Expansion Space and Thermal Stability of Microencapsulated *n*-Octadecane

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ABSTRACT: 5.0–50.0 vt% of cyclohexane was mixed with 95.0–50.0 vt% of *n*-octadecane as the oil-phase during the emulsion process in the *in situ* polymerization of melamine-formaldehyde. By heat-treating the microcapsules in an oven at 100°C, the cyclohexane was removed and expansion space was formed inside the microcapsules. The microcapsules were characterized by using FTIR, SEM, DSC, TGA, and gas chromatography. When the microcapsules are heat-treated at temperatures higher than 180°C, Tm, ΔHm, Tc, and ΔHc of the microcapsules decrease. The attenuation of enthalpy of the microcapsules containing expansion space is obviously lower than that of the control sample, however. The permeability of the microcapsule shell decreases with the increase of cyclohexane content. There is a maximum between the thermal stabilities of the microcapsules and the cyclohexane contents. The microcapsules synthesized with 30.0–40.0 vt% of cyclohexane have the highest thermal stabilities, with 230°C and 289°C in air and nitrogen atmosphere, respectively. The thermal stable temperatures are approximately 67°C and 102°C higher than that of the control sample, respectively. The expansion space inside the microcapsules allows the *n*-octadecane to expand in the temperature rising process and exert lower pressure to the shell, therefore keeping the shell intact and increasing the thermal stabilities of the microcapsules. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 390–396, 2005

Key words: microencapsulation; structure-property relations; microcapsule; thermal property; expansion space

INTRODUCTION

Microcapsules are tiny particles that have core materials surrounded with wax, salts, clays, macromolecules, metals, etc.[1] The core materials can be drugs, paper coatings, enzymes, dyes, fragrant oils, solvents, salts, etc. Microcapsules using micro-particles as the core material were applied in electronic ink[2]; a microencapsulated healing agent was studied in automatic healing composites.[3] Microencapsulated phase change materials (MicroPCMs) have been studied as active or pumped coolants[4–7] in solar and nuclear heat storage systems for decades.[8,9] Microencapsulated water and phase change materials were studied in microclimate environmental controls.[10] MicroPCMs have also been used in thermoregulated fibers, fabrics, and foams recently.[11] Thermal stability of the microcapsule is crucial for the manufacture of thermoregulated fibers and fabrics.[12,13] Selecting an appropriate shell to improve the thermal stability of MicroPCMs has been studied for years.[14,15] Previous experimental results show that the highest thermal stable temperature of MicroPCMs with a melamine-urea-formaldehyde shell is approximately 200°C,[14] and the MicroPCMs expand and contract during the phase change process of the core with an order of magnitude of 10%.[6] Dimples are formed on the surface of the microcapsules after solidification of the core, which is attributed to the lower contract coefficient of the shell than that of the core. Moreover, SEM, TGA, and DSC experiments indicate that diffusion through the microcapsule shell in the heat treatment process is the major mode by which the capsules lost the core materials.[12,13] Therefore, adding expansion space inside microcapsules would increase their thermal stability.

EXPERIMENTAL

Materials

n-Octadecane (95 wt %) was purchased from Union Lab, Supplies Limited, Hong Kong. Cyclohexane, heptane, citric acid (98 wt %), and triethanolamine (95 wt %) were purchased from Tianjin Chemical Regents Inc. Melamine (98 wt %) and formaldehyde (37 wt %) were a product of Tianjin Resins Material Factory and Jinan Organic Chemical Plant, respectively. Emulsion of sodium salt of styrene-maleic anhydride copolymer (TA, solid content 19 wt %) was a product of Shanghai Leather Chemical Works.

TABLE I
Cyclohexane Content in Series A

Sample no.	A_0	A_1	A_2	A_3	A_4
Cyclohexane/ml	0.0	5.0	9.0	15.0	30.0
n-Octadecane/g	40.0	40.0	40.0	40.0	40.0
Cyclohexane content in the oil phase/vt%	0.0	8.8	15.0	22.6	36.8
TA/g	20.0	20.0	20.0	20.0	20.0

Fabrication of microcapsules

Prepolymer solution synthesis. The prepolymer solution was prepared by mixing 10.0 g of melamine, 19.5 mL of formaldehyde, and 20 mL of distilled water. Then the pH of the mixture was adjusted to 8.5 with triethanolamine and stirred at 70°C until it became clearly transparent.

Emulsion preparation. A predetermined weight of melted *n*-octadecane and a predetermined volume of cyclohexane as shown in Tables I and II were used as the oil phase. Different content of TA was used as the emulsifying agent. The temperature of the emulsion process was kept at below 45°C to decrease the evaporation of cyclohexane. The mixture of *n*-octadecane, cyclohexane, TA, and 250 mL of distilled water were emulsified with a homo mixer (Shanghai Xinrui Mechanical and Electrical Equipments Inc., MBE-100L) at a stirring rate of 9000 rpm for about 90 min. The pH of the emulsion was adjusted to 5.0 with 10 wt % solution of citric acid.

Microcapsule fabrication. The prepolymer solution was added into the emulsion in droplets while the emulsion was stirred at a rate of 500 r/min. After all of the prepolymer was added, it was continuously stirred for 120 min. Then the pH of the emulsion was adjusted with 50 wt % triethanolamine solution to 9.0, and the *in situ* polymerization was terminated. The emulsion was filtered after being cooled down to 25°C, and the microcapsules were washed with distilled water at 60°C until pH 7.0 was reached. The cyclohexane inside the microcapsules was removed after drying the microcapsules in an oven at 100°C until their weights were constant.

Microcapsule characterization

FTIR spectra of shell and samples were obtained by using spectrophotometer (Perkin–Elmer system 2000,

TABLE II
Cyclohexane Content in Series B

Sample no.	B_0	B_2	B_3	B_4	B_5
Cyclohexane/ml	0.0	10.3	15.4	20.6	25.7
n-Octadecane/g	40.0	32.0	28.0	24.0	20.0
Cyclohexane content in the oil phase/vt%	0.0	20.0	30.0	40.0	50.0
TA/g	30.0	30.0	30.0	30.0	30.0

TABLE III
Calculated Volume Expansion Ratio of *n*-Octadecane at Different Temperature

Temperature/°C	Melted density/ g · cm^{-3}	Volume expansion ratio/%
160	0.6978	11.3
200	0.6738	15.3
240	0.6498	19.6
280	0.6258	24.2
300	0.6138	26.6
315	0.6048	28.5

wave numbers from 400 to 4000 cm^{-1}) at room temperature.

The phase change properties of the heat-treated microcapsules were measured by using a differential scanning calorimeter (DSC, Perkin–Elmer DSC7) at a rate of 10°C/min in a nitrogen atmosphere from −20 to 100°C, waiting for 3 min, then cooling to −20°C at the same rate. The mass of the sample was 6.0 ± 1.0 mg. To indicate the thermal stability of the microcapsules, the average attenuation of enthalpy is estimated by comparing the enthalpy of the sample heat-treated at temperatures T and 100°C, that is:

$$\text{Average attenuation of } \Delta H = [(\Delta Hm$$

$$+ \Delta Hc \text{ of sample heat-treated at temperature T})/$$

$$(\Delta Hm + \Delta Hc \text{ of sample heat-treated at 100 °C}) - 1]$$

$$\times 100 \quad (1)$$

The surface morphology and diameter were obtained by using a scanning electronic microscope (SEM, Philips XL30). The heat-treated microcapsules at 100°C were placed on a stainless steel SEM stub and gold-coated. The diameters of the microcapsules were measured on the SEM photos. More than 200 microcapsules were counted. The diameter distribution was processed with Origin 6.0 Professional.

Microcapsules were placed on a glass flake and heat-treated on a heating stage at a temperature rising rate of 10°C/min. The samples were removed from the heating stage when the predetermined temperature was reached and subsequently cooled to room temperature. The surface morphology of the gold-coated heat-treated sample was measured by using SEM.

The microcapsules were heat-treated in an oven at a predetermined temperature for 30 min. The accuracy of the temperature was ± 5°C. The curve of the weight loss ratio of the microcapsules and temperature were measured by using a thermogravimetric analyzer (TGA, Japan Regaku Standard TG-DTA and NETZSCH STA 409 PC/PG) at a rate of 10°C/min in the atmosphere of air and nitrogen, respectively. The

TABLE IV
Phase Change Properties of Heat-Treated Microencapsulated *n*-Octadecane at Various Temperatures

Heat-treated temperature/°C	Tm/°C	ΔHm/J · g^{-1}	Tc/°C			ΔHc/J · g^{-1}	Average attenuation of ΔH/%
			α	β	γ		
100	36.1	166	25.1	20.4	12.0	165	0
120	36.2	164	25.5	20.1	10.8	165	−1
140	35.8	164	25.3	19.3	10.4	164	−1
160	34.9	156	25.4	18.5	11.3	156	−6
180	29.2	85	17.2	11.0	4.6	86	−48
200	26.1	48	16.3	7.7	2.5	50	−70
220	24.4	44	14.1	7.2	1.4	48	−72

Tm—peak temperature in the DSC heating curves, whose accuracy is less than ±0.5°C; ΔHm—melting enthalpy, whose accuracy is less than ±5%; Tc—peak temperature in the DSC cooling curves, whose accuracy is less than ±0.5°C. The crystallization process was divided into multiple peaks, α, β, and γ; ΔHc—crystallization enthalpy, whose accuracy is less than ±5%; Average attenuation of ΔH=[(ΔHm+ΔHc of sample heat-treated at temperature T)/(ΔHm+ΔHc of sample heat-treated at 100°C) − 1 × 100.

temperature of 5 wt % weight loss was recorded as the thermal stable temperature (T_d) of the microcapsules.

Microcapsules with 0.0, 30.0, and 50.0 vt% cyclohexane and their heat-treated samples at 160°C for 30min were conditioned in a silicagel desiccator for 96 h. 0.2 g dry microcapsules were mixed with 25 mL of heptane (density 0.685 g/cm^3) at 25°C for 16 h. The obtained mixture was measured by gas chromatography (GC, Shimadzu GC-9A, SE-52/25 mL, column temperature 200°C, detector temperature 320°C, air 0.5 kg/cm^2, H$_2$ 0.7 kg/cm^2, N$_2$ 50 mL/min).

Model of microcapsule containing expansion space

The crystal density of *n*-octadecane is 0.93 g/cm^3,[16] and the melted density at 28°C is 0.777 g/cm^3.[16] The volume change ratio of *n*-octadecane during the phase change process was estimated with eq. (2):

$$\text{Volume change ratio (\%)} = (\rho_c/\rho_a - 1) \times 100 \quad (2)$$

where ρ_c is the crystal density of *n*-octadecane and ρ_a is the melted density of *n*-octadecane at 28°C. The volume change ratio of *n*-octadecane during the phase change process is 19.7 vt% according to eq. (2). The

compression deformation corresponding to the yield point of the melamine-formaldehyde shell is approximately 19 ± 1%,[17] and the deformation at bursting was 70 ± 1%.[18] Therefore, the shell is not destroyed by the contraction of the core during the crystallization process. The temperature coefficient of density ($\Delta\rho/\Delta t$) in the liquid phase of normal paraffin with 21 to 30 carbon atoms is 6×10^{-4} g/(cm^3·°C).[19] The volume expansion ratios of *n*-octadecane at 100–315°C are estimated using these parameters,

$$\rho_t = \rho_0 - (T - 28) \times 0.0006 \quad (3)$$

$$\text{Vt (\%)} = (\rho_0/\rho_t - 1) \times 100 \quad (4)$$

where T is the temperature (°C); ρ_t, the density of melted *n*-octadecane at T; ρ_0, the amorphous density of *n*-octadecane at 28°C; and Vt, the volume expansion ratio of melted *n*-octadecane at temperature T compared with 28°C. The calculation results are listed in Table III. The boiling point of *n*-octadecane is approximately 315°C.[12] Therefore, the maximum volume expansion ratio from melting to boiling point is below 28.5 vt%. If the expansion space were equivalent to the
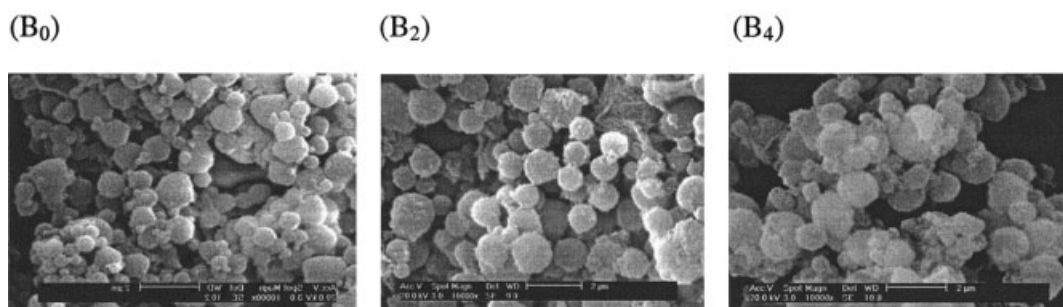

(B₀)   (B₂)   (B₄)

Figure 1 SEM micrographs of microcapsules using B₀—0.0 vt% cyclohexane; B₂—20.0 vt% cyclohexane; B₄—40.0 vt% cyclohexane.

TABLE V
Effects of Cyclohexane on Thermal Stability of MicroPCMs with Changed Core Weight*

| Sample no | D. R./μm | W.A.D./μm | Tm/°C | ΔHm/J.g^{-1} | Tc/°C | | | ΔHc/J.g^{-1} | T$_d$/°C | |
					α	β	γ		Air	N$_2$
A$_0$	0.2–2.6	1.2	34.9	160	25.4	18.6	11.4	158	166	187
A$_1$	0.2–2.2	1.1	36.5	159	25.7	21.0	11.0	156	171	199
A$_2$	0.2–1.8	1.0	36.0	156	25.4	20.9	11.6	156	170	200
A$_3$	0.2–1.4	0.9	35.3	156	25.4	21.0	11.8	152	169	206
A$_4$	0.2–1.4	0.8	33.3	153	23.0	16.5	9.7	150	230	268

* Diameter was obtained by measuring SEM micrographs; D.R.—diameter range; W.A.D.—weight-average diameter; All of the microcapsules were heat treated at 160°C for 30 min; T$_d$—the temperature of 5% weight loss in TGA curve, whose accuracy is ±5°C.

volume expansion ratio inside the microcapsule, the shell would not be destroyed by the expansion of the core in the temperature rising process.

Volatile solvent(s) is encapsulated in the microcapsule by adding solvent(s) in the oil phase during the emulsion process. Because of the difference of diffusion rate of the volatile solvent and *n*-octadecane, the solvent is removed by heat-treating the microcapsules in an oven for a period of time. As the contract coefficient of the shell is lower than that of *n*-octadecane, expansion space is formed inside the microcapsule.

RESULTS AND DISCUSSION

The phase change properties of microencapsulated *n*-octadecane (A$_0$) after being heat-treated at 100–220°C are listed in Table IV. When the microcapsule is heat-treated at temperatures higher than 180°C, the Tm, Tc, ΔHm, and ΔHc of the microcapsule decrease. The melting point of the 180°C heat-treated sample is significantly lower than that of the 160°C, and peak α disappears in the cooling curves. The average attenuation of enthalpy of the 180°C heat-treated sample is approximately 48% of the enthalpy of the 100°C heat-treated sample. The decrease of Tm, Tc, ΔHm, and ΔHc indicate the decomposition or evaporation of *n*-octadecane during the heat treatment process.[14]

SEM micrographs of samples using different contents of cyclohexane are shown in Figure 1. Their diameters are in the range of 0.2–1.8 μm. The surface of the microcapsule without cyclohexane is smooth. The dimple on the control microcapsule, which is attributed to the lower contract coefficient of the shell than that of the core, is small.[6] Some floccules and concaves appear on the surfaces of microcapsules with 20.0 vt% and 40.0 vt% cyclohexane. These concaves are mainly attributed to cyclohexane escaping from the microcapsules and the formation of expansion space, and the shrinkage of *n*-octadecane from the melting state to the crystal state.

The average diameters, phase change properties, and thermal stable temperatures of the microcapsules (series A) are listed in Table V. As the cyclohexane content increases, the measured average diameters of the microcapsules decrease. According to Akiyama and coworkers, the decrease of microcapsule diameter tends to reduce the thermal stability.[15] However, as shown in Table V, when the cyclohexane content in the oil phase increased from 8.8 to 22.6 vt%, both the temperatures of 5% weight loss in air and nitrogen atmosphere increase slightly. Furthermore, the thermal stable temperatures of microcapsules with 36.8 vt% cyclohexane in the air and nitrogen atmosphere are 230°C and 268°C, approximately 67°C and 81°C higher than that of microcapsules without cyclohexane, respectively.

The phase change properties of heat-treated microcapsules with 36.8 vt% cyclohexane at 100–220°C are listed in Table VI. When the heat treatment tempera-

TABLE VI
Phase Change Properties of Heat-Treated Microcapsules with 36.8 vt% Cyclohexane at Various Temperatures for 30min

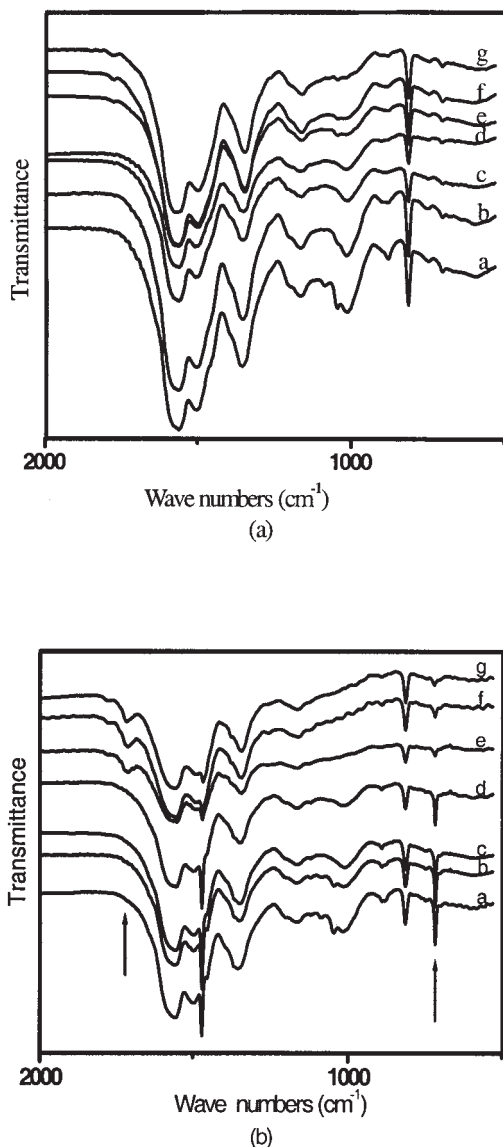| Heat-treated temperature/°C | Tm/°C | ΔHm/J · g^{-1} | Tc/°C | | | ΔHc/J · g^{-1} | attenuation of ΔH/% |
			α	β	γ		
100	33.3	153	23.0	16.5	9.7	−150	0
140	33.3	153	22.5	16.6	9.5	−149	−1
160	32.9	152	21.4	11.3	9.5	−152	0
180	28.0	94	22.6	10.2	—	−106	−34
200	26.5	95	20.0	2.9	—	−95	−37
220	26.8	98	18.8	1.9	—	−91	−38

Figure 2 FTIR spectra of heat-treated shell (a) and micro-capsule without cyclohexane (b) at a—Untreated; b—120°C; c—140°C; d—160°C; e—180°C; f—200°C; g—220°C.

significantly lower than the average attenuation of enthalpy of microcapsules without cyclohexane (48%, Table IV). The average attenuation of enthalpy of heat-treated microcapsules with 36.8 vt% cyclohexane stays almost stable when the temperature further increases. The concentration of cyclohexane in the microcapsule after polymerization is not known; however, the addition of cyclohexane in the oil phase indeed increases the thermal stability of the microcapsule.

The FTIR spectra of heat-treated shell and microcapsules with 36.8 vt% cyclohexane at different temperatures are shown in Figure 2. As the heat treatment temperature increases, the absorption peak in the spectra of the microcapsules at 718 cm^{-1}, which is attributed to rock vibration in the plane of $-CH_2-$, becomes weak. By contrast, a strong absorption peak at 1718 cm^{-1} that is attributed to the carboxyl group appears in the spectra of samples with heat-treated temperatures higher than 180°C. No corresponding peak strength change was observed on the spectra of shells heat-treated at 120–220°C, however. The appearance of this peak indicates that some of the $-CH_2-$ groups in *n*-octadecane were oxidized and turned into carboxyl groups.

The phase change properties and thermal stabilities of microcapsules with constant core weight (series B) are listed in Table VII. As the cyclohexane content increases, Tm and Tc are almost constant. The ΔHm and ΔHc decrease gradually with the increase of cyclohexane content, however. That is attributed to the increase of cyclohexane content inside the microcapsule. The "expansion space" is formed inside the microcapsules after removing the cyclohexane by heat treatment. The formation of expansion space as a concave on the shell of the microcapsule has been proved by the SEM micrographs in Figure 1. In this study, it is supposed that the average decrease of enthalpy was equivalent to the expansion space ratio inside the microcapsule. The expansion space ratio is 5 to 28%, significantly lower than the cyclohexane content in the oil phase. This may be explained by the evaporation of cyclohexane during the emulsion process.

The thermal stable temperatures of microcapsules with constant core weight in the atmosphere of air and nitrogen rise at the beginning, and then descend with

ture is higher than 180°C, the Tm and Tc decrease slightly, but the ΔHm and ΔHc decrease significantly. The average attenuation of enthalpy of the heat-treated microcapsule at 180°C is approximately 34%,

TABLE VII
Effects of Cyclohexane on Phase Change Properties and Thermal Stability of MicroPCMs with Constant Core Weight

Sample no	Tm/°C	ΔHm/J · g⁻¹	Tc/°C α	Tc/°C β	Tc/°C γ	ΔHc/J · g⁻¹	Average decrease of ΔH/%	T_d/°C Air	T_d/°C N₂
B_0	35.7	156	23.9	20.9	12.2	155	0	165	185
B_2	34.5	148	23.4	18.6	11.6	148	−5	169	207
B_3	33.9	133	23.2	18.1	12.1	133	−14	173	285
B_4	33.9	129	25.5	18.9	11.6	128	−17	215	289
B_5	33.5	113	23.6	16.9	12.2	111	−28	172	234

TABLE VIII
Phase Change Properties of Heat-Treated Microcapsules with 40.0 vt% Cyclohexane at Various Temperatures for 30min

Heat-treatment temperature/°C	Tm/°C	$\Delta Hm/J \cdot g^{-1}$	Tc/°C			$\Delta Hc/J \cdot g^{-1}$	Average attenuation of ΔH/%
			α	β	γ		
100	35.4	127	19.6	11.6	−0.5	−128	0
140	35.4	123	19.0	11.5	2.4	−125	−3
160	35.4	118	18.5	10.9	3.4	−120	−7
180	33.9	113	21.1	9.2	—	−118	−9
200	28.9	62	14.5	4.6	—	−66	−50
220	27.3	57	12.6	3.5	—	−60	−54

the increase of cyclohexane content. The thermal stable temperature of microcapsules fabricated with 40.0 vt% cyclohexane resulted in an "expansion space" value of 17%, while the thermal stable temperatures in the air and nitrogen are 215°C and 289°C, respectively. The expansion space of microcapsules with 50.0 vt% cyclohexane is 28%, higher than the 19% of elastic deformation of the melamine-formaldehyde shell of the microcapsules.[17] The thermal stable temperatures in the air and nitrogen of microcapsules with 28% expansion space are 172°C and 234°C, respectively. The plastic deformation of the shell after removing 28% of the cyclohexane from the microcapsules may cause the shell to be broken to some extent, therefore decreasing the thermal stability.

The phase change properties of heat-treated microcapsules with 40.0 vt% cyclohexane at 100–220°C are listed in Table VIII. When the heat treatment temperature is higher than 180°C, the Tm and Tc decrease

slightly, but ΔHm and ΔHc decrease significantly. The average attenuation of enthalpy of the heat-treated microcapsules with 40.0 vt% cyclohexane at 180°C is approximately 9%, significantly lower than the average attenuation of enthalpy of the microcapsules without cyclohexane (48% in Table IV) and lower than the average attenuation of enthalpy of microcapsules (series A, 34% in Table VI).

The SEM micrographs of heat-treated microcapsules with 40.0 vt% cyclohexane at various temperatures are shown in Figure 3. When the heat-treated temperature is below 200°C, the changes of morphology are not very significant. The shells of heat-treated samples at 220°C and 240°C shrink corresponding to the microcapsules losing *n*-octadecane in the cores, however.

The leakages of *n*-octadecane from microcapsules in heptane are listed in Table IX. The leakages of untreated and 160°C heat-treated samples are almost the
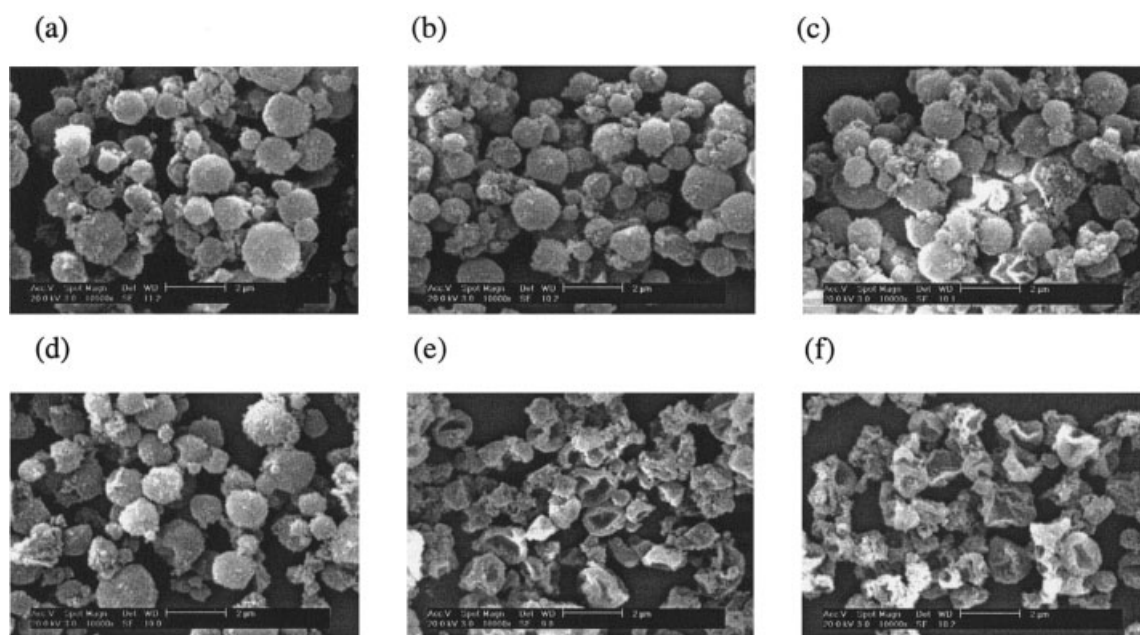

Figure 3 SEM micrographs of heat-treated microcapsules with 40.0 vt% cyclohexane to (a) 140°C; (b) 160°C; (c) 180°C; (d) 200°C; (e) 220°C; (f) 240°C.

TABLE IX
Leakage of *n*-Octadecane from Microcapsules in Heptane*

Sample no	Heat treatment	Wm/%	Ws/%	Wr/%
B_0	Untreated	1.168	0.53	71.0
	160°C/30min	1.168	0.53	71.4
B_3	160°C/30min	1.168	0.18	29.0
B_5	Untreated	1.168	0.05	8.6
	160°C/30min	1.168	0.04	7.5

* Wm—MicroPCMs content in heptane = $100 \times$ weight of microcapsules/weight of heptane; Ws—Leakage of *n*-octadecane in heptane was measured by GC; Wr—the ratio of spilled *n*-octadecane in all of the *n*-octadecane = $100 \times$ Ws $\times \Delta Hm_0/(Wm \times \Delta Hm)$, $\Delta Hm_0 = 244.68$ J · g−1.

same. Therefore, heat treatment that induces crosslinking of the shell has no effect on the permeability of microcapsules. As the cyclohexane content increases, the leakage of *n*-octadecane in heptane and the ratio of leaked *n*-octadecane in all of the *n*-octadecane decrease significantly. Adding cyclohexane in the oil phase makes the microcapsule contain expansion space after drying in the oven at 100°C. The existence of expansion space in the microcapsule allows the *n*-octadecane to expand and exerts lower pressure on the shell in the temperature rising process, therefore decreasing the permeability of *n*-octadecane and increasing the thermal stability of the microcapsules.

CONCLUSIONS

Microencapsulated *n*-octadecane containing 5.0–50.0 vt% of cyclohexane was synthesized by *in situ* polymerization of melamine-formaldehyde. By heat-treating the microcapsules in an oven at 100°C, the cyclohexane was removed and approximately 5–28 vt% of expansion space was formed inside the microcapsules. The existence of expansion space in the microcapsule allows the *n*-octadecane to expand in the temperature rising process and exerts lower pressure on the shell. Therefore, it decreases the permeability of *n*-octade-

cane and increases the thermal stability. The maximum thermal stable temperatures in air and nitrogen atmosphere are approximately 67°C and 102°C higher than that of the control sample, respectively.

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