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Thermal stability and permeability of microencapsulated *n*-octadecane and cyclohexane

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Abstract

Microencapsulated phase change materials (MicroPCMs) used as thermal insulating coating and fabrics are usually required to have a prominent thermal stability and a lower permeability. MicroPCMs with a prominent thermal stability and a lower permeability were fabricated by feeding an appropriate content of cyclohexane into *n*-octadecane followed by heat-treatment at a suitable condition. Microcapsules containing 18–19% reserved expandable space are synthesized at 30–40 wt.% cyclohexane in the oil phase, which have a highest thermal resistant temperature −270 °C, and a lower permeability, less than 1.2%. The weight loss of microcapsules is mainly attributed to the leakage of *n*-octadecane from some broken capsules, so improving their uniformity can efficiently enhance their thermal stability and lower the permeability.

Keywords: Microcapsules; Phase change material; Thermal stability; Permeability

1. Introduction

Microencapsulated phase change materials (MicroPCMs) have been widely studied since the late of 1970's [1]. They are used as active or pumped coolants [2–6], solar and nuclear heat storage systems [7], packed bed heat exchangers [8], thermal insulating coating [9] and fabrics [10–12]. Furthermore, MicroPCMs are hopefully employed in the microclimate environmental control on vegetation and seeds [13]. Super-cooling of MicroPCMs was investigated in the 1990's [14–16], and it was availably prevented by feeding paraffin of an appropriate contents into microcapsules with *n*-octadecane as a core in the early 2000's [17]. Thermal stability of MicroPCMs, however, was studied rarely up to now. Yoshioka obtained a microcapsule with a high thermal resistance in which the capsule shell comprised organopolysiloxane [18]. Tadaaki synthesized microcapsules with an aromatic polyamide shell that had prominent thermal stability by the interfacial polymerization [19]. In addition, a thermoexpandable microcapsule which showed a high thermal resistance after thermoexpansion were invented, and the microcapsule was composed of a polymer shell and an expandable agent such as propane therein [20–23]. However, there is still little information available on the thermal stability of microcapsules. Although permeability of MicroPCMs was characterized in ethyl alcohol by means of spectrophotometer [24], permeability of thermoexpandable microcapsules with phase change material and an expandable agent had never been investigated systemically. In this paper, thermal stability and permeability of microencapsulated *n*-octadecane and cyclohexane were studied in detail.

2. Experimental

2.1. Materials

Melamine (purity 97%, Tianjin Resin Factory) and formaldehyde (37 wt.% aqueous solution, A.R., Tianjin Chemical Reagent Factory) were used as shell-forming

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monomers; *n*-octadecane (purity 98%, Union Lab. Supplies Limited, Hong Kong) was used as core material. Cyclohexane (A.R., Tianjin Chemical Regents, Inc.) was used as an expandable agent. Petroleum ether (density 0.655 g ml^{-1}, A.R., Beijing Chemical Plant) was used as an extracting solvent. An emulsifier, TA (sodium salt of styrene–maleic anhydride copolymer, 19 wt.% aqueous solution) was obtained from Shanghai Leather Chemical Works.

2.2. Fabrication of microcapsules

An oil phase of *n*-octadecane (density 0.775 g cm^{-3}) and cyclohexane (density 0.775 g cm^{-3}) (Table 1) was prepared. An amount of 20 g of TA were dissolved in 300 ml of distilled water to form an emulsion. The resultant emulsion was heated to 45 °C. The oil phase was added to the emulsion, and the mixture was emulsified mechanically with a stirring speed of 8000 rpm for 90 min to form an oil-in-water system in a 1000 ml kettle equipped with circulated cooling water. The prepolymerization was carried out in a 250 ml three-neck round-bottomed flask equipped with a mechanical stirrer. A 19.5 ml of formaldehyde, 10 g of melamine and 20 ml of distilled water were added to the flask, respectively. The pH of the mixture was regulated to 8–9 with triethanolamine. The prepolymer was prepared at 70 °C with a stirring speed of 250 rpm until the mixture became transparent. The emulsion was shifted to 1000 ml three-neck round-bottomed flask after the pH was regulated to 4–5. Then the prepolymer was slowly added into the emulsion system to start in situ polymerization at 70 °C with a stirring speed of 100 rpm. After the prepolymer was added, the reaction was continued with a stirring speed of 600 rpm for 180 min. The resultant microcapsules were filtered and washed with distilled water at 80 °C for twice to remove remaining reactants and TA, and then dried in an oven at 100 °C.

2.3. Extraction experiment of microcapsules

A 2.0000 g (W_0) of dried microcapsules were sealed in a filter paper bag. The bag with microcapsules was dried for 3 h in an oven at 100 °C, cooled at a vacuum desiccator and weighed exactly (W_1). This bag was immerged in petroleum ether in the extraction vessel for 16 h, and then microcapsules were extracted by petroleum ether at 85 °C for 2 h (8 cycle h^{-1}). The bag was taken out, dried for 3 h in an oven at 100 °C, cooled at a vacuum desiccator and weighed exactly (W_2). The weight loss of microcapsules α_1 can be calculated by

$$\alpha_1 = \frac{W_1 - W_2}{W_0} \times 100\% \quad (1)$$

The weight loss of microcapsules α_2 can be also calculated approximately according to the measured enthalpies.

$$\alpha_2 \approx \frac{(|\Delta H_1| - |\Delta H_2|)}{|\Delta H_0|} \times 100\% \quad (2)$$

where $|\Delta H_1|$ and $|\Delta H_2|$ are the enthalpies of microcapsules without extraction and extracted microcapsules, respectively (J g^{-1}); $|\Delta H_0|$ is the melting enthalpy of *n*-octadecane, and here is about 245 J g^{-1}.

2.4. Characterization of the microcapsules

Microcapsules were dispersed uniformly on a small glass plate and then gold-coated. The morphology and dispersibility of microcapsules containing *n*-octadecane and cyclohexane were observed through a scanning electronic microscopy (SEM, PHILIPS, XL 30 ESEM).

Microcapsules were heat-treated in an oven at 100 °C till their constant weights and then heat-treated at 160 °C for 30 min. The thermal properties of microcapsules were measured using a differential scanning calorimetry (DSC, Perkin-Elmer, DSC7) at a heating or cooling rate of 10 °C min^{-1} under a nitrogen (N_2) atmosphere. The three heating-cooling cycles were carried out for each sample. The mass of the sample was 6 ± 1mg. The uncertainties of temperature and enthalpy measurements are ±0.5 °C and ±5%, respectively. The thermal resistant temperatures of microcapsules were obtained by using a thermogravimetry (TG, NETZSCH, STA409 PC/PG TG-DTA) at a heating or cooling rate of 10 °C min^{-1} under a nitrogen (N_2) atmosphere. Here, the thermal resistant temperature ($T_{0.05}$) is defined as the temperature at which 5% weight loss occurred.

The extracting solution, petroleum ether and *n*-octadecane were analyzed by a gas chromatography (GC, Shimadzu, GC-9A). An amount of 2 μl of sample was injected into the Chromatogram column (SE-54/30 m, column temperature T_{column} = 120 °C, temperature of injection port T_{INJ} = 280 °C) and detected by flame ionization detector (FID); the flow velocities of a carrier gas (N_2), an auxiliary gas (air) and a

Table 1
Cyclohexane contents and polymerization condition

Sample no.	Control	C_1	C_2	C_3	C_4	C_5
n-Octadecane (g)	40.0	32.0	28.0	24.0	20.0	16.0
Cyclohexane (g)	0	8.0	12.0	16.0	20.0	24.0
Cyclohexane contents in the oil phase (wt.%)	0	20.0	30.0	40.0	50.0	60.0
Melamine (g)	10.0					
Formaldehyde (37 wt.% solution) (ml)	19.5					
TA (19 wt.% solution) (g)	20.0					
Stirring speed (rpm)	8000					

combustion gas (H_2) were 50, 500 and 100 ml min^{-1}, respectively.

2.5. Calculation of reserved expandable space

It is assumed that cyclohexane in microcapsules can be removed completely from microcapsules by heat-treatment. Because the density of cyclohexane (0.777 g cm^{-3}) is equal to that of *n*-octadecane (0.777 g cm^{-3}) at the room temperature, the reserve expandable space (RES) of microcapsules can be calculated approximately by

$$\mathrm{RES} \approx \frac{1 - \Delta H_s}{\Delta H_{control}} \times 100\% \quad (3)$$

where $\Delta H_{control}$ and ΔH_s are the enthalpies of control and microcapsules with cyclohexane (C_1–C_5), respectively (J g^{-1}).

3. Results and discussion

3.1. Morphology of MicroPCMs with cyclohexane

The micrographs of microcapsules synthesized at 40 wt.% cyclohexane in the oil phase are shown in Fig. 1. The sizes of the microcapsules mainly range from 1 to 2 μm and their average diameter is approximately 1.3 μm. The sizes of the microcapsules are affected by the stirring rate in the emulsion process, emulsifier content and cyclohexane content in the oil phase, etc., and the results have been reported elsewhere [25]. Before heat-treated, microcapsules have smooth and compact surfaces, and have spherical profiles; however, a majority of microcapsules show large concaves after they are heat-treated at 160 °C for 30 min. For control capsules without cyclohexane after heat-treated at 160 °C for 30 min, only some tiny concaves are shown on several microcapsules due to the incomplete shrinkage of the capsule shell, thermal expandable melamine–formaldehyde resin. Therefore, these large concaves are mainly attributed to cyclohexane escaping from microcapsules and the shrinkage of *n*-octadecane transition from melting state to crystal state.

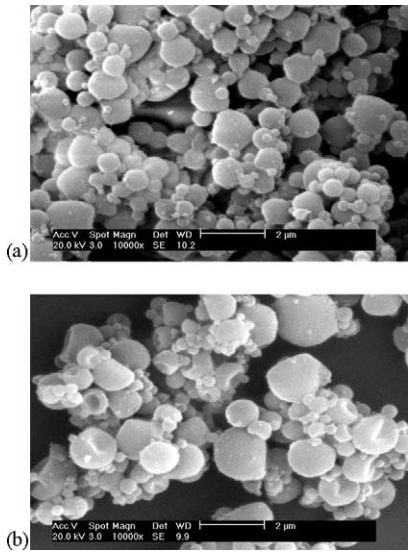

Fig. 1. Micrographs of microcapsules synthesized at 40 wt.% cyclohexane in the oil phase. (a) Untreated microcapsules; (b) microcapsules heat-treated at 160 °C for 30 min.

3.2. Relationship of cyclohexane contents and RES

Cyclohexane in microcapsules can be removed by heat-treatment since the boiling point is only 80.7 °C. Microcapsules are not considered to contain cyclohexane when they are heat-treated at 100 °C till the constant weight. The enthalpies measured by DSC for microcapsules heat-treated at 160 °C for 30 min are shown in Table 2. Their enthalpies are attributed to the phase transition of *n*-octadecane in microcapsules. It decreases with the increase of cyclohexane contents in the oil phase, which indicates that the cyclohexane contents in untreated microcapsules increase. The volume of cyclohexane removed from microcapsules is considered as RES of microcapsules, so RES increase as increasing the cyclohexane contents in the oil phase. However, the relationship between RES and the cyclohexane contents is not linear due to cyclohexane volatilization, TA loss and unencapsulated *n*-octadecane in the process of microcapsule fabrication. RES is 18 and 19% when the cyclohexane contents in the oil phase are 30 and 40 wt.%, respectively.

3.3. Thermal stability of microcapsules containing n-octadecane and cyclohexane

MicroPCMs with melamine–formaldehyde resin as a capsule shell had better be heat-treated at 160 °C for 30 min in order to improve their thermal stability [26]. Fig. 2 shows TG diagrams of the microcapsules synthesized at different cyclohexane contents in the oil phase after heat-treated for 30 min at 160 °C. Obviously, when cyclohexane contents in the oil phase exceed 30 wt.%, the inflexion near 200 °C disappears in the TG diagrams of microcapsules (C_2–C_5), which is beneficial to enhance the thermal stability of microcapsules.

Thermal resistant temperatures of microcapsules synthesized at different cyclohexane contents in the oil phase after heat-treated at 160 °C for 30 min are shown in Table 2. With

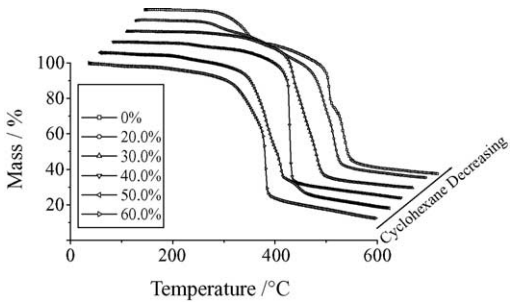

Fig. 2. TG diagrams of microcapsules synthesized at different cyclohexane contents in the oil phase after heat-treated at 160 °C for 30 min.

Table 2
Thermal properties and RES of microcapsules heat-treated at 160 °C for 30 min

Sample no.	Cyclohexane contents in the oil phase (wt.%)	Enthalpy (ΔH) (J g^{-1})	Reserve expandable space (RES) (%)	Thermal resistant temperature ($T_{0.05}$) (°C)
Control	0	166	0	190
C_1	20.0	138	17	210
C_2	30.0	136	18	280
C_3	40.0	135	19	270
C_4	50.0	108	35	240
C_5	60.0	102	39	230

the increase of cyclohexane in the oil phase, the thermal resistant temperatures first enhance and subsequently lower. The microcapsules with 18–19% RES, which were synthesized at 30–40 wt.% cyclohexane in the oil phase, possess the maximum thermal resistant temperature, about 270 °C. It demonstrates that the appropriate RES can improve the thermal stability of microcapsules.

3.4. Permeability of microcapsules

Determination of petroleum ether, *n*-octadecane and an extracting solution has been performed using gas chromatography (GC). Petroleum ether shows up at two retention times of 0.33 and 0.65 min, and *n*-octadecane shows up at 7.32 min. Besides the peaks characterized petroleum ether, the chromatogram given by the extracting solution of microcapsules synthesized at 20 wt.% cyclohexane in the oil phase highlights only one peak identical to the peak given by *n*-octadecane. So does in control or any other microcapsule with cyclohexane. It indicates microcapsules lose mainly *n*-octadecane after extracted by petroleum ether.

Permeability of microcapsules can be characterized by the weight loss of extracted microcapsules, which is calculated by a weight method or an enthalpy method. The weight loss of microcapsules synthesized at different cyclohexane contents in the oil phase is shown in Table 3. Calculated by either a weight method or an enthalpy method, the weight loss of extracted microcapsules with cyclohex-

Table 3
The weight loss of extracted microcapsules with cyclohexane

Sample no.	Cyclohexane contents in the oil phase (wt.%)	Weight method			Enthalpy method		
		M_1 (g)	M_2 (g)	α_1 (%)	$\lvert\Delta H_1\rvert$ (J g^{-1})	$\lvert\Delta H_2\rvert$ (J g^{-1})	α_2 (%)
Control	0	2.7456	2.5772	8.4	166	149	6.9
C_1	20.0	2.8502	2.8311	1.0	129	123	2.4
C_2	30.0	2.8109	2.8006	0.5	117	115	0.8
C_3	40.0	2.6174	2.6022	0.8	133	130	1.2
C_4	50.0	2.7915	2.7765	0.8	109	103	2.4

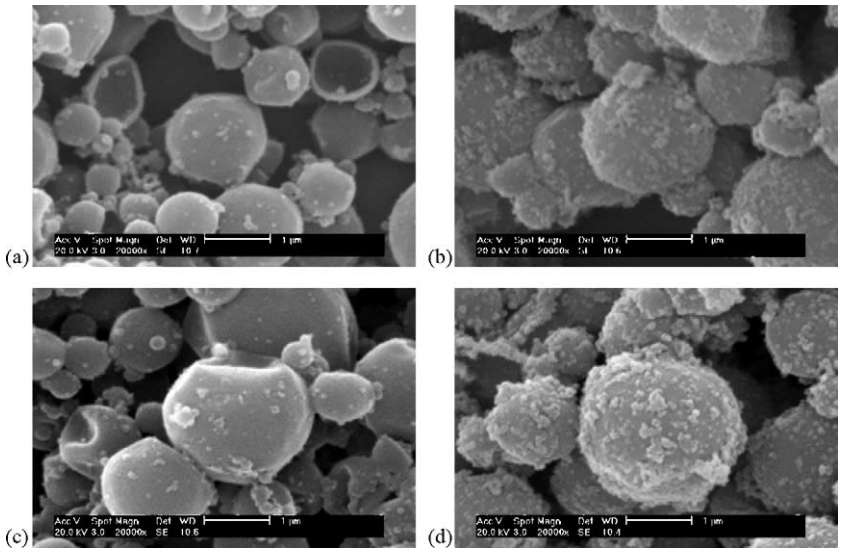

Fig. 3. Micrographs of control with (a) or without extraction (c); the microcapsules synthesized at 40 wt.% cyclohexane in the oil phase with (b) or without extraction (d).

ane is less than that of control. Especially, and the weight loss of microcapsules synthesized at 30–40 wt.% cyclohexane in the oil phase (C_2 and C_3) is extraordinarily little, just 0.5–0.8% (by a weight method) or 0.8–1.2% (by an enthalpy method). It indicates that these microcapsules have a prominent compactibility, which is corresponding to their thermal stability.

Fig. 3 shows micrographs of control and the extracted microcapsules synthesized at 40 wt.% cyclohexane in the oil phase. Several extracted microcapsules without cyclohexane are broken, as shown in Fig. 3(a). By contraries, the extracted microcapsules synthesized at 40 wt.% cyclohexane in the oil phase are hardly broken, shown in Fig. 3(b). In the micrographs of microcapsules without extraction, as shown in Fig. 3(c and d), however, neither microcapsule with cyclohexane nor control capsule is broken. Therefore, the weight loss of microcapsules is not mainly attributed to the exudation of *n*-octadecane from the integrated microcapsules, but mainly to the leakage of *n*-octadecane from some broken capsules. This phenomenon exists not only in the extraction experiment, but also in the thermogravimetric experiment. It demonstrates that improving the uniformity of microcapsules may become the efficient method to enhance their thermal stability and lower their permeability. The thermal stability of microcapsule can be enhanced by increase the stirring speed or the emulsifier content which increase the uniformity of microcapsules [25]. Microcapsules synthesized at 30–40 wt.% cyclohexane in the oil phase have a prominent thermal stability just because RES formed by cyclohexane escaping from microcapsules leads to enhance thermal stability of each microcapsule.

4. Conclusions

MicroPCMs with a prominent thermal stability and a lower permeability have been synthesized by adding cyclohexane of proper contents into the core. Cyclohexane contents in the oil phase have a dramatically effect on morphology, thermal stability and permeability of microcapsules after heat-treated. After microcapsules are heat-treated at 100 °C to their constant weight, and then heat-treated at 160 °C for 30 min, the reserved expandable space can be formed to enhance the thermal stability of microcapsules due to cyclohexane escaping completely from microcapsules. Microcapsules with 18–19% reserved expandable space are synthesized at 30–40 wt.% cyclohexane in the oil phase. These microcapsules have a highest thermal resistant temperature, about 270 °C, and their weight loss is less than 1.2% after they are immerged in petroleum ether for 16 h and then extracted by petroleum ether. Because the weight loss of microcapsules is mainly attributed to the leakage of *n*-octadecane from some broken capsules, improving the uniformity of microcapsules can be an efficient method to enhance their thermal stability and lower their permeability.

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