Preparation and Characterization of Double-MF Shell MicroPCMs Used in Building Materials

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ABSTRACT: A kind of double-shell heat energy storage microcapsule was prepared used melamine formaldehyde (MF) resin as shell material, and the properties of the microcapsules were investigated. A phase change material, with melt point of 24°C and phase transition heat of 225.5J/g, was used as core. The microcapsules would be used in indoor walls to regulate the temperature and save energy. The surface morphological structure was examined by means of scanning electron microscopy. The strength of the shell was evaluated through observing the surface change after pressure by means of scanning electron microscopy. The average diameter of the microcapsules was 5 μm $\sim$ 10 μm. Diameter of 1 μm $\sim$ 5 μm could also be obtained by using different stirring speeds. The globular surface was smooth and compact. The thickness was 0.5 μm $\sim$ 1 μm. Also, the melting point of the microcapsules was 24.7°C, nearly equal to the pure phase change material. The DSC results make clear that the polymer shell of the microcapsules does not influence the properties of the phase change material. It was also found that the avoiding penetration property of the double-shell microcapsules was better than that of single shell, and the average diameter of 5 μm was better than 1 μm. With the increase of ratio of the core material, the compactability decreased, and the shell thickness decreased. The mass ratio of core and shell was 3 : 1 to ensure that the microcapsules had good heat storage function. The measuring test showed that the microcapsules did not rupture at a pressure of 1.96 $\times$ 10^5 Pa. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1755–1762, 2005

Key words: microcapsules; in suit polymerization; phase change material; heat energy storage; penetration property

INTRODUCTION

Microcapsules have been used in carbonless copying paper, liquid crystals, adhesives, insecticides, cosmetics, pharmaceutical and medical applications, and so on. Microcapsules are particles composed of a shell, which protects the core material. 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, phase change material (PCM) has been studied and applied for thermal energy storage. As PCM can absorb, store, and release large amounts of latent heat over a defined temperature range while it itself changes phase, it can be used in many fields. Microcapsulation of PCM (microPCMs) offers a measure to solve the supercool problem and interfacially combine with circumstance materials. MicroPCMs have been used in functional fiber,[1,2] solar energy utilizers,[3] heat energy transfers,[4] agriculture,[5] and building materials.[6]

The objective of this study was to synthesize microcapsules containing a composite phase change material of size 5μm for application in indoor wall controlling temperature, which would save energy and make the indoors comfortable. The microPCMs were prepared by using in-suit polymerization with a prepolymer of melamine-formaldehyde, and we then characterized the properties such as shape, diameter distribution, thermal properties, strength, shell thickness, and penetration property.

EXPERIMENTAL

Materials

The prepolymer of melamine-formaldehyde was obtained from Shanghai JQ Chemistry Co. of China, with solid content of 50%. The composite phase change materials prepared by Energy Sources and Low Emission Research Institute of Hebei University of Technology were applied as the core material. The phase change temperature was 24°C, and the phase change quantity of heat was 225.5J/g. Styrene maleic anhydride copolymer solid (Scripte-520) was used as dispersant. Nonionic surfactant, NP-10 [poly (ethylene glycol) nonylphenyl] from Sigma Chemical, was used as an emulsifier.

Preparation of microcapsules

The encapsulation was carried out in a 500 mL three-neck round-bottomed flask equipped with a conden-

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sator and a tetrafluoroethylene mechanical stirrer. First, 10g of styrene-maleic anhydride and 0.8g of NaOH were dissolved in 100 mL, 50°C water, with pH value of 4 ~ 5 after 2h. 32g core was added to the aqueous surfactant solution, and the mixture was emulsified mechanically at a stirring rare of 2500 r/min for 10min using a QSL high-speed dispersemachine. Then the emulsion in the bottle was dipped in a steady temperature flume and stirred at a speed of 1500 r/min while 16g prepolymer was added dropwise at a speed of 0.5 mL min^{-1}. The shell formed after 1.5h by raising the temperature to 60°C slowly. Then another 16g prepolymer was dropped in the bottle at the same dropping speed. Then the temperature was elevated to 75°C. After 1h, the temperature dropped to atmospheric temperature. The resultant microcapsules were filtered and washed with water and dried in a vacuum oven.

Measurements

Photos of the shape of the microcapsules were taken by optical microscope. The surface morphological structure was examined by means of an XL30 PHILIPS scanning electron microscopy. The size and diameter distribution was obtained by using a POP (III) laser diameter distribution machine. The thermal properties of the microcapsules containing phase-change material were evaluated using differential scanning calorimetry (DSC, Dupont 2910) and the phase-change temperature of the microcapsules. The mass of the core material content was measured from the heat of fusion (ΔH_f) of the PCM. The microcapsules were buried in glutin and, by cutting the air-dried glutin to thin slices, we got the thickness of the shell of the microcapsules by SEM. The microcapsules were put into two pieces of glass and suffered press. The rigidity of the shell was evaluated through observing the surface change after pressure by means of scanning electron microscopy. The penetration property was characterized in ethyl alcohol with density of 0.97g/mL by means of a 722-spectrophotometer.

RESULTS AND DISCUSSION

Shape of the microcapsules

An optical microphotograph and SEM photographs of the microcapsules containing phase-change material are shown in Figure 1. The optical microphotograph was taken after polymerization in water. It shows that the diameter of the microcapsules is uniform. There is no conglutination between particles.

After the microcapsules were dried in a vacuum oven at 40°C for 24 h, the morphologies can be seen from the SEM photographs, shown in Figure 2. The surface of most of the microcapsules was smooth, and

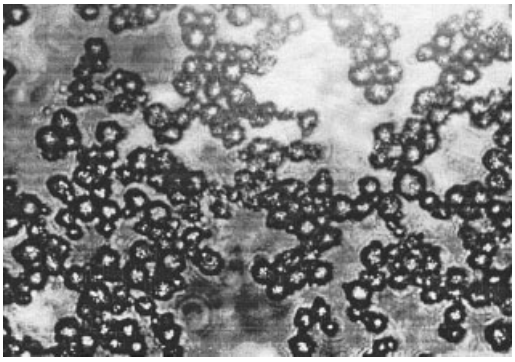

Figure 1 Optic micrograph of microPCMs in water.

the shape was very regularly global with diameter of about 5 μm, as Figures 2a and 2b show. As the core material could not have been encapsulated completely and the shell material also could not be absolutely covered on the cores, in Figure 2c there was a little polymer pilling between microcapsules.

Dropping the speed of the shell material could control the morphology of the microcapsules. Microcapsules, both magnified 20,000 SEM in Figures 2d and 2e, were gotten by dropping the speed of 1 mL · min^{-1} and 0.5 mL · min^{-1}. With the increase of dropping speed of the core material, the surface was rougher. The reason is probably that the prepolymer of melamine-formaldehyde will not capsulate on the core slowly and tightly at rapid dropping speed.

Diameter distribution

The particle diameter size distribution and cumulative distribution of the prepared melamine resin microcapsules containing phase change material are shown in Figure 3. The average diameter was different at different stirring rates. As curve 3a shows, the size of the particles was below 2 μm and cumulative distribution was 100% at 1.8 μm, by stirring at the rate of 3000 r/min. By contrast, the size of the particles was below 25 μm and cumulative distribution was 100% at 25 μm, by stirring at the rate of 1500 r/min in curve 3b. The size distribution of the prepared microcapsules in this study was narrow. Apparently, we could control the average diameter of the microcapsules by stirring speed. To ensure that the microcapsules had enough shell rigidity, we closed the stirring speed of 2500 r/min, and got the 5 μm ~ 10 μm average diameter microPCMs just as Figure 3c shows.

Thermal characteristics of the microcapsules

The thermal characteristics of the microcapsules containing phase change material are shown in Figures 4 and 5 by use of TG and DSC. According to TG analysis

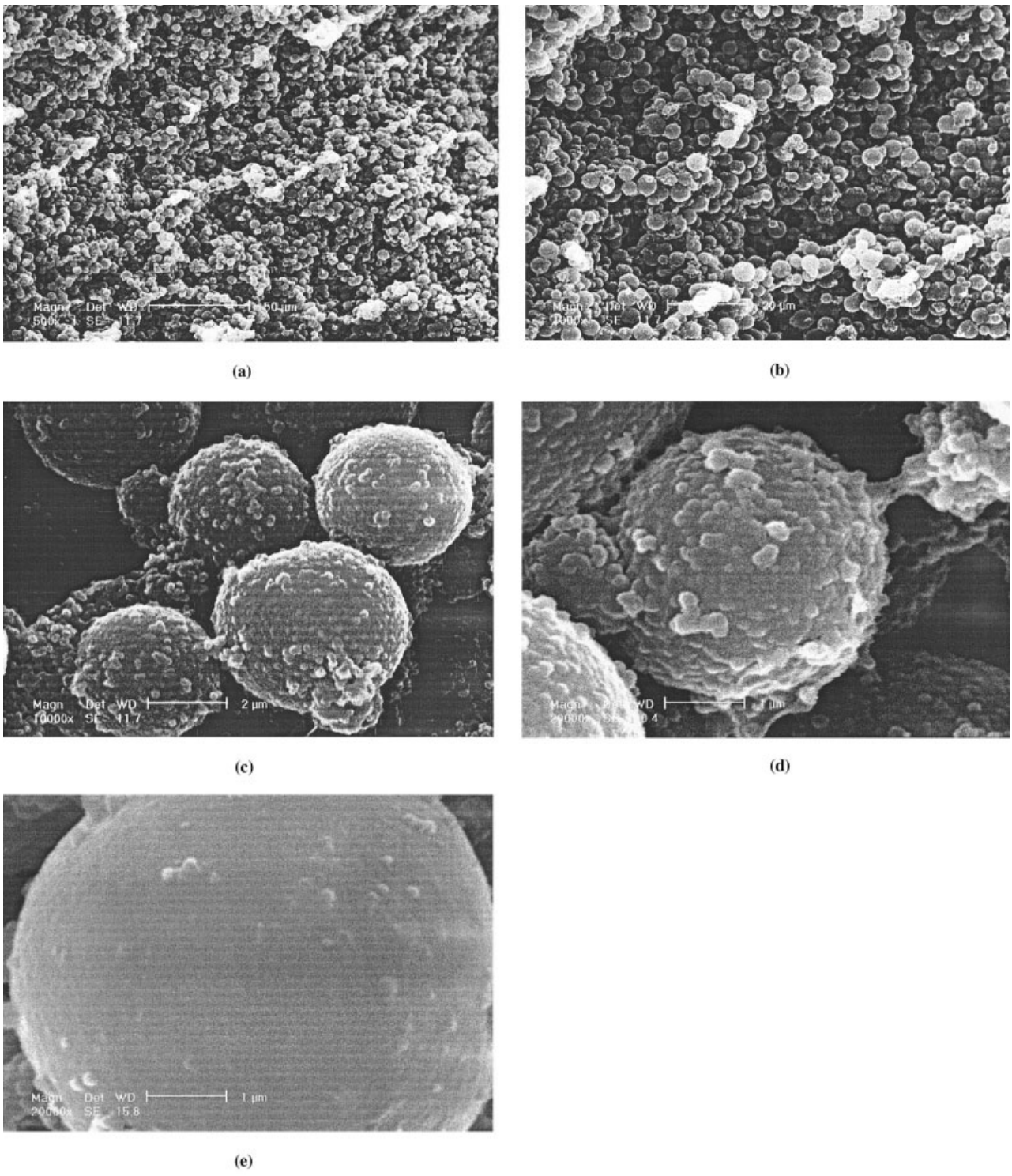

Figure 2 SEM micrographs of surface of microcapsules.

presenting residual weight (%) of material by temperature change, the microcapsules' weight was decreased with increasing temperature. Pure phase change material lost weight at the temperature of 137°C and was lost completely at 207°C. The loss of weight was rapid. By contrast, microcapsules containing phase change material lost weight at the temperature of nearly 100°C. The lost weight was some water and other little molecule ingredients. From 271°C, because of the cracking of the shell of the microcapsules, the weight loss was more rapid and was lost completely at 440°C. The microcapsules' weight loss ratio was lower than that of pure phase change material, obviously. Thus, it proved that the double-

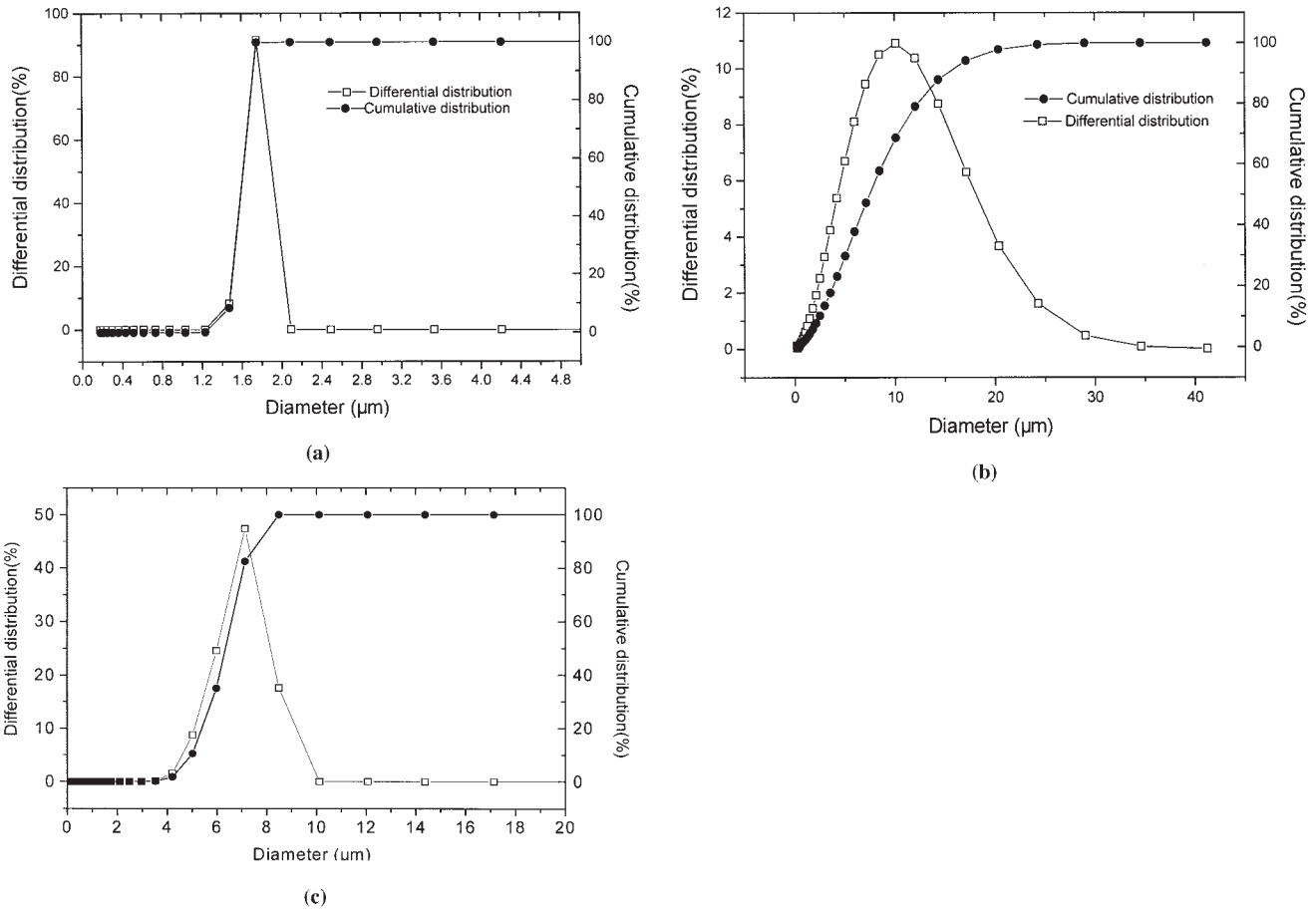

Figure 3 Diameter distribution and cumulative distribution of microcapsules.

layer polymer shell protected the phase change material and prevented the phase change material from releasing.

DSC results present information about polymer properties, such as changes of the temperature of melting point and phase transition heat. Figure 5a

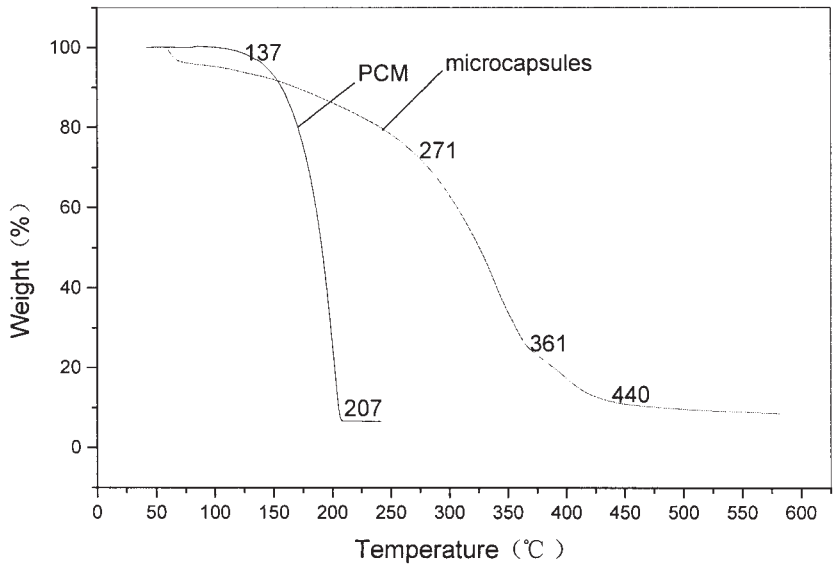

Figure 4 Curve of TG of microcapsules.

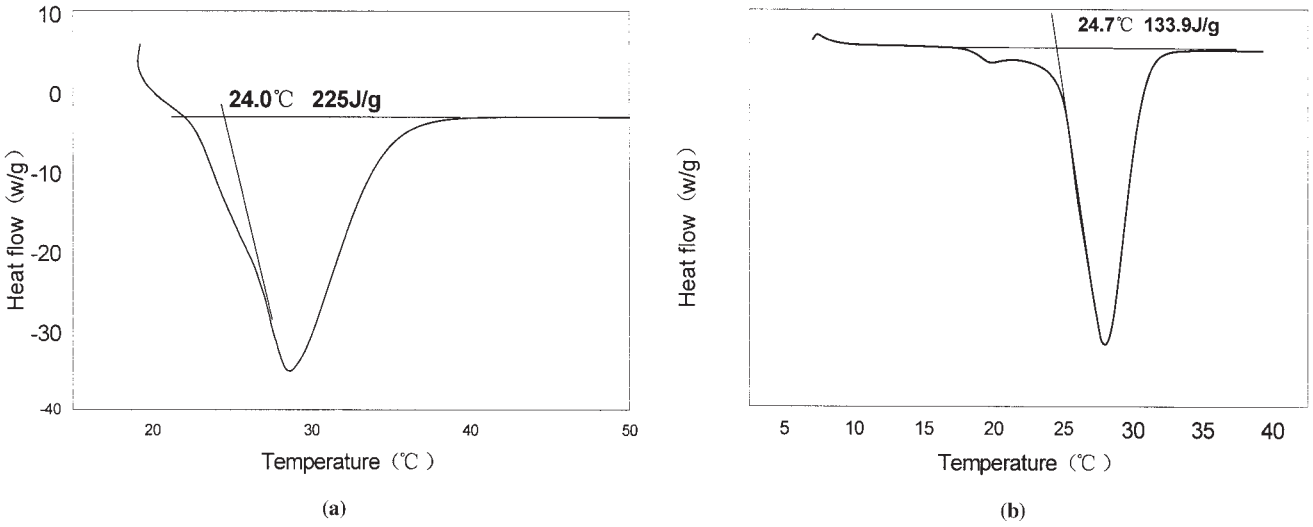

Figure 5 DSC curves of microcapsules.

shows the DSC properties of pure phase change material. Its melting point was 24.0°C and the phase change heat was 225.5J/g. As the double-layer microcapsules containing phase change material consisted of the core material and the shell material with the weight ratio of 1 : 1, the microcapsules' absorbed heat was 113.9 J/g. Also, the melting point of the microcapsules was 24.7°C, nearly equal to the pure phase change material just as Figure 5b shows. The DSC results make it clear that the polymer shell of microcapsules does not influence the properties of the phase change material. Obviously, the microcapsules prepared in this study can be utilized successfully.

Shell strength of the microcapsules

The microcapsules containing phase change material need certain rigidity when utilized in practice. Sun and Zhang[7,8] investigated the strength of microcapsules made of three different shells by a micromanipulation technique. Single microcapsules were compressed to large deformation or rupture, and the force being imposed on them was measured simultaneously. This method required special apparatus and it was difficult to see the surface shape changes as they occurred. Also, when the microPCMs were used in practice, the strength of a single microcapsule did not reflect the actual strength, as the microcapsules were piled together.

In this study, we adapted a new method to test the strength. As Figure 6 shows, microcapsules were put between two pieces of glass and suffered press. The rigidity of the shell was evaluated through observing the surface change after pressure by means of scanning electron microscopy. The results showed the average diameter of the microcapsules was 5μm, and the globular surface was smooth and compact. After press, as Figures 7a, 7b, and 7c show, there were concaves on the microcapsules. According to increasing the strength of press, some little microcapsules were caved into large ones, as shown in Figure 7d. But two were not ruptured. From SEM micrographs of the surface of the microcapsules after press, a yield point, could be observed, just as the deformation needed mixture force.

It was also found that the mechanical intensity of double-shell microcapsules was better than that of single shell. A yield point about 1.1×10^5Pa was found, and when the press was beyond that point, the microcapsules showed plastic behavior.

Thickness of shell

The thickness of the microcapsule shell was related to the diameter, the ratio of mass of the core and the shell, and the process of microcapsulation. It was necessary to investigate the shell, for the thickness would affect the strength and penetration property of the

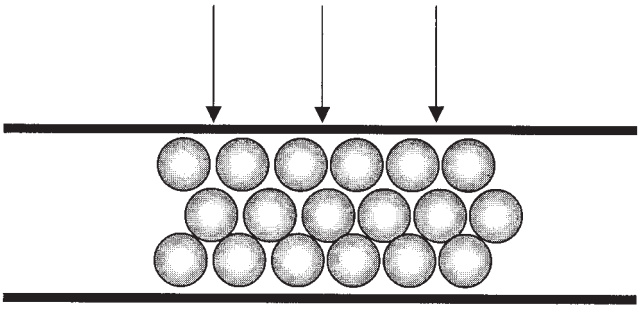

Figure 6 Sketch map of press on microcapsules.

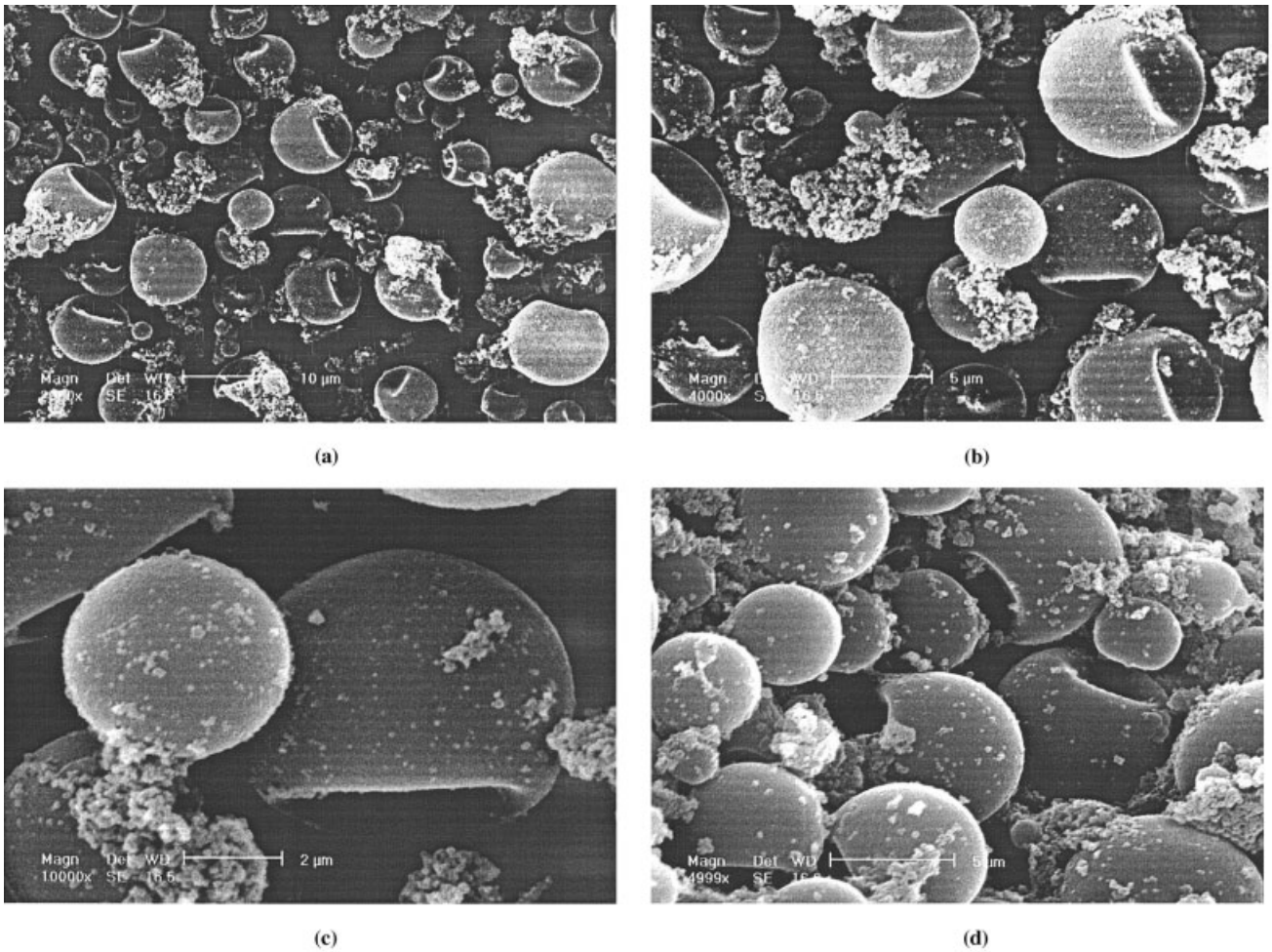

Figure 7 SEM micrographs of surface of microcapsules after press.

microcapsules. There were direct methods, such as using in-bed in resin, and indirect methods such as using microscope photos of the second focus of the microcapsule made by phase separation. To observe the double-shell shell, we adapted the methods of embedding the microcapsules in glutin, and got SEM images of the slices.

As Figure 8a shows, the dried microcapsules scat-

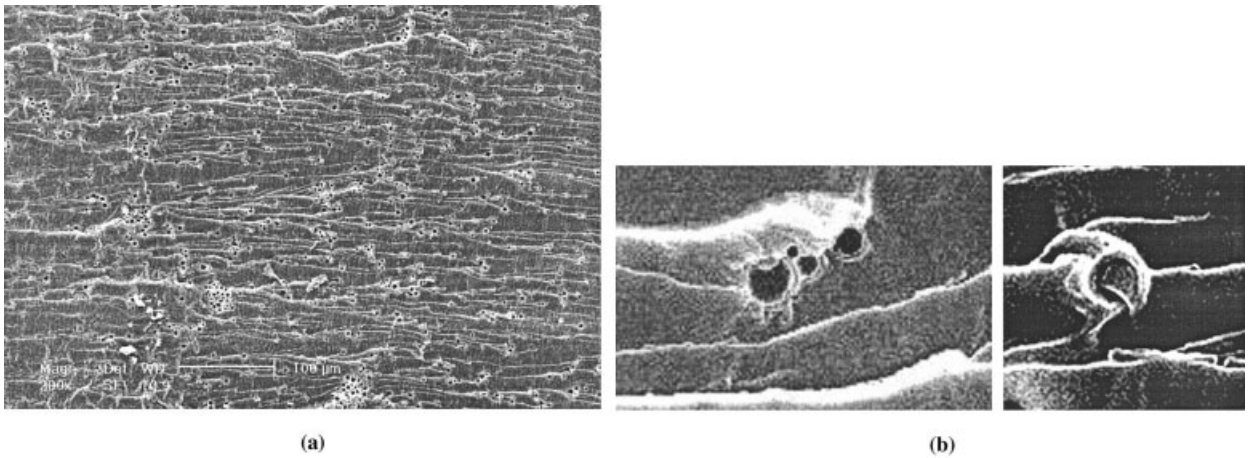

Figure 8 SEM micrographs of slices of microcapsules in glue.

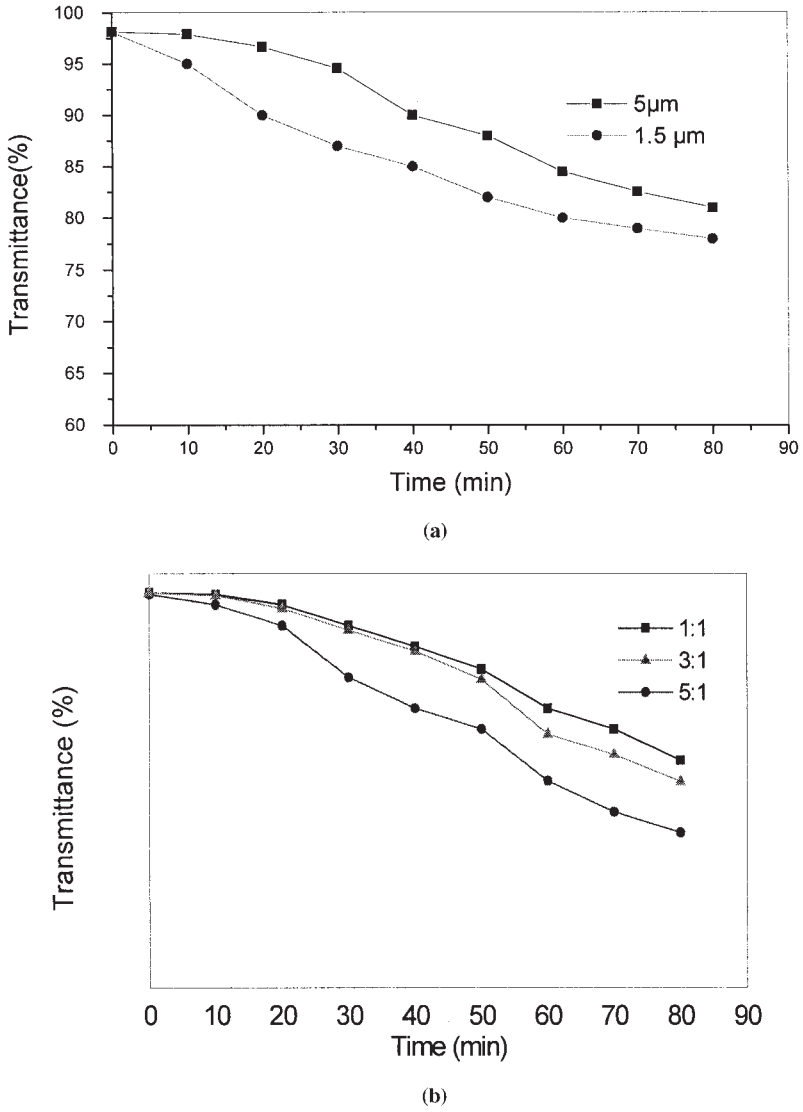

Figure 9 Penetration properties of microcapsules.

tered in glutin separately. We could see the black caves in the resin that was caused by a slice being taken out of the core material at the same time. But the shell material conglutinated with the glutin and was still keeping shape, as Figure 8b shows. From the SEM micrographs, we could measure the thickness of the shells. The average thickness was 0.5 ~ 1 μm. Attention must be paid to the fact that this thickness may not be the maximum thickness of the diameter. For this reason, the measured shell thicknesses just give an average value and information of the double-shell visualization.

Penetration property

Penetration property was another main property and is studied mostly in the pharmaceutics field to get the property of releasing slowly. In this study, we hoped the MF shell protecting the phase change material would not be affected by the outer materials and environment. That would make the core safe, not strained, and the microPCMs would have a long life in practice.

The penetration property of different average diameter microPCMs was evaluated using a 722-spectrophotometer in ethyl alcohol with density of 0.97 g/mL. From changes in transmittance of light, we got the core material penetrating time. In this process, the ethyl alcohol should be airproofed to avoid volatility. The average diameter microPCMs of 5 μm and 1.5 μm were tested, as Figure 9a shows. Obviously, the penetration of 5 μm was slower than that of 1.5 μ. The reason for this might be that the smaller the average of the microcapsules, the larger the surface area for penetration.

As microcapsulation proceeded, the core material was dispersed by mechanical stirring. The diameter of

the dispersed core determined the average diameter of the microPCMs. So at the same stirring speed and different mass ratios of core and shell material, that would get different thicknesses of shell, as well as different penetration properties. The different mass ratios of core and shell microPCMs penetration property was shown in Figure 9b. The penetration property of the mass ratio of core and shell 1 : 1 was slower than that of 3 : 1 and 5 : 1.

CONCLUSION

In this study, melamine resin microcapsules with double-layers containing phase change material were prepared, and the shape of the microcapsules, the size distribution, thermal properties, and shell rigidity were investigated. The microcapsules have a smooth and globular surface, a narrow size distribution, and a double-layer shell. Also, the average diameter of the microcapsules was from 1 μm to 20 μm, with compact shells. The microcapsules did not influence the properties of the pure phase change material. A yield point about 1.1×10^5Pa was found, and when the press was beyond that point the microcapsules showed plastic behavior.

References

1. Hittle, D. C.; Andre, T. L. A. ASHRAE Transactions 2002, 108, 175.
2. Holman, M. E. Am Society Mechan Engineers 1999, 44, 235.
3. Mulligan, J. C.; Colvin, D. P.; Bryant, Y. G. J Spacecraft Rockets 1996, 33, 278.
4. Inaba, H.; Kim, M.-J.; Horibe, A. Transactions of the Japan Society of Mechanical Engineers, Part B. 2002, 68, 161.
5. Cartwright, D. K.; Bryant, Y. G.; Colvin, D. P. Am Society Mechan Engineers 1999, 44, 241.
6. Hawlader, M. N. A.; Uddin, M. S.; Zhu, H. J. Intl J Solar Energy 2000, 20, 227.
7. Sun, G.; Zhang, Z. J Microencapsulation 2001, 18, 593.
8. Sun, G.; Zhang, Z. J Microencapsulation 2002, 242, 307.