Preparation and Characterization of Polyurethane Microcapsules Containing *n*-Octadecane with Styrene-Maleic Anhydride as a Surfactant by Interfacial Polycondensation

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ABSTRACT: A series of polyurethane microcapsules containing a phase change material (PCM) of *n*-octadecane was successfully synthesized by an interfacial polymerization in aqueous styrene-maleic anhydride (SMA) dispersion with diethylene triamine (DETA) as a chain extender reacting with toluene-2,4-diisocyanate (TDI). The average diameter of microPCMs is in the range of 5–10 μm under the stirring speed of 3000–4000 rpm. Optical and SEM morphologies of microPCMs had ensured that the shell was regularly fabricated with the influence of SMA. FTIR results confirmed that the shell material was polyurethane and the SMA chains associated on core material reacted with TDI forming a part of shell material. The shell thickness was decreasing in the range of 0.31–0.55 μm with the molar ratio of DETA/TDI from 0.84 to 1.35 and the weight of core material increasing from 40 to 80% (wt %). By controlling the weight ratio of PCM as 40, 50, 60, 70, and 80% in microPCMs, it was found using DSC that the T_m and T_c of microPCMs were in the range of 29.8–31.0°C and 21.1–22.0°C and an obvious phase change had been achieved nearly the same temperature range of that of PCM. The results from release curves of microPCM samples prepared by 1.4, 1.7, and 2.0 g of SMA indicated the release properties were affected by the amount of the dispersant, which attributed to the emulsion effect and shell polymerization structure. The above results suggest that the shell structure of microPCMs can be controlled and the properties of microPCMs determined by shell will perform proper practical usage. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4996–5006, 2006

Key words: microcapsules; phase change material; styrene-maleic anhydride; polyurethane; interfacial polycondensation

INTRODUCTION

Microencapsulation is a widely accepted technique, and has been used in carbonless copying papers, liquid crystals, adhesives, cosmetics, insecticides, pharmaceutical, and medical applications.[1] Microcapsules have a core-shell structure to protect specific functional materials from or to release them into an outer phase for a long period of time.[2] Usually, the shell of microcapsules composes of natural or synthetic polymers with different morphological and physicochemical properties. In recent years, phase change materials (PCMs) have attracted ever-increasing attention since they can absorb or release large latent heat at their melting points as surrounding temperature increases or decreases. Thus, they can be potentially used in active or pumped coolants, solar and nuclear heat storage systems, and heat exchangers.[3] Although very high latent heat can be obtained, the bulk PCMs are not easy to handle in practical application. The recent advances of microcapsules containing PCMs (microPCMs) have provided an interesting alternative for using PCMs in the manufacture of thermoregulated fibers, fabrics, foams, and building materials.[4–8] To date, melamine-formaldehyde (MF) resin,[9,10] urea-formaldehyde (UF) resin,[11,12] and polyurethane (PU)[7,13,14] are usually selected as microcapsule shell materials for the PCMs protection. However, there may exist ineluctable remnant formaldehyde after forming the shell through polymerization, such as using MF and UF resins, which causes environmental and health problems. Generally speaking, it is hard to find an effective means to eliminate formaldehyde that is dissociative and continuously releasing from the products.

In this regard, PU is the promising polymer material in the field of microPCMs. Generally, a convenient technology is applied by polycondensating two complementary monomers to obtain PU-shell microcapsules. This method has been widely used in making flame-retarded, functional oil, and artificial organ PU-shell microcapsules.[15–19] It starts with making an emulsion of two immiscible phases (i.e., oil and water, O/W). Each phase contains a dissolved specific monomer that is able to react with the other monomer present in the other phase. In earlier studies of PU-shell microcapsules, (TDI),[7,16] hexamethylene diisocianate (HMDI)[20] and isophorone diisocyanate (IPDI)[21] are employed as the oil soluble monomers. To make the emulsion stable, certain surfactants or polymers are usually added to the continuous and/or the dispersed phase. Subsequently, these additives form an adsorption layer at the liquid-liquid interface, which may affect the polycondensation polymerization more or less.[20] After forming the nascent shell, the following polycondensation reaction is a diffusion-controlled process since it must occur at the O/W interfaces. As a result, capsule-like structured particles can BE formed with the particle size depending on the initial emulsion conditions and formation process parameters, such as emulsion rate, reaction condition, and molar ratio of monomers.

In addition, after the fabrication, the physical properties of microcapsules are determined basically by shell molecular structures, such as crosslinkage, chain segment and molecular weight. So it is very important to research the molecular structures for the shells following the special protected core material. Especially, it is necessary to evaluate the physicochemical properties of shell for the microPCMs that are absorbing and releasing latent heat and avoiding contamination caused by surrounding materials. The perfect shell structure will ensure the PCMs inside capsules for a long service time. In previous PU-shell microcapsule literatures, the molecular structures have been designed to achieve proper properties of shell for different core materials through the methods of regulation of surfactant, costabilizer, and water.[22–25] These additions are considered to cause side reaction between hydroxyl group (—OH) and isocyanate group (—OCN). For example, Hong[22] had prepared PU-shell microcapsules with different soft segments and evaluated the average particle size and distributions, morphologies, loading content, and release behavior of polyurethane particles. And Chang[23] claimed that the permeability properties of PU-shells could be attributed to a structural change of the microcapsule shell surface as the result of the interaction between the protective colloid and the dispersing medium. Also, it is found that the microPCMs release profiles are strongly dependent on the particle size distribution

and particle morphologies primarily depended on structure.[24]

Above all, there has been much attention on designing for proper PU-shell structures. However, there was litter information available focusing on the PU-shell microPCMs, especially relationship of shell structure and the stability and thermal properties of microPCMs. The aim of this research was to prepare a series of novel PU-shell microPCMs containing n-octadecane, which were fabricated by interfacial polycondensation between toluene-2,4-diisocyanate (TDI) and diethylene triamine (DETA). n-Octadecane is usually a PCM desirable for usage in thermal storage and releasing for its availability in a reasonable phase change temperature range and its large amount latent heat.[25] The latent heat of n-octadecane is 241.2 J/g and its melting point (T_m) is 28°C. Styrene maleic anhydride (SMA) copolymer solid was used as a nonionic dispersant in this preparation. The effect of the mass ratio of two monomers on the morphology and particle size distribution was evaluated by different characterization methods. And the influence of various parameters such as surfactant concentration and its ratio to core material were examined. We also investigated the effect of dispersant on the shell structure. To understand the thermal properities of microPCMs, the factors influencing thermal stability were examined with regard to the structure of MicroPCMs.

EXPERIMENTAL

Materials

The microcapsule shell was synthesized from TDI and DETA monomers, which were both purchased from Nankai University Special Reagent for forming the microcapsule shell by using an interfacial polymerization process. n-Octadecane (purity 98% minimum) was the core material as PCM purchased from Tianjin Chem. Reagent Co. Nonionic surfactant, SMA (Scripset®520, Hercules) was used as a dispersant. All the chemicals were of reagent grade and used without further purification.

Preparation of microcapsules

The concept of the microcapsules preparation method is based on the polycondensation reaction of hydrophilic and lipohilic monomers at the interface of an O/W submicronic emulsion. The fabrication procedure can be illustrated as shown in Figure 1. Initially, n-octadecane and lipophilic monomers TDI were dissolved in 20 mL of acetone as an oil phase. Different weight of SMA solid was dissolved in 40 mL of distilled water to adjust the pH value to 10 by using 0.1 mol/L NaOH solution to form a serious
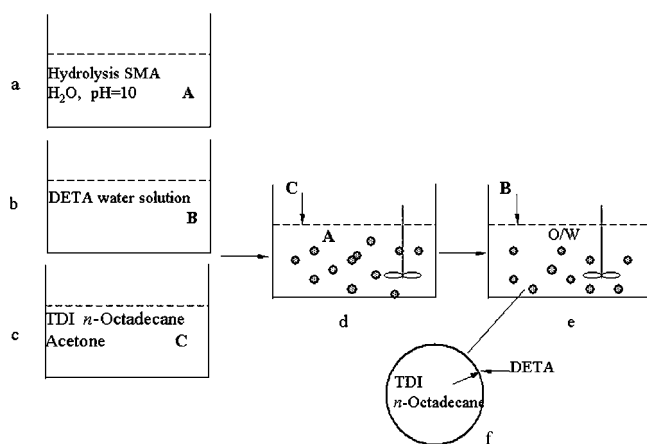
Figure 1 Schematic of the preparation of microcapsules containing *n*-Octadecane. (a) part A: mixture of water and hydrolysis SMA by 0.01 mol/L NaOH, pH = 10; (b) part B: DETA water solution; (c) part C: mixture of TDI, *n*-octadecane and acetone; (d) part C added into part A with stirring rate of 3000 rpm; (e) part B dipped into the O/W emulsion; (f) the interfacial polycondensation reaction between DETA and TDI at the O/W interface.

microPCMs. Then the oil phase was slowly dipped into the aqueous phase under magnetic stirring at a speed of 1000–4000 rpm for 2 min. Then a measured DETA was diluted in 20 mL of distilled water, and then slowly added into the emulsion system to ignite the interfacial polycondensation. The microcapsules were formed by progressive interfacial polycondensation reaction between DETA and TDI at the interface of hydrolysis SMA in water submicronic emulsion. After 2 h, the colloidal solution was then concentrated by evaporation under reduced pressure at 40°C to about 20 mL.

Characterization

After the microPCMs fabrication, 1 mL of the colloidal solution was extracted and spread on a stainless glass sheet (1 ×3 cm^2). Photographs of the microcapsules retained in emulsion were taken by an optical microscope (MiVnt Image analyze system, China). The morphologies of microPCMs dried in a vacuum oven at 40°C for 24 h were examined by means of a XL30 PHILIPS scanning electron microscopy (SEM). SEM experiments were performed at 10 kV after carefully coating with gold-palladium without cracking the shells. The size and diameter distribution was obtained by using a laser diameter distribution machine (Microtrac S3500). The thickness of shells can be achieved from the SEM images of cross section of microcapsules. The thickness of a microcapsule shell was calculated by a MiVnt Image analyze system automatically. At least 50 shells of each sample microcapsule were measured and the average data was recorded. The reagents and microcapsules

were analyzed on a Perkin-Elmer 1760-X FTIR spectrometer. The thermal analyses of microPCMs were carried out on a DSC analyzer (Perkin–Elmer, DSC7). The mass of the core material content was measured from the heat of fusion (ΔH_f) of PCM. Ten milligram of the dried microPCMs sample was tested with a heating rate of 5°C/min with nitrogen as the purging and protective gas. Each sample was analyzed at least twice and the average value was recorded. The thermal stability characterization was performed on a Dupont SDT-2960 TGA analyzer at a scanning rate of 5°C/min in a flow of 40 mL/min nitrogen. The penetration property of microcapsules was characterized in ethyl alcohol whose density was 0.97 g/mL by means of a 723PC spectrophotometer (Shanghai Cany Precision Instrument, China).

RESULTS AND DISCUSSION

Mechanism of SMA in PU-shell formation

Controlling the polymeric capsule morphology is of importance, since the permeation characteristics of capsule membranes is strongly dependent on the membrane structure. In earlier works, several surfactants have been used to obtain the stable oil phase particles. For example, NP-10 [poly (ethylene glycol) nonylphenyl] was used as a surfactant and the results showed that cetyl alcohol and poly (vinyl alcohol) made the side reaction between its —OH groups and the —NCO groups to form PU-shell.[7]

In this research, we select hydrolyzed SMA as a polymeric surfactant, which is soluble in water and sufficiently amphiphilic to be adsorbed by surfaces and interfaces, particularly by dispersed solid or liquid phases. The mechanism of this surfactant is that hydrolyzed SMA plays two important roles during the formation of microcapsules: dispersant and anionic polyelectrolyte.[11] Figure 2(a) depicts chemical structures of SMA and its hydrolyzed form. SMA molecules can hydrolyze in water by sodium hydroxide (NaOH) and form carboxyl (—OOH) groups. These hydrophilic polar groups, alternatively arranged along the SMA backbone chains, thus associate with water molecules and trimly cover the oil droplet surface with hydrophobic groups oriented into oil droplet and hydrophilic groups out of oil droplet. This orientation of molecular groups results in a relatively strong electron negative field on the surface of oil particles. Anionic polyelectrolyte hydrolyzed SMA has anionic carboxyl groups that can interact with positively charged particles below the ζ potential.[26]

Figure 2(b,d) shows the reaction scheme of shell formation process. The PU-shell is formed by reaction of DETA amine (—NH$_2$) groups with —NCO groups from TDI at the interface. Interfacial poly-
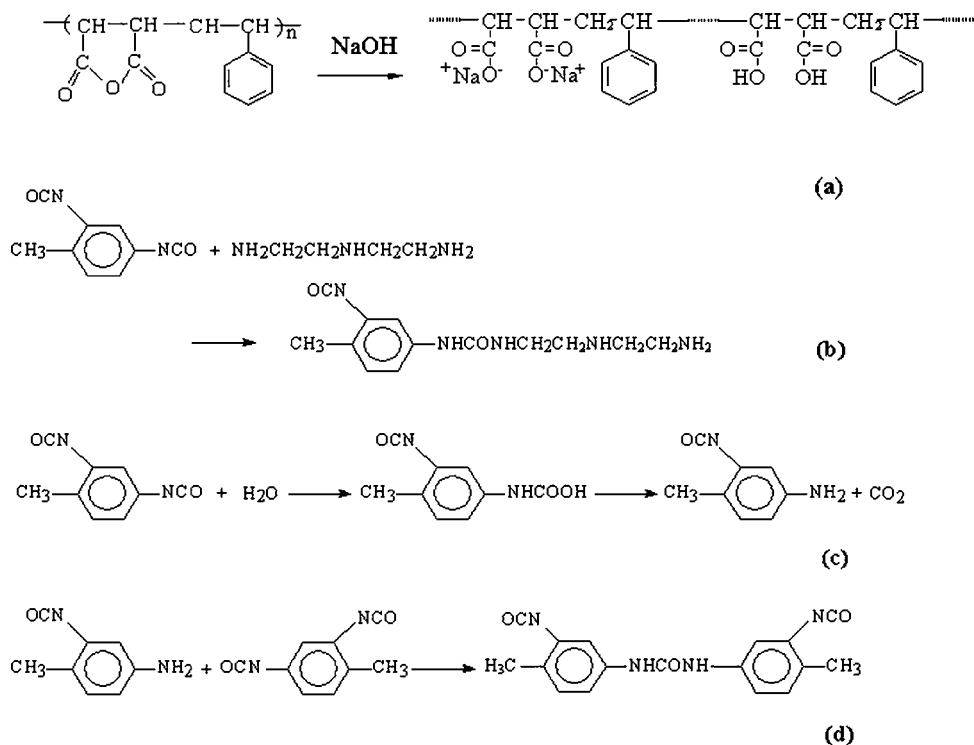
Figure 2 PU-shell forming reaction process, (a) chemical structures of styrene maleic anhydride (SMA) alternating copolymer and hydrolysis polymer; (b) reaction of the amine groups of DETA with isocyanate group of TDI; (c) reaction of isocyanate group of TDI with H_2O; (d) reaction of isocyanate group of TDI with $-NH_2$.

merization of TDI and DETA occurs rapidly at room temperature. On the other hand, TDI monomers can be hydrolyzed slowly at the interface to form $-NH_2$ groups, which react with TDI to form the PU microcapsule shell. The latter interfacial reaction occurs on the oil side of the interface.

Morphologies of microcapsules

Figure 3 shows optical microphotographs of microcapsules in different cases. Under rigorous stirring, the oil phase containing TDI can be quickly dispersed into the bulk if added dropwise [Fig. 3(a)]. The TDI monomer may take a side reaction with H_2O molecule; however, TDI will mainly react with DETA at the interfaces. Then, after covered by hydrolyzed SMA, the reaction between TDI and water may be greatly retarded without influencing the particle shape. In 2 h reaction, the PU-shell microcapsules formed have global shape and are well dispersed in water [Fig. 3(b)]. It can be reflected by image that the shell forming reaction is perfect as there is no obvious polymer filling in water.

Figure 4 shows the SEM morphologies of treated and dried microcapsules. In Figure 4(a), the final microcapsules are found to be piled with a thickness of about 100 µm formed by deposition mechanism. It is very interestingly noted that the PU-shell micro-

capsules are individually distributed without excessive conglutination among each other. In Figure 4(b), the surface of microcapsules is mostly smooth and the shape is regularly spherical with a diameter of about 5–10 µm. Some polymer filling the interstitials of the between microcapsules can be observed, possibly due to the incomplete encapsulation of the core material or the shell material could not absolutely cover the cores.

Particle size distribution

Figure 5 presents the particle diameter size distribution and cumulative distribution of the prepared microPCMs under various agitation rates. It is clear that the average diameter varies at different agitation rates from 1000 to 4000 rpm. The size of the particles, obtained at a stirring rate of 1000 rpm, has a wide bimodal distribution and the average particle size is below 10 µm with 70% cumulative distribution shown in Figure 5(a). The bimodal distribution still exists in the case of 2000 rpm. Contrastingly, the particle size distribution becomes narrow ranging from 1 to 20 µm and cumulative distribution is 100% under 20 µm. When the stirring speed is between 3000 and 4000 rpm, the average particle diameter of microPCMs turns to be 10 and 5 µm, respectively. In the meantime, the particle size distribution becomes
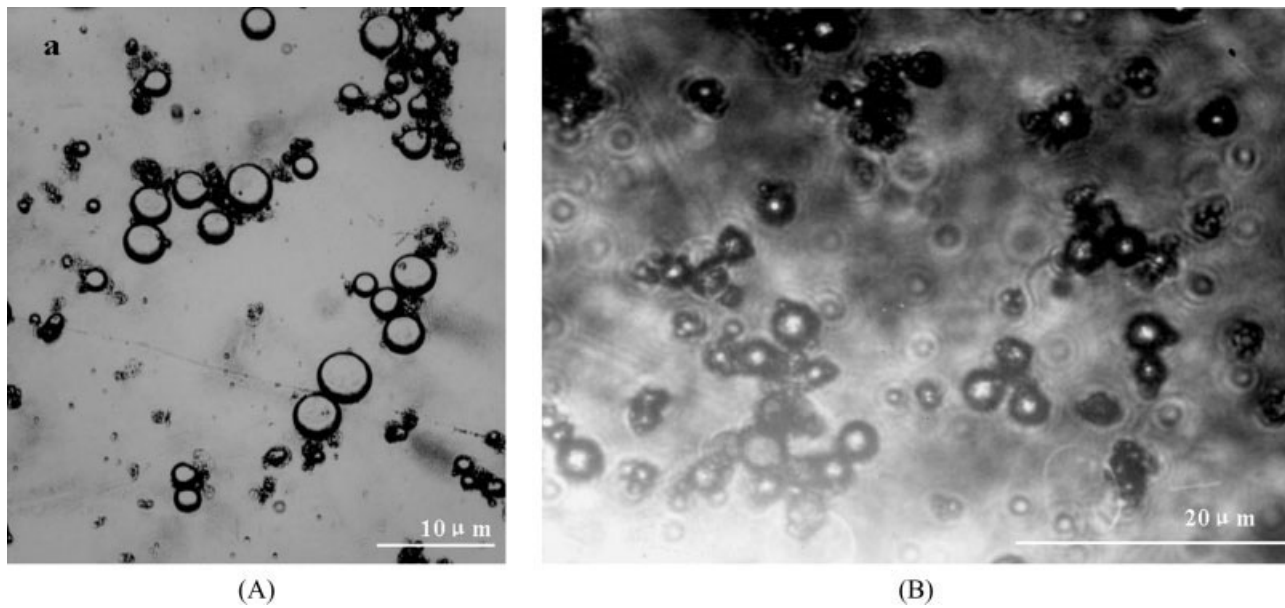
Figure 3 Optical microphotographs of microcapsules: (a) core material and dispersed by hydrolyzed SMA in water for 5 min; (b) Microcapsules in water.

narrow and also changes from bimodal mode to single mode. Generally, the particle size distribution of microcapsules is mainly controlled by the stirring speed. The above results indicate that 3000–4000 rpm is proper to achieve microcapsules with homogeneous diameter.

Structure of microcapsules

FTIR analysis of shell material enables to determine the chemical structure of the shell polymer containing chemical bonds. To achieve the pure PU-shell

material avoiding the influence of core material, the piled PU-shell microcapsules were blended in paraffin. After the blend was dried in room temperature, it was carefully cut to obtain the cross section by an ultramicrotome (RMC MT-7000). The half-shelled microcapsules were put into alcohol for removing PCM and paraffin. Then the shells were washed again with distilled water. In addition, it is very interesting that we can achieve the morphologies of the inside of the shell and the shell thickness after the pure shell material has been dried at 40°C for 2 h. Figure 6 shows the typical cross-sectional view
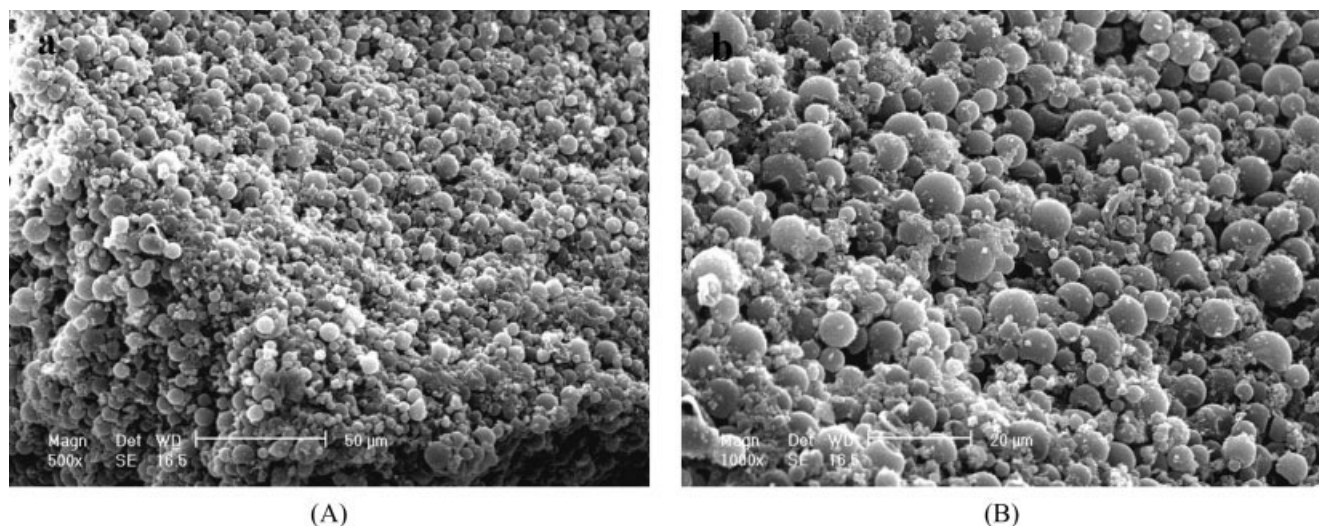

Figure 4 SEM photographs of single-layer microcapsules dried in a vacuum oven at 40°C for 24 h, (a) surface morphology of piled microcapsules, (b) the rough surface morphology of single-layer microcapsules.
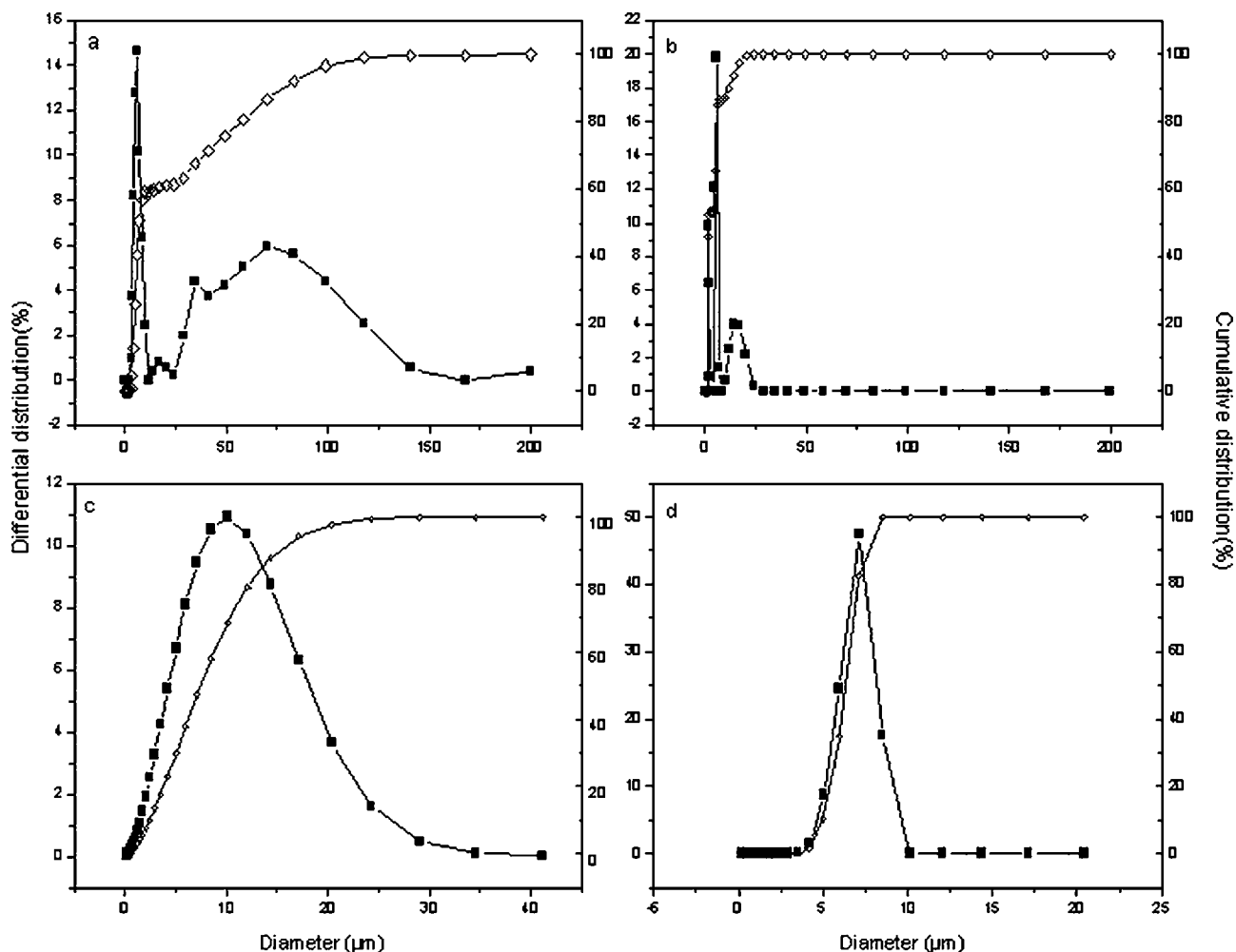
Figure 5 Microcapsule article size distribution, (■) Differential distribution (%) and (◇) Cumulative distribution (%) fabricated by emulsion rate of (a) 1000, (b) 2000, (c) 3000, (d) 4000 rpm.

of microcapsules. Obviously, it is seen that inside of the shell is rather smooth and the shell thickness about 0.3–0.5 μm.

In FTIR analysis study, it is necessary to understand the reality reaction degree of TDI. This information can be achieved from the core material in shells. The core material in shells was separated from half of the cross section as the above-mentioned method by a centrifugal machine (Biofuge[®] Pico Barkey, Germany). Figure 7(a) shows the FTIR spectrum of the core material. It has two absorption bands at 2275 cm^{-1} and 1573–1542 cm^{-1}, which are assigned to the unreacted —NCO group coming from TDI. Figure 7(a,b) both show an absorption band at 3471–3381 cm^{-1} for the N—H stretching vibration, which may result in the formation of the strong hydrogen bonds on the shell side. C—H stretching vibrations of aliphatic diamine are shown at 2868, 1660, and 1726 cm^{-1} for the C=O stretching of urethane. The sharp C—H stretching vibration for case (b) indicates that the SMA chain associated on core material could have reacted with TDI and

formed a part of shell material. These FTIR results have confirmed that the shell of microcapsules is polyurethane.
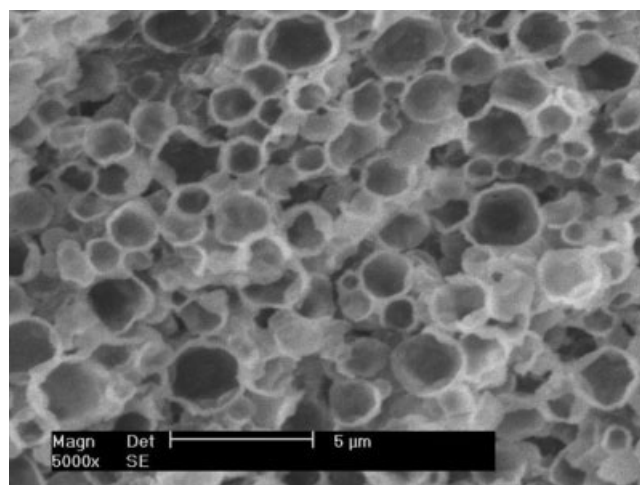

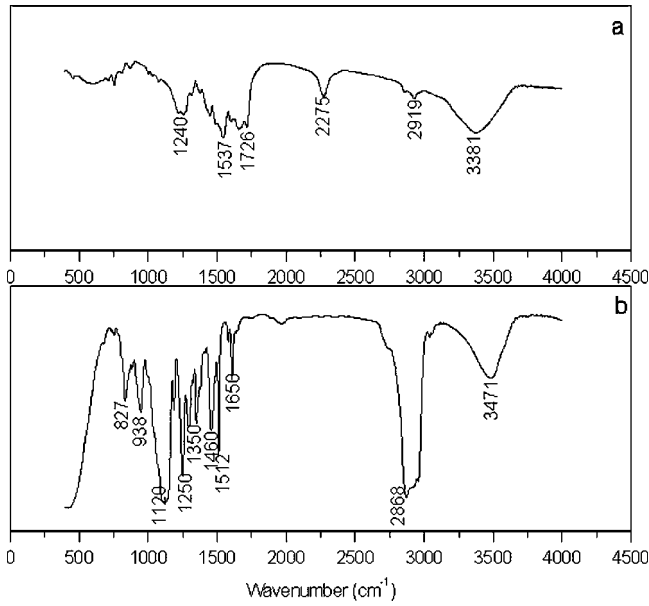**Figure 6** SEM image of cross section for the PU-shell microcapsules.

Figure 7 FTIR spectra of PU microcapsules shell, (a) 6.0 mg TDI without DETA and SMA, (b) 6.0 mg TDI, 4.0 mg DETA and 3.0 mg SMA.

Molar ratio of DETA/TDI effect on the properties of microcapsules

The physical properties of microcapsules including the shell thickness, average particle size, and dry weight have been studied for better understanding the effect of DETA/TDI molar ratio. It needs to be mentioned that the employed amount of surfactant is a factor influencing the colloidal stability because the size of the droplets, directly dispersed after primary equilibration, depends on the amount of surfactant in the emulsion progress. Thus, to research the influence of molar ratio of DETA/TDI from 0.84 to 1.35 on the properties of microcapsules, the same amount of 1.5 g SMA is applied with 3000 rpm emulsion rate to fabricate microPCMs containing 30 g n-octadecane.

Table I shows the properties of microcapsule samples coded D-1–D-10 prepared by various DETA/TDI molar ratios (6 g TDI). The shell thickness is decreasing in the range of 0.31–0.55μm with the weight of core material increasing from 40 to 80% (wt %). When the core particle size retains the same range mainly controlled by the same stirring rate of 3000 rpm, the more shell material leads to the larger shell thickness.

With the shell material weight increasing, the average particle size of microcapsules is changed from 5.0 to 5.2 μm following the increasing of shell thickness. Standard deviation (σ) is a characteristic parameter to describe the distribution degree of particle size, which may be expressed as follows:

$$X = \frac{1}{n}\sum_{i}^{n} x_i \qquad (1)$$

$$\sigma = \sqrt{\frac{\sum_{i}^{n}(x_i - X)^2}{n}} \qquad (2)$$

where x_i and X are the average particle size of a sample and the total average particle size of microPCMs, respectively. Table I shows that the distribution degree value is almost 28 for different molar ratios of DETA/TDI.

Another parameter, the dry weight (W_E), is considered to quantify the yield of microcapsules obtained. Ideally, W_E can be calculated as the following:

$$W_E = W_{SMA} + W_{TDI} + W_{DETA} \qquad (3)$$

Where W_{SMA}, W_{TDI}, and W_{DETA} are the weight of SMA, TDI, and DETA, respectively. The experimental dry weight of microcapsule samples are usually smaller than ideal W_E because of the loss of shell material and uncompleted encapsulation of core material. Thus, the dry weight may not really reflect the encapsulation ratio of core material. There is no

TABLE I
Different Molar Ratio of DETA/TDI Effect on the Properties of Microcapsules

Sample number	DETA (g)	TDI (g)	DETA/TDI (molar ratio)	SMA (g)	Shell thickness (μm)	Average particle size (μm)	Standard deviation (σ)	Theoretic dry weight of microcapsules (g)	Experimental dry weight of microcapsules (g)
D-1	3.0	6.0	0.84	1.5	0.31	5.0	28.63	12.0	10.01
D-2	3.2	6.0	0.90	1.5	0.31	5.1	28.28	12.2	11.02
D-3	3.4	6.0	0.95	1.5	0.32	5.1	27.22	12.4	11.00
D-4	3.6	6.0	1.01	1.5	0.35	5.1	27.40	12.6	11.04
D-5	3.8	6.0	1.07	1.5	0.35	5.1	28.28	12.8	11.24
D-6	4.0	6.0	1.12	1.5	0.40	5.1	28.28	13.0	11.20
D-7	4.2	6.0	1.18	1.5	0.45	5.2	28.58	13.2	12.04
D-8	4.4	6.0	1.24	1.5	0.50	5.2	28.02	13.4	12.40
D-9	4.6	6.0	1.30	1.5	0.54	5.2	28.44	13.6	12.51
D-10	4.8	6.0	1.35	1.5	0.55	5.2	28.28	13.8	12.52

Sample number	Shell thickness (μm)	*n*-Octadecane weight (%)	T_m (°C)	T_c (°C)	ΔH_f (J/g)	ΔH_c (J/g)	MicroPCMs efficiency (%)
P-40	0.36	40	31.0	21.1	115.0	110.4	93.4
P-50	0.35	50	30.8	20.9	113.4	110.0	92.3
P-60	0.30	60	30.5	21.4	110.0	111.2	91.7
P-70	0.30	70	30.5	22.0	117.5	111.0	94.7
P-80	0.24	80	29.8	22.0	117.5	111.4	94.9

large difference between the data of theoretic dry weight (12.0–13.8 g) and experimental dry weight of microcapsules (10.01–12.52 g) as shown in Table I. It indicates that DETA and TDI have high reactive ratio with fewer by-product with the DETA/TDI molar ratio increasing. And the core material may be largely capsulated without the variety of DETA/TDI molar ratios.

Thermal properties

The thermal properties of the microPCMs were evaluated using DSC and TGA. Table II presents the melting point (T_m), the crystallization temperature (T_c), the latent heat of fusion (ΔH_f), and the heat of crystallization (ΔH_c) of *n*-octadecane encapsulated in microcapsules measured using DSC. By controlling of the weight ratio of PCM as 40, 50, 60, 70, and 80% in microcapsules, a series of microPCMs were obtained coded as P-40, P-50, P-60, P-70, and P-80,

respectively. These samples were prepared by reacting PCM with DETA/TDI monomers (molar ratio of 1.01 : 1 DETA = 3.6 g) at emulsion rate of 3000 rpm. The DSC data show the P-40–P-80 samples have a T_m of 31.0, 30.8, 30.5, 30.5, 29.8°C and T_c of 21.1, 20.9, 21.4, 22.0, 22.0°C, respectively. Obviously, microPCMs have a phase change over the temperature range as that of the pure PCM, and ΔH_f and ΔH_c were accord with the weight ratio of the PCM in microPCMs. From these results, it can be concluded that the PU-microPCMs may have no significant effect on the melting behavior of *n*-octadecane.

Moreover, the PCM encapsulation ratio determines the efficiency of microPCMs, which can be calculated by means of heat flow in DSC. MicroPCMs efficiency is calculated by using the following formula:

$$\Phi = \frac{\Delta H_{f,\text{MicroPCMs}} + \Delta H_{c,\text{MicroPCMs}}}{\Delta H_{f,\text{PCM}} + \Delta H_{c,\text{PCM}}} \tag{4}$$
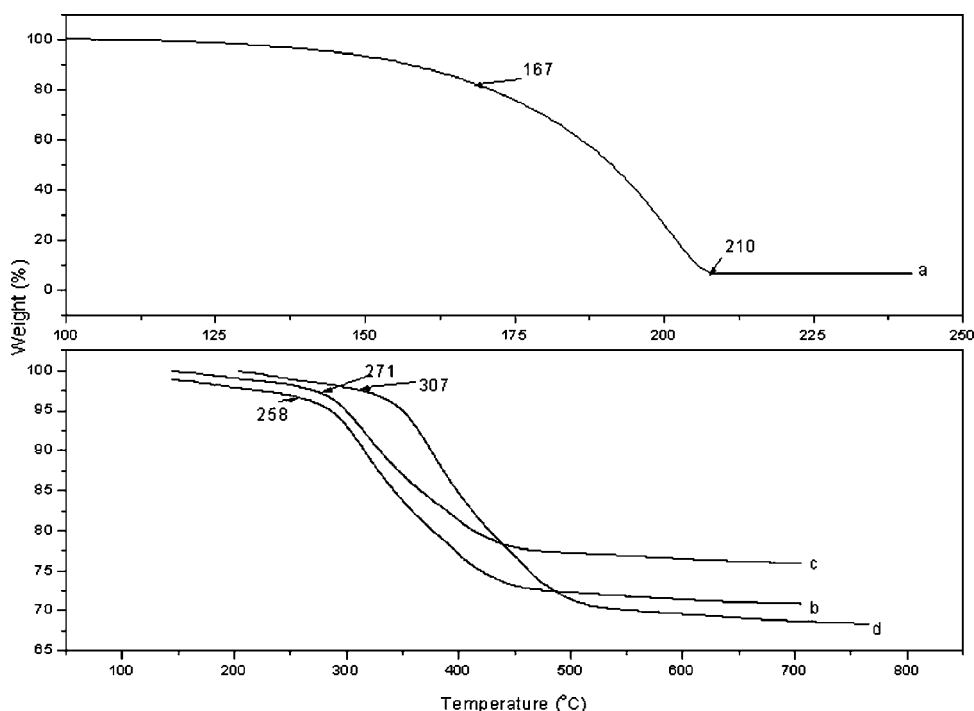

Figure 8 TGA curves of microcapsules containing *n*-octadecane with different content of SMA. (a) Pure PCM; (b) 1.4 g SMA, (c) 1.7 g SMA; (d) 2.0 g SMA.
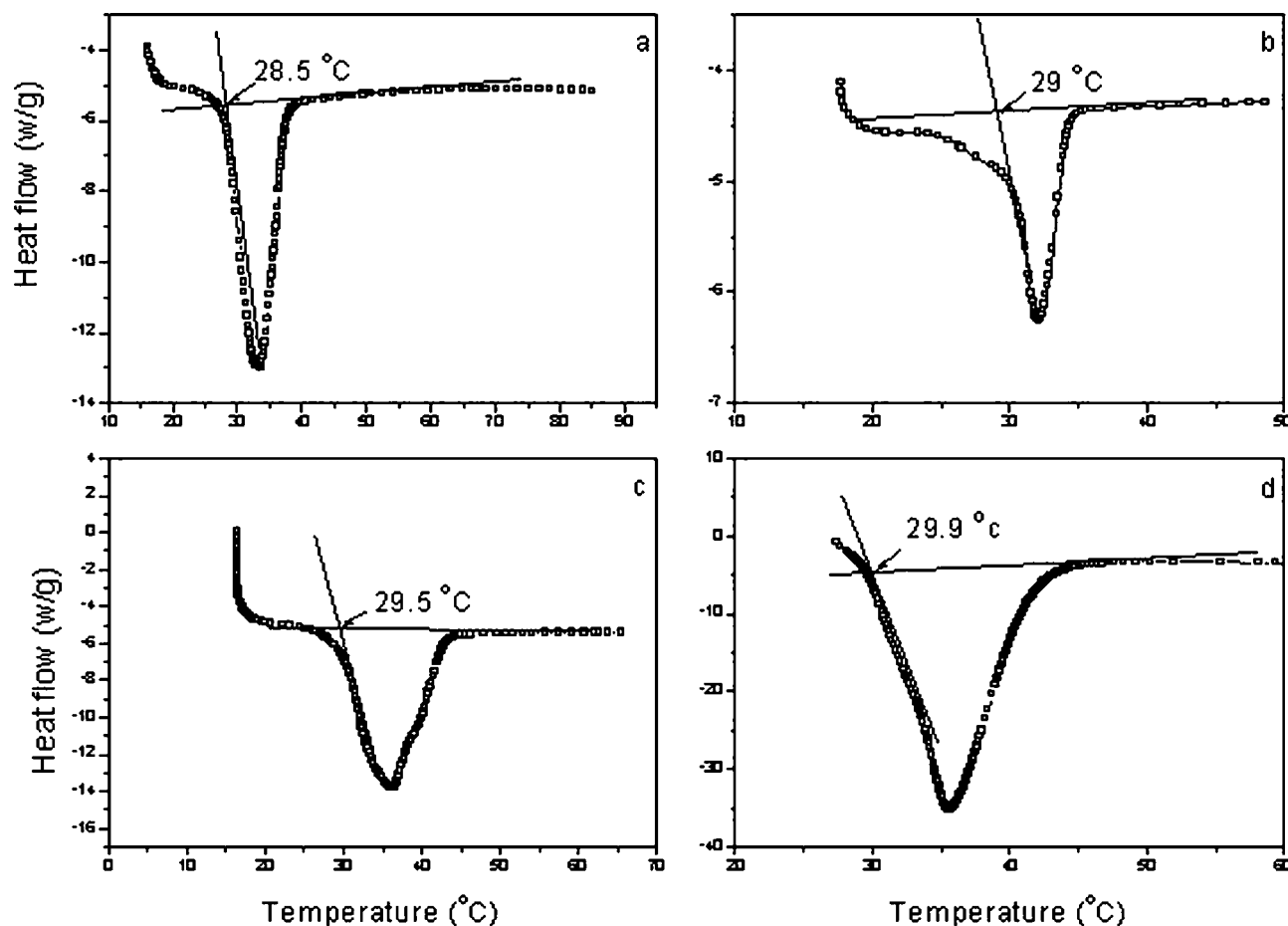
Figure 9 DSC curves of microcapsules containing 10 g *n*-octadecane fabricated with molar ratio DETA/TDI of 1.01, 3.6 g DETA and different content of 1.4, 1.6, 1.8, and 2.0 g SMA.

where $\Delta H_{f,\text{MicroPCMs}}$ and $\Delta H_{c,\text{MicroPCMs}}$ are the latent heat of fusion and the heat of crystallization of microPCMs; $\Delta H_{f,\text{PCM}}$ and $\Delta H_{c,\text{PCM}}$ are the latent heat of fusion and the heat of crystallization of PCM, respectively. According to formula (4), the efficiency of microPCMs P-40–P-80 is 93.4, 92.3, 91.7, 94.7, and 94.9%, respectively. The nearly same values indicate that the PU-shell do not affect the heat transmitting properties of pure PCM and the latent heat can be exchanged freely. Furthermore, it can be concluded that the PU-shell microPCMs has a high efficiency in storage and releasing heat.

Figure 8 shows the TGA curves of pure *n*-octadecane and microPCMs. The data are obtained by increasing the temperature at a rate of 5°C/min from room temperature to 700°C. In Figure 8(a), pure PCM starts to lose weight at approximately 167°C, and it completely loses its weight at 210°C. The TGA curve of pure PCM is sharp because it is composed of alkane molecules with a lower decompose temperature. Comparably, the TGA curve has two steps for encapsulated PCM and is quite different for vari-

ous SMA contents, as shown in Figure 8(b,d). The lost weight temperature are 258, 271, and 307°C for microPCMs fabricated with 1.4, 1.7, and 2.0 g SMA. The following conclusions can be drawn from these results. Firstly, it can be concluded that shells with seldom cracking have encapsulated the PCM. Otherwise, the microPCMs will have a nearly same decomposed temperature with bulk uncapsulated PCM out of shells or leaking from shells. Secondly, the microPCMs fabricated with 2.0 g SMA begins to lose weight at a higher temperature of 258°C, which suggest that the amount of SMA could significantly influence the structural compactness of microcapsules. Thirdly, it may be concluded that the PCM encapsulated ratio is increased from the first-step lost weight ratio of microPCMs.

Effect of amount of SMA on encapsulated ratio and release behavior

The encapsulated ratio and controlled release of the capsules are important physical properties influenc-
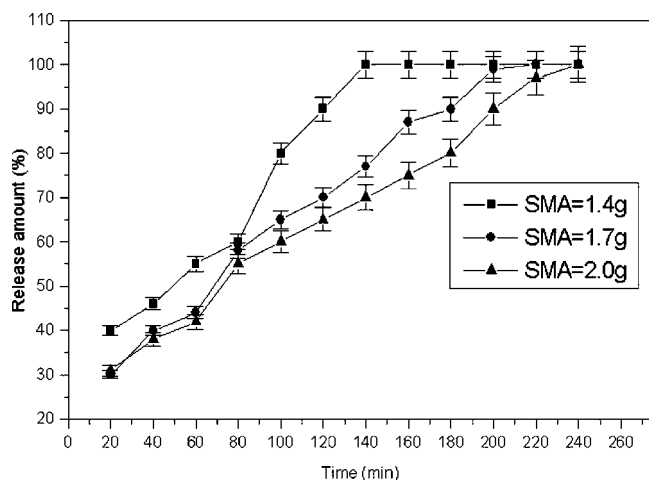
Figure 10 Release behavior of PU-shell microcapsules of different amount of SMA.

ing the microcapsules practical usage, which strongly depend on capsule shell structure.[26] In this study, the shell structure fabricated by interfacial polymerization on PCM particles is based on the first-step of the emulsion by using emulsification. So the amount of SMA will greatly influence the effect of emulsion and loading account. Also, controlling the polymer release behavior is important since the permeation characteristics of the capsule membranes can depend quite strongly on the membrane structure. DSC was used to measure the fusion heat ($\Delta H_{f,\text{MicroPCMs}}$) of microPCMs fabricated by using different SMA contents. The method to evaluate the encapsulated ratio is calculated by the afore mentioned formula (5):

$$L = \frac{H_{\text{microPCMS}}}{\Delta H_{f,\text{PCM}} \times m_{\text{PCM}}} \quad (5)$$

where $\Delta H_{f,\text{MicroPCMs}}$ is the calculated heat fusion of microPCMs by DSC, $\Delta H_{f,\text{PCM}}$ is latent heat of fusion of PCM, m_{PCM} is total weight of PCM in emulsion.

Figure 9 shows the DSC curves of four microPCM samples prepared with DETA/TDI (molar ratio of 1.01, 3.6 g DETA), 10 g n-octadecane with various weights of 1.4, 1.6, 1.8, and 2.0 g SMA. Apparently, it can be seen that their T_m is in the range of 29–29.9°C, which is nearly equal to the T_m of pure PCM. Also, $H_{\text{microPCMs}}$ value of microPCMs, calculated from the integral of the curves area using software Origin 6.0 Professional, increase with more increase of SMA, which is attributed to the increase in the encapsulation content by better emulsion effect.

Release profiles of n-octadecane from 50 g microcapsules were examined in 200 mL ethyl alcohol as an extraction solvent (density was 0.97 g/mL) at 200 rpm. The data of release amount (wt%) of the

n-octadecane was measured and conversed through transmittance of spectrophotometer. Figure 10 shows release carvers of microPCMs samples prepared by 1.4, 1.7, and 2.0 g of SMA. As shown in the profiles, there is an obvious influence of the different content SMA on microcapsule samples release behavior. A sample with less usage of SMA will bring the release rate of core material from PU-shell sharply increasing after the initial release on the capsules shell. Theses phenomena may be attributed to the emulsion effect and shell polymerization structure.

CONCLUSIONS

A series of PU-shell microPCMs containing n-octadecane is successfully prepared with particle size distribution properly controlled by the emulsion-stirring rate ranging between 1000–4000 rpm. FTIR results have confirmed that the PU-shell microcapsules are successfully fabricated by interfacial polymerization between TDI and DETA with SMA as a dispersant. Molar ratio of DETA/TDI is found to be a factor for the shell thickness and the dry weight of microcapsules. Thermal analysis results indicate that the PU-shell microPCMs samples fabricated by 3000 rpm emulsion rate with DETA/TDI molar ratio of 1.01 (DETA = 3.6 g) nearly do not affect the thermal transmitting properties of encapsulated PCM. Moreover, SMA influences the shell structure and its amount may be related to the microcapsule release properties.

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