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ARTICLE TYPE

Do encapsulated heat storage materials really keep original thermal properties?

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Encapsulation of Rubitherm®27 (RT27), which is one of commercially supplied heat storage materials, by polystyrene (PS), polydivinyl benzene (PDVB) and polymethyl methacrylate (PMMA) was carried out using conventional radical microsuspension polymerization. The products were purified to remove free RT27 and free polymer particles without RT27. In the cases of PS and PDVB microcapsules, the latent heats of melting and crystallization for RT27 (ΔH_m* and ΔH_c*, J/g-RT27) were obviously decreased by the encapsulation. On the other hand, those of PMMA microcapsules were the same as pure RT27. Supercooling phenomenon was observed not only for PS and PDVB but also PMMA microcapsules. These results indicate that the thermal properties of the heat storage materials encapsulated depended on the kind of polymer shells, that is, the encapsulation by polymer shell changed thermal properties of RT27. This is quite different from the idea of other groups in the world, in which they has discussed the thermal properties based on the ΔH_m and ΔH_c values expressed in J/g-capsule assuming that the thermal properties of heat storage materials are not changed by the encapsulation. Hereafter, this report should raise an alarm to the "wrong" common knowledge to develop the encapsulation technology of heat storage materials.

Introduction

Heat storage or phase change materials (PCMs) are the materials that change their status with temperature. They are, respectively, solid or liquid at the temperatures lower or higher than the transition temperature.[1, 2] Because of the environment concerning, they are attractive for many industrial applications such as solar heat storage,[3-12] textile,[13-19] and air conditioning of building.[20-23] Paraffin wax such as octadecane (OD), hexadecane (HD), dodecanol (DD) and nonadecane (ND) is one group of PCMs that melt and crystallize at a wide range of temperature making them attractive for many applications. They are also cheap, non-toxic, chemical inert and moderate thermal energy storage, but low thermal conductivity. To overcome this disadvantage, the encapsulation of PCMs is an interesting alternative.[2, 7] Therefore, a numerous of researches have been carried out on micro- and nanoencapsulation of PCMs using different polymer shells with various techniques. For example, microencapsulated OD with resorcinol-modified melamine-formadehyde or polyurea containing different soft segments was synthesized by in situ polymerization[24] or interfacial polycondensation,[25] respectively. Three types of paraffin waxes (HD, OD and ND) were encapsulated through complex coacervative of natural and biodegradable polymer, gum arabic gelatin mixture.[26] Polystyrene (PS),[27-30] poly(styrene-methacrylate)[31, 32] and poly(styrene-butyl acrylate)[33] micro- and nanoencapsulations of various PCMs were carried out by both microsuspension and miniemulsiom polymerizations. The polymethyl methacrylate (PMMA) capsules with encapsulated OD,[34, 35] *n*-octacosane[8], *n*-DD[36] and HD[37] were prepared by miniemulsion polymerization. However, to our knowledge, most of all researches have not focused on the influence of polymer shell on the thermal properties of the encapsulated paraffin wax. They calculated % loading of the wax in the capsules using latent heats (ΔH) in the unit of J/g-capsule comparing to those of the pure wax, assuming that the latent heats of the encapsulated paraffin wax are the same as those of the pure one. It is reasonable to evaluate the thermal storage ability based on J/g-capsule in the industrial field, but we consider that it is "wrong" in the academic aspect. Even in these two years, the thermal properties of encapsulated heat storage materials have been discussed based on the "wrong" idea over 70 articles reported in various Journals. In order to develop the encapsulation technology of heat storage materials, it should be discussed based on ΔH* in the unit of J/g-heat storage materials as described below.

In our previous articles, we have successfully prepared polydivinylbenzene (PDVB) microcapsules with encapsulated HD[38-41] and OD[42-45] by microsuspension polymerization utilizing a *S*elf *a*ssembly of *P*hase *S*eparated *P*olymer (SaPSeP) method.[46] It was found that the latent heats of the encapsulated waxes, heats of melting (ΔH_m*) and crystallization (ΔH_c*), in the microcapsule (J/g-wax) were always much lower than those of pure waxes, which may be due to incomplete phase separation of PDVB shell and waxes core. The microsuspension copolymerization of PDVB with polar acrylate component improved the latent heats (ΔH_m*, ΔH_c*: J/g-the encapsulated waxes).[40] In these ways, the thermal properties of the encapsulated waxes depended on the kinds of polymer shells. Therefore, we should not discuss the heat storage ability based on the assumption that the latent heats of the encapsulated paraffin wax were the same as those of the pure one. However, our statement may encounter criticism because our

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prepared polymer microcapsules with encapsulated waxes had crosslinked structure, which is different from many reports where uncrosslinked microcapsules have been prepared.

In this article, we therefore will prove the validity of our idea that thermal properties strongly depends on the kind of polymer shell using uncrosslinked microcapsules with the encapsulated heat storage materials that have often been synthesized in the other groups as described above.

Experiment

Materials

Methyl methacrylate (MMA) (Aldrich, Wisconsin, USA; purity, 99%) and styrene (S) (Aldrich, Wisconsin, USA; purity, 99%) were purified by passing through the column packed with basic aluminium oxide. RT27 (Rubitherm Technologies GmbH, Berlin, Germany; Commercial grade) was used as received. Divinyl benzene (DVB; Aldrich, Wisconsin, USA; purity, 80%) was washed with 1 M sodium hydroxide (NaOH; BDH Prolabo, Leuven, Belgium) solution to remove polymerization inhibitors before use. Reagent-grade benzoyl peroxide (BPO; Merck, Munich, Germany) was purified by recrystallization. Poly(vinyl alcohol) (PVA; Aldrich, Wisconsin, USA; degree of saponification 87-90 %; molecular weight 3-7x10^4 g/mol) was used received.

Microcapsule preparation

PMMA/RT27, PS/RT27 and PDVB/RT27 microcapsules were prepared by conventional radical microsuspension polymerization (microsuspension CRP) under the conditions listed in Table 1. Firstly, monomer, RT27 and BPO (8 wt% relative to monomer) were homogeneously mixed as oil phase. It was then poured into a PVA aqueous solution (1 wt%) and homogenized at 5,000 rpm for 5 min to form oil-in-water emulsion. Secondly, the obtained emulsion was subsequently transferred to round bottom flask, sealed with silicone rubber septum and purged with vacuum/N_2 cycle five times. It was finally polymerized at 80 °C for 8 h at a stirring rate of 200 rpm.

Table 1 Recipe for the preparation of PMMA/RT27, PS/RT27 and PDVB/RT27 microcapsules by microsuspension CRP [a] of monomer/RT27 droplets [b] (monomer/RT27 = 50/50, w/w) with BPO as initiator

Ingredients		
Monomer [c] (g)	2.50	2.50
RT27 (g)	-	2.50
BPO (g)	0.20	0.20 (8 wt% relative to monomer)
PVA aqueous solution (1 wt%) (g)	45.00	45.00

Abbreviations: MMA, methyl methacrylate; DVB, divnylbenzene; RT27, Rubitherm®27; BPO, benzoyl peroxide; PVA, polyvinyl alcohol

[a] 80 °C, 8 h.

[b] Homogenized at 5,000 rpm for 5 min.

[c] MMA, DVB or S.

Washing process of microcapsules

Each dispersion prepared by the microemulsion CRP was kept overnight at room temperature. Floated microcapsules were dispersed in a formed upper layer. The lower aqueous layer (containing free polymer particles without RT27) was replaced with deionized water three times or until giving the bright aqueous medium to remove free polymer particles without RT27. PMMA/RT27, PS/RT27 and PDVB/RT27 microcapsules (approximately 1g) or the microcapsules mixed with pure RT27 were washed with 2-propanol (5 g) for 30 to 120 seconds to remove unencapsulated wax and impurities.

Characterization of microcapsules

The prepared microcapsules were observed with an optical microscope (OM, SK-100EB&SK-100ET, Seek Inter Co. Ltd., Thailand) and scanning electron microscope (SEM, JSM-6510, JEOL, JEOL ltd., Japan) to investigate the inner structure of the microcapsules and the morphology of the surface, respectively. For SEM observation, one drop of each polymer dispersion was placed on a nickel SEM stub and dried before being coated with Au. For the measurement of thermal properties, free polymer particles were first removed from each dispersion and then the microcapsules were washed with 2-propanol before dried in vacuum oven. The RT27 content in the dried microcapsules was determined by thermogravimetric analyzer (TGA, TGA 4000, Perkin-Elmer, USA) at a heating rate of 5 °C/min. The latent heats (ΔH_m and ΔH_c) and the crystallization (T_c) and melting (T_m) temperatures of the encapsulated RT27 in dried microcapsules after washing were measured with a differential scanning calorimeter (DSC, DSC 4000, Perkin-Elmer, USA) under a N_2 flow in a scanning temperature range of -20-40 °C and at heating/cooling rate of 5 °C/min. To compare the ΔH_m and ΔH_c values of the encapsulated RT27 in the washed microcapsules containing different amounts of RT27, ΔH_m* and ΔH_c* values were given in unit of joules per 1 g of encapsulated RT27 (J/g-RT27). These values were calculated using the following equation (1) from the heating/cooling peak areas of the DSC thermogram and the RT27 content in each washed microcapsule obtained from the TGA analysis, which did not contain free polymer particles and/or unencapsulated RT 27.

$$A = \left[\frac{B}{C}\right] \text{x } 100 \qquad (1)$$

Where

A = ΔH_m* and ΔH_c* of the encapsulated RT27 in unit of joules per 1 g of encapsulated RT27 (J/g-RT27)
B = ΔH_m and ΔH_c of the encapsulated RT27 in unit of joules per 1 g (J/g-capsule) obtained from the DSC thermogram
C = % loading (experiment) of RT27 in the washed microcapsules obtained from the TGA thermogram

The theoretical % loading of RT27 in the washed microcapsules was also calculated by equation (2) using % conversion and % free polymer particles. Encapsulation efficiency (%) was calculated using the equation (3).

$$\text{\% loading (theory)} = \left[\frac{W_{wax}}{(W_{wax} + W_m \text{ (\% conversion - \% free polymer)}/100)}\right] \text{x}100 \qquad (2)$$

where W_{wax} and W_m are weights of RT 27 and monomer, respectively, in the polymerization recipe shown in Table 1.

$$\text{Encapsulation efficiency (\%)} = \left[\frac{\text{\% loading (experiment)}}{\text{\% loading (theory)}}\right] \times 100 \quad (3)$$

Results and discussion

Microcapsule formation

Oil droplets consisting of monomer, RT27 and BPO were homogeneously dispersed in a PVA aqueous solution. When the polymerization proceeded, polymer molecules having above critical chain length precipitated in the oil phase, resulting in phase separation therein. The polymer molecules moved to the oil droplet interface because of their higher hydrophilicity and formed capsule shell with encapsulated RT27 core. Figure 1 shows optical micrographs of the prepared polymer microcapsules containing RT27 with various polymer shells (PMMA, PS and PDVB) at room temperature. In the case of PMMA microcapsules (Fig. 1a) they had a nonspherical shape with voids at the surface, while in the cases of PS and PDVB microcapsules (Fig. 1b and c) they had a spherical shape.

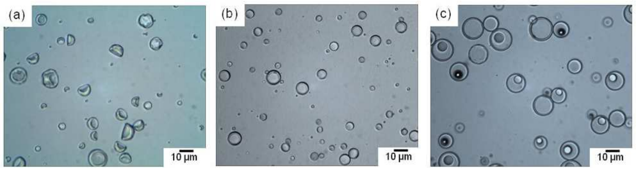

Fig. 1 Optical micrographs of PMMA/RT27 (a), PS/RT27 (b) and PDVB/RT27 (c) microcapsules prepared by microsuspension CRP of MMA/RT27, DVB/RT27 and S/RT27 droplets, respectively, at 80 °C for 8 h.

After washing with 2-propanol, the shapes of PMMA and PDVB microcapsules were not changed (respectively, Fig. 2a, a' and c, c'), while a part of PS microcapsules were broken (Fig. 2b, b') with a gentle washing. These photographs indicate that RT27 existed as core in each polymer shell, because each polymer is insoluble in RT27. PS was not appropriate for waxes encapsulation although some groups reported that spherical PS microcapsules were successfully prepared under similar conditions.[27-30]

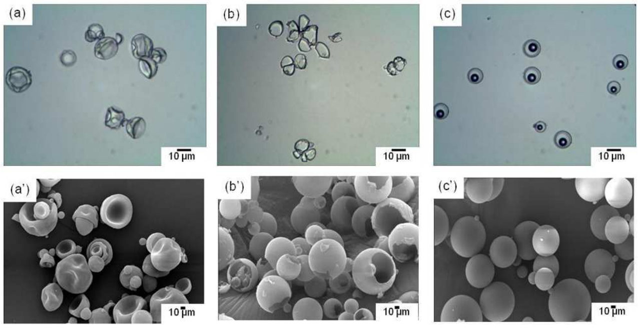

Fig. 2 Optical (a, b, c) and SEM (a', b', c') micrographs of PMMA/RT27 (a, a'), PS/RT27 (b, b') and PDVB/RT27 (c, c') microcapsules after washing with 2-propanol.

When the dispersions of the microcapsules were kept overnight, all microcapsules floated on the top layer (Fig.3) because the total density of the microcapsule is lower than that of water (densities of RT27, PMMA, PS and PDVB were, respectively, 0.76, 1.18, 1.04 and 1.04 g/ml). In the case of PMMA/RT27 (Fig. 3a), the lower aqueous layer was heavily turbid although the PMMA microcapsules did not exist there. This indicates that emulsion polymerization of PMMA occurred at the same time in the system in addition to the microsuspension CRP, resulting in a lot of free PMMA particles (without RT27). The amount of the free PMMA particles, of which number-average diameter measured with dynamic light scattering was about 200 nm, was 45 wt% relative to total PMMA. In the case of PS/RT27, quite brighter lower aqueous layer was observed, in which a small amount of free PS particles and a rather amount of broken PS microcapsules without RT27 existed. The total PS amount was 42 wt%. In the case of PDVB/RT27, although the lower aqueous medium looked somewhat bluish turbid (Fig. 3c), in which very few particles having above 65 nm in diameter were observed, emulsion polymerization could be neglected because there was no residue polymer after drying the aqueous medium. This indicates that the PDVB was used 100 % for the encapsulation.

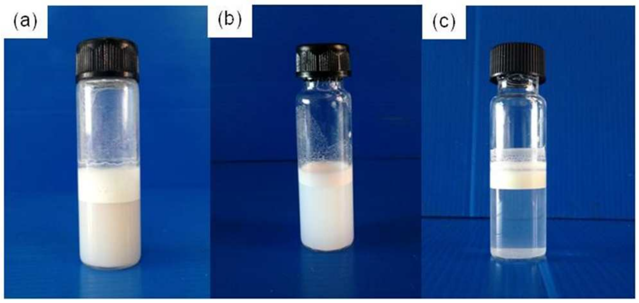

Fig. 3 Photos of aqueous dispersions of PMMA/RT27 (a), PS/RT27 (b) and PDVB/RT27 (c) microcapsules prepared by microsuspension CRP.

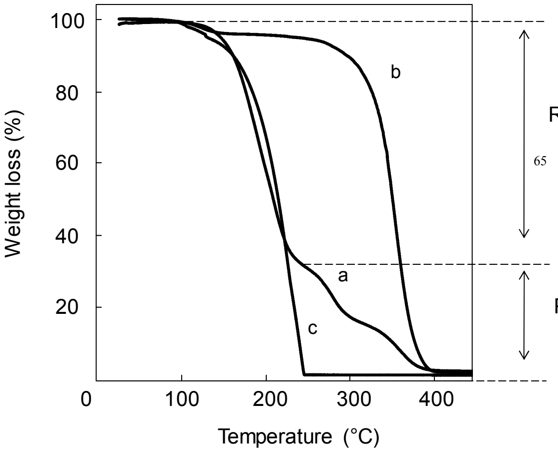

Fig. 4 TGA thermograms of pure RT27 (a), PMMA (b) and washed PMMA/RT27 microcapsules after removal of free PMMA particles and washing with 2-propanol for 90 seconds (c).

Figure 4 shows TGA thermograms of PMMA, pure RT27 and the washed PMMA/RT27 microcapsules (after the removal of the free PMMA particles) with 2-propanol for 90 seconds. The decomposition temperature of pure RT27 was 70 to 250 ˚C, while it was 250-400 ˚C for PMMA. In the case of the PMMA/RT27 microcapsules, the degradation was two steps. The first step was the degradation of the encapsulated RT27 from about 80-250 °C, which was slightly higher than that of pure RT27 because of the encapsulation. The second step was the decomposition of PMMA from 250-400 °C with two transition curves, although in the cases of PS/RT27 and PDVB/RT27 microcapsules only one transition curve was observed (data omitted). The reason why the two-step degradation of PMMA shell was observed is unclear now, but it might be based on that the PMMA shell contained low molecular weight component. This point will be discussed in a following article.

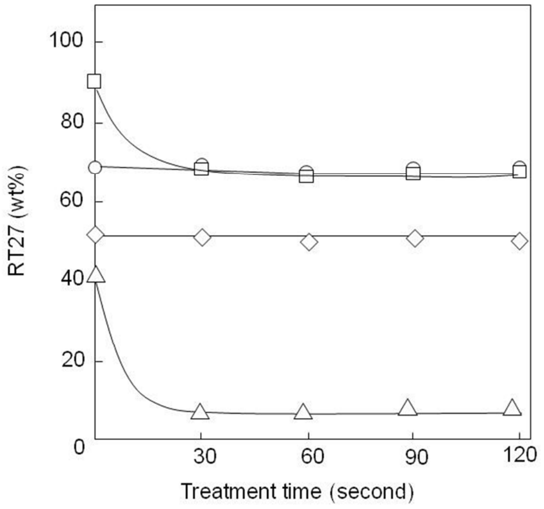

Fig. 5 Weight % of RT27 in PMMA/RT27 (○), PS/RT27 (Δ) and PDVB/RT27 (◊) microcapsules after removal of free particles and in a mixture of the PMMA/RT27 microcapsules and pure RT27 (□) as a function of the washing with 2-propanol.

To estimate % loading of RT27 in each microcapsule, as shown in Fig. 4, the removal of the free polymer particles and the washing of the microcapsules with 2-propanol were carried out before the TGA measurement. 2-Propanol is miscible with RT27 and the monomers, while it is a nonsolvent for PMMA, PS and PDVB. Although Rodriguez and coworker[27] also prepared PS/RT27 microcapsules and washed them with methanol, we did not use it for washing because it is immiscible with RT27. To clarify the washing efficiency with 2-propanol, in addition to PMMA, PS and PDVB microcapsules after the removal of the free polymer particles, a mixture of the PMMA microcapsule and pure RT27 was washed with 2-propanol as a function of washing time. The results are shown in Fig. 5. In the case of PMMA/RT27 microcapsules, the RT27 content was always constant at 70 wt% over the washing process (120 seconds). In case of the mixture of the washed PMMA/RT27 microcapsules and pure RT27, in which the RT27 content was 90 wt%, the RT27 content decreased to 70 wt% by 30 seconds washing and then kept constant, which well accorded with that in the unwashed PMMA/RT27 microcapsule. These indicate that the decrease of the RT27 content from the mixture is due to the complete removal of the pure RT27 mixed with them. The experimentally obtained % loading of RT27 in the washed PMMA microcapsules (70 wt%) was accord with calculated value using % conversion (80 %) and % of free PMMA particles (45 %) in the polymerization system. % Loading of RT27 encapsulated by PDVB was always constant at 49 wt% over the washing. These results indicate that RT27 used in the microsuspension CRPs of MMA and DVB was completely encapsulated by PMMA and PDVB, respectively. RT27 content in PS microcapsule was decreased from 40 wt% to 8 wt% after 30 seconds washing. This indicates that a rather amount of PS/RT27 microcapsules were broken in the washing process.

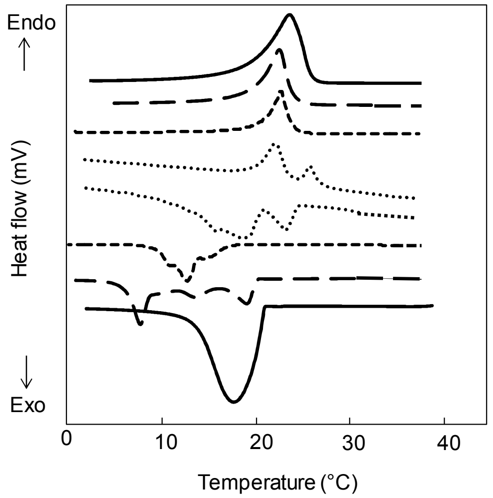

Fig. 6 DSC thermograms of pure RT27 (——) and encapsulated RT27 in the PMMA (– – –), PDVB (- - - -) and PS (··········) microcapsules after removing free particles and washing with 2-propanol.

Thermal properties of encapsulated RT27 in microcapsules

Figure 6 shows DSC thermograms of pure RT27 and encapsulated RT27 in the PMMA, PS and PDVB microcapsules after removing free polymer particles and washing with 2-propanol. Where, the scale of Y-axis is not indicated to clearly show them without overlapping. Melting points, T_m values of the encapsulated RT27 for PMMA, PS and PDVB microcapsules were about 23 °C closed to that of pure RT27 (25 °C). On the other hand, crystallization temperature, T_c values of the encapsulated RT27 for PMMA, PS and PDVB microcapsules were 9, 18 and 12 °C, respectively. The decrease of T_c was called supercooling. Such a supercooling was still observed even at the lower cooling rate, although ΔT (= T_m – T_c) was somewhat decreased from 14 to 12 ˚C by decreasing the cooling rate from 5 to 1 ˚C/min. It is generally understood that the crystallization of waxes is induced by impurities. The supercooling of encapsulated wax in the microcapsule seems to be based on "compartmentalization effect" or "homogeneous nucleation" because the impurities located in a microcapsule cannot induce the nucleation of wax encapsulated in the other microcapsules[47, 48]. Therefore, in the dispersion systems, the multiple peaks of RT27 might be based on the different amounts of impurities in each microcapsule, which should result in the different nucleation efficiency.

Table 2 % Loading and latent heats (ΔH_m and ΔH_c) of the encapsulated RT27 in PMMA, PS and PDVB microcapsules (after removal of free particles and washing with 2-propanol) prepared by the microsuspension CRP

	% Loading (wt%)[a]	ΔH_m (J/g-sample)[b]	ΔH_m^* (J/g-RT27)[c]	ΔH_c (J/g-sample)[b]	ΔH_c^* (J/g-RT27)[c]
Pure RT27	-	-	162	-	168
PMMA/RT27	70	114	164	116	167
PS/RT27 (before separation of the broken PS particles)	10	2.1	21	2.6	26
PS/RT27 (after separation of the broken PS particles)	8	9	112	8	100
PDVB/RT27	49	63	127	65	133

[a]. Measured with TGA
[b] Measured with DSC.
[c] Calculated from equation (1)

Table 2 shows % loading and latent heats of the encapsulated RT27 in the PMMA, PS and PDVB microcapsules after removal of free particles and washing with 2-propanol, measured by DSC, where two types of latent heats (ΔH_m, ΔH_c and ΔH_m^*, ΔH_c^*) are shown. The former two, of which unit is J/g-sample, were directly measured with DSC. The latter two, of which unit is J/g-RT27, were obtained with both DSC and TGA data. In the case of PMMA microcapsules, ΔH_m^* and ΔH_c^* values were 164 and 167 J/g-RT27, respectively, which were almost the same as those (162 and 168 J/g-RT27, respectively) of pure RT27. It is very interesting that the reduction of latent heats of RT27 encapsulated by PMMA shell was not observed. On the other hand, in the case of PDVB microcapsules, ΔH_m^* and ΔH_c^* values of the encapsulated RT27 were, respectively, 127 and 133 J/g-RT27, which were lower than those of the pure RT27. These results well accorded with the results of PDVB/HD[38-41] and PDVB/OD[42-45] microcapsules in the previous articles, in which the ΔH_m* and ΔH_c* of the encapsulated HD and OD were decreased by the PDVB encapsulation. Moreover, in the PS microcapsules, from which the broken microcapsules (without RT27) were separately removed by triplicate sedimentation procedure, ΔH_m* and ΔH_c* values were further decreased to 112 and 100 J/g-RT27, respectively. Such decreases in the latent heats of the encapsulated RT27 is clearly different from the idea given by the other groups who assumed that ΔH_m^* and ΔH_c^* of the encapsulated waxes[3-5, 8, 9, 13, 27, 29-32, 49-51] are the same as those of the pure ones. We conclude that the encapsulation by polymer shell does not always keep thermal properties of RT27, which depends on the kind of polymers.

Table 3 shows % loading of RT27 and encapsulation efficiencies (%) of RT27 by polymer shells. % Loading values were obtained by the following three ways: 1) theoretical value calculated using % conversion and wt% of free polymer particles (equation (2)); 2) experimental value measured directly with TGA based on the authors' idea; 3) calculated value by equation (4) using ΔH_m (J/g-sample) and ΔH_{RT27} based on the other groups' idea [27, 31, 33, 35, 49, 52-54]. The % loadings measured from TGA measurement of the washed microcapsules well accorded with the theoretical ones. The calculated % loading values (based on the other groups' idea) for PS and PDVB microcapsules were lower than the measured ones (based on the authors' idea), although in the case of PMMA microcapsule they were the same, because ΔH_m* (J/g-RT27) was equal to ΔH_{RT27}.

Encapsulation efficiencies of RT27 obtained using equation (3) were 100 % in the microsuspension CRPs of MMA and DVB. However, in the case of MMA, a lot of free PMMA particles were produced as already described above. This serious problem will be improved in a following article. In the case of DVB such a problem could be neglected but ΔH_m* (J/g-RT27) was lower than ΔH_{RT27}. This problem will also be improved in the next article[55].

On the other hand, the encapsulation efficiencies calculated from equation (5) based on the definition that has so far been applied by many other groups in the world were lower than those obtained using equation (3) except for PMMA microcapsule. We understand that it is no problem to estimate the heat storage ability of the encapsulated RT27 by $\Delta H_{capsule}$ (J/g-capsule) in the industrial application. However, in academic aspect, when ΔH_m* (J/g-RT27) is not equal to ΔH_{RT27}, we should emphasize to make serious mistakes in the research strategy planned under assuming that ΔH_m* and ΔH_c* of heat storage materials are not changed by the encapsulation with polymer shell. This paper should raise an alarm to the "wrong" common knowledge that has been applied over the years in the world and must disturb the development of the encapsulation technology of heat storage materials such as wax by polymer shell.

Table 3 % loadings of the encapsulated RT27 in PMMA, PS and PDVB microcapsules (after removing free particles and washing with 2-propanol) prepared by the microsuspension CRP and encapsulation efficiencies (%) of RT27 that are shown based on definitions applied of our group and many other groups

Microcapsule	% Loading			Encapsulation efficiency (%)	
	Other groups' idea[a]	Experiment[b]	Theory[c]	Authors' idea[d]	Other groups' idea[e]
PMMA/RT27	70	70	74	~100	~100
PS/RT27	5	8	75	10	7
PDVB/RT27	35	49	52	~100	75

[a] Calculated from $(\Delta H_m/\Delta H_{RT27}) \times 100$ (4)
[b] Measured with TGA
[c] Calculated from equation (2)
[d] Calculated from equation (3)
[e] Calculated from {(% loading obtained eq. (4) / % loading (theory))   (5)

Conclusions

The latent heats (ΔH_m* and ΔH_c*) of the encapsulated RT27 by PDVB and PS were quite lower than those of the pure RT27. On the other hand, the encapsulation by PMMA did not change it, although its microsuspension CRP gave a lot of free PMMA particles without RT27. In all microcapsules, supercooling phenomenon was observed. These indicate that encapsulation efficiencies of heats storage materials in many papers reported by the other groups in the world calculated assuming that the thermal properties of heat storage materials are not changed by the encapsulation are "wrong", which must disturb the development of encapsulation technology of heat storage materials. Hereafter, this report should raise an alarm to the "wrong" idea that has so far commonly been adapted.

Acknowledgement

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