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# Preparation and Properties of Phase-Change Heat-Storage UV Curable Polyurethane Acrylate Coating

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**ABSTRACT:** Phase-change heat-storage UV curable polyurethane acrylate (PUA) coating was prepared by applying microencapsulated phase change materials (microPCMs) to PUA coating. MicroPCMs containing paraffin core with melamine-formaldehyde shell were synthesized by *in situ* polymerization. The effect of stirring speed, emulsification time, emulsifier amount, and core/shell mass ratio on particle size, morphology, and phase change properties of the microPCMs was studied by using laser particle size analyzer, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopic analysis, scanning electron microscopy, and differential scanning calorimetry. The results showed that the diameter of the microcapsules decreased with the increase of stirring speed, emulsification time, and emulsifier amount. When the mass ratio of emulsifier to paraffin is 6%, microcapsules fabricated with a core/shell ratio of 75/25 have a compact surface and a mean particle size of 30 $\mu$m. The sample made under the above conditions has a higher efficiency of microencapsulation than other samples and was applied to PUA coating. The dispersion of microPCMs in coating and heat-storage properties of the coating were investigated. The results illustrated that the phase-change heat-storage UV curable PUA coating can store energy and insulate heat. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41266.

**KEYWORDS:** applications; properties and characterization; synthesis and processing

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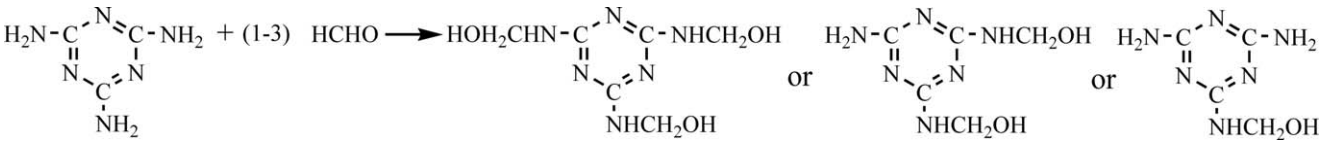
## INTRODUCTION

Compared to traditional solvent based coatings, UV curable coatings can not only reduce volatile organic compound (VOC) but also increase productivity and save energy.[1–5] Polyurethane acrylate (PUA) is one of the common oligomers used in UV curable coatings because of its outstanding chemical and physical properties.[6,7]

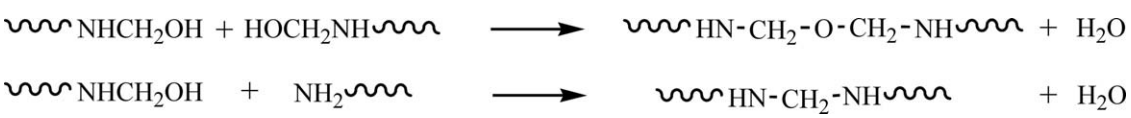
Since many energy sources are intermittent and energy crisis is now up to us, energy storage plays a more important role today,[8] which puts forward high request to the heat-storage properties of the UV curable coatings.

Thermal energy storage has attracted an increasing attention recently by using phase change materials (PCMs), which can absorb, store and release large amount of latent heat during phase-change process.[9] However, most PCMs melt and crystallize repeatedly during use, therefore it is important to avoid their leakage and decrease their supercooling.[10] Microencapsulated PCMs (microPCMs) provide an effective way to solve these problems as they can increase heat transfer area, reduce PCMs' reactivity towards the outside environment and control the changes in the storage material volume as phase change occurs.[11] MicroPCMs have been widely used in building materials,[12,13] fabrics,[14,15] packed bed heat exchangers,[16] foams,[17] and so on.

A lot of literatures have reported the fabrication and properties of microPCMs containing PCMs as core materials. Hong and Park used sodium lauryl sulphate as emulsifier and poly(vinyl alcohol) (PVA) as protective colloid to prepare microcapsules with Margin oil as core material and melamine-formaldehyde resin as shell material by *in situ* polymerization. The particle size of the microcapsules was below 10 $\mu$m.[18] Zhang and Wang fabricated microcapsules with *n*-octadecane as core and melamine-formaldehyde resin as shell by in situ polymerization. They used styrene-maleic anhydride copolymer (SMA) as emulsifier and the diameter of the microcapsules was ~15 $\mu$m.[19] Mao et al. prepared microcapsules with paraffin as core and urea-formaldehyde resin as shell by *in situ* polymerization. The average diameter was below 10 $\mu$m.[20] Alkan et al. fabricated microcapsules using docosane as core and PMMA as shell. The results showed that the samples had compact and smooth surface with a mean size below 0.16 $\mu$m.[21] Zhang and Wang used TDI and EDA as reactive monomer to prepare microcapsules with *n*-octadecane as core and polyurea as shell by interfacial



Scheme 1. The reaction mechanism of synthesis of MF prepolymer.



Scheme 2. The reaction mechanism of the formation of shell material.

polymerization. The particle size of the microcapsule was below 10 $\mu$m.[22] Su et al. used TDI and DETA as reactive monomers to fabricate microcapsules with average diameter below 10 $\mu$m.[23] Although the microPCMs could be prepared using different materials, the mechanical strength and permeability of microcapsules by using MF resin as shell material are better than those by using other materials for its high crosslinking density.[24]

The objective of this study is to fabricate a kind of heat-storage UV curable coating by applying microPCMs to PUA coating. Just as we have known, common PUA coating cannot store energy and insulate heat. By applying microPCMs to PUA coating, we are able to make the heat-storage PUA coating, which can be used in architectural heat preservation. The microPCMs based on paraffin core and melamine-formaldehyde (MF) shell was synthesized by *in situ* polymerization. The influence of stirring speed, emulsification time, emulsifier amount, and core/shell mass ratio on the morphology, phase change properties, and efficiency of encapsulation of the microcapsules were discussed. The dispersion of microPCMs in PUA coating and heat-storage properties of the coating was also investigated.

## EXPERIMENTAL

### Materials

Melamine with purity above 99% and formaldehyde (37 wt % aqueous solution) used as shell-forming monomers were purchased from Sinopharm Chemical Reagent, Ltd. Paraffin (phase change temperature is 28°C) was supplied by Shanghai Joule Wax Industry, Ltd, and was used as core material. Styrene-maleic anhydride copolymer (SMA) as emulsifier was obtained by Cray Valley Hydrocarbon Specialty Chemicals, USA. Sodium hydroxide and hydrochloric acid used as pH regulators were also purchased from Sinopharm Chemical Reagent, Ltd. Aliphatiy urethane diacrylate oligomer and 2-hydroxy-2-methyl-phenyl-propan-1-one (Darocure 1173) were kindly supplied by Hangzhou Kewang Special Ink, Ltd.

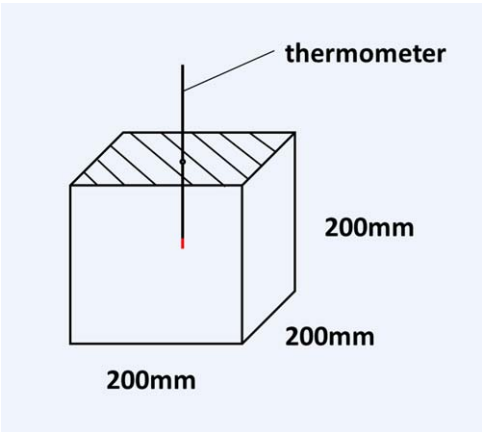
### Preparation of MicroPCMs

The microencapsulated paraffin was fabricated through *in situ* polymerization. The procedure included the synthesis of melamine-formaldehyde (MF) prepolymer solution, the preparation of PCM emulsion and the formation of shell material.

In a typical recipe, 0.6 g of SMA and 100 mL of distilled water were mixed and adjusted to pH 9 with dilute sodium hydroxide solution. Then the mixture was stirred at 70°C for 2 h. Ten grams of paraffin was melted at 70°C and then added into the above solution at 70°C. The mixture was stirred at a stirring speed of 1000 rpm for 60 min to prepare the PCM emulsion. The obtained emulsion was adjusted to pH 4 with diluted hydrochloric acid. 1.5 g of melamine, 5 mL of 37 wt % formaldehyde aqueous solution and 10 mL of distilled water were mixed together and adjusted to pH 9 with dilute sodium hydroxide solution. Then the mixture was stirred at 70°C for 0.5 h to prepare MF prepolymer aqueous solution. The reaction mechanism of synthesis of MF prepolymer was shown in Scheme 1. The MF prepolymer solution was added dropwise into the above emulsion to start an *in situ* polymerization at 70°C with a stirring speed of 300 rpm. After all of the MF prepolymer solution was added, the mixture was stirred for another 2 h. Finally, the reaction was terminated as the pH of the mixture was adjusted to 9 with dilute sodium hydroxide solution. The reaction mechanism of the formation of shell material was shown in Scheme 2. The resultant microcapsules were filtered and washed with 30 wt % hot ethanol-water solution to remove unreacted material. The wet powders were dried in a vacuum oven at 80°C for 24 h.

### Preparation of Heat-Storage UV-Curable Coating

A certain amount of PUA oligomer and microPCMs were mixed and stirred at 70°C. Then 3 wt % photoinitiator (Darocure 1173) was added into the above mixture. The coating with a




Scheme 3. Diagram of self-made equipment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

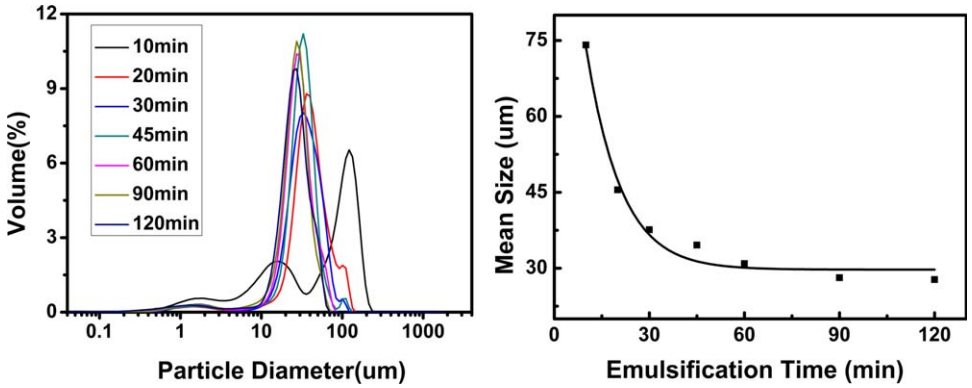



**Figure 1.** Particle size of microcapsules prepared under different emulsification time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

thickness of 2.5 mm was prepared by multilayer coating and the single layer's thickness is 0.5 mm. Every coating was cured in the UV irradiation apparatus (1 kW) for 15 s. The distance between samples and UV lamp was 20 cm.

### Characterization

The chemical structure of paraffin, MF prepolymer, and microcapsule was analyzed by a NICOLET 5700 infrared spectrometer (Thermo Electron, USA). The samples were ground and mixed with KBr to make pellets, and the spectrum was collected in the frequency range of 400–4000 $cm^{-1}$ with a resolution of 4 $cm^{-1}$ by averaging 16 scans.

The chemical composition of the microPCMs was investigated by VG ESCALAB MARK II X-ray photoelectron spectroscopy equipped with a Mg K$\alpha$ X-ray source (h$\gamma$ = 1253.6 eV). All the spectra were recorded at 0–1060 eV with a step internal of 0.5 eV.

Thermal storage properties of microcapsules were measured by a TA Q200 differential scanning calorimetry (DSC, TA Instruments, New Castle, DE) at a heating and cooling rate of 10°C/min under a flow of nitrogen gas. Each sample with a weight of 7–10 mg was encapsulated into an aluminum pan. The temperature ranges of the heating and cooling cycle were −20 to 80°C and 80 to −20°C, respectively.

The dried samples were adhered to the sample stage and sprayed with gold. The surface morphology of microcapsules was observed with a field emission scanning electron microscope (FESEM, CorlzeisD Utral 55, Germany).

The mean diameter and diameter distribution of microcapsules were measured by a Laser Particle Size Analyzer (LS-230, Coulter, USA).

The dispersion of microPCMs in PUA coating was observed with a polarizing optical microscope (Eclipse E600W Pol, Nikon, Japan).

The heat-storage properties of the coating were measured by self-made equipment shown in Scheme 3. A box with an open side (200 × 200 × 200 $mm^3$) was made by 30 mm thick foamed polystyrene board. The open side was coated by the PUA coating. A thermometer was placed inside the box to measure the temperature change. The equipment was heated to 38°C and then cooled down to 18°C.

## RESULTS AND DISCUSSION

### Effect of Emulsification Time and Stirring Speed on Particle Size of Microcapsules

The emulsification time and stirring speed may affect the particle size of microcapsules. Therefore, the effect of the emulsification time and stirring speed on the particle size of microcapsules was studied. The diameter of microcapsule made in different emulsification time is shown in Figure 1. When the

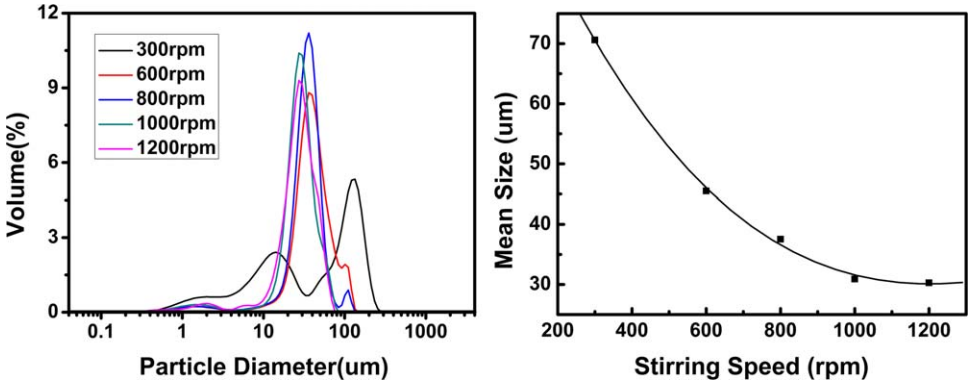



**Figure 2.** Particle size of microcapsules prepared under different stirring speed. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

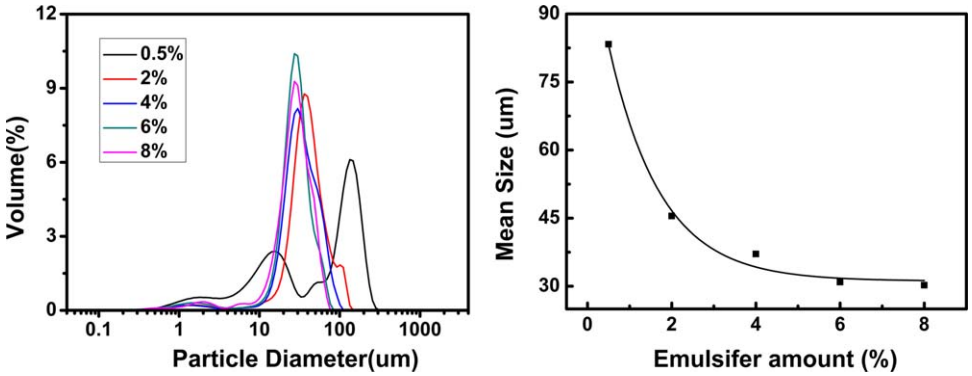



**Figure 3.** Particle size of microcapsules prepared with different emulsifier amount. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

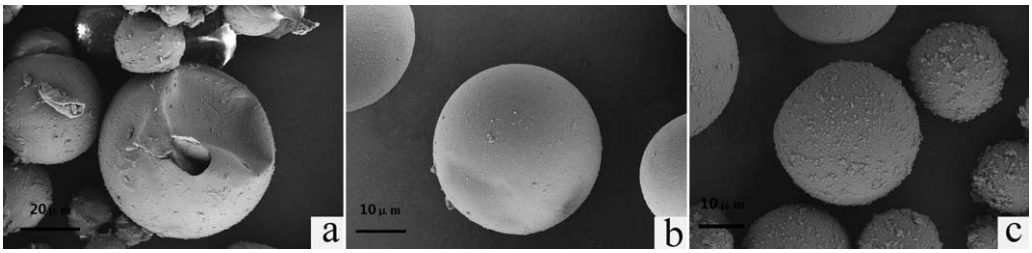



**Figure 4.** Morphology of microcapsules prepared with different SMA amount (SMA amount (a) 2%, (b) 6%, (c) 8%.

emulsification time is as short as 10 min, there are two peaks in the size distribution curve and the mean size is as large as 74.09 $\mu$m. As the emulsification time increases, one of the peaks gradually becomes small. When the emulsification time is longer than 60 min, there is only one peak in the curve. It also can be seen that the mean size decreases as the emulsification time increases. When the emulsification time is longer than 60 min, the mean size almost do not change with the emulsification time and remains at 30 $\mu$m. The result indicates that when the emulsification time is short, the core material cannot be evenly and steadily dispersed and 60 min can be considered as the minimum emulsification time in this study.

The diameter of microcapsule made under different stirring speed is shown in Figure 2. The curve shows two peaks when the stirring speed is as low as 300 rpm and the mean size is 70.60 $\mu$m. One of the peaks becomes small as the stirring speed

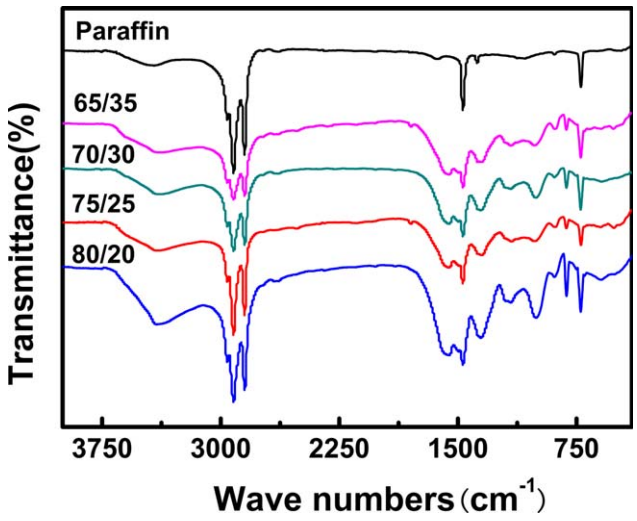



**Figure 5.** FTIR spectra of paraffin and microcapsules prepared with different core/shell mass ratio. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

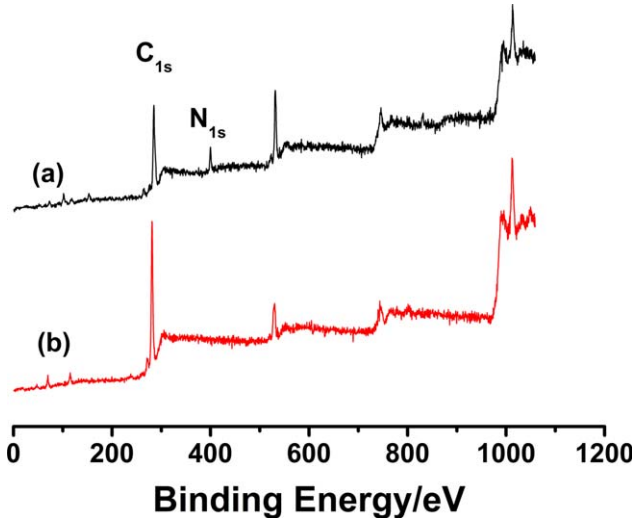



**Figure 6.** XPS survey scan spectra of microPCMs under different time of argon bombarding (time of argon bombarding (a) 0 min, (b) 5 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

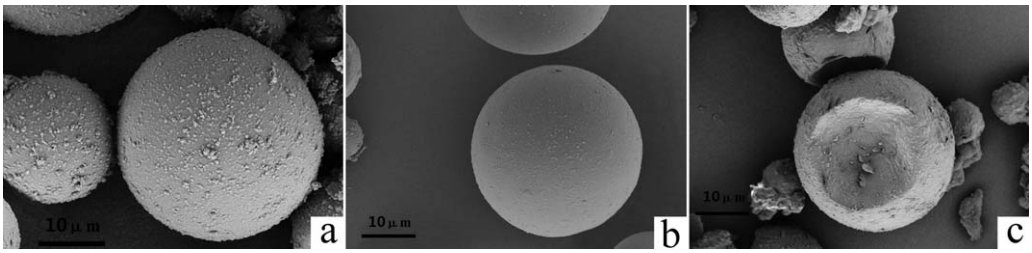



**Figure 7.** Morphology of microcapsules prepared with different core/shell mass ratio (core/shell mass ratio (a) 65/35, (b) 75/25, (c) 80/20.

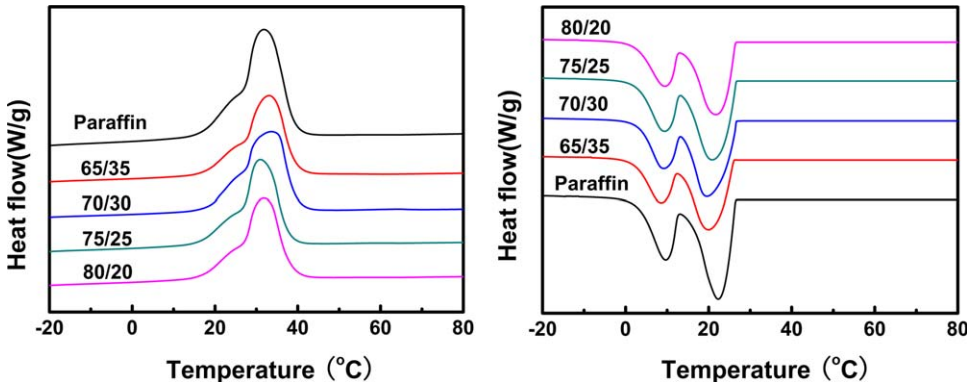



**Figure 8.** DSC thermograms of paraffin and the microcapsules prepared with different core/shell mass ratio. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increases. When the stirring speed reaches 1000 rpm, there is only one peak in the size distribution curve. The mean size decreases as the stirring speed increases and tends to maintain at 30 $\mu$m when the stirring speed is higher than 1000 rpm. The result illustrates that low stirring speed leads to unsteady emulsion and the particle size of microcapsule prepared under low stirring speed is not even. As the stirring speed increase, the shear that the core droplets bear will increase, resulting in the breakup of large droplets and the formation of small droplets if the emulsifier is sufficient enough to prevent the small droplets from recoalescing. One thousand rpm can be considered as the appropriate stirring speed in this study.

### Effect of Emulsifier Amount on Properties of Microcapsules

The effect of emulsifier is based on the recoalescence prevention as well as reducing the interfacial tension between two immiscible phases. Hence, the particle size and morphology while changing the emulsifier amount was studied. Figure 3 shows the diameter distribution of microcapsules prepared with different emulsifier amount. When the mass ratio of emulsifier to PCM is 0.5%, there are two peaks in the distribution curve and the mean size is as large as 83.32 $\mu$m. The results also show that when the amount of emulsifier is less than or equal to 2%, in addition to large particles there are a certain number of small particles. When the emulsion is stored for a while, the small droplets tend to recoalesce. These results illustrate that the emulsifier is not sufficient to prevent the droplets from recoalescing. As the amount of emulsifier further increases, the peak with large particle diameter gradually disappears, which indicates that the core material can be dispersed into small particles when the emulsifier amount increases. When the amount of emulsifier is higher than 6%, the mean size tend to maintain at 30 $\mu$m. Moreover, the diameter distribution is narrow with only one peak in the curve when the mass ratio of emulsifier to PCM is higher than 6%. Therefore, 6% can be considered as the appropriate emulsifier amount to prepare microcapsules with appropriate particle size.

**Table I.** Phase Change Properties of Paraffin and the Microcapsules Prepared with Different Core/Shell Mass Ratio

| Sample | $\Delta H_m$ (J/g) | $C_t$ (%) | $C_e$ (%) | $E$ (%) |
|---|---|---|---|---|
| 65/35 | 80.06 | 65 | 63.3 | 97.3 |
| 70/30 | 88.13 | 70 | 69.7 | 99.5 |
| 75/25 | 93.97 | 75 | 74.3 | 99.1 |
| 80/20 | 88.03 | 80 | 69.6 | 87.0 |
| Paraffin | 126.48 | - | - | - |

Figure 4 shows the morphology of microcapsules prepared with different SMA amount. When the mass ratio of SMA to paraffin is 2%, the microcapsules are irregular spherical with some fragment and some of the microcapsules are damaged, because of the insufficient amount of emulsifier for preparing compact microcapsules. When the SMA amount is 6%, the microcapsules are spherical and compact with a smooth surface. As the SMA amount reaches 8%, a little rough surface is found. This can be attributed to the excessive emulsifier, which can cause high charge density on the core droplets, resulting in a fast

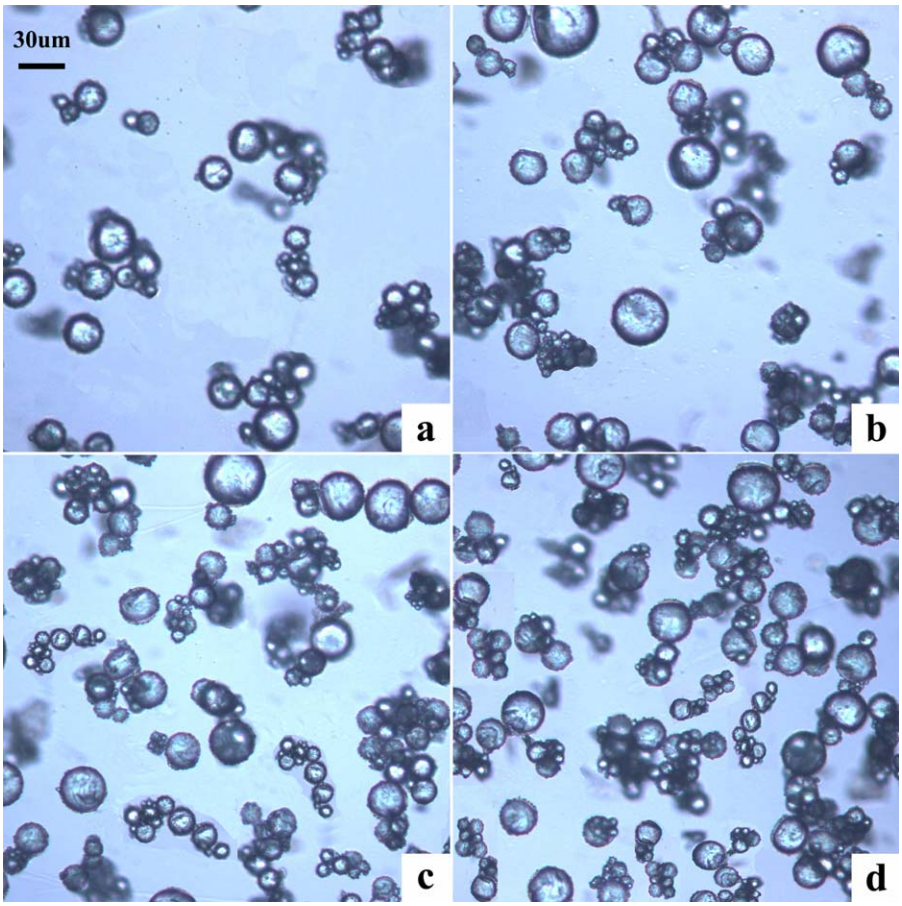



**Figure 9.** Dispersion of microPCMs in PUA coating (microPCMs/PUA weight ratio (a) 5/95, (b) 10/90, (c) 15/85, (d) 20/80. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

deposition of the MF resin onto the surface of the microcapsules. The results illustrate that 6% is the appropriate emulsifier amount to prepare spherical and compact microcapsules with a smooth surface.

### Effect of Core/shell Mass Ratio on Properties of Microcapsules

The FTIR spectra of paraffin and the microcapsules prepared with different core/shell mass ratio is presented in Figure 5. The strong and wide absorption peaks at 3417 $cm^{-1}$ are attributed to the O—H and N—H stretching vibrations. The peaks at 1559 and 812 $cm^{-1}$ are assigned to the triazine ring. The weak peak at l163 $cm^{-1}$ is corresponding to the C—O—C stretching vibrations. The peak at 1009 $cm^{-1}$ is attributed to C—O stretching vibrations. The multiple strong peaks at 2918 and 2850 $cm^{-1}$ are associated with C—H stretching vibrations of methyl and methylene groups.

The characteristic peaks of paraffin at ~2918 and 2850 $cm^{-1}$ can be observed in the microcapsules, indicating that paraffin has been encapsulated. Moreover, the characteristic peaks of MF resin at ~1559 and 812 $cm^{-1}$ are also found, indicating that paraffin has been encapsulated with MF resin as shell material.

XPS analysis was also used to determine the chemical composition of the microPCMs. From the survey scan (Figure 6), peaks at about 285 and 400 eV were observed, which ascribed to $C_{1s}$ and $N_{1s}$, respectively. Just as we have known, the shell material contains nitrogen while the core material does not contain nitrogen. When the shell was intact, peak at about 400 eV could be observed, which prove the existence of nitrogen. After 5 min of argon bombarding, the peak at about 400 eV was barely observed because shell was broken and then core was exposed. This result can also indicate that paraffin has been encapsulated.

Figure 7 shows the morphology of microcapsules prepared with different core/shell mass ratio. When the core/shell mass ratio is 65/35, the microcapsule is spherical and compact with a rough surface. It can be explained that excessive MF resin will enhance the deposition of MF resin on the surface of the microcapsule, resulting in a rough surface. When the core/shell mass ratio is 75/25, spherical, and compact microcapsules with a smooth surface are observed. As the core/shell mass ratio reaches 80/20, some of the microcapsules are found broken, due to the insufficient MF resin, which is not enough to encapsulate the core material compactly. The result indicates that 75/25 is the optimal core/shell mass ratio for the synthesis of the microcapsules.

The phase change behavior of the paraffin and microcapsules was investigated by DSC, and the thermograms are displayed in Figure 8. It can be seen that the melting and crystallizing temperature of the pure paraffin and the paraffin in microcapsules

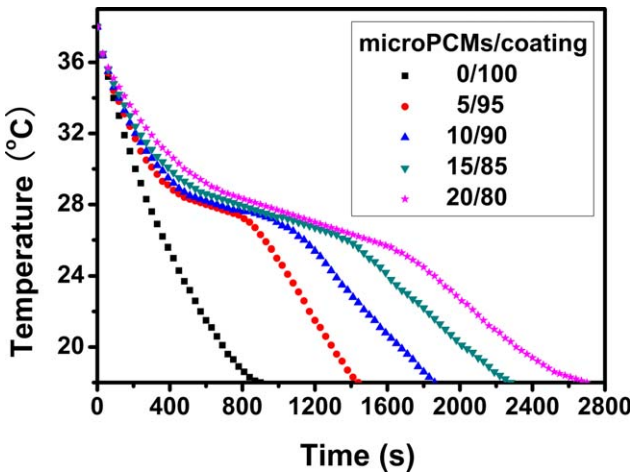



**Figure 10.** Heat-storage properties of coatings with different microPCMs content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

are almost the same. However, the enthalpy of the paraffin in microcapsules is smaller than that of the pure paraffin. This is because the shell materials do not change its phase during the test. It is the core material that provides latent heat.

The melting and crystallization properties of all the samples are obtained from DSC analysis and summarized in Table I. Theoretical ($C_t$) and experimental ($C_e$) amounts of encapsulated paraffin were calculated through eqs. (1) and (2), respectively. The efficiency of microencapsulation ($E$) was obtained from eq. (3).

$$C_t = \frac{W_p}{W_p + W_{\mathrm{MF}}} \times 100\% \quad (1)$$

$$C_e = \frac{\Delta H_m}{\Delta H_p} \times 100\% \quad (2)$$

$$\mathrm{E} = \frac{C_e}{C_t} \times 100\% \quad (3)$$

where $W_p$ and $W_{MF}$ are the initial weights of paraffin and MF resin, respectively. $\Delta H_m$ is the enthalpy of melting for the microcapsules, and $\Delta H_p$ is the enthalpy of melting for paraffin.

When the core/shell mass ratio is lower than 75/25, the efficiency of microencapsulation is almost 100%. However, when the core/shell mass ratio is 80/20, the efficiency of microencapsulation reduced to 87.0%. The result demonstrates that when the core/shell mass ratio is high, the core material cannot be compactly encapsulated and the shell of the microcapsule is loose and porous, resulting in the leakage of core material. Thus, the efficiency of microencapsulation is low. The results also conform that the core/shell mass ratio of 75/25 is the optimal value to prepare microcapsules.

### Properties of Heat-Storage UV Curable PUA Coating

Phase-change heat-storage UV curable PUA coating was prepared by applying microPCMs to PUA coating. Coatings with different microPCMs/coating mass ratio were prepared to investigate the dispersion of microPCMs in PUA coating. Figure 9 shows the dispersion of microPCMs in PUA coating. It was found that the microPCMs are spherical and compact. The result demonstrated that the shell was not broken during the dispersion process and microPCMs can be well dispersed in PUA coating.

To study the heat-storage properties of coatings with different microPCMs content, the temperature change inside the self-made box was investigated. Figure 10 shows the temperature change during the cooling process. A platform at about 28°C can be observed in the curve. As the microPCMs/coating weight ratio increases, the platform becomes wider and the time that the inside temperature decreases from 38 to 18°C increases as well. The results demonstrate that the microPCMs change phase and release energy during the test, resulting in the slow temperature change inside the box.

## CONCLUSION

The micro-PCMs based on paraffin core and MF resin shell were prepared by *in situ* polymerization. The FTIR spectra confirmed that the paraffin was encapsulated by the MF shell. Stirring speed, emulsification time, and emulsifier amount have a great influence on the particle size of the microcapsules. The diameter decrease with the increase of the stirring speed, emulsification time, and emulsifier amount. The core/shell mass ratio has a significant effect on the phase change properties of the microcapsules. The samples prepared with a core/shell mass ratio of 75/25 have a good phase change properties and a high efficiency of encapsulation.

Phase-change heat-storage UV curable PUA coating was prepared by applying microPCMs to PUA coating. The results illustrated that PUA coating of microPCMs had good heat-storage properties and can insulate heat, meanwhile, the dispersion of microPCMs in PUA coating is also good.

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