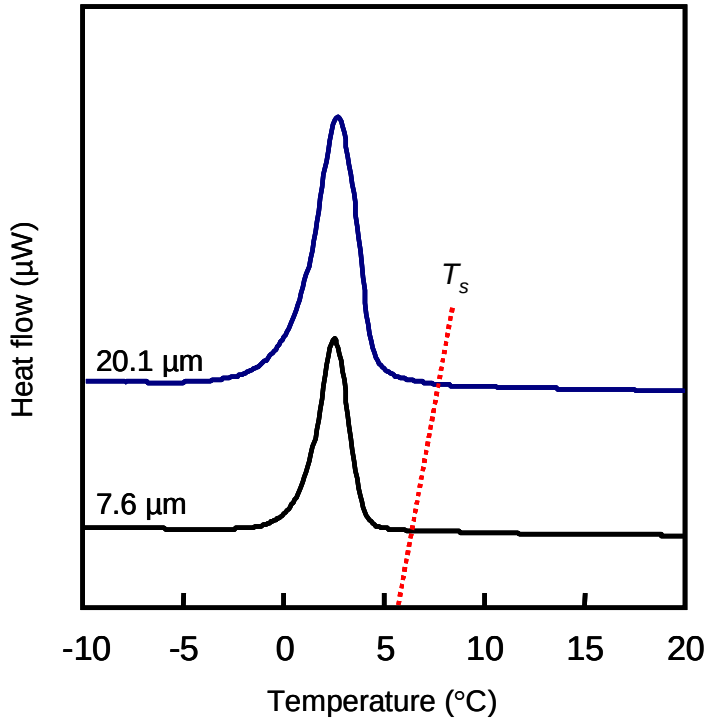

Fig. 8 DSC thermograms of encapsulated HD of PDVB/HD (DVB/HD = 2/3, w/w) dispersion measured with DSC at a scanning rate of 5 °C/min. Numbers on thermograms indicate particle diameters

Solidification of encapsulated HD in capsule particles

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 with regards to application as heat storage materials. 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 in PDVB particles 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 in order 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

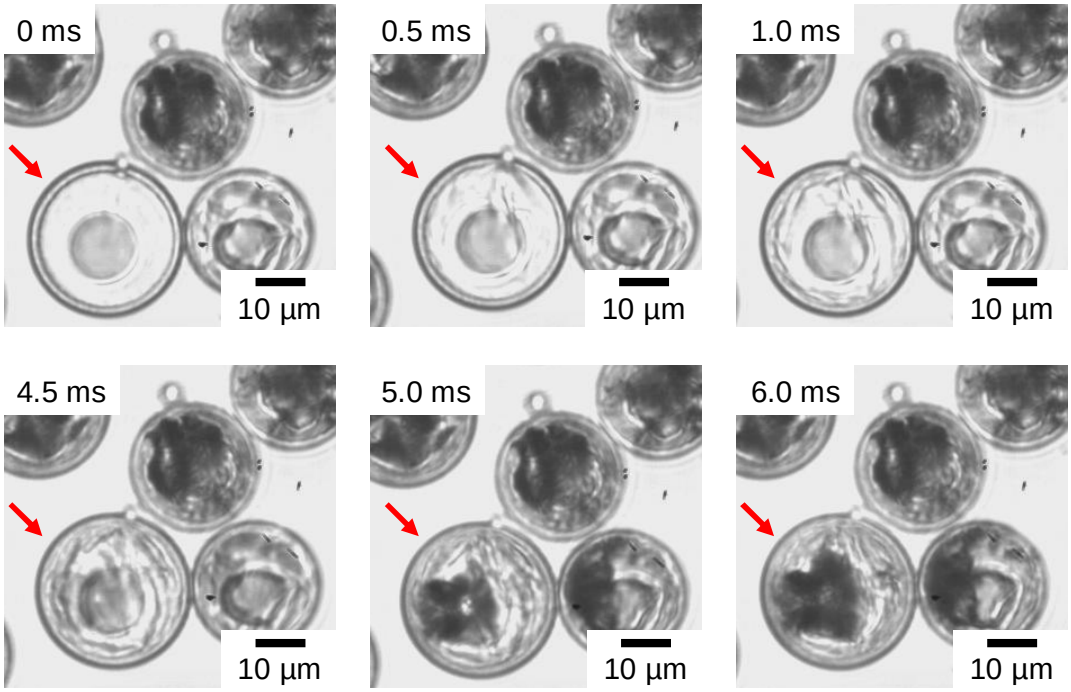

Fig. 9 Optical micrographs (with high speed camera) of solidification of HD encapsulated in PDVB (DVB/HD = 2/2, w/w) particles during cooling at 5 °C/min

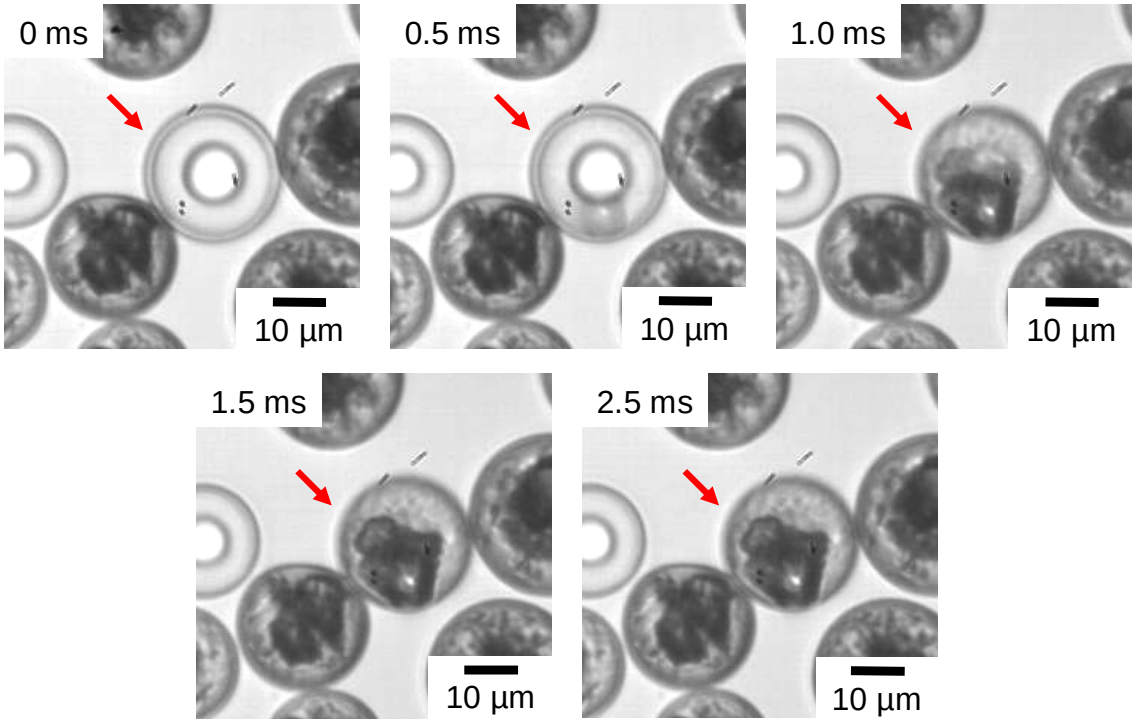

Fig. 10 Optical micrographs (with high speed camera) of solidification of HD encapsulated in PDVB (DVB/HD = 2/3, w/w) particles during cooling at 5 °C/min

interface of the polymer shell and HD, and continued until completely solidified. Solidification time of HD encapsulated in PDVB particle 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 sufficient 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 due to the decrease of total interfacial area of water domains in encapsulated HD cores.

Acknowledgement

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).

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Chapter 3

Thermal properties of hexadecane encapsulated in cross-linked capsule particles with water and/or air domains

Introduction

Polymer particles with hollow structures are attractive because of numerous industrial applications such as microcapsules, hiding or opacifying agents in coating and molding compositions [1-6]. We have succeeded in preparing approximately 5-μm-sized, monodisperse, cross-linked polymer particles with a single hollow center by 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 was named the Self-assembling of Phase Separated Polymer (SaPSeP) method and the mechanism was proposed [11]. Initially, PS dissolved in DVB/toluene droplets homogeneously. As the polymerization proceeds, polyDVB (PDVB) chains precipitate in the droplet because of cross-link. They are trapped near the interface based on surface coagulation and gradually piled at the inner interface resulting in a cross-linked PDVB shell. PS dissolved in toluene and DVB are repelled gradually to the inside. After the completion of polymerization, toluene and dissolved PS are entrapped by the PDVB shell, then toluene in the hollow evaporates by drying, and PS clings to the inner wall of the shell uniformly. On the basis of this mechanism, hollow polymer particles were also prepared by micro-suspension 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 accelerator for phase separation of PDVB formed during the polymerization [13]. The phase separation in

the early stage is the first required point for the formation of the hollow structure because at low conversion the PDVB can move and adsorb at the interface of the droplets due to low viscosity. The second required point is the preferential adsorption of PDVB at the interface of the droplets over PS previously dissolved therein to form PDVB shell. Micro-suspension polymerization of DVB droplets containing *n*-hexadecane (HD) yielded HD capsulated particles where HD as nonsolvent worked 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 and adsorb there to form the polymer shell. That is, the SaPSeP method is applicable not only to the preparation of hollow particles but also to the encapsulation of HD.

Heat storage materials can absorb and release the 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 numbers of heat storage materials that melt and solidify at a wide range of temperatures, making 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. Encapsulation of these materials is associated with many advantages such as provide 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 heating and air conditions of building [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. studied the melting and solidification processes of microencapsulated *n*-tetradecane and *n*-dodecane with gelatin shell prepared by complex coacervation. The microcapsule diameters were in the range of 5-1000 μm [23]. Zhang et al.

reported the preparation of phase change microcapsules and nanocapsules containing *n*-octadecane with melamine-formaldehyde shell [24] and the crystallization of microencapsulated n-alkanes in urea-melamine-formaldehyde shell [25] prepared by in situ polycondensation. Supercooling of encapsulated *n*-alkanes was clearly observed in either case. The preparation of polyurea microcapsule with encapsulated HD by interfacial polycondenzation used for thermal energy storage was also reported by Zou et al. [26]. It was shown that heat of melting 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 micro-suspension polymerization utilizing the SaPSeP method of micron-sized, comparatively monodisperse DVB/HD droplets prepared by the Shirasu Porous Glass (SPG) membrane emulsification method [27, 28]. The heat of melting (H_m), which corresponds to the heat of solidification (H_s), of the pure HD used was approximately 230 J/g, and its melting temperature (T_m), which corresponds to its solidification temperature (T_s), was approximately 15 °C. It was found that H_s of HD encapsulated in PDVB particles was much lower than that of the pure HD. Moreover, T_s of the encapsulated HD was also approximately 10 °C lower than that of the pure HD while T_m still remained at 15 °C [29]. These phenomena are of course negative with regards to application as heat storage materials. However, the problem with the reduction of H_s of the encapsulated HD was improved by the copolymerization of acrylic monomer 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, eventually resulting 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 article, to clearly understand the influence on the thermal properties of encapsulated HD of the water domain, thermal properties of encapsulated HD in cross-linked capsule particles containing a water and/or air domain are studied from the viewpoint of heat storage application.

2. Experimental

Materials

DVB (Nippon Steel Chemical, Tokyo, Japan; purity, 96%) was washed with 1 N NaOH and distilled water to remove inhibitors before use. Poly(vinyl alcohol) (PVA) (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 micro-suspension polymerization

The organic phase of DVB/HD of 2/2 (w/w) consists of DVB (3.3 g), HD (3.3 g) and BPO (0.1 g; 4 wt% of monomer) whereas that of DVB/HD of 2/3 (w/w) consists of DVB (2.6 g), HD (4.0 g) and BPO (0.1 g; 4 wt% of monomer). Emulsification was carried out using the SPG membrane emulsification technique (SPG Technology, Japan)

employing a microporous glass membrane with pore sizes 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 PVA in 50 g of water). The resulting emulsions were transferred to glass ampoules, degassed using several N_2/vacuum cycles and sealed off. The polymerizations were carried out at 70 °C for 24 h shaking the ampoules horizontally at a rate of 80 cycles/min (3-cm strokes). The prepared particles were observed with an optical microscope (ECLIPSE 80i, Nikon Corporation, 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 dispersion 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 clearly observation. The instantaneous evaporation rate of water was determined by differentiation of the weight-loss curve.

Measurement of thermal properties and thermal stability of HD encapsulated in cross-linked capsule particles

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

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

3. Results and discussion

Formation and influence of water domain in encapsulated HD

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 the SPG membrane method. Generally, the size distribution of monomer droplets prepared by mechanical stirring is very broad. However, utilizing the SPG emulsification technique fairly uniform droplets can be obtained. The coefficient of variation (CV) is usually approximately 10% [32, 33]. By carrying out 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) are 18.9 μm and 11.5% whereas those of PDVB/HD (DVB/HD = 2/3, w/w) are 19.9 μm and 10.0%, respectively. At the ratio of DVB/HD = 2/2 (w/w) (Fig. 1a), spherical capsule particles with smooth outer surface were obtained. No porous structure was observed in the shell with transmission electron microscope of ultrathin cross section sample [30]. The P(S-DVB) particles having high mechanical strength and smooth surface with no porous structures were also prepared by suspension polymerization by Tanaka et al [34]. Cho et al. also reported the preparation of monodisperse PDVB macrobeads without the porous structure [35]. In addition, a single domain was observed in the encapsulated HD core. The single domain was not observed in the capsule particles just after the polymerization at 70 °C. This suggests that any domain has not formed yet or very fine domains, which are not visible with optical microscope, have

formed due to 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) [36]. The calculated shrinkage volume is 5.6%. During cooling from 70 °C 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 particles. Cooling after the polymerization increases the density of HD leading to the formation of space inside the capsule particles. The calculated volume shrinkage of HD at 20 °C is 2.6% based on the densities of HD at 20 °C and 70 °C, which are 0.773 and 0.738 g/cm^3, respectively [37]. Then, the calculated total volume shrinkage is 8.2% of particle. 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 a water domain in the HD core if the shell strength is sufficient to withstand the external pressure [31].

On the other hand, in the case of DVB/HD = 2/3 (w/w) (Fig. 1b), nonspherical (dimple) particles were formed. As discussed in previous articles [30, 31], it seems that this shape deformation occurred as a result of shrinkage of the monomer phase during the polymerization after cross-linked shell formation based on 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 water domain, the evaporation behaviors of water from the capsule particles both with and without water domain were studied by TG/DTA. 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 ratio) of PDVB/

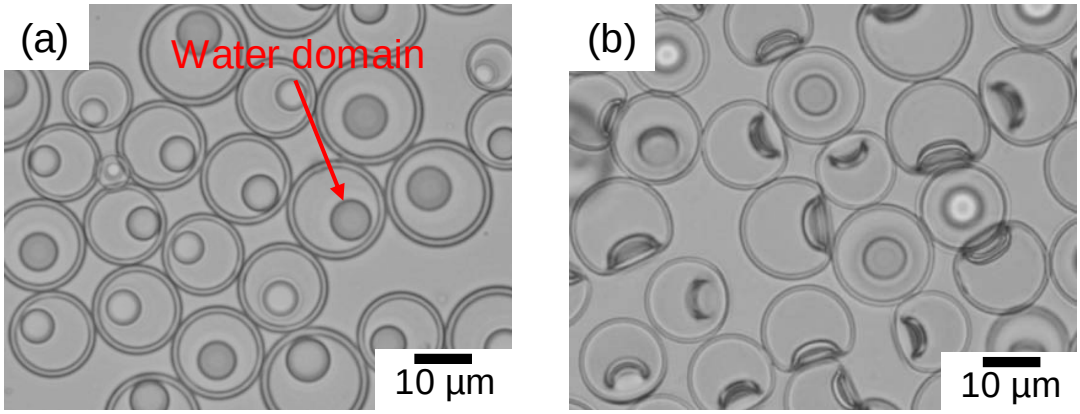

Fig. 1 Optical micrographs of PDVB/HD particles in aqueous dispersed state, produced by micro-suspension polymerization utilizing the SaPSeP method of DVB/HD droplets prepared with SPG emulsification method (pore size, 3.9 µm). DVB/HD (w/w): (a) 2/2; (b) 2/3

HD particles. In their final drying stages, the rate of the weight loss from the aqueous dispersions of the PDVB/HD (DVB/HD = 2/2, w/w) was slower than that of the particle of DVB/HD = 2/3 (w/w). This seems 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 corresponding 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 is much slower than that of free water because the water in the particles must diffuse through the hydrophobic polymer shell. On the other hand, the particles without any water domain showed only one step (I) due to the evaporation of aqueous medium as shown in Fig. 3 [38]. These results could support our assumption that the water domain was formed inside PDVB/HD of DVB/HD = 2/2 (w/w) particles.

The thermal properties of the encapsulated HD were measured with DSC. Figure 4 shows DSC thermogram of aqueous dispersion of PDVB/HD (DVB/HD = 2/2, w/w) particles.

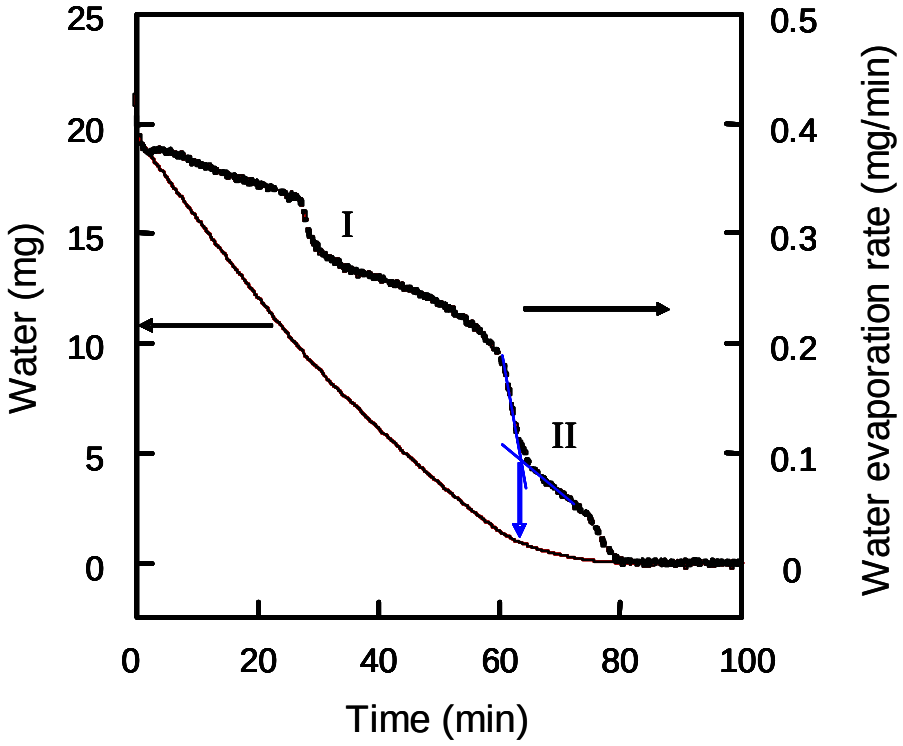

Fig. 2 Weight-loss curve based on the evaporation of water at 30 °C from aqueous dispersions of PDVB/HD (DVB/HD = 2/2, w/w) particles and an evaporation rate curve obtained by differentiation of the weight-loss curve

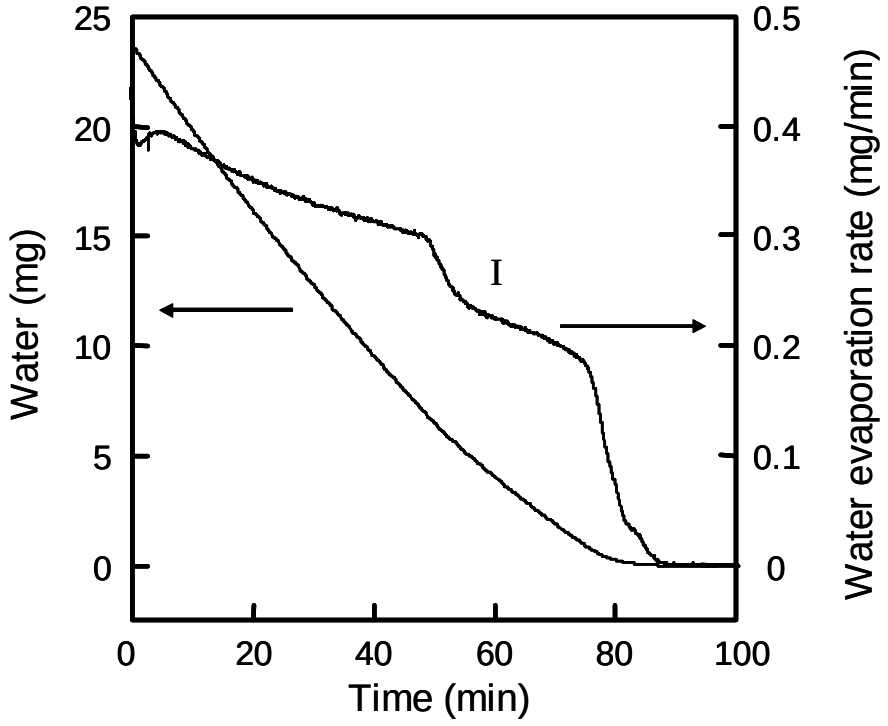

Fig. 3 Weight-loss curve based on the evaporation of water at 30 °C from aqueous dispersions of PDVB/HD (DVB/HD = 2/3, w/w) particles and an evaporation rate curve obtained by differentiation of the weight-loss curve

The solidification peak of water was observed in cooling curve at approximately -20 °C while melting peak was observed in heating curve at approximately 0 °C. These peaks in the temperature descending and ascending processes should correspond to heat-evolving peak of water in both medium and water domain inside the capsule particles. However, because the volume of water domain is extremely low in comparison with aqueous medium, heat-evolving of the water domain must be neglected. Therefore, using the water solidification curve, it is difficult to discuss the existence of water domain. Moreover, it was found that the water solidification peak inclined in temperature descending process, which may be due to the increase of sample temperature because of large amount of heat-evolving of solidification of the whole aqueous medium. To clearly study the influence of water domain on the thermal properties of encapsulated HD, the solidification peak was focused.

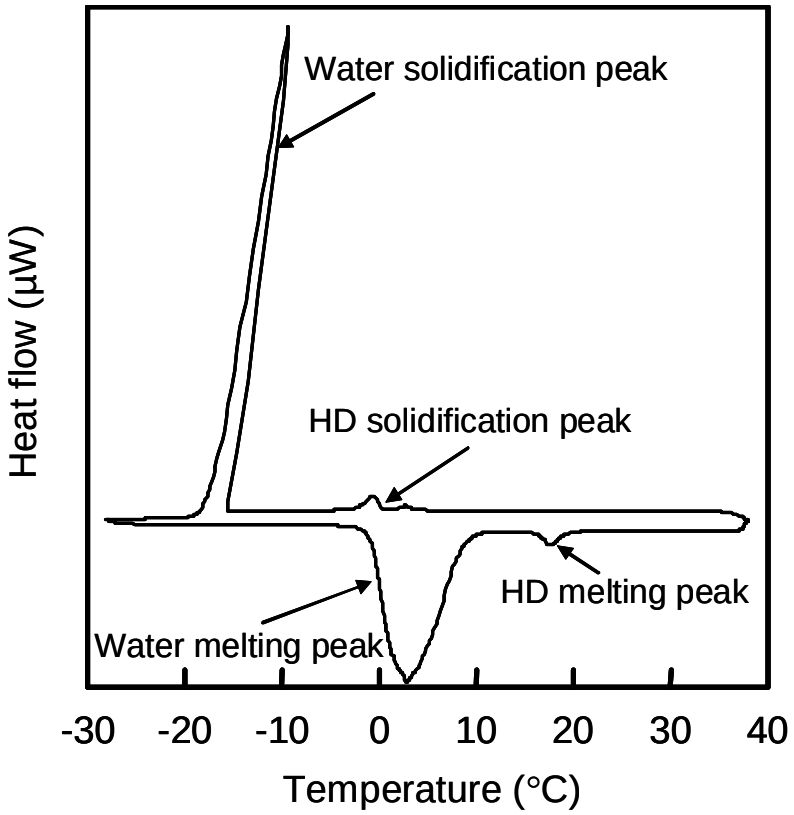

Fig. 4 DSC thermogram of aqueous dispersion of PDVB/HD (DVB/HD = 2/2, w/w) particles recorded with a scanning rate of 5 °C/min

DSC thermograms of HD encapsulated in PDVB particles with different DVB/HD weight ratios were shown in Fig. 5. In both cases, T_s of the encapsulated HD decreased from that of pure HD while T_m still remained at 15 °C. The reason of T_s decreasing may be based on a compartmentalization effect that is impurities located in capsule particle can not induce the nucleation of HD encapsulated in the other particles [30]. In the bulk system, it is known that there is an impurity that works as a trigger for the nucleation resulting in heterogeneous nucleation [23, 39]. In emulsion, the numbers of impurity that usually cause heterogeneous nucleation as in bulk phase are distributed among a large number of isolated droplets. Therefore, the probability for heterogeneous nucleation for all droplets is drastically reduced resulting in the decrease of 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-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-HD and T_{s1} = 6 °C for the first peak, and H_{s2} = 123 J/g-HD and T_{s2} = 1 °C for the second peak. This lower temperature-side peak (H_{s2}, T_{s2}) is 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 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 (162 J/g-HD) with DVB/HD = 2/3 (w/w), however, lower than that of pure HD. On the basis of the formation mechanism of hollow polymer particle [11], the polymer molecules formed in the monomer droplet separate and adsorb at the inner interface, resulting in cross-linked shell encapsulating HD. The interfacial interaction of polymer shell at the inner interface and encapsulated HD may disturb the solidification of encapsulated HD contacting with the inner shell leading to the decrease of H_s. To clarify this assumption, the copolymerizations of DVB and acrylic acid monomers were carried out [30]. It was found that an increase in hydrophilicity of P(DVB-BA) chains with

increasing of BA content should enhance the phase separation between the copolymer chains and HD, eventually resulting in the complete isolation of the HD core from the polymer shell. This HD core seems to be more smoothly solidified than incompletely isolated HD locating in the inner interface of polymer shell, resulting in the increasing of H_s with the BA content. This is more obvious in the case of P(DVB-EA) capsule particles because of higher hydrophilicity of EA than BA unit. However, the influence of the incorporation of acrylic monomers to the shell was not observed on T_s of encapsulated HD.

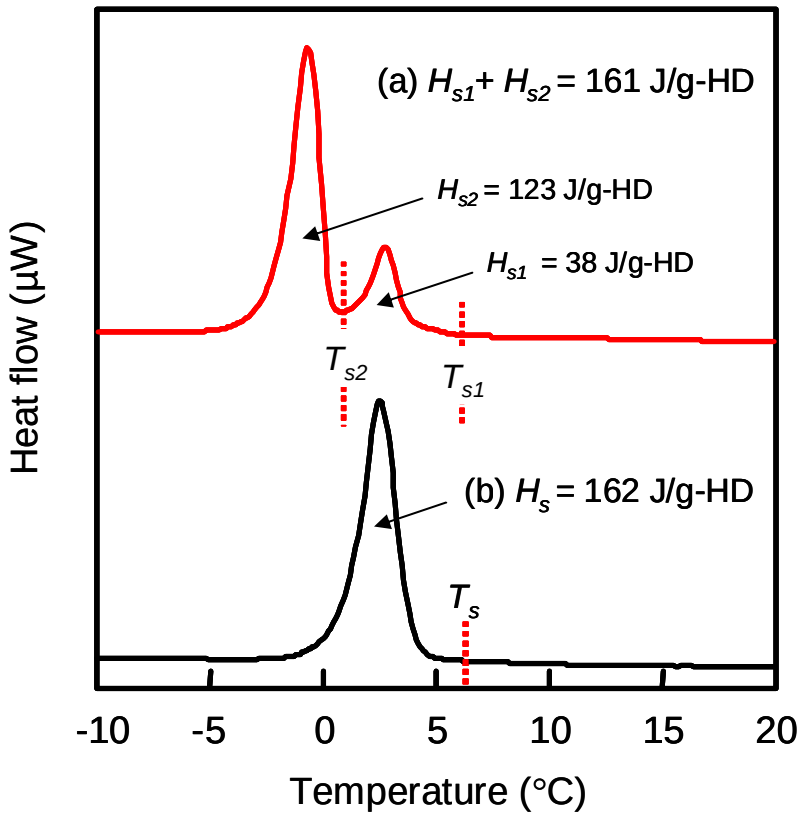

Fig. 5 DSC thermograms of encapsulated HD in PDVB particles in aqueous dispersion, produced by micro-suspension polymerization of DVB/HD droplets prepared by the SPG (pore size, 1.1 μm) emulsification method. DVB/HD (w/w): (a) 2/2; (b) 2/3

Thermal properties of encapsulated HD with water or air domain

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 changing drying time of the dispersion samples. Samples dried at 70 °C for 15-30 min were still at the wet state whereas those for ≥ 45 min were at dry state (no aqueous medium was observed).

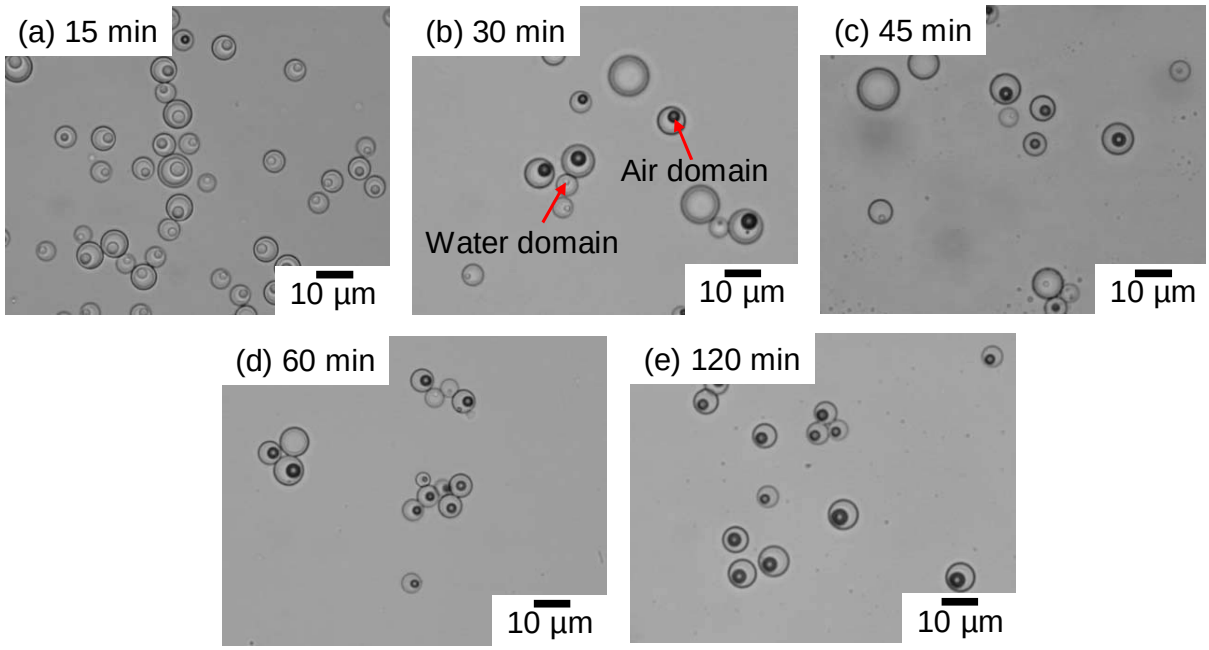

Fig. 6 Optical micrographs of PDVB/HD (DVB/HD = 2/2, w/w) particles (SPG pore size, 1.1 µm) redispersed in water at room temperature after drying at 70 °C for different times (min): (a) 15; (b) 30; (c) 45; (d) 60; (e) 120

Figure 6 shows optical micrographs taken just after redispersion in water (to avoid 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 black ring). After 120 min drying, all water domains were replaced with air domains, indicating that the formation of air domains is due to the evaporation of water from the HD core.

Figure 7 shows optical micrographs taken just after redispersion in water of dried

nonspherical PDVB/HD (DVB/HD = 2/3, w/w) capsule particles at 70 °C for 60 and 120 min. No air domains were observed even though the capsule particles were dried for 120 min. This also supports the above idea that the evaporation of the water domain in the HD core resulted in the formation of the air domain.

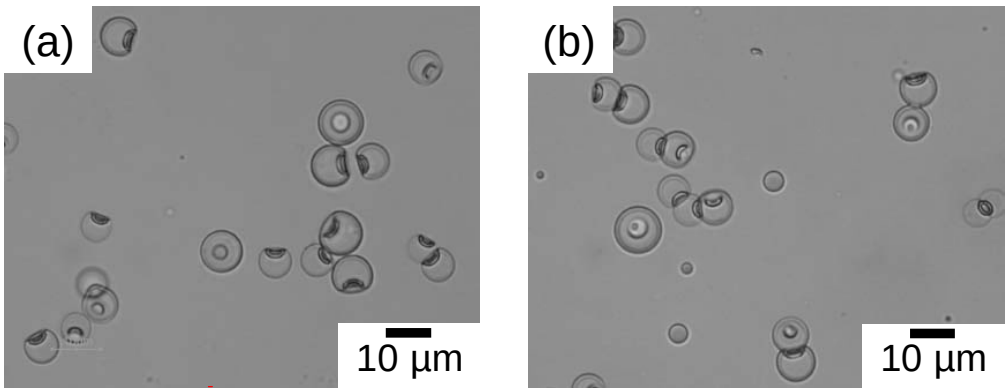

Fig. 7 Optical micrographs of the nonspherical PDVB/HD (DVB/HD = 2/3, w/w) particles (SPG pore size, 1.1 μm) redispersed in water at room temperature after different drying times at 70°C (min): (a) 60; (b) 120

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 at different dry states. The wet samples dried for 15 and 30 min (Fig. 6a, b) exhibited bimodal peaks similarly to that of the original particles in the aqueous dispersed state. After 45 min drying, at which point a considerable percentage of the water domains were replaced with air domains (Fig. 6c), the lower temperature-side peak (T_{s2} = 1 °C) decreased, resulting in reversal of the peak sizes of T_{s1} and T_{s2}, although the peak was still 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 DSC thermograms showed a sharp single peak. These results indicate that the lower temperature-side peak is due to the influence of the water

domain in the HD core [31]. On the other hand, the presence of water or air domains does 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-HD).

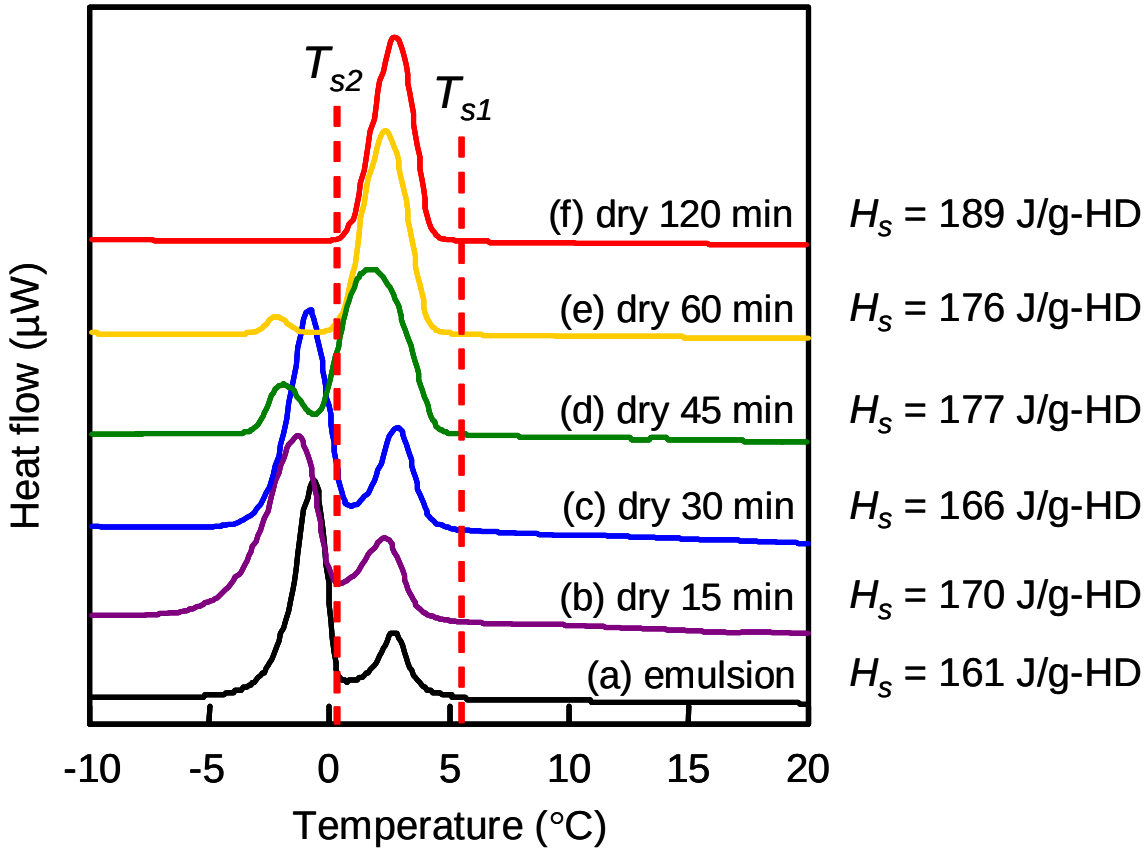

Fig. 8 DSC thermograms of encapsulated HD in the PDVB/HD (DVB/HD = 2/2, w/w) particles in aqueous dispersed state (a) and at dry states (b-g) for different drying times (min): (b) 15; (c) 30; (d) 45; (e) 60; (f) 120

Influence of water or air domain in encapsulated HD in 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 by using a SPG membrane with 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 has already repenetrated into the HD core inside the capsule particles. During the redispersion period, several small domains gradually coagulated, resulting in a single large water domain in each HD core. Because the incompletely dried particles still contain water in the shell, water may penetrate the shell from the aqueous medium into the core, leading to the several small water domains, and eventually a single domain, in the HD core.

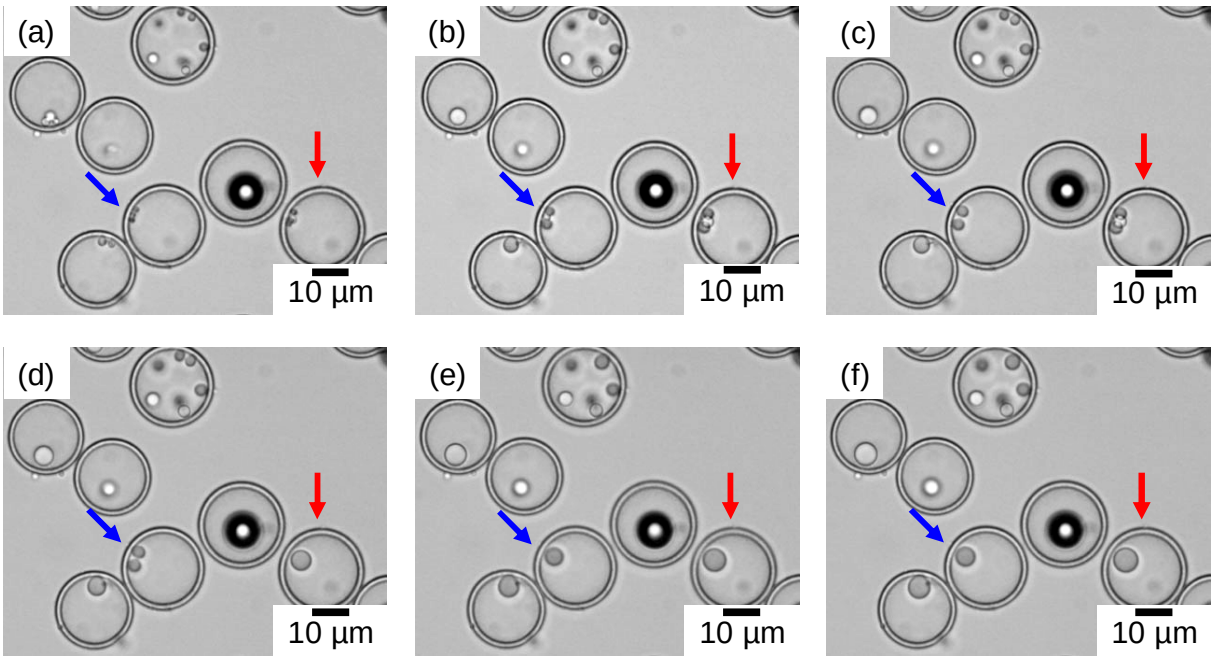

Fig. 9 Optical micrographs of incompletely dried PDVB/HD particles (70 °C, 45 min), produced by micro-suspension polymerization of DVB/HD (2/2, w/w) droplets prepared by the SPG (pore size, 3.9 µm) emulsification method, redispersed in water for a few minutes at room temperature

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

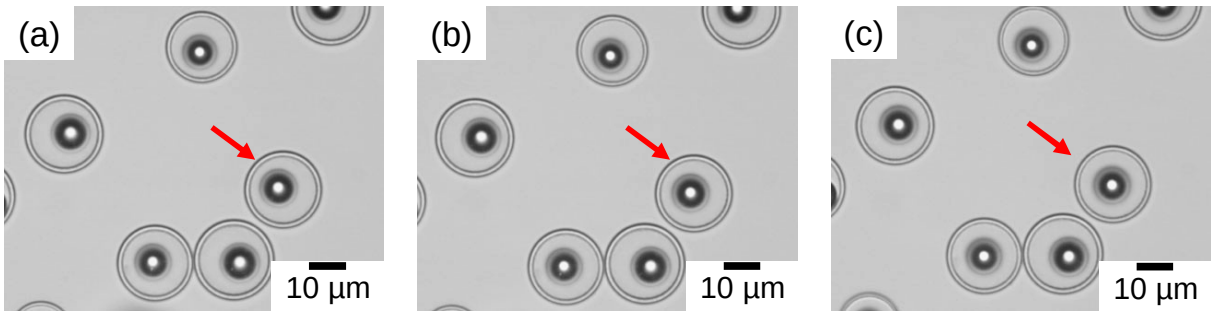

Fig. 10 Optical micrographs of completely dried PDVB/HD particles (70 °C, 120 min), produced by micro-suspension polymerization of DVB/HD (2/2, w/w) droplets prepared by the SPG (pore size, 3.9 µm) emulsification method, redispersed in water for a few minutes at room temperature

Figure 11 shows DSC thermograms of the encapsulated HD in the PDVB/HD particles (DVB/HD = 2/2, w/w) redispersed in water after drying for different times. The results are consistent with the above findings, i.e. the incompletely dried particles (drying times: 30, 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. 11b) than in the dry state (Fig. 8d), possibly due to water penetration from the aqueous medium during the DSC measurement. On the other hand, the lower temperature-side peak was not clearly observed for completely dried particles (120 min) (Fig. 11d), in which no water domain reappeared anymore in the HD core despite there being sufficient time for penetration of water during the DSC measurement. This indicates that once an air domain appears in place of the water domain, water penetration cannot occur. This seems 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.

It can be concluded that complete removal of water domain in the HD core of the particles leads to disappearance of the lower temperature-side peak. Thus, the encapsulated

HD without water domain but with air domain needed shorter time and higher temperature to complete the solidification than the ones with 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.

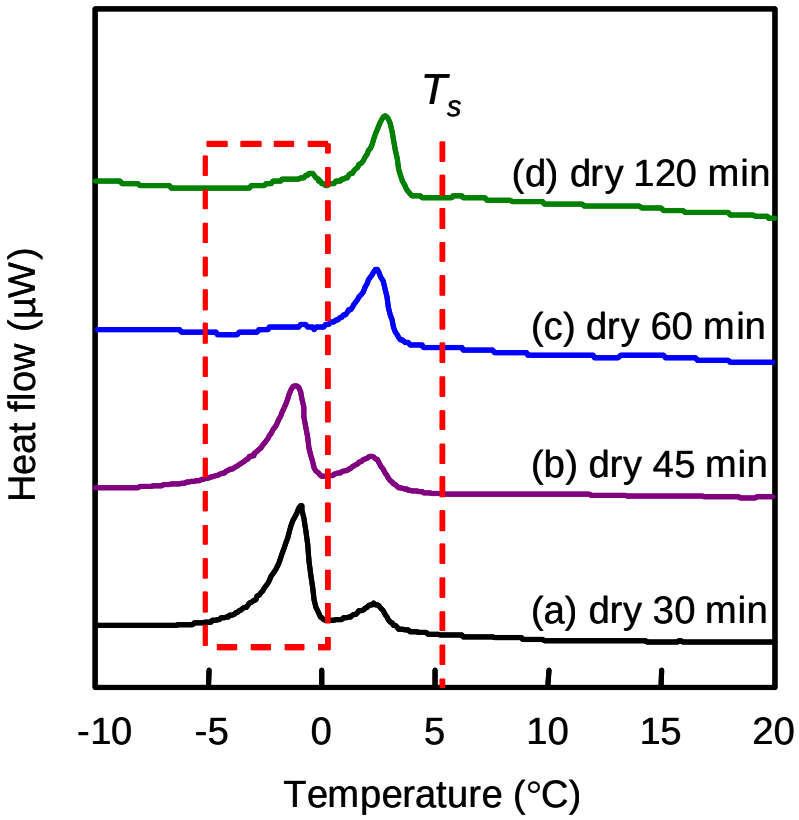

Fig. 11 DSC thermograms of encapsulated HD in PDVB/HD (DVB/HD = 2/2, w/w) particles (SPG pore size, 1.1 μm) redispersed in water at room temperature after drying at 70 °C for different drying times (min): (a) 30; (b) 45; (c) 60; (d) 120

Thermal stability of encapsulated HD with air domain

The air domain was also found in the HD core inside the particles after DSC measurement with aqueous 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 DVB/HD of 2/3 (w/w) (red circle in Fig. 12). This difference may be due to the presence/absence of water domain in the HD cores. During solidification, the shrinkage of the encapsulated HD led to the formation of air domain. To study the effect of the air domain formed in the HD core on the thermal stability with long-term thermal cycled of the encapsulated HD, accelerated 100 melting/freezing cycles without flow of capsule particles in aqueous dispersion were continuously measured with DSC.

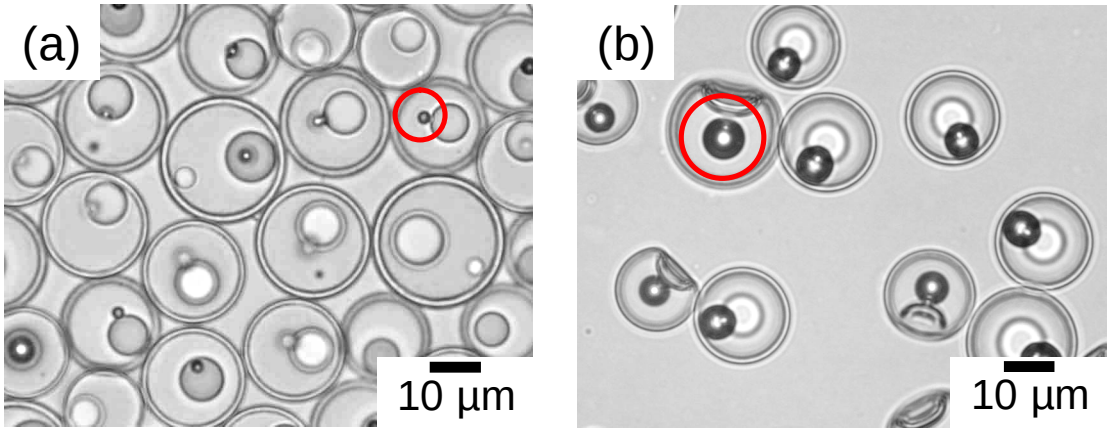

Fig. 12 Optical micrographs taken after DSC measurement from -10 to 30 °C for 4 scans of PDVB/HD particles produced by micro-suspension polymerization of DVB/HD droplets prepared by SPG (pore size, 3.9 µm) emulsification method. DVB/HD (w/w): (a) 2/2; (b) 2/3

Figure 13 shows DSC thermograms of various thermal cycles of the encapsulated HD in PDVB particles having DVB/HD ratio (w/w) of 2/2. Both melting and freezing curves of the encapsulated HD did not change significantly throughout 100 cycles. Although the air domain of the particles having DVB/HD ratio of 2/3 (w/w) was larger than that of the other ones, a similar result was obtained (Fig. 14). Therefore, it is concluded that the presence of the air domain did not affect the stability of the encapsulated HD in either case.

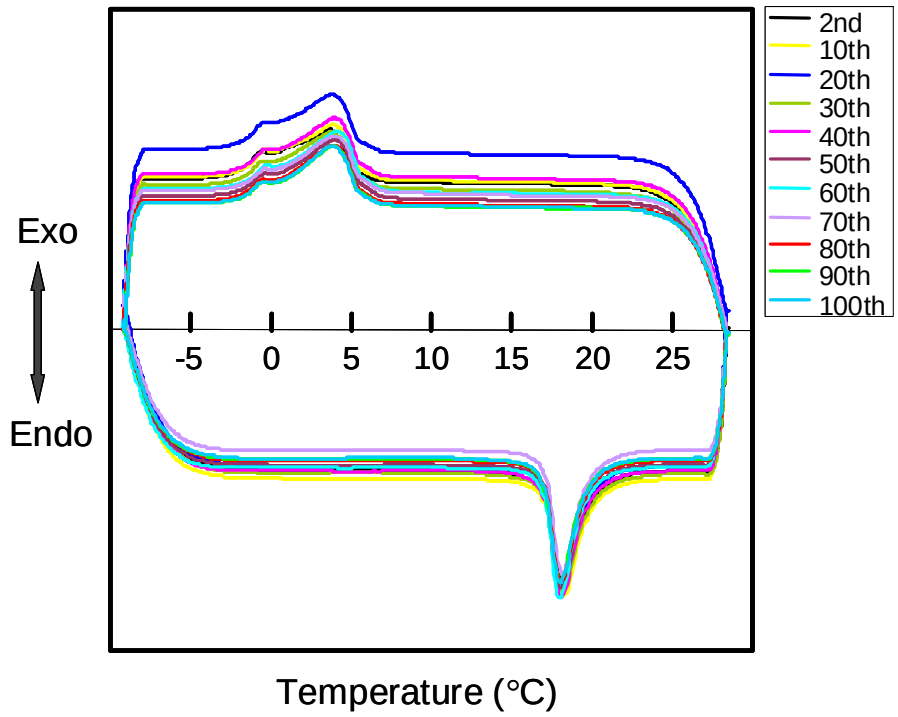

Fig. 13 DSC thermograms for various melting/freezing cycles of encapsulated HD in the PDVB (DVB/HD = 2/2, w/w) particles (SPG pore size, 3.9 μm) in aqueous dispersed state measured with a scanning rate of 5 °C/min

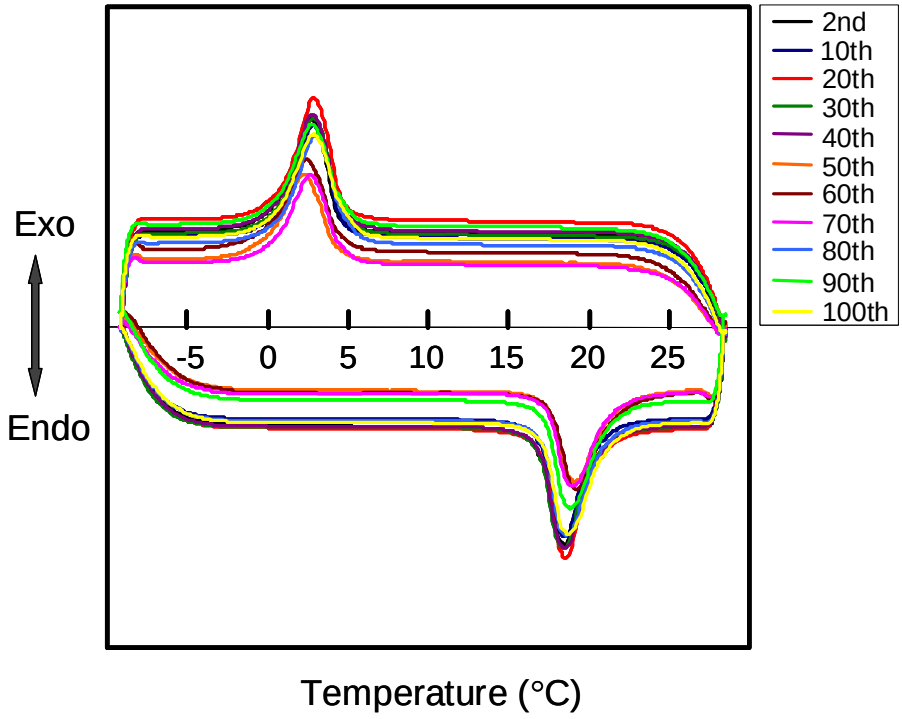

Fig. 14 DSC thermograms for various melting/freezing cycles of encapsulated HD in the PDVB (DVB/HD = 2/3, w/w) particles (SPG pore size, 3.9 μm) in aqueous dispersed state measured with a scanning rate of 5 °C/min

Conclusions

The thermal property of HD encapsulated in micrometer-sized, monodisperse PDVB capsule particles produced by micro-suspension polymerization utilizing 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 retarded its solidification in heat storage applications. However, this influence gradually decreased with an increase in the drying time due to 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.

Acknowledgement

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).

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Chapter 4

Influence of residual monomer on water domain formation and thermal properties of encapsulated hexadecane in poly(divinylbenzene) capsule particles

Introduction

In recent years, microencapsulation of phase change materials (PCMs) have attracted for many applications such as air conditions of building, solar heat storage and thermal adaptable fibers [1-3]. Many methods have been studied to prepare microcapsules for heat storage application. Yamagishi et al. studied the melting and solidification processes of microencapsulated *n*-tetradecane and *n*-dodecane with gelatin shell prepared by complex coacervation. The microcapsule diameters were in the range of 5-1000 μm [4]. Zhang et al. reported the preparation of phase change microcapsules and nanocapsules containing *n*-octadecane with melamine-formaldehyde shell by in situ polymerization [5]. The preparation of phase change microcapsules with phenolic resin shell and n-hexadecane (HD) core by phase separation technique was reported by Jiang et al. [6]

We proposed the technique named the Self-assembling of Phase Separated Polymer (SaPSeP) method in preparing approximately 5-μm-sized, monodisperse, cross-linked polymer particles with a single hollow at the center by seeded polymerization of divinylbenzene (DVB)/toluene-swollen polystyrene (PS) particles prepared by the dynamic swelling method [7-11]. The shells of PS/PDVB composite particles at various DVB conversions were not observed for the particles just after the polymerization. On the other hand, after evaporation of DVB and toluene, the shell layer was found at all conversions. This

seems to be based on the similar refractive indexes of PDVB and mixture of DVB and toluene. On the basis of the proposed mechanism [11], hollow polymer particles were also prepared by 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 accelerator for phase separation of polyDVB (PDVB) formed during the polymerization [13]. Microsuspension polymerization of DVB droplets containing HD yielded HD capsulated particles where HD as nonsolvent worked 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. That is, the SaPSeP method is applicable not only to the preparation of hollow particles but also to the encapsulation of HD.

Recently, we reported the preparation of PDVB capsule particles with encapsulated HD, a paraffin wax, as heat storage materials by microsuspension polymerization utilizing the SaPSeP method of micron-sized, comparatively monodisperse DVB/HD droplets prepared by the Shirasu Porous Glass (SPG) membrane emulsification method [15, 16]. The heat of melting (H_m), which corresponds to the heat of solidification (H_s), of the pure HD used was approximately 230 J/g, and its melting temperature (T_m), which corresponds to its solidification temperature (T_s), was approximately 15 °C. It was found that H_s of HD encapsulated in PDVB particles was much lower than that of the pure HD. Moreover, T_s of the encapsulated HD was also approximately 10 °C lower than that of the pure HD while T_m still remained at 15 °C [17]. These phenomena are of course negative with regards to application as heat storage materials. However, the problem with the reduction of H_s of the encapsulated HD was improved by the copolymerization of acrylic monomer such as butyl acrylate [18]. This seems to be based on the fact that the copolymerization of polar monomers enhances the phase separation of copolymer chains in HD, eventually resulting 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 [19]. Moreover, thermal properties of HD encapsulated in cross-linked capsule particles containing water and/or air domains are also studied from the viewpoint of heat storage application [20].

In this article, the influence of residual monomer on the formation of water domain and thermal properties of encapsulated HD are studied to clearly understand the preparation of cross-linked capsule particles encapsulating HD for heat storage application.

Experimental

Materials

DVB (Nippon Steel Chemical, Tokyo, Japan; purity, 96%) was washed with 1 N NaOH and distilled water to remove inhibitors before use. Poly(vinyl alcohol) (PVA) (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 Inc., Kyoto, Japan; guaranteed reagent grade) was used as received.

Table 1 Recipes for the production of PDVB capsule particles with encapsulated HD by micro-suspension polymerization [a)] of comparatively monodisperse DVB/HD (2/2, w/w) droplets prepared by the SPG membrane emulsification method [b)]

Ingredients		Initiator concentration (wt%)			
		0.5	1.0	2.0	4.0
DVB	(g)	3.3	3.3	3.3	3.3
HD	(g)	3.3	3.3	3.3	3.3
BPO	(g)	0.02	0.04	0.08	0.16
PVA	(g)	0.5	0.5	0.5	0.5
Water	(g)	50	50	50	50
Conversion [c)]	(%)	68	87	94	100

[a)] N_2, 70 °C, 24 h, 80 cycles/min (3-cm strokes)

[b)] SPG membranes (pore sizes: 1.1 µm)

[c)] Measured with gas chromatograph

Abbreviations: DVB, divinylbenzene; PDVB, poly(DVB); HD, *n*-hexadecane; BPO, benzoyl peroxide; PVA, poly(vinyl alcohol)

SPG membrane emulsification and micro-suspension polymerization

The homogeneous solutions of DVB, HD and BPO were dispersed as droplets in PVA aqueous solution with the SPG membrane with pore sizes 1.1 µm (SPG Technology Co., Ltd., Japan). The resulting emulsions were transferred to glass ampoules, degassed using several N_2/vacuum cycles and sealed off. Micro-suspension polymerizations of the monomer dispersions were carried out at 70 °C for 24 h under nitrogen atmosphere in sealed glass tubes

under the conditions listed in Table 1. The tubes were horizontally shaken at 80 cycles/min (3-cm strokes). The prepared particles were observed with an optical microscope (ECLIPSE 80i, Nikon Corporation, Tokyo, Japan).

Measurement of transmittance

The solution polymerizations of DVB in HD with various BPO initiator concentrations were carried out in a spectrophotometer cell under nitrogen atmosphere at 70°C. The transmittances of the solutions were measured by a Hitachi Model 100-50 spectrophotometer at 550 nm. Since the solutions before polymerization had a yellowish appearance, this wavelength was chosen to avoid the influence of absorption.

Measurement of thermal properties of HD encapsulated in cross-linked capsule particles

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

Results and discussion

Preparation and observation of capsule particles

The variations in the transmittance of the solutions at 550 nm during solution polymerizations of DVB in HD with various BPO concentrations at 70 °C were shown in Fig. 1. The transmittance of the solutions drastically decreased after a certain polymerization time indicating that phase separation occurred during the polymerization. The start of the phase separation became short with an increase of BPO concentration due to an increase of

polymerization rate. Conversions of DVB in microsuspension polymerizations at 70 °C for 24h were 68, 87, 94 and 100% for BPO concentrations of 0.5, 1.0, 2.0 and 4.0 wt%, respectively, as shown in Table 1.

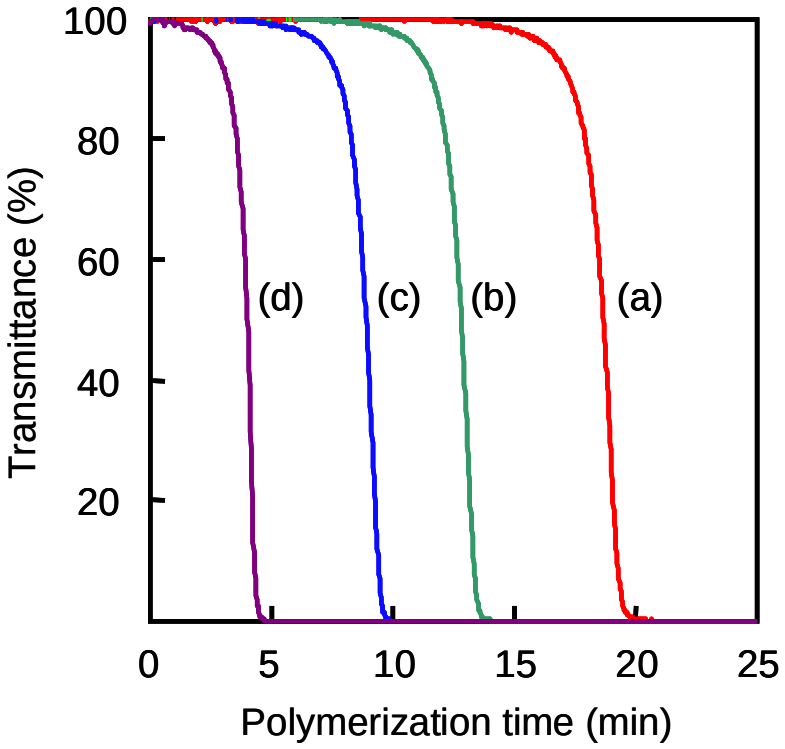
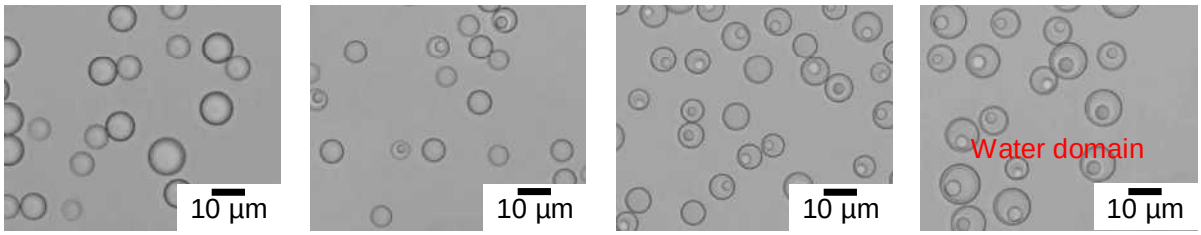


Fig. 1 Transmittances as a function of polymerization time of DVB in HD (DVB content, 50 wt%) solution with various BPO concentrations at 70°C. BPO (wt% of DVB): (a) 0.5; (b) 1; (c) 2; (d) 4

The preparation of PDVB particles encapsulating HD was carried out by microsuspension polymerization with various initiator concentrations at 70°C of DVB/HD (2/2, w/w) droplets prepared by the SPG membrane method under the conditions listed in Table 1. Figure 2 shows optical micrographs at room temperature of PDVB/HD particles. The particles were comparatively monodisperse. In all cases, spherical capsule particles with smooth outer surface were formed even though in the case of the longest phase separation time. This indicates that phase separation occurred in an early stage of polymerization due to

the presence of HD working as accelerator of phase separation. At BPO = 0.5 wt% (Fig. 2a), no any water domains were observed in the encapsulated HD. When BPO concentration increased, a single water domain was found in the HD core (Figs. 2b-d). The percentage of capsule particles containing the water domain increased with BPO concentration.

Fig. 2 Optical micrographs of PDVB/HD particles, produced by microsuspension polymerizations of DVB/HD (2/2, w/w) droplets with various BPO concentrations prepared by the SPG membrane emulsification method. BPO (wt% of DVB): (a) 0.5; (b) 1; (c) 2; (d) 4



As discussed in previous articles [19, 20], a single domain was formed due to the shrinkage of DVB/HD core phase with the polymerization (5.6%) after the cross-linked shell formation based on the different densities of DVB and PDVB (0.91 and 1.04 g/cm^3, respectively) [21]. Besides, during cooling from 70 to 25 °C, a single domain gradually appeared in each particle and the domain size increased with decreasing temperature. 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 2.6% based on the densities of HD at 20 and 70 °C, which are 0.773 and 0.739 g/cm^3, respectively [22]. The total volume shrinkage is 8.2%. 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 a water domain in the HD core if the shell strength is sufficient to withstand the external pressure.

The disappearance of the water domain in the HD core at low conversion (Fig. 2a) suggests that any water domain was not formed or it has already formed but was not visible with optical microscope. These may be due to the influence of residual monomer in capsule particles. The similar refractive indexes of water (1.3329 at 20 °C [21]) and mixture of DVB and HD (1.5835 [23] and 1.4348 [24] at 25 °C, respectively) may hinder the observation of water domain. The very small water domain formed in the HD core containing DVB may not be observed by optical microscope. Furthermore, this residual DVB may affect the shrinkage of DVB/HD core with the polymerization and during cooling after the polymerization. The total volume shrinkage of particles containing residual DVB increases with conversion. To clarify whether water domain formed or not in the HD core, thermal properties of encapsulated HD are measured with DSC.

Thermal properties of encapsulated HD

The thermal properties of the encapsulated HD were measured with DSC. Figure 3 shows DSC thermograms of HD encapsulated in PDVB particles prepared with different initiator concentrations. 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 a BPO = 0.5 (wt%) (Fig. 3a), a single peak of the encapsulated HD due to solidification was observed with H_s = 163 J/g-HD and T_s = -2 °C. On the other hand, for BPO = 1.0 (wt%) (Fig. 3b), at which point a few percentage of water domains were formed, the peak was slightly bimodal with T_{s1} = 1 °C for the first peak, and T_{s2} = -4 °C for the second peak. When BPO concentration increased corresponding with an increase of the percentage of the water domains, the lower temperature-side peak (T_{s2}) increased resulting in reversal of the peak sizes of T_{s1} and T_{s2} although the peaks were still bimodal. For BPO = 2.0 (wt%) (Fig. 3c), the peak was bimodal with T_{s1} = 5 °C, and T_{s2} = -1 °C whereas T_{s1} = 6 °C, and T_{s2} = 1 °C in the case of BPO = 4.0 wt%. The lower

temperature-side peak gradually appeared with increasing BPO concentration. These lower temperature-side peaks are due to the influence of the water domain in the HD core [19, 20]. This result indicates that a single water domain was not formed in the encapsulated HD at low conversion containing high amount of residual DVB. Therefore, there was an influence of residual DVB on the formation of water domain in the HD core and T_s of the encapsulated HD. However, it was found that the total H_s were not much different in all cases indicating that there is no significant influence of water domain on H_s of encapsulated HD [19, 20].

In all cases, T_{s1} values of the encapsulated HD were lower than that of the pure HD called supercooling. In the case of BPO = 4 wt% (conversion = 100%), T_{s1} was about 6 °C, i.e. approximately 9 °C lower than that of pure HD. We reported that the reason of T_s decreasing may be based on a compartmentalization effect that is impurities located in capsule particle can not induce the nucleation of HD encapsulated in the other particles [18]. In the bulk system, it is known that there is an impurity that works as a trigger for the nucleation resulting in heterogeneous nucleation [25]. In emulsion, the numbers of impurity that usually cause heterogeneous nucleation as in bulk phase are distributed among a large number of isolated droplets. Therefore, the probability for heterogeneous nucleation for all droplets is drastically reduced.

Moreover, it was found that T_{s1} of the encapsulated HD also decreased with BPO concentration. It seems to be due to the influence of residual monomer in capsule particles. The presence of some residual DVB molecules lowered the T_s of the encapsulated HD. It is well known that the decrease in the freezing point of a solution occurs when a solute is added to a solvent called freezing point depression, a colligative properties [26-27]. When a solute is dissolved in a solvent, the solute molecules lower the rate at which molecules in the liquid return to the solid state. The tendency to melt reflects the tendency of the solid to become disordered. When a solute is available to mix with the solvent, the tendency to melt is

enhanced because the resulting solution is more disordered than the pure solvent would be. The enhanced tendency to melt means that melting can occur at lower temperature than it does in the absence of the solute. In other words, the melting and hence the freezing points are lowered by the solute. Therefore, the freezing point of a solvent with a solute is lower than that of a pure solvent.

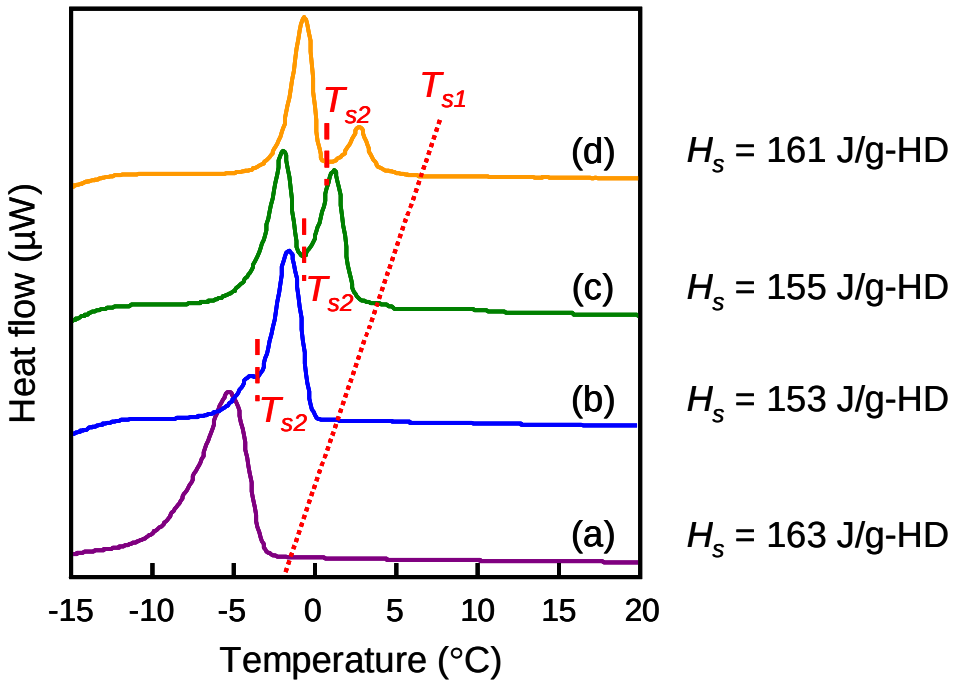


Fig. 3 DSC thermograms of encapsulated HD in PDVB particles in aqueous dispersion, produced by microsuspension polymerization of DVB/HD droplets prepared by the SPG emulsification method under the conditions listed in Table 1. BPO (wt% of DVB): (a) 0.5; (b) 1.0; (c) 2.0 and (d) 4.0

Influence of residual monomer on water domain formation and thermal properties of encapsulated HD

To clearly understand the influence of residual monomer on the formation of water domain in the encapsulated HD, conversion-time of DVB/HD (2/2, w/w) microsuspension polymerization was studied at 70 ºC. The polymerization smoothly preceded until reach 100% conversion.

The prepared particles at each conversion were observed with optical microscope at room temperature (Fig. 4). The particles at 30 min (conversion = 16%) were nonspherical (dimple) without water domain. Cooling after the polymerization led to the shrinkage of HD core resulting in the formation of space inside the capsule particles [18, 19]. Because, at low conversion, the shell strength was insufficient to withstand the external pressure, part of the shell buckled before water penetration. As conversion increased, spherical particles were obtained because of an increasing of the shell strength as a result of an increase of the shell thickness. At 2.5h (conversion = 37%), the polymer shell layer was not clearly observed which seems to be based on the similar refractive indexes of PDVB (1.6150 at 20 °C [21]) and mixture of DVB and HD. Moreover, no any water domains were observed. The amount of the water domain increased with conversion. This result well accorded with Fig. 2. Therefore, it supports that the presence of residual monomer in the particles affects the formation of the water domain in the HD core.

Thermal properties of encapsulated HD at each conversion were shown in Fig. 5. This is consistent with the previous result (Fig. 3) that the lower temperature-side peak gradually appeared with increasing conversion due to an increasing of the percentage of water domains. The presence of the water domain only affects T_s of encapsulated HD. Then, similar H_s were obtained in either case. In addition, T_{s1} of encapsulated HD also decreased with reducing of conversion which may be due to the influence of residual monomer in capsule particles as already mentioned (Fig. 3).

To confirm our assumption**,** the evaporation of residual DVB was performed. After residual DVB was evaporated, a single water domain was observed in each capsule particle (Fig. 6). This supports our assumption that the existence of residual monomer in capsule particles prevented the formation of water domain in the HD core. The bimodal solidification curve of encapsulated HD was obtained (Fig. 7) because of the influence of the water domain.

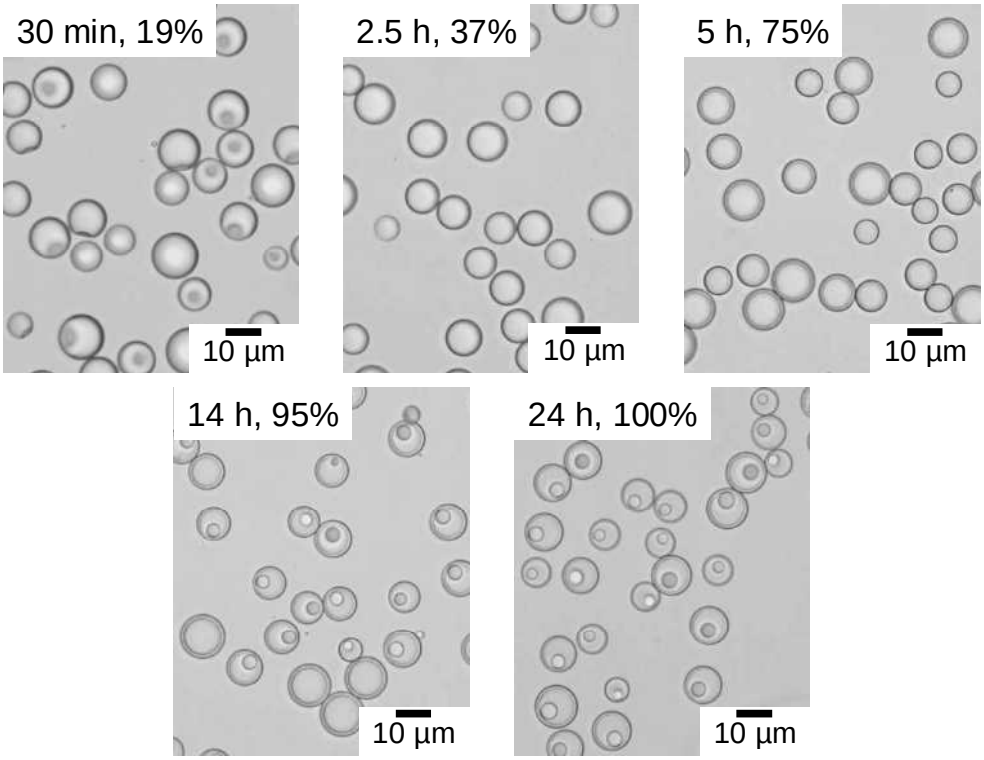


Fig. 4 Optical micrographs at various conversions of PDVB/HD particles, produced by microsuspension polymerizations using BPO = 4 wt%. Numbers on photographs indicate polymerization times and conversions

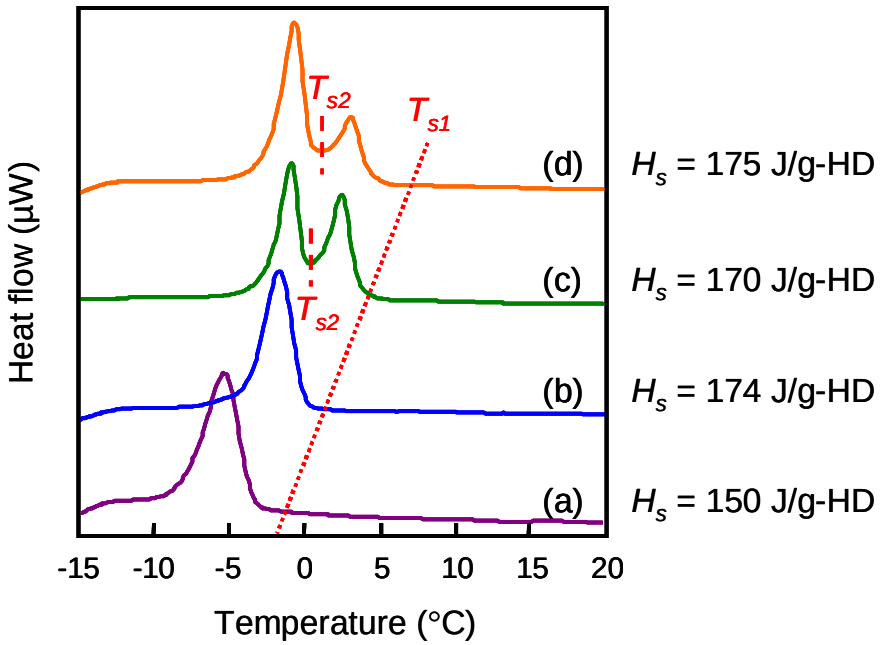


Fig. 5 DSC thermograms at various conversions of encapsulated HD in PDVB capsule particles, produced by microsuspension polymerization using BPO = 4 wt%. Conversions (%): (a) 37, (b) 75, (c) 95 and (d) 100

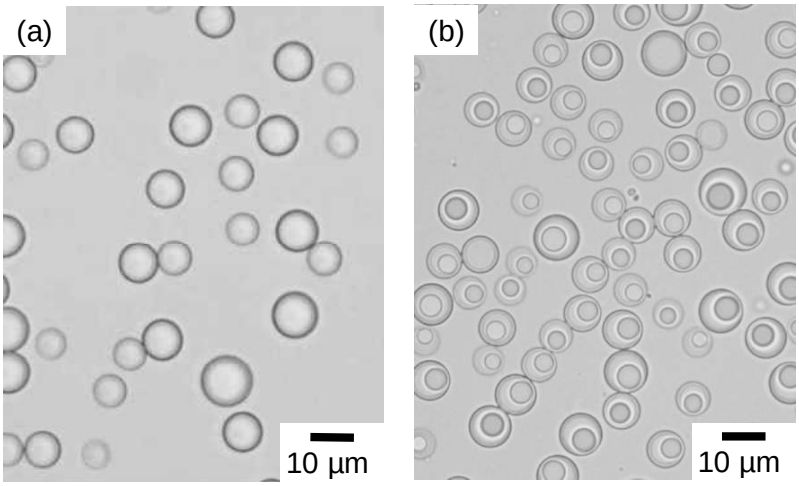


Fig. 6 Optical micrographs of PDVB/HD particles, produced by microsuspension polymerizations of DVB/HD droplets (BPO = 0.5 wt%) prepared by the SPG membrane emulsification method (a) before and (b) after residual DVB evaporation

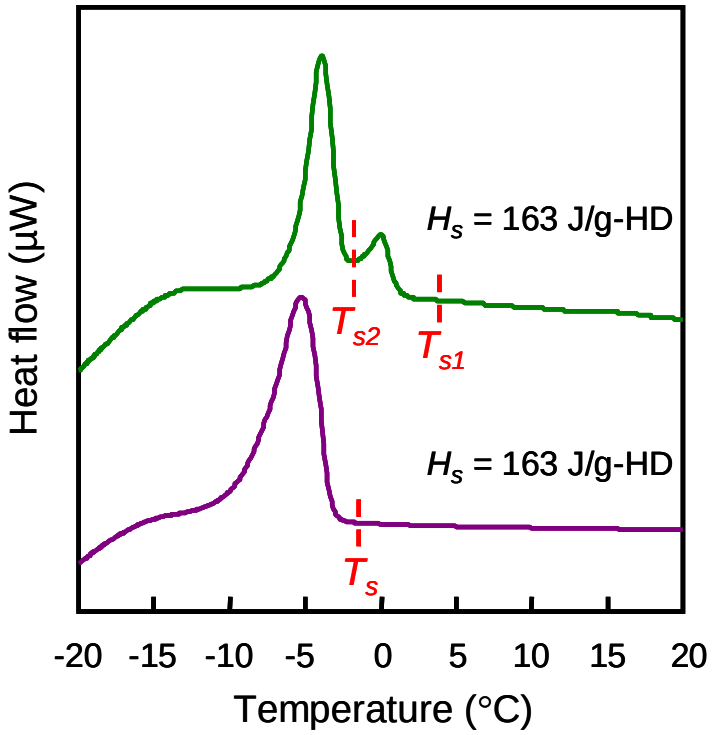


Fig. 7 DSC thermograms of encapsulated HD (——) before and (——) after residual DVB evaporation in PDVB particles, produced by microsuspension polymerizations of DVB/HD droplets (BPO = 0.5 wt%) measured at a scanning rate of 5°C/min

The T_{s1} increased from -1 to 5 °C whereas H_s was not changed (163 J/g-HD). In addition, the shell layer was observed because of the evaporation of residual DVB in capsule particles [11].

It can therefore be concluded that the water domain formation and T_s of encapsulated HD were affected by the presence of residual monomer in the capsule particles.

Conclusions

The presence of residual monomer in capsule particles influence on the formation of a single water domain in the HD core inside micron-sized, monodisperse PDVB capsule particles produced by microsuspension polymerization utilizing the SaPSeP method. It may affect the shrinkage of DVB/HD core with the polymerization and during cooling after the polymerization. Moreover, it also affects the thermal properties of the encapsulated HD. The residual monomer led to the decrease of T_{s1} of the encapsulated HD, which is negative with regards to application as heat storage capsule. However, this influence gradually decreased with an increase of the conversion as by increase of initiator concentration or polymerization time.

Acknowledgement

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).

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Chapter 5

Effect of shell strength on shape and performance of cross-linked capsule particles encapsulating hexadecane in recycle usage

Introduction

Recently, microencapsulation of phase change materials (PCMs) is attractive for many industrial applications such as air conditions of building, solar heat storage and thermal adaptable fibers [1-5]. Paraffin waxes are useful as one group of numerous numbers of heat storage materials that melt and solidify at a wide range of temperatures, making them attractive for many applications. They 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 such as provide large heat transfer area and control the volume change of the storage materials as phase change occurs [6].

We proposed the technique named the Self-assembling of Phase Separated Polymer (SaPSeP) method in preparing approximately 5-μm-sized, monodisperse, cross-linked polymer particles with a single hollow at the center by seeded polymerization of divinylbenzene (DVB)/toluene-swollen polystyrene (PS) particles prepared by the dynamic swelling method [7-11]. Micron-sized, nonspherical polymer particles with “rugby ball” and “red blood corpuscle”-like were produced by seeded polymerization of (DVB/vinylbiphenyl (VBP)/xylene)-swollen PS particles dispersion [12]. The studied of the shape transformation of cross-linked PS/P(DVB-VBP) particles showed that the shell strength was an important key for the shape transformation. On the basis of the proposed mechanism [11], hollow polymer particles were also prepared by microsuspension polymerization of DVB/toluene

droplets containing dissolved PS and benzoyl peroxide (BPO), although they were polydisperse [13]. The PS dissolved in the DVB/toluene droplets worked as accelerator for phase separation of polyDVB (PDVB) formed during the polymerization [14]. Microsuspension polymerization of DVB droplets containing *n*-hexadecane (HD) yielded HD capsulated particles where HD as nonsolvent worked as PS in the SaPSeP method [15]. 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 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.

We reported the encapsulation of HD, one of paraffin waxes used as heat storage materials, in PDVB particle produced by microsuspension polymerization utilizing the SaPSeP method of micron-sized DVB/HD droplets prepared by the Shirasu Porous Glass (SPG) membrane emulsification technique [16, 17]. The heat capacity of pure HD is approximately 230 J/g defined as heat of melting (H_m) and heat of solidification (H_s) while melting (T_m) and solidification (T_s) temperatures are approximately 15 °C. It was found that H_s of HD encapsulated in PDVB particle was much lower than that of pure HD. Moreover, T_s of the encapsulated HD was also lower approximately 10 °C than that of pure HD while T_m still remained at 15 °C [18]. These phenomena are, of course, negative to apply it for heat storage materials. However, the problem in the decrease of H_s of encapsulated HD was improved by the copolymerization of hydrophilic acrylic monomer such as butyl acrylate. This seems to be based on the fact that the copolymerization of hydrophilic monomer enhances the phase separation of copolymer chains and HD, eventually resulting in the complete isolation of the HD core from the polymer shell [19]. Moreover, it was also found that the deformation of capsule particles depended on the shell thickness and the encapsulated HD content [20].

A solar thermal system with energy storage materials undergoes one melting/freezing cycle per day which can be called a normal cycle. However, a repeated melting/freezing cycles test conducted in the laboratory with a hot plate or similar system is called accelerated thermal cycle test [21]. The experimental studies of accelerated cycle tests on heat storage materials have been reported to study their performances [21-23]. The stability of the microcapsules is required for thermal storage application. The volumetric expansion or shrinkage of the core material, which accompanies the thermal cycle, damage on microcapsule shell from inside of the particles. Furthermore, pumping and mixing associated with the emulsion flow may cause distortion of the microcapsules due to the induction of shear stress [24]. Therefore, it is important to investigate the stability of prepared capsule particles associated with the applications.

In this article, the influence of capsule shell strength on the shape and performance of cross-linked particles encapsulating HD in recycling usage of heat storage application are studied.

Experimental

Materials

DVB (Nippon Steel Chemical, Tokyo, Japan; purity, 96%) was washed with 1 N NaOH and distilled water to remove polymerization inhibitors before use. Butyl acrylate (BA) (Nacalai Tesque Inc., Kyoto, Japan; extra pure reagent grade) was purified by distillation under reduced pressure. Poly(vinyl alcohol) (PVA) (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 Inc., Kyoto, Japan; guaranteed reagent grade) was used as

received.

Table 1 Recipes for the preparation of PDVB and P(DVB-BA) capsule particles with encapsulated HD by microsuspension polymerization [a)] of comparatively monodisperse DVB/HD and (DVB-BA)/HD droplets, respectively, prepared by the SPG membrane emulsification method [b)]

Ingredient		DVB/HD (w/w)			
		2/3		2/2	2/1
		DVB/BA (w/w)			
		100/0	20/80		
DVB	(g)	2.6	0.5	3.3	4.4
BA	(g)	0	2.1	0	0
HD	(g)	4.0	4.0	3.3	2.2
BPO	(g)	0.1	0.1	0.1	0.1
PVA	(g)	0.5	0.5	0.5	0.5
Water	(g)	50	50	50	50

[a)] N_2, 70 °C, 24h, 80 cycles/min (3-cm strokes)

[b)] SPG membrane (pore size: 1.1, 3.9 and 5.3 µm)

Abbreviations: DVB, divinylbenzene; BA, butyl acrylate; HD, *n*-hexadecane; BPO, benzoyl peroxide; PVA, poly(vinyl alcohol)

SPG membrane emulsification and microsuspension polymerization

Emulsification was carried out using the SPG membrane emulsification technique (SPG Technology Co., Ltd., Japan) employing a microporous glass membrane with pore sizes

1.1, 3.9 and 5.3 μm. A homogeneous solution of monomers, HD and BPO was dispersed as droplet in PVA aqueous solution. Microsuspension 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 for DVB homopolymer (PDVB) and DVB-BA copolymer [P(DVB-BA)] particles. The tubes were horizontally shaken at 80 cycles/min (3-cm strokes). Capsule particles were observed with an optical microscope (ECLIPSE 80i, Nikon Corporation, Tokyo, Japan).

Measurement of thermal properties and thermal recycle stability of HD encapsulated in cross-linked capsule particles

H_s, T_s, H_m and T_m of HD encapsulated in capsule particle dispersions were measured in an aluminum pan with a differential scanning calorimeter (DSC) (DSC 6200, Seiko Instruments Inc., Chiba, Japan) under a N_2 flow with a scanning rate of 5 °C/min.

For thermal recycle stability test, accelerated 100 melting/freezing cycles without particles flow of capsule particles in aqueous dispersion were continuously measured in an aluminum pan under a N_2 flow with a scanning rate of 5 °C/min.

Measurement of compressive strength

The strength property of the polymer particles in the dry state was measured at room temperature by using a micro-compression testing machine (Shimadzu DUH-W201) with a 50 μm diameter flat indenter at a rate of 0.13 mN/s. The micro-compression device was equipped with an optical microscope, thus enabling approximate estimation of the diameter of the single particle being tested, and thus also enabling one to select particles of suitable size within the distribution for testing. The particles tested were all in the approximate diameter range of 21 μm ± 1 μm (SPG pore size, 3.9 μm). The compressive strength (σ_B) is related to

the breaking load (*P*) and the particle diameter (*d*) according to Eq. (1) [25-28].

$$\sigma_B = a\frac{P}{d^2} \quad (1)$$

where "a" is a constant, the value of which depends on the relationship between the compressive and tensile stress in the center of the particle [25, 26, 29]. Eq. (1) was derived for a pair of concentrated loads (sharply pointed forces) being applied to a particle [27]. Each data reported (Table 3) corresponds to the average of 20 independent measurements.

Measurement of the amount of broken particles

The capsule particle dispersions (solid content: 6.5 wt%) were individually homogenized at various times and speed and then observed with optical microscope to measure the amount of broken particles based on ≥ 150 particles.

Results and discussion

Preparation and properties of capsule particles

The prepared capsule particles were observed with optical microscope. Figure 1 shows optical micrographs of comparatively monodisperse PDVB particles with encapsulated HD produced by microsuspension polymerization of various ratios of DVB/HD droplets prepared by the SPG emulsification technique under the condition listed in Table 1. At the DVB/HD = 2/1 (w/w) (Fig.1a), the porous particles were formed instead of hollow structure particles. The phase separation in the early stage is the first required point for the formation of the hollow structure by the SaPSeP method because at low conversion the PDVB can move and adsorb at the interface of the droplets due to low viscosity. At high DVB content, the critical chain

length to phase separated of PDVB chains formed in the droplets was high resulting in late phase separation of them. Therefore, these porous particles were prepared under the condition where phase separation in the droplets did not occurred in the early stage of polymerization. When the DVB/HD = 2/2 w/w (Fig. 1b), the spherical particles with hollow structure were obtained. The formation of the hollow particles is due to the increase of HD content that promotes phase separation of PDVB chains and HD in the droplets [15]. In addition, single water domain was observed in encapsulated HD inside capsule particle. As discussed in the previous article [20], some water domains may be formed due to 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. Moreover, during cooling from 70 °C to 25 °C, the single domain appeared in each particle and the domain size increased with the decrease of temperature. 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 2.6% based on the densities of HD at 20 °C and 70 °C, which are 0.773 and 0.739 g/cm^3, respectively [30]. 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 sufficient to withstand the external pressure. In the case of DVB/HD = 2/3, w/w (Fig. 1c), nonspherical (dimple) particles, which did not contain a water domain, with smooth outer surface were formed. This is due to the decrease of capsule shell thickness leading to the reduction of shell strength. As discussed in the previous articles [19, 20, 31], this shape deformation was taken place by shrinkage of the monomer phase during the polymerization. Because the shell strength was insufficient to withstand the outer pressure, a part of the shell buckled before the penetration of water leading to the deformation of the particle shape.

Thermal properties of encapsulated HD in capsule particles were measured with DSC.

Figure 2 shows DSC thermograms of HD encapsulated in PDVB particle having various weight ratios of DVB/HD. 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 = 2/1 (w/w) (Fig. 2a) which is porous particles, a single peak of encapsulated HD due to solidification was found. However,

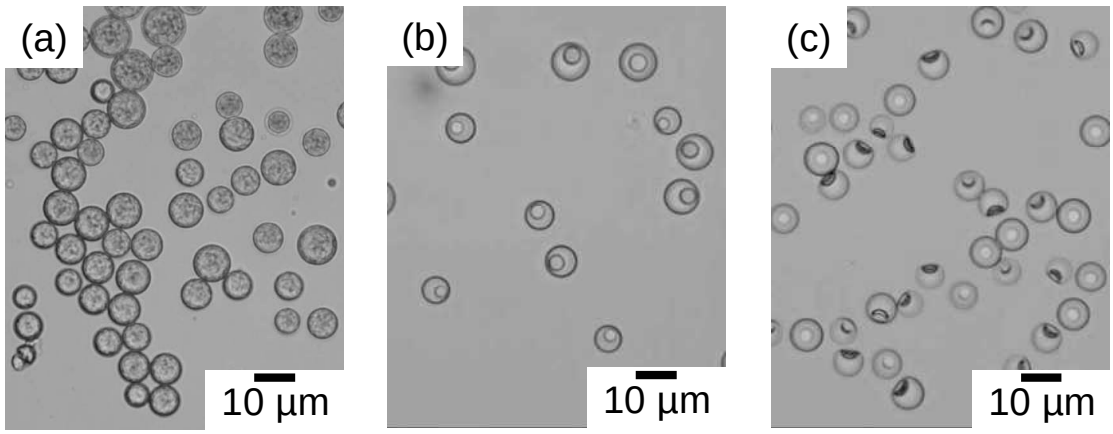

Fig. 1 Optical micrographs of PDVB with encapsulated HD, produced by micro-suspension polymerizations utilizing the SaPSeP method of DVB/HD droplets prepared by the SPG (pore size: 1.1 µm) emulsification method under the conditions listed in Table 1. DVB/HD (w/w): (a) 2/1; (b) 2/2; (c) 2/3

H_s (90 J/g-HD) was much decreased from that of pure HD while T_s was increased to 10 °C, i.e. only approximately 5 °C lower than that of pure HD. These phenomena seem to be due to the effect of high interfacial area between polymer and HD [18, 19]. On the other hand, in the case 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}) was 161 J/g-HD. It is due to the influence of water domain formed in the HD core. 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 as discussed in the previous article [20, 31]. In the case of DVB/HD = 2/3 (w/w), a sharp single peak was observed and its H_s and T_s values were 162 J/g-HD and 6 °C, respectively, which was almost the same as that (161 J/g-HD) with DVB/HD of 2/2 (w/w).

In this study, from the viewpoint of heat storage material, only hollow particles encapsulating HD will be considered to avoid the leakage of HD as phase change occurs.

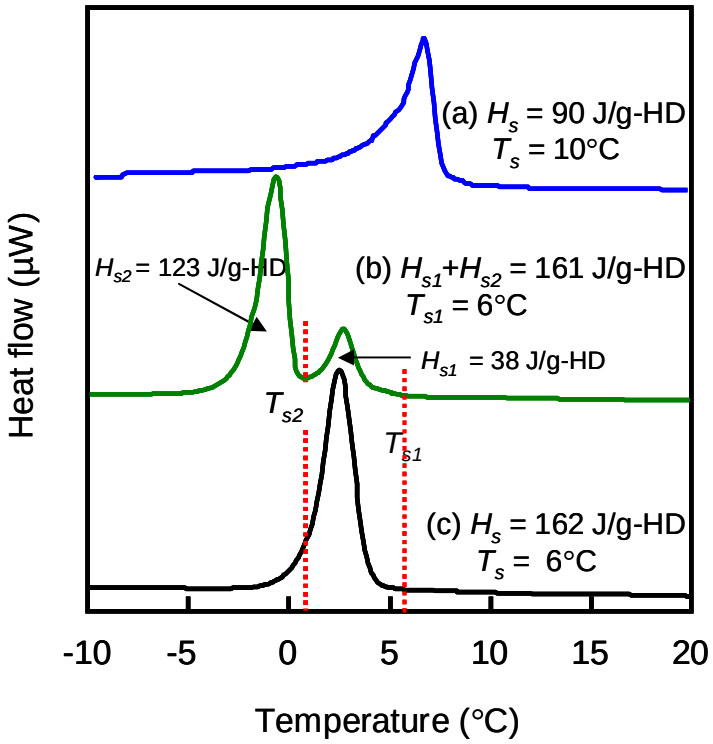

Fig. 2 DSC thermograms of encapsulated HD in PDVB particles at various weight ratios of DVB/HD prepared under the conditions listed in Table 1. DVB/HD (w/w): (a) 2/1; (b) 2/2; (c) 2/3

Compressive strength

To investigate the effect of shell strength on the performance of capsule particles in the application, the compressive strength was measured for both PDVB and P(DVB-BA) capsule particles. The micro-compression testing machine enables measurement of individual

particles, and the results thus truly represent the strength of a single particle. Similar experimental approaches to measure mechanical properties of polymer particles have been reported for cross-linked P(S-DVB) particles [32] and cross-linked poly(ethylene glycol) particles [33]. The primary data obtained by the compression tests are load (mN) vs. deformation (μm) as shown in Fig. 3 for a representative sample (PDVB (DVB/HD = 2/3, w/w)). The breaking load (*P*) and the deformation at break were defined based on the point at the beginning of the plateau region as indicated in Fig. 3. The compressive strength was subsequently calculated from Eq. (1).

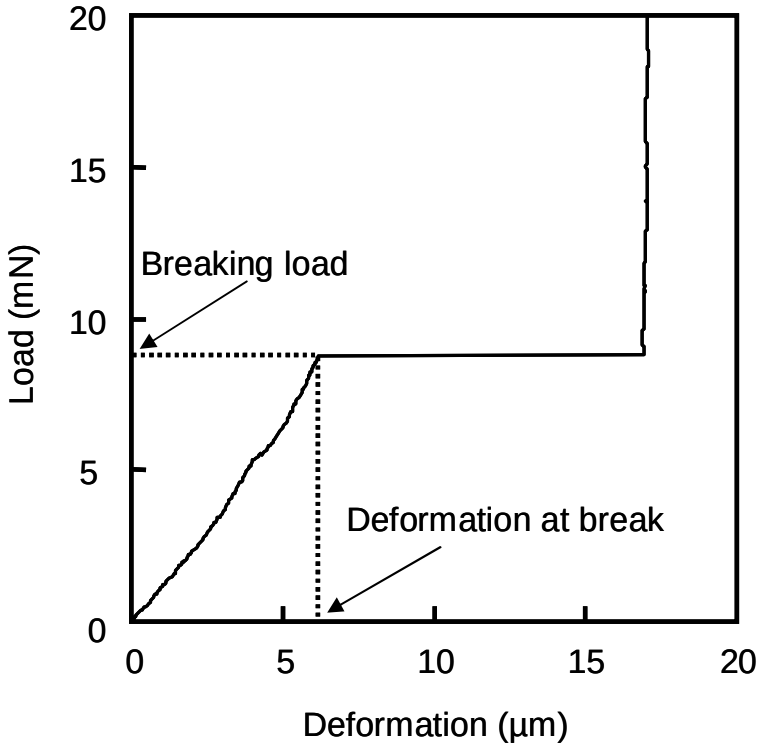

Fig. 3 The relationship between load and deformation measured with micro-compression testing machine at a rate of 0.13 mN/s of PDVB/HD (DVB/HD = 2/3, w/w) particle

Table 2 shows average compressive strengths measured with micro-compression testing machine of PDVB (DVB/HD = 2/2 and 2/3, w/w) and P(DVB-BA) [(DVB-BA)/HD = 2/3; DVB/BA = 20/80, w/w] particles. It was found that PDVB (DVB/HD = 2/2 (w/w)

particles has the highest compressive strength which is 21 MPa. When capsule shell thickness (corresponding with polymerization recipes) was decreased (DVB/HD = 2/3, w/w), the decrease of shell strength was observed. Moreover, the decrease of cross-linked density and glass transition temperature (T_g) by copolymerization of DVB and BA (DVB/BA = 20/80, w/w) was also resulted in the decrease of capsule shell strength, i.e. approximately 8 MPa.

Table 2 Average compressive strengths of various capsule particles (diameter 21±1 μm), produced by microsuspension polymerizations of DVB/HD and (DVB-BA)/HD droplets prepared by the SPG emulsification method under condition listed in Table 1

Polymers	Average strength (MPa)
PDVB/HD	
DVB/HD = 2/2	21.2
DVB/HD = 2/3	16.4
P(DVB-BA)/HD	
(DVB/HD = 2/3; DVB/BA = 20/80)	8.0

The amount of broken particles

In addition, the stability of capsule particle was determined in the term of the amount of broken particles after the shear stress was applied by homogenization at various times and speeds as shown in Fig. 4. Figure 4a shows the percentage of broken particles at various homogenization times of 500 and 4000 rpm. At low shear stress condition (500 rpm), the percentages of broken particles slowly increased with homogenization time. However, it is noted that the amount of broken particles of all three capsules were not much different at any homogenization times. Otherwise, in the case of high shear stress condition (4000 rpm), the

amount of broken particles drastically increased with homogenization time especially those of P(DVB-BA) capsule particle. Moreover, large difference of the amount of broken particles of all three capsule particles was also observed. In the case of DVB/HD = 2/2 (w/w), the amount of broken particles slowly increased while they much increased with time in the case of DVB/HD = 2/3 (w/w). The effect of homogenization time on the capsule shell strength is more obvious in the case of P(DVB-BA) particle. The percentages of broken particles drastically increased until higher than 20% at 30 min.

Figure 4b shows the percentage of broken particles at various homogenization speeds for 10 min. It was found that there is no significant difference of the percentage of broken particles for all three capsule particles at low homogenization speed (100, 500 rpm). The amounts of broken particles are lower than 5%. The percentage of broken particles increased with the increase of speed especially those of P(DVB-BA) capsule particle. In the case of PDVB (DVB/HD = 2/2, w/w) particle, the amount of broken particles were quite constant, i.e. lower than 5%. In contrast, in the case of PDVB (DVB/HD = 2/3, w/w) particle, they gradually increased and differ from the former particle at high homogenization speed. The effect of homogenization speed on the capsule shell strength is more obvious in the case of P(DVB-BA) particle. The percentages of broken particles drastically increased with the increase of speed until reach approximately 10% of broken particles at 4000 rpm. It can be noted that there is the large difference of the amount of broken particles between PDVB and P(DVB-BA) particles at long homogenization time and high speed. This seems to be due to the decrease of cross-linked density and T_g of copolymer particles.

Therefore, the stability of capsule particles was insignificant different under low shear stress condition while the large different was observed under strong condition. This is the result of capsule shell thickness, cross-linked density and T_g effecting on the capsule shell strength.

The effect of particle size on capsule stability was also studied. Figure 5 shows the amount of broken particles of PDVB/HD (DVB/HD = 2/2, w/w) having various particle diameters. The amount of broken particles slightly increased with particle diameter. Yamagishi et al. also found that the breakage rates of gelatin particles encapsulated tetradecane decrease as the capsule sizes decrease. Smaller size microcapsules were more durable and withstood the stress from the slurry flow [24].

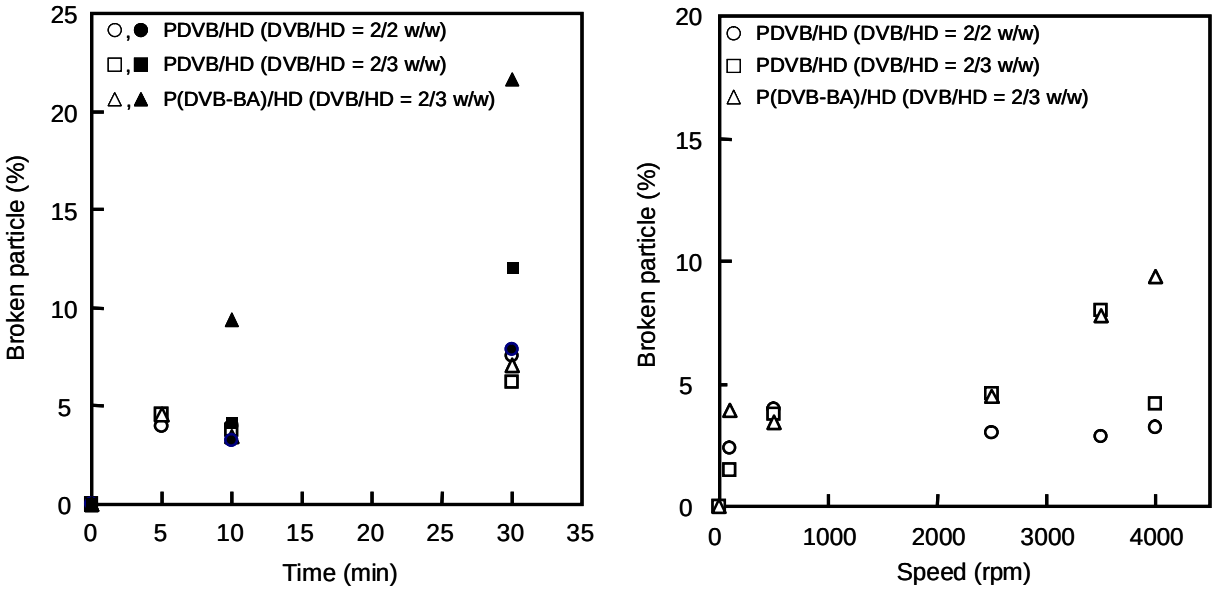

Fig. 4 The percentage of broken particles at various (a) homogenization time (min): (○, □, △) at 500 rpm; (●, ■, ▲) at 4000 rpm and (b) homogenization speed (rpm) for 10 min of various cross-linked capsule particles (diameter: 20 μm; solid content: 6.5 wt%)

Performance of capsule particles in thermal recycles

From the viewpoint of heat storage application, the effect of thermal cycle on the thermal properties of HD encapsulated in both PDVB and P(DVB-BA) particles (SPG pore size, 3.9 μm) were investigated with DSC for accelerated 100 melting/freezing cycles without particle flow. Figure 6a shows DSC thermograms of various thermal cycles of encapsulated

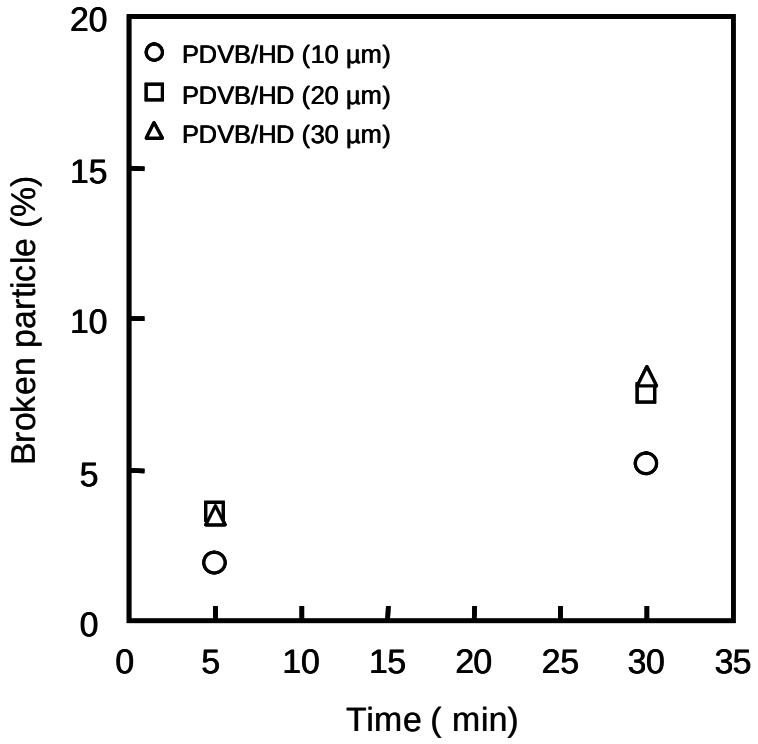

Fig. 5 The percentage of broken particles homogenized at 2,500 rpm for 5 and 30 min of PDVB/HD (DVB/HD = 2/2, w/w) capsule particles (solid content: 6.5 wt%). Particle diameters (μm): ○ 10; □ 20; △ 30

HD in PDVB (DVB/HD = 2/2, w/w) particles. This can be seen that both melting and freezing curves of encapsulated HD have not had major change throughout 100 cycles. Their thermal properties in the term of H_m, H_s, T_m and T_s were shown in Fig. 6b. It also showed that the thermal properties of cycled encapsulated HD in PDVB particles were insignificantly changed during this test. It confirmed that the capsule particles were not broken because no pure HD peak due to the leakage of encapsulated HD by the thermal cycle was observed. These phenomena are also observed in the case of PDVB (DVB/HD = 2/3, w/w) particles although its shell strength is lower than that of the previous ones. Figure 7a shows DSC thermograms of various thermal cycles of encapsulated HD in PDVB/HD (DVB/HD = 2/3, w/w) and its thermal properties were shown in Fig. 7b.

Thermal recycle stability test was also carried out for P(DVB-BA) capsule particles.

Figures 8a and b show DSC thermograms and thermal properties, respectively, of various thermal cycles of encapsulated HD in P(DVB-BA) (DVB/HD = 2/3; DVB/BA = 20/80, w/w). Although its shell strength is much lower than that of PDVB capsule particles due to the decrease of cross-linked density and T_g as already discussed in the previous section, the significant change was not observed from thermal stability test throughout these 100 melting/freezing cycles.

It can therefore be concluded that both PDVB and P(DVB-BA) capsule particles have sufficient performance for heat storage application within this thermal recycle testing condition.

Conclusions

Comparatively monodispersed PDVB and P(DVB-BA) particles with encapsulated HD were prepared by microsuspension polymerization utilizing the SaPSeP method at different DVB/HD ratios to study the effect of capsule shell strength on the shape and performance of cross-linked capsule particles from the viewpoint of heat storage application. It was found that PDVB particles of different shell thicknesses resulted in the different shell strengths and particle shapes. The thicker shell, spherical particle consisting of a single water domain, showed higher shell strength than the thinner one which is nonspherical without water domain. The copolymerization of DVB and BA decreased the capsule shell strength due to the decrease of cross-link density and T_g. However, their performances in the term of thermal recycle usage tested by DSC were insignificant different. Their thermal properties of encapsulated HD showed insignificantly changed throughout accelerated 100 melting/freezing cycles.

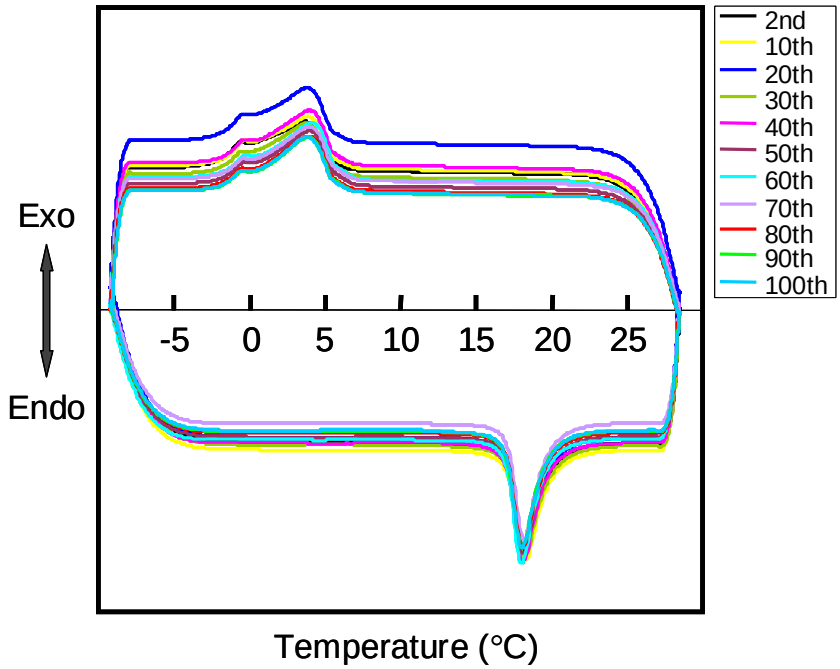

Fig. 6a DSC thermograms of various melting/freezing cycles of HD encapsulated in PDVB particles, produced by microsuspension polymerization utilizing the SaPSeP method of DVB/HD (2/2, w/w) droplets prepared by the SPG (pore size, 3.9 µm) under the conditions listed in Table 1

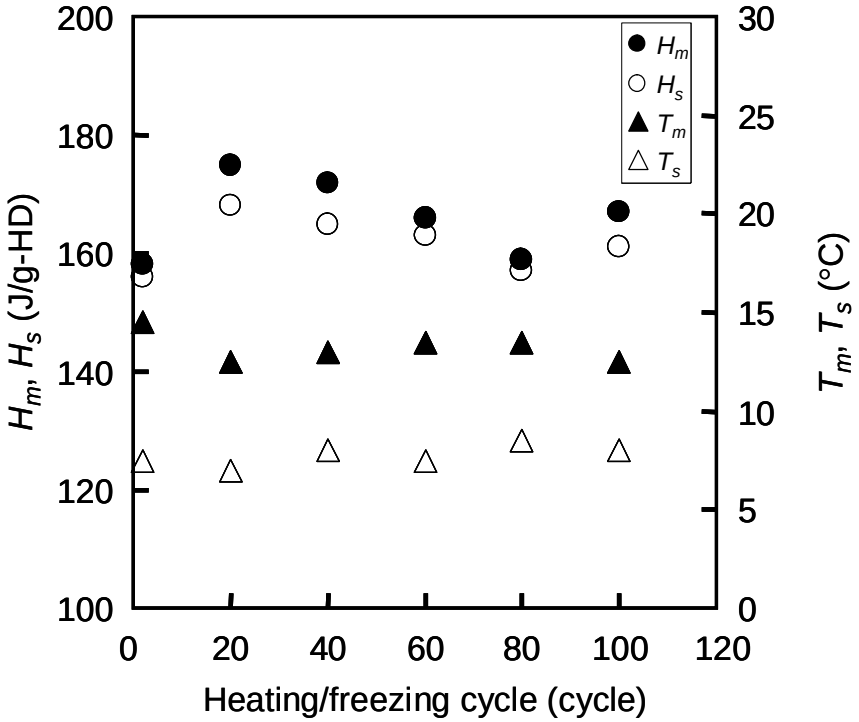

Fig. 6b Thermal properties of various melting/freezing cycles of HD encapsulated in PDVB particles, produced by microsuspension polymerization utilizing the SaPSeP method of DVB/HD (2/2, w/w) droplets prepared by the SPG (pore size, 3.9 µm) under the conditions listed in Table 1

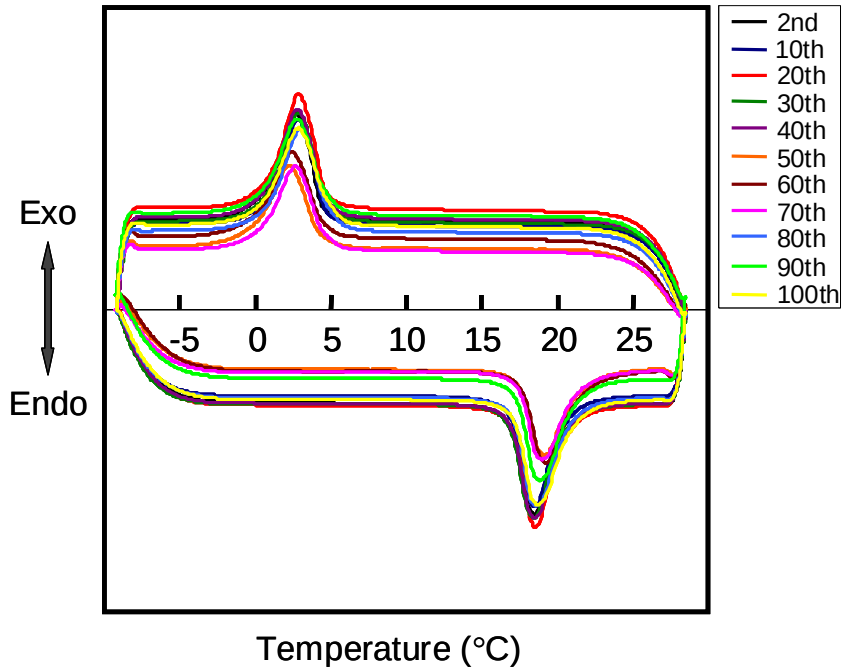

Fig. 7a DSC thermograms of various melting/freezing cycles of encapsulated HD in PDVB particles, produced by microsuspension polymerization utilizing the SaPSeP method of DVB/HD (2/3, w/w) droplets prepared by the SPG (pore size, 3.9 µm) under the conditions listed in Table 1

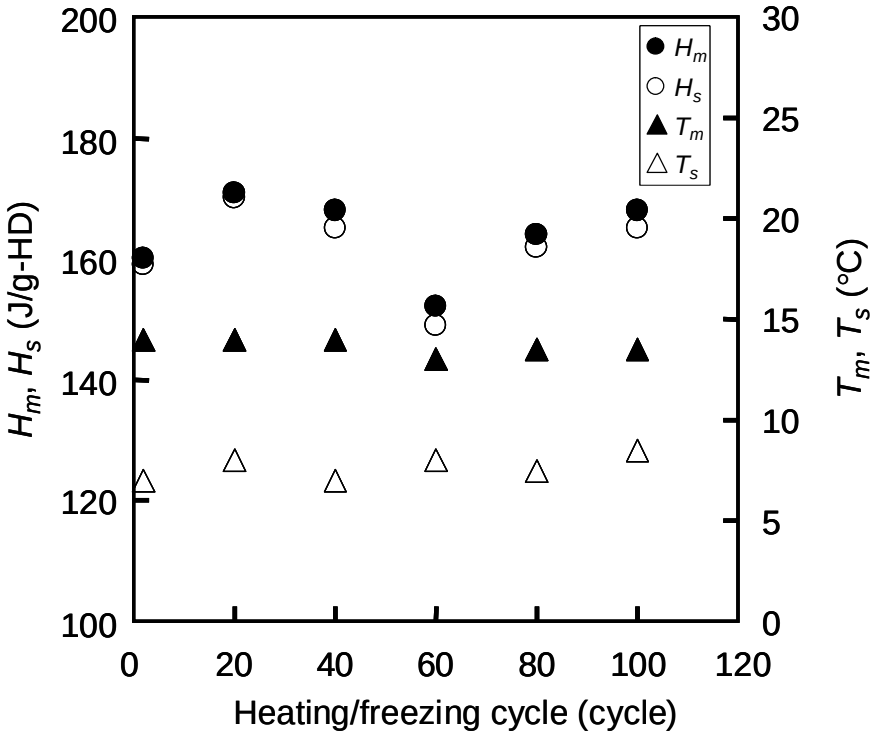

Fig. 7b Thermal properties of various melting/freezing cycles of encapsulated HD in PDVB particles, produced by microsuspension polymerization utilizing the SaPSeP method of DVB/HD (2/3, w/w) droplets prepared by the SPG (pore size, 3.9 µm) under the conditions listed in Table 1

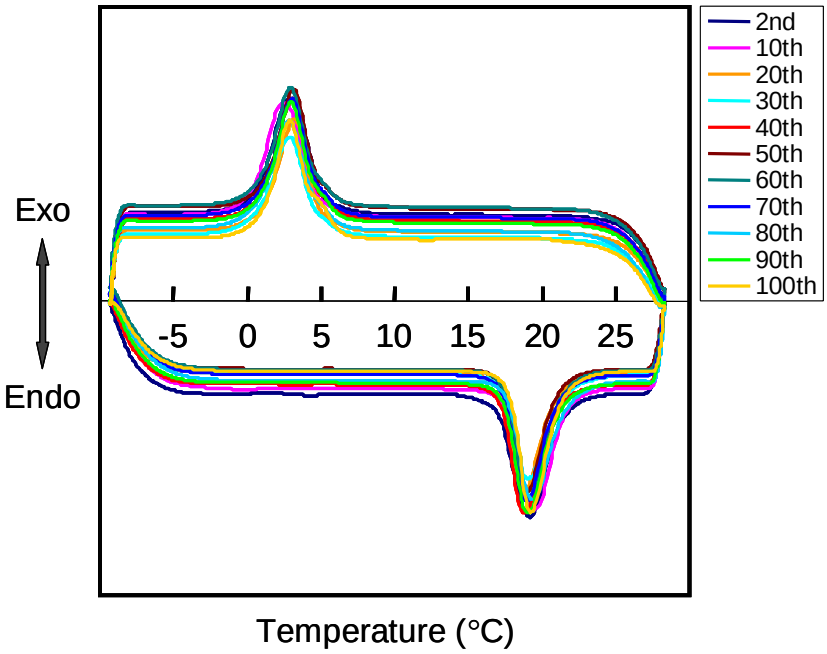

Fig. 8a DSC thermograms of various melting/freezing cycles of encapsulated HD in P(DVB-BA) (DVB/BA = 20/80, w/w) particles, produced by microsuspension copolymerization utilizing the SaPSeP method of (DVB-BA)/HD (2/3, w/w) droplets prepared by the SPG (pore size, 3.9 µm) under the conditions listed in Table 1

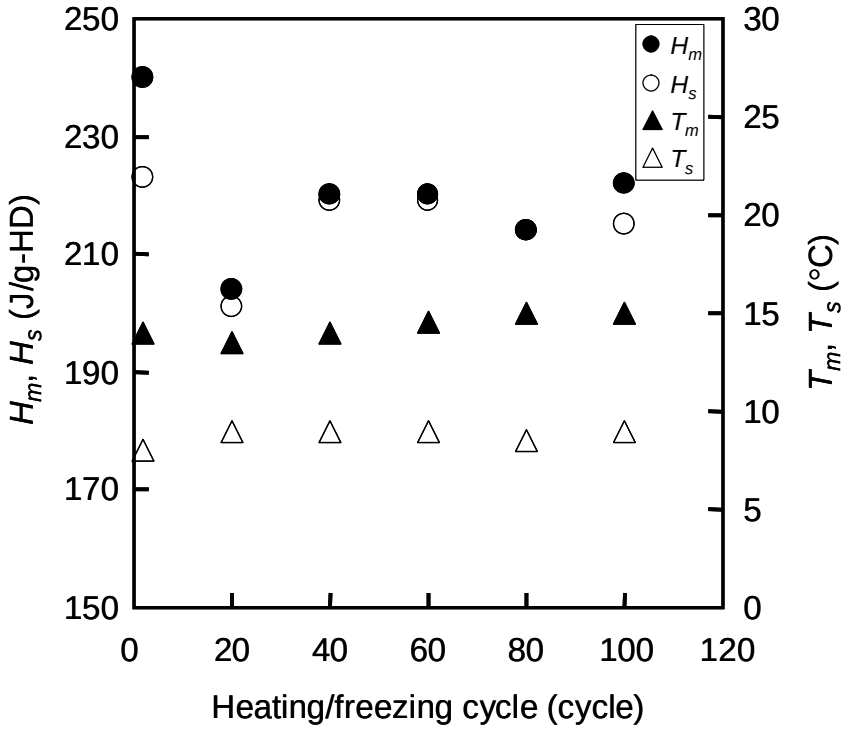

Fig. 8b Thermal properties of various melting/freezing cycles of encapsulated HD in P(DVB-BA) (DVB/BA = 20/80, w/w) particles, produced by microsuspension copolymerization utilizing the SaPSeP method of (DVB-BA)/HD (2/3, w/w) droplets prepared by the SPG (pore size, 3.9 µm) under the conditions listed in Table 1

Acknowledgement

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).

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Conclusions

The production of micron-sized, monodisperse cross-linked capsule particles encapsulating HD by microsuspension polymerization utilizing the SaPSeP method of monomer(s)/HD droplets prepared by the SPG membrane emulsification technique was studied. The presence of HD accelerated phase separation of PDVB formed in the droplets even in an early stage of the polymerization. The phase separated PDVB moved toward the interface of the droplets to form capsule particles. The thermal properties of encapsulated HD and performance in thermal recycle of capsules were determined from the viewpoint of heat storage application. The results have been summarized here.

In **Chapter 1**, monodispersed DVB copolymer particles with encapsulated HD were prepared by microsuspension copolymerization utilizing the SaPSeP method. The H_s of HD encapsulated in PDVB particles was much decreased from that of pure HD which is negative with regards to application as heat storage materials. However, it was improved by the copolymerization of hydrophilic acrylic monomer. This seems to be based on the finding that the copolymerizations of hydrophilic monomer enhance the phase separation of copolymer chains and HD, eventually resulting in the complete isolation of the HD core from the polymer shell. This HD core seems to be more smoothly solidified than incompletely isolated HD locating in the inner interface of polymer shell, leading to the increase of H_s with hydrophilic monomer content.

In **Chapter 2**, 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 gradually formed with the increase of their sizes during cooling from 70 °C to room temperature. This is because the

density of HD increases with the decrease of temperature leading to the formation of space inside the capsule particles. When the shell strength is sufficient 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. 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, this influence gradually decreased with an increase of the particle diameter, which seems to be due to the decrease of total interfacial area of water domains in encapsulated HD cores.

In **Chapter 3**, the thermal property of HD encapsulated in micron-sized, monodisperse PDVB capsule particles produced by microsuspension polymerization utilizing the SaPSeP method was influenced by a single water domain formed in the HD core. In DSC thermograms, pure HD had a single peak due to solidification (T_s) at 15 °C, whereas the encapsulated HD containing a water domain had two peaks of T_{s1} and T_{s2}, at 6 and 1 °C, respectively. This water domain led to the partial decrease of T_s ($\rightarrow T_{s2}$) of the encapsulated HD in the capsule particles, which retarded its solidification in heat storage applications. However, this influence gradually decreased with an increase in the drying time due to 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 was also found in the encapsulated HD core after solidification because of shrinkage of the HD. The presence of the air domain in the HD core did not affect the thermal properties and stability of the encapsulated HD.

In **Chapter 4**, the presence of residual monomer in capsule particles influenced on the formation of a single water domain in the HD core inside micron-sized, monodisperse PDVB capsule particles produced by microsuspension polymerization utilizing the SaPSeP

method. It may affect the shrinkage of DVB/HD core with the polymerization and during cooling after the polymerization. Moreover, it also affected the thermal property of the encapsulated HD. The residual monomer led to the decrease of T_{s1} of the encapsulated HD, which is negative with regards to application as heat storage capsule. However, this influence gradually decreased with an increase of the conversion as by increase of initiator concentration or polymerization time.

In **Chapter 5**, comparatively monodispersed PDVB and P(DVB-BA) particles with encapsulated HD were prepared by microsuspension polymerization utilizing the SaPSeP method at different DVB/HD ratios to study the effect of capsule shell strength on the shape and performance of cross-linked capsule particles from the viewpoint of heat storage application. It was found that PDVB particles of different shell thicknesses resulted in the different shell strengths and particle shapes. The thicker shell, spherical particle consisting of a single water domain, showed higher shell strength than the thinner one which is nonspherical with out water domain. The copolymerization of DVB and BA decreased the capsule shell strength due to the decrease of cross-link density and T_g. However, their performances in the term of thermal recycle usage tested by DSC were not significant different. Their thermal properties of encapsulated HD showed insignificantly changed throughout accelerated 100 melting/freezing cycles.

The field of capsule particle preparation is of great interest and rapidly grows in recent years for various applications. The micron-sized, monodisperse cross-linked capsule particles encapsulating HD are successfully prepared by microsuspension polymerization utilizing the SaPSeP method. The problems with the encapsulation on thermal properties of encapsulated HD, supercooling and reduction of H_s and H_m, were improved. However, further works are still required to prepare excellent capsule particles with high performance for heat storage application.

Publication List

Chapter 1

"Preparation of divinylbenzene copolymer particles with encapsulated hexadecane for heat storage application"

P. Chaiyasat, Y. Ogino, T. Suzuki, H. Minami, M. Okubo

Colloid Polym. Sci., **286**, 217-223 (2008)

Chapter 2

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

P. Chaiyasat, Y. Ogino, T. Suzuki, M. Okubo

Colloid Polym. Sci., **286**, 753-759 (2008)

Chapter 3

"Thermal properties of hexadecane encapsulated in poly(divinylbenzene) particles"

P. Chaiyasat, T. Suzuki, H. Minami, M. Okubo

J. Appl. Polym. Sci., submitted

Chapter 4

"Influence of residual monomer on water domain formation and thermal properties of encapsulated hexadecane in poly(divinylbenzene) capsule particles"

P. Chaiyasat, Y. Ogino, T. Suzuki, M. Okubo

in preparation

Chapter 5

"Effect of capsule shell strength on the shape and performance of cross-linked capsule particles with encapsulated hexadecane in recycling usage"

P. Chaiyasat, Y. Ogino, T. Suzuki, M. Okubo

in preparation