

# Fabrication and Thermal Properties of MicroPCMs: Used Melamine-Formaldehyde Resin as Shell Material

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**ABSTRACT:** An in-situ polymerization process prepared a series of melamine formaldehyde (MF) microcapsules containing phase change material (PCM) as core material. The phase change temperature of this PCM was 24°C and its phase transition heat was 225.5 J/g. The microencapsulated phase change materials (MicroPCMs) were bedded in in-door-wall materials to store and release heat energy, which would economize heat energy and make the in-door condition comfortable. We investigated the structural formation mechanism by microscope and scanning electron microscopy (SEM). The superficial morphology measurements indicated the optimal shell material dropping rate 0.5 mL

min<sup>-1</sup>, double-shell, and temperature elevating speed 2°C/10 min. The results obtained in the present investigation were reasonably understood on the basis of getting determinate rigidity and compacted shell. Also, the observed results were used to control the mass of shell material to get desired thickness of shell. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1522–1528, 2006

**Key words:** microcapsule; in-situ polymerization; heat energy; phase change material; structure; melamine formaldehyde

## INTRODUCTION

Microcapsules are tiny particles that contain active agent or core material surrounded by a coating or shell.<sup>1</sup> The diameters of microcapsules are usually in the range of 1–1000 μm. Microencapsulation is a widely used technique, which have been used in carbonless copying paper, functional textiles, liquid crystals, adhesives, insecticides, cosmetics, food, spice, pharmaceutical, aquaculture and medical applications,<sup>2</sup> etc. The protective shell usually is a natural or a synthetic polymer, and the core ingredient can be a solid or a liquid material.

In recent years, much attention is focused on energy problems and many researchers have done the research and development. Phase change material (PCM) has been widely studied and applied for thermal energy storage.<sup>3–5</sup> As PCM can absorb, store, and release large amounts of latent heat over a defined temperature range while itself changes phase, it can be used in many fields. Microencapsulated phase change materials (MicroPCMs) have attracted more and more

attention since the 1990s.<sup>6</sup> MicroPCMs offer a measure to solve the supercool problem and interfacially combine with circumstance materials.<sup>7</sup> MicroPCMs have been synthesized with urea-formaldehyde, crosslinked nylon, melamine-formaldehyde (MF), gelatin-formaldehyde, and polyurethane<sup>6,8–14</sup> as shell materials, which are usually used at a temperature lower than 150°C. These MicroPCMs were used in functional fiber, solar energy utilize, heat energy transfers, agriculture, and building materials.<sup>3,9,10,15–21</sup>

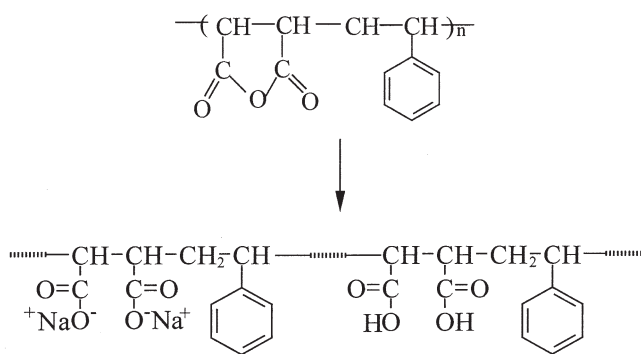
MicroPCMs should have appropriate properties, such as superficial morphology, diameter distribution, thermal prosperities, shell mechanical strength, shell thickness, penetration property, etc. Especially, for the microPCMs, the shell properties, including mechanical strength, shell thickness, and shell penetration, which affect stability of microcapsules, are the main characteristics needed in application.<sup>22</sup> Much microcapsule researches have focused on the preparation and characterization, or the functional application.

However, structural formation process of microPCMs has rarely been studied as a key problem. It is the basic of to getting determinate rigidity and compacted shell, by depositing shell on core particulates. Also, relationship of the process details of emulsification and core-shell structures is of great value, but few were reported.

Based on the afore-mentioned facts and motivated by this, the aim of this research is to synthesize micro-

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**Figure 1** Chemical structures of styrene maleic anhydride random copolymer and hydrolysis polymer.

capsules containing a composite PCMs for application in indoor wall to control temperature, which would save energy and make comfort indoors. The microPCMs were prepared by using in situ polymerization with prepolymer of MF. We investigated structural formation process of microPCMs by microscope and scanning electron microscopy (SEM) analysis for the cross sections of microcapsules, which revealed the systematic formations of deposit structures followed by the formation of core-shell structures. Moreover, the superficial morphology measurements indicated the optimal shell material dropping rate. Also different shell material dropping rate affected the thermal properties of microPCMs. The microPCMs preparation was interpreted in terms of the structural formation of the microcapsules.

## EXPERIMENTAL

### Materials

The prepolymer of melamine-formaldehyde (MF) was obtained from Shanghai JQ chemistry Ltd. Co. of China, whose solid content was  $50 \pm 2$  wt %. The composite PCMs that were prepared by Energy sources and Low emission Research Institute of Hebei

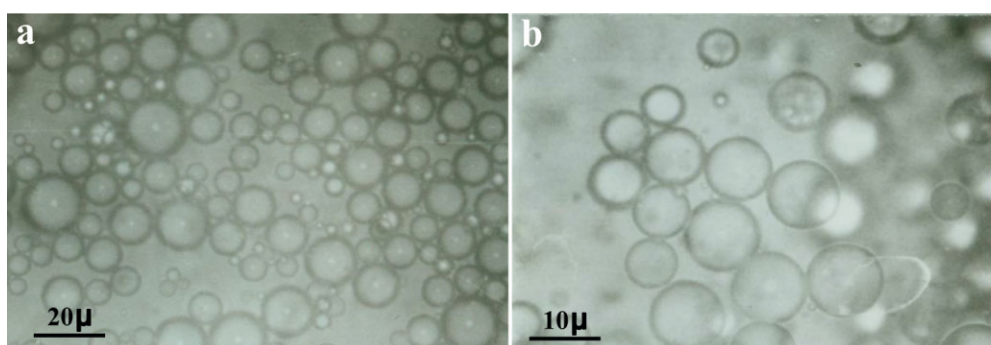
University of Technology was applied as core material. The temperature of solid-liquid phase change was  $24^\circ\text{C}$  and phase change quantity of heat was  $225.5$  J/g. Styrene maleic anhydride random copolymer solid (Scripte-520) was used as a dispersant. Nonionic surfactant, NP-10 [poly (ethylene glycol) nonylphenyl] obtained from Sigma Chemical was used as an emulsifier.

### Synthesis of microPCMs

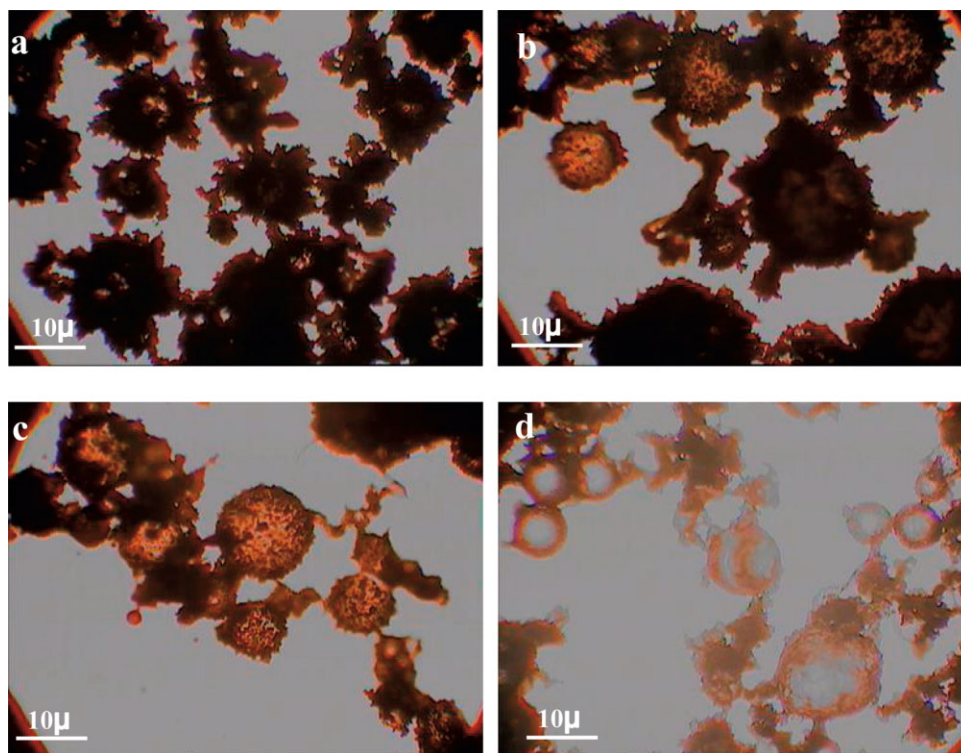
The encapsulation was carried out in a 500-mL three-neck round-bottomed flask equipped with a condenser and a tetrafluoroethylene mechanical stirrer. First, 10 g styrene-maleic anhydride, 0.2 g nonionic surfactant NP-10, as emulsifying agents, and 0.8 g NaOH were dissolved in 100 mL,  $50^\circ\text{C}$  water, whose pH value was 4–5 after 2 h. Thirty two grams core was added to the aqueous surfactant solution, and the mixture was emulsified mechanically under a vigorous stirring rate of 3000 r/min for 10 min using QSL high-speed disperse-machine (Shanghai Hongtai Ltd., Shanghai, China). Then dropped the emulsion in the bottle dipped in steady temperature flume and stirred at a speed of 1500 r/min, and dropped 16 g prepolymer at a rate of  $0.5$  mL  $\text{min}^{-1}$ . The shell formed after 1.5 h by heating slowly to temperature of  $60^\circ\text{C}$ . Then another 16 g prepolymer was dropped in bottle at the same dropping rate. Then the temperature elevated to  $75^\circ\text{C}$ . After polymerization for 1 h, temperature was dropped slowly at  $2^\circ\text{C}/\text{min}$  to room temperature. The resultant microcapsules were filtered and washed with water and dried in a vacuum oven.

### Testing

The method of studying the structural formation process of microPCMs is to observe the photos of emulsion, which batch extraction during the microcapsules formation process. One ml of the microcapsules in emulsion was paved on a stainless glass slice and



**Figure 2** Optical microphotographs of core material (PCM) emulsified by styrene-maleic anhydride at different stirring rate: (a) 2000 r/min; and (b) 2500 r/min. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 3** Optical microphotographs of microPCM, made by different shell material dropping rate of dropping all once (a),  $5 \text{ mL min}^{-1}$  (b),  $1 \text{ mL min}^{-1}$  (c), and  $0.5 \text{ mL min}^{-1}$  (d). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

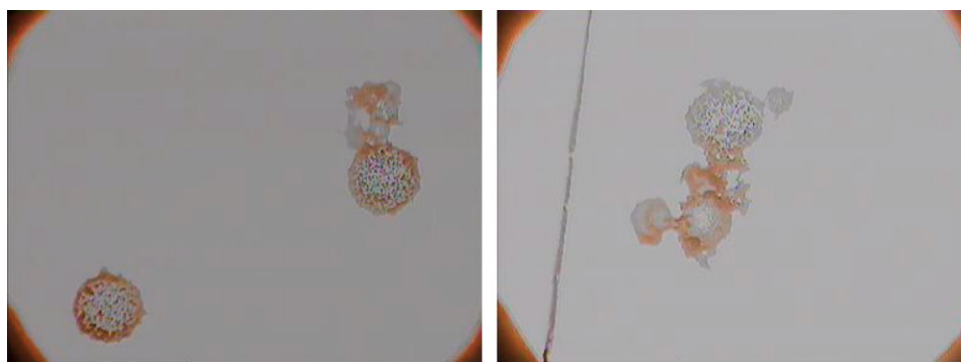
air-dried; photos of the morphology of the microcapsules were taken by optical microscope. After microcapsules were dried in a vacuum oven at  $40^\circ\text{C}$  for 24 h, the surface morphological structure was examined by means of an XL30 PHILIPS scanning electron microscopy (SEM). The thermal properties of the dry microcapsules were observed by using a differential scanning calorimeter (DSC, Perkin-Elmer, DSC7) at a rate of  $10^\circ\text{C}/\text{min}$  in a nitrogen atmosphere. FTIR transmittance of pure PCM, microcapsules, and the shell material were obtained by using a Perkin-Elmer

2000 spectrophotometer (wave-numbers  $400\text{--}4000 \text{ cm}^{-1}$ ).

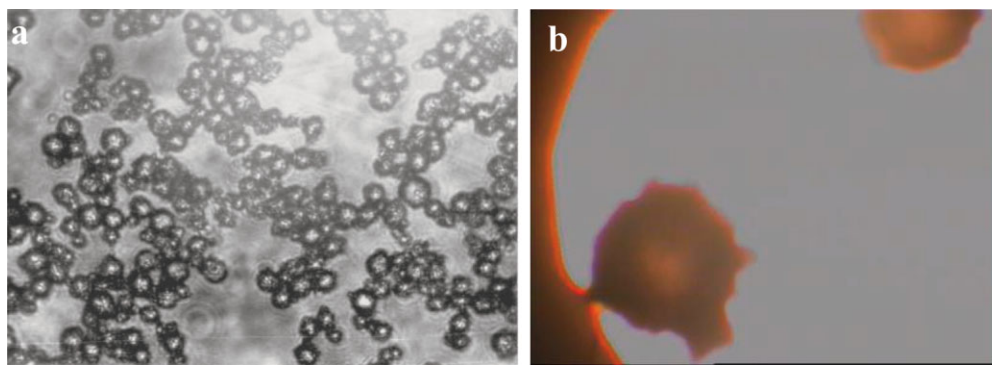
## RESULTS AND DISCUSSION

### Effect of emulsification

We have studied<sup>22</sup> that mass ratio of core and shell of MicroPCMs was 3 : 1 to ensure the microcapsules had good heat storage function. With the increase of ratio of core material, the compatibility decreased, whereas



**Figure 4** Optical microphotographs of microPCM, made by different temperature elevating speed of  $2^\circ\text{C}/10 \text{ min}$  (a) and  $5^\circ\text{C}/10 \text{ min}$  (b), at the same liquid shell material dropping rate of  $0.5 \text{ mL min}^{-1}$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 5** Optical microphotographs of double-shell microPCM, showing the microcapsules surface are smooth and compact. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

shell thickness decreased. Also though we studied the  $\zeta$  potential, we found that the optical mass of styrene-maleic anhydride was 15% (mass rate of core material). As a kind of polymer emulsion, its molecules will be hydrolysis by NaOH. The  $-\text{COO}$  group insert and directionally arrange on core surface. Prepolymer has affinity for these particulates by static. The reaction of microencapsulation took place under acid and heat effect on the surface of PCM particles of emulsion, which formed membrane of capsule. Figure 1. shows chemical structure of styrene-maleic anhydride.

The optical microphotographs of core material emulsified by styrene-maleic anhydride at different stirring rate are shown in Figure 2(a), 2000 r/min; and Figure 2(b), 2500 r/min. Apparently, we could control the average diameter of microcapsules by stirring speed. To ensure that the size distribution of microcapsules was narrow and shell had enough rigidity, we choose the stirring speed of 2500 r/min, got the 5–10  $\mu\text{m}$  average diameter microPCMs, just as shown in Figure 2(b).

### Analysis of structure formation

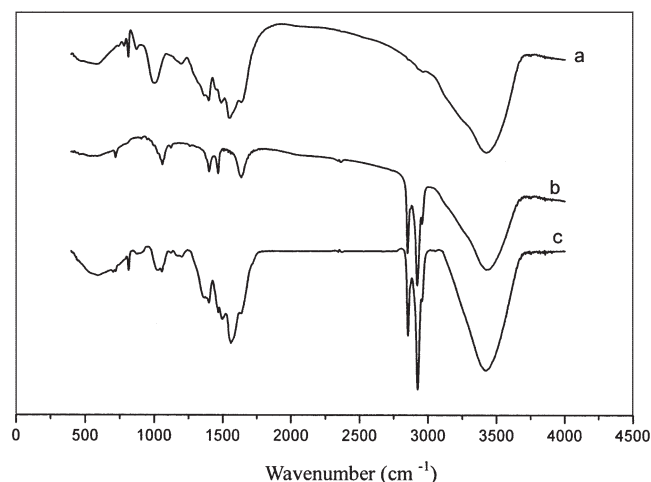
Optical microphotographs of microcapsules containing PCM emulsified 3000 r/min were taken on the study of structural formation process during polymerization in water. We studied the facts of shell material dropping rate, different dropping times, and different temperature elevating speed.

First, to get details of the process, we extracted one drop of the microcapsule dispersion 4 times each at the end of encapsulation after temperature elevating speed of  $10^\circ\text{C}/10$  min, which were placed on a glass plate and air-dried, photos of the shape of the microcapsules were taken by optical microscope. It was easy to obtain the diameter of the microcapsules and shell material deposit morphologies from the photographs. Figure 3 (a–d) shows the photographs of different shell material dropping rates of dropping all directly,  $5\text{ ml min}^{-1}$ ,  $1\text{ ml min}^{-1}$ , and  $0.5\text{ ml min}^{-1}$ , respectively. Dropping rate of shell material could control the morphology of micro-

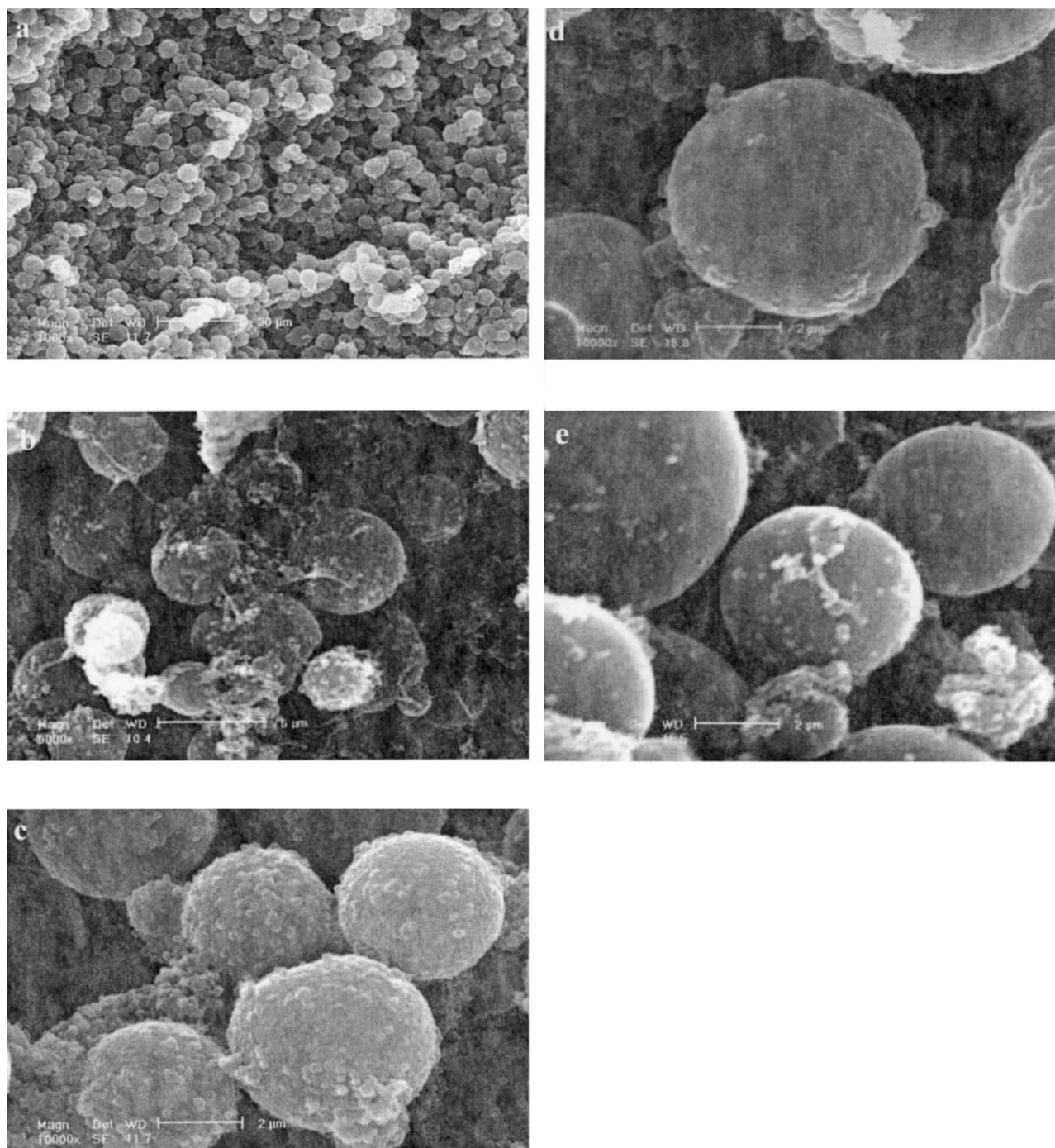
capsules. With the increase of dropping rate of shell material, the surface was rougher. Moreover, when the shell material dropped all once, as Figure 3(a) shows, the shell thickness was not regular and not accordant. The reason is that the prepolymer of MF will not capsule on core slowly and tightly at a rapid dropping rate. So at same core emulsify stirring speed and same mass ratio of core and shell material, different thicknesses of shell also get different penetration property. In this study, we hoped the MF shell to protect the PCM not affected by the outer materials and environment. That would make the core safe not stained and the microPCMs to have a long life in practice. Dropping rate of  $0.5\text{ mL min}^{-1}$  was perfect, as studied<sup>22</sup> earlier.

As the core material could not be encapsulated completely and the shell material also could not absolutely cover the core, in Figure 3(d) there was little polymers pilling between microcapsules

At the same liquid shell material dropping rate of  $0.5\text{ mL min}^{-1}$ , Figure 4 shows different temperature elevating speed of  $2^\circ\text{C}/10$  min, Figure 4(a) and  $5^\circ\text{C}/10$



**Figure 6** FTIR spectra of microPCMs and shell polymer, (a) shell polymer; (b) microcapsule; (c) pure PCM.

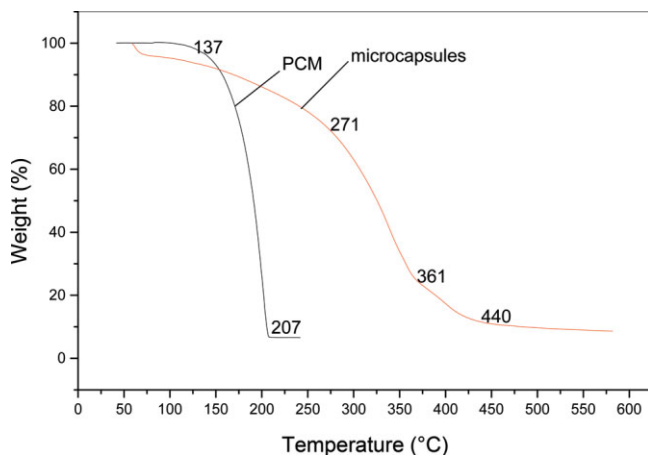


**Figure 7** The SEM photographs of double-shell microcapsules morphologies, dried in a vacuum oven at 40°C for 24 h. (a)  $\times 1000$ , (b)  $\times 5000$ , (c)–(e)  $\times 10,000$ .

min, Figure 4(b). The temperature elevated to 75°C from the shell material dropping over. After 1 h, the temperature dropped to room temperature and microcapsules solution was diluted. Figure 4(b) shows there was some polymers, which was not deposited covering microcapsules.

Above all, the shell material was dropped continuously and formed single-shell. The double-shell microPCMs were prepared by dropping shell material

twice. First, dropped the emulsion in the bottle dipped in steady temperature flume and stirred at a speed of 1500 r/min while 16 g prepolymer was added at a speed of 0.5 mL min<sup>-1</sup>. The shell formed after 1.5 h by elevating the temperature to 60°C slowly. Then another 16 g prepolymer was dropped in bottle at the same dropping rate. Then the temperature elevated to 75°C. As Figure 5 shows, the double-shell microcapsules surface are smooth and compact.



**Figure 8** TG curves of pure PCM and double-layer microPCMs. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

### IR spectra of microPCMs

FTIR spectra of pure PCM, melamine formaldehyde copolymer, and microencapsulated PCM are shown in Figure 6(a) shell prepolymer; b. microcapsule; c. pure PCM). The strong adsorption peaks of the pure PCM at  $1570\text{--}1236\text{ cm}^{-1}$  are associated with the aliphatic C—H stretching vibration. As PCM was capsulated, the peak disappeared. But core material cannot be capsulated completely, pure PCM adsorption peaks at  $2935\text{--}2852\text{ cm}^{-1}$  was still existing.

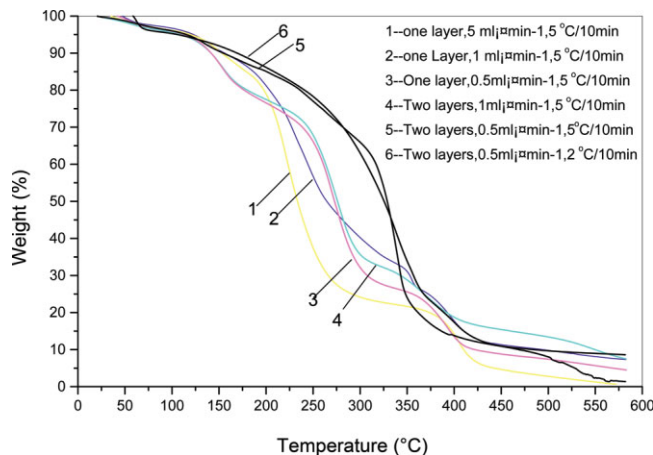
### Surface morphologies

After double-shell microcapsules were dried in a vacuum oven at  $40^\circ\text{C}$  for 24 h, SEM photographs reflected the surface morphologies. As Figure 7(a) ( $1000\times$ ) shows, the surface of most of the microcapsules was smooth and the shape was very regularly global, with average diameter of about  $5\ \mu\text{m}$ . The core material could not be encapsulated completely and the shell material also could not absolutely cover on the core, in Figure 7(b) ( $5000\times$ ), there was little polymer pilling between microcapsules. With the increase of dropping rate of shell material, Figure 7(c–e) ( $10,000\times$ ), the surface was rougher. This is probably because the prepolymer of MF will not capsule on core slowly and tightly at rapid dropping rate. The surface is smooth and shell protects the PCM not affected by the outer materials and environment.

### Thermal properties

The thermal characteristics of the microcapsules containing PCM are shown in Figures 8–10, using of TG and DSC.

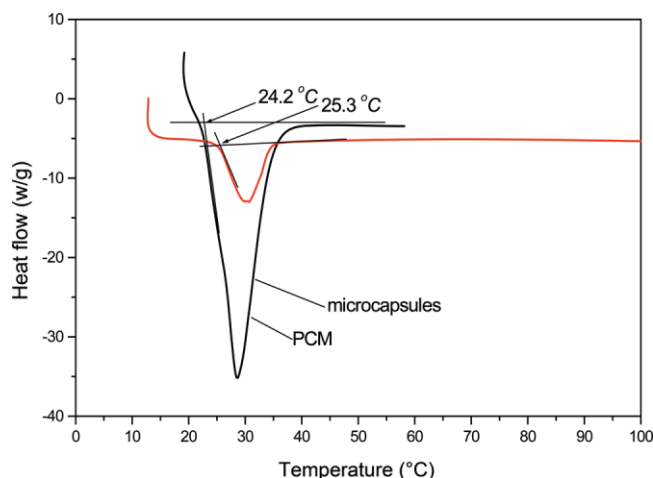
According to TG analysis presenting residual weight (%) of material by temperature change, the



**Figure 9** TG curves of microPCMs made by different layers, shell prepolymer dropping rate, and temperature elevating speed. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

microcapsules weight was decreased with increasing temperature. In Figure 8, pure PCM lost weight at the temperature of  $137^\circ\text{C}$  and lost completely at  $207^\circ\text{C}$ . The loss of weight was rapid. Contrastively, microcapsules containing PCM lost weight at the temperature of nearly  $100^\circ\text{C}$ . The lost weight was some water and other little molecule ingredients. From  $271^\circ\text{C}$ , because of the cracking of shell of microcapsules, the weight loss was more rapid and was lost completely at  $440^\circ\text{C}$ . Microcapsules weight loss ratio was lower than that of pure PCM obviously. Thus, it proved that the double-layer polymer shell protected the PCM.

To know the compactness of different encapsulation effect, we compared TG curves of the following microPCMs made by different layers, shell prepolymer dropping rate, and temperature elevating speed, such



**Figure 10** DSC curves of same weight of pure PCM and microPCMs. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

as that shown in Figure 9. Obviously, the best is the microcapsules of two layers,  $0.5 \text{ mL min}^{-1}$  dropping rate,  $2^\circ\text{C}/10 \text{ min}$  temperature elevating speed. It also can be found that the lost weight temperature of two layers microPCMs is higher than that of one layer. Thus, it proved that the double-layer polymer shell protected the PCM compacter.

Figure 10 shows DSC curves of same weight of pure PCM and microPCMs. As microcapsules were composed of PCM and shell material, phase change heat of microPCMs was less than that of pure PCM. Also, onset temperature of melting peak is 1 degree higher than that of pure PCM. The reason is that the shell polymer has a resistance of thermal transition. But it will not affect storage and release heat energy, which will economize heat energy and make the in-door condition comfortable.

### CONCLUSIONS

In this study, the factors influencing thermal stability were investigated in relationship with the shell structures of microPCMs. Thus, this study has demonstrated that the shell structures of microPCMs can be controlled by structural formation process, including shell material speed of  $0.5 \text{ mL min}^{-1}$ , temperature elevating speed of  $2^\circ\text{C}/10 \text{ min}$ , and shell material dropping twice. To get perfect thermal properties, surface morphologies and shell structure of microcapsules are crucial. The investigation by DSC shows the melt point of PCM in shell does not change and the heat transmit is obvious.

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