

Preparation and Characterization of Polyurea/Polyurethane Double-Shell Microcapsules Containing Butyl Stearate Through Interfacial Polymerization

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ABSTRACT: Double-shell microcapsules containing butyl stearate were prepared through interfacial polymerization. The outer shell is polyurea formed through polymerization of toluene-2,4-diisocyanate (TDI) and diethylene triamine, and the inner shell is polyurethane (PU) formed through polymerization of TDI and polypropylene glycol 2000 (PPG2000). Styrene maleic anhydride copolymer was used as emulsifier. The effects of core to monomer ratio and dosage of PPG2000 on core content and encapsulation efficiency of microcapsules were investigated. The core content has a maximum at core to monomer ratio of 3–4, and the encapsulation efficiency has a

maximum value of 95% at core to monomer ratio of 2. The prepared microcapsules were smooth and compact and have an obvious latent heat of 85 J/g. The shell structure of microcapsules was polyurea and PU. The average diameter of the microcapsules was 1–5 μm . The stabilities of the double-shell microcapsule, such as anti-ethanol wash and antiheat properties are obviously improved than those of single-shell microcapsule. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 3377–3383, 2011

Key words: microcapsules; polyurea; polyurethane; phase change material; butyl stearate; interfacial polymerization

INTRODUCTION

Microcapsule is a kind of small particles, which contain an active agent or core material surrounded by a coating or shell.¹ Microencapsulated phase change materials (microPCMs) are a kind of microcapsules, which containing phase change materials (PCM).^{2–4} MicroPCMs are not easily affected by the surrounding environment because of the protection of the shell, it can absorb, store, and release large amounts of latent heat over a certain temperature range when experiencing a phase transition.⁵ MicroPCMs can be conveniently applied in solar and nuclear heat storage systems,⁶ building energy saving,⁷ textile fibers,⁸ garments,⁹ foam plastics,¹⁰ coating, and composite materials.^{11,12}

At present, melamine formaldehyde (MF), urea formaldehyde (UF), and polyurethane (PU) are usually selected as shell materials for microPCMs. However, there may exist ineluctable remnant formaldehyde when MF and UF resins are selected as shell materials, as is known, formaldehyde is harmful to environment and health. So, PU is the promising

polymer material in the preparation of microPCMs. Interfacial polymerization is a convenient technology to obtain PU shell microcapsules reacted by two monomers.

There are some reports about microPCMs containing octadecane prepared through interfacial polymerization.^{13–15} However, encapsulation effect is not satisfied due to poor intersolubility for octadecane and toluene-2,4-diisocyanate (TDI). To improve the intersolubility, cyclohexane is usually added. However, the improvement of solubility is limited, because cyclohexane and octadecane are all nonpolar materials. In addition, cyclohexane decreased the energy storage density of microPCMs. In the presented investigation, butyl stearate was selected as PCM. As a polar material, it has complete miscibility with TDI and has a high latent heat, and its phase change temperature is close to octadecane.

In recent years workers in this field have paid more attention to improve the core contents, thermal stability and compactness of microPCMs.^{15–18} In the related reports temperature raising, prolonging reaction time and higher stirring speed are all helpful to improve the stability of microPCMs, but the effect is limited. In the previous investigations most reports were focused on single-shell microPCMs, however, seldom reports on double-shell microPCMs were

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TABLE I
The Bath Compositions Used for Preparing MicroPCMs

Core to monomer ratio (wt/wt)	Butyl stearate (g)	TDI (g)	DETA (g)	PPG2000 (g)	Monomers (g)
1.5	13.1	5.0	2.75	1.0	8.75
2.0	17.5	5.0	2.75	1.0	8.75
3.0	23.4	5.0	2.80	0	7.8
3.0	24.8	5.0	2.77	0.5	8.25
3.0	26.3	5.0	2.75	1.0	8.75
3.0	27.7	5.0	2.72	1.5	9.22
3.0	29.1	5.0	2.70	2.0	9.7
4.0	35.0	5.0	2.75	1.0	8.75
7.0	61.3	5.0	2.75	1.0	8.75

found. In the presented investigation, double-shell microPCMs were prepared. The outer shell is polyurea formed by polymerization of TDI and diethylene triamine (DETA), and the inner shell is PU formed by unreacted or residual isocyanate reacting with PPG2000 in the inner surface of the polyurea shell. The effect of weight ratio of core material to shell material (core-to-monomer ratio) and encapsulation efficiency were investigated. The thermal property, surface morphology, and chemical structures of microPCMs were characterized by differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and FTIR. The stability to water wash, ethanol wash, and heat property was investigated as well.

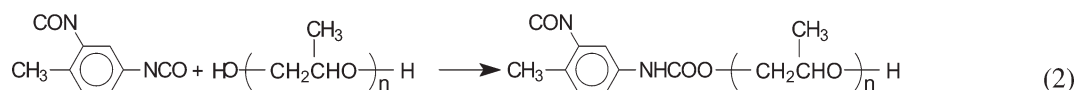
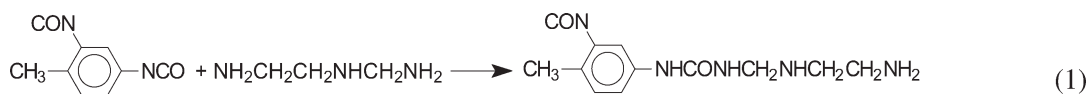
EXPERIMENTAL

Materials

Butyl stearate and PPG2000 (Sinophram Chemical Reagent, China), DETA (Shantou Xilong Chemical Factory, China), TDI (Chengdu United Chemical & Pharmaceutical, China), and styrene maleic anhydride (SMA; Scripset®520, Hercules) were used throughout the investigation. All these chemicals were reagent grade and used without further purification.

Preparation of microcapsules

TDI, butyl stearate, and PPG2000 were mixed well at around 30°C to form an hydrophobic solution, the detailed amounts are shown in Table I. A total of 1.5 g of SMA was dissolved in 200 mL of distilled water and used as the emulsifier, and then the pH was adjusted to 8 by using a 0.1 mol/L NaOH aqueous solution. Two grams of DETA was dissolved in 20-mL distilled water to form a DETA solution. Firstly, the SMA solution was added to a 500-mL beaker, and then the hydrophobic solution was gradually added to the former system under stirring at 5000 rpm, and the stirring was continued for 8 min to form the oil-in-water emulsion. Fifteen milliliters of the DETA solution was slowly added to the emulsion with stirring at 800 rpm to initiate the interfacial polymerization, and the reaction was carried out for 30 min at 30°C, and then the bath was raised to 70°C to promote the reaction of TDI and PPG2000, and the reaction was continued for 180 min. The remaining 5 mL of DETA solution was added to the system. The reaction was continued for another 45 min. The reactions of TDI with DETA and with PPG2000 are shown in Formula 1 and Formula 2. The formed microcapsules were filtered, washed thoroughly in distilled water at 60°C to remove the unused monomers and core materials and then dried at 40°C in an oven for 12 h.



Characterization of microcapsules

Actual core content

The actual core content of microcapsules (C_a) is defined as:

$$C_a(\%) = \left(\frac{\Delta H_m}{\Delta H_{PCM}} \right) \times 100 \quad (3)$$

where, ΔH_m and ΔH_{PCM} represent, respectively, the phase transition heat of the microcapsules (J/g) and the phase transition heat of the pure PCM. In this case, PCM is butyl stearate. The phase transition heat was measured using Mettler Toledo DSC822 attached intra cooler. The samples were scanned at a rate of 3°C/min in N₂ atmosphere.

Theoretical core content

The theoretical core content (C_t) is defined as:

$$C_t(\%) = \left(\frac{W_{PCM}}{W_{PCM} + W_m} \right) \times 100 \quad (4)$$

where, W_{PCM} and W_m ($W_m = W_{PPG2000} + W_{DETA} + W_{TDI}$) represent, respectively, the weight of PCM and the total weight of the core materials and the monomers.

Encapsulation efficiency

The encapsulation efficiency (E) is defined as:

$$E(\%) = \left(\frac{C_a}{C_t} \right) \times 100 \quad (5)$$

Surface characterization

The morphology of the microcapsules was examined using an optical microscope (OLYMPUS CX41-32RFL) and a JSM 6460 SEM.

FTIR spectra

Infrared spectra of microcapsule were analyzed using a Nicolet 5700 Fourier transform infrared spectrophotometer.

Distribution of particle size

The size and diameter distribution of the microcapsules was obtained by using a Malvern MS2000 laser diameter distribution machine.

RESULTS AND DISCUSSION

Effect of core-to-monomer ratio

Although the dosage of PPG2000 is 1 g, the values of the actual core content (C_a), theoretical core con-

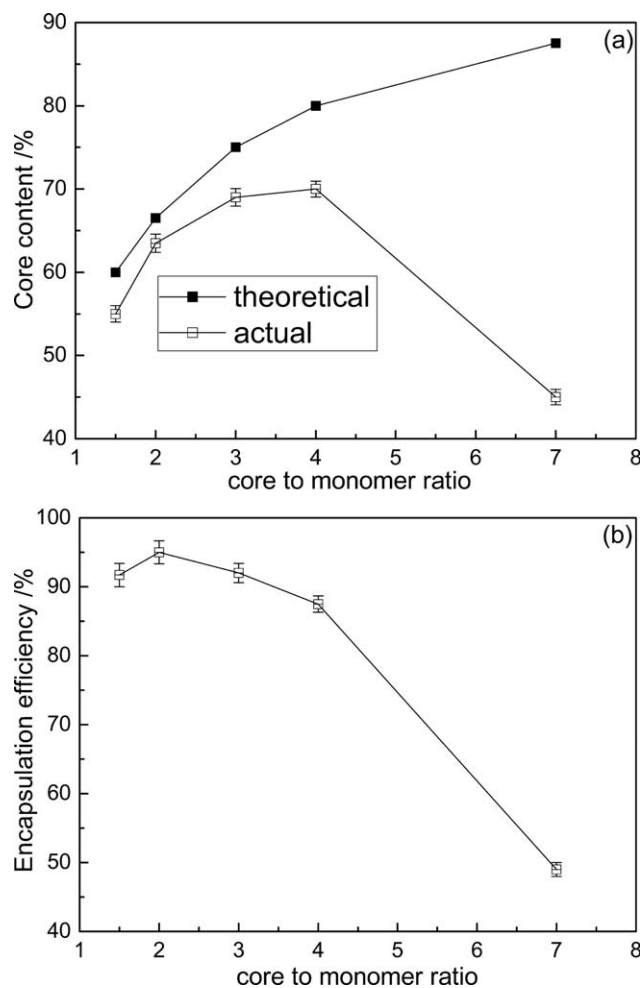


Figure 1 Effect of core to monomer ratio on (a) core content and (b) encapsulation efficiency. The error bar represents the means \pm standard error of three experiments.

tent (C_t), and encapsulation efficiency (E) against the core-to-monomer ratio are plotted in Figure 1. It can be seen from Figure 1(a) that at a high core-to-monomer ratio, the C_a is very low, whereas the C_t is at the maximum. This suggests that the amount of monomer is not sufficient to form shell of microcapsules, and the loss of core material is very high at this stage. As the core-to-monomer ratio is lowered, the C_t decreases as expected, whereas the C_a increases owing to a better shell formation around the core. The C_a decreases after reaching a critical point at the core-to-monomer ratio of 4, which indicates that core-to-monomer ratio of 3–4 is sufficient to form stable shell around the core material. Any further increase in monomer content only adds the dead weight to the microcapsules, resulting in lower core content. On the other hand, E is very high at low core-to-monomer ratio, as is shown in Figure 1(b), because enough TDI is present in oil droplets to form proper polymeric shells, and it has a maximum value of 95% at core to monomer ratio of 2.

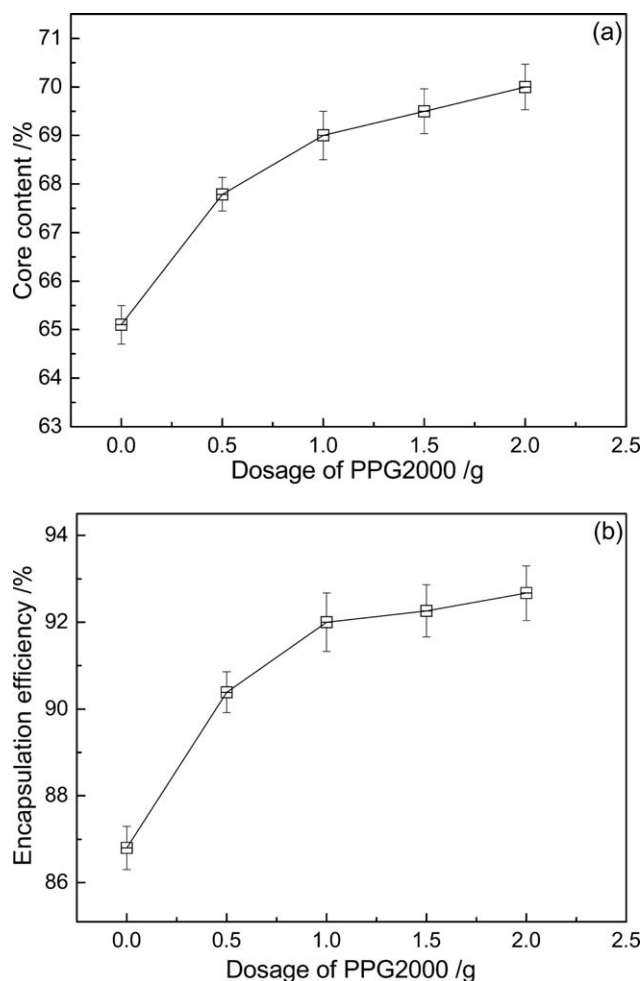


Figure 2 Effect of the dosage of PPG2000 on (a) core content and (b) encapsulation efficiency of microPCMs. The error bar represents the means \pm standard error of three experiments.

Effect of the dosage of PPG2000

In this article, double-shell microcapsules were prepared through interfacial polymerization. The outer shell is polyurea formed through polymerization of TDI and DETA, and the inner shell is PU formed through unreacted or residual isocyanate reacting with PPG2000 in the inner surface of the polyurea shell. Although the core-to-monomer ratio is 3, the C_a and the E against the weight of the PPG2000 are plotted in Figure 2. As shown in Figure 2(a), the C_a and E of the double-shell microcapsules formed with the addition of PPG2000 are obviously improved contrasting to the single-shell microcapsules formed without PPG2000, and with the increasing content of PPG2000, C_a and E raise slightly, which is because more weight of shell formed by TDI conversion reacted with adequate PPG2000. It can be seen from Figure 2 that the suitable dosage of PPG2000 is 1 g, more dosage has little

help for C_a and E and only increase the weight of shell.

FTIR spectra of the microcapsules

The FTIR spectra of the pure PCM and double-shell microPCMs (core-to-monomer ratio is 3, dosage of PPG2000 is 1 g) are illustrated in Figure 3.

In Figure 3(a), 1739 cm^{-1} corresponds to the stretching vibration of C=O. In Figure 3(b), 3310 cm^{-1} corresponds to the stretching vibration of N—H, and 1643 cm^{-1} corresponds to the bending vibration of N—H. There is no obvious peak present at 2220 \sim 2280 cm^{-1} , which suggests that N=C=O has completely reacted. The characteristic stretching vibrations of 1,2,4-triple substitution on benzene ring are 966 and 852 cm^{-1} . The in-plane and out-of-plane bending vibrations of C—H at benzene ring are 721 and 1070 cm^{-1} , respectively. The stretching vibrations of C—H in methyl and methylene are 2924 and 2854 cm^{-1} . The stretching vibration of C—O—C is 1238 cm^{-1} . The stretching vibration of ether bond is 1117 cm^{-1} , and the stretching vibrations of poly-oxypropylene are 1379 and 1024 cm^{-1} . These FTIR results have confirmed that the shell of microcapsules is composed of polyurea and PU.

Surface morphology of microcapsules

Figure 4 (a) shows an optical photograph of the microcapsules in the slurry state and (b) a SEM photograph of the microcapsules in the powder state (core to monomer ratio is 3; dosage of PPG2000 is 1 g).

In Figure 4(a), the optical photograph was taken after polymerization in water. It shows that the diameter of the microPCMs is uniform, the agglomeration between particles of the microcapsules was not

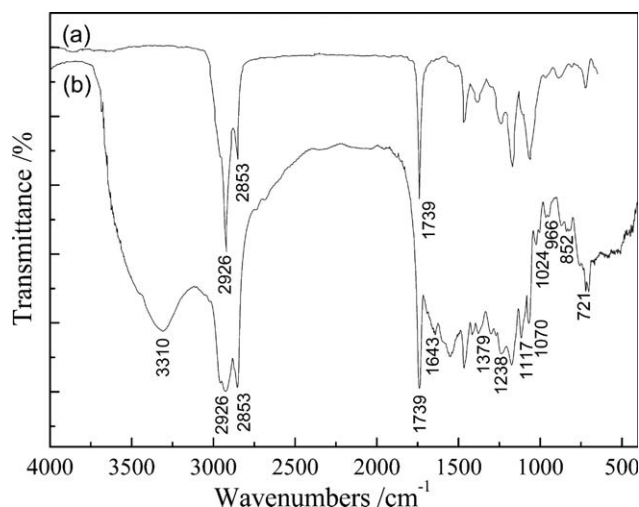


Figure 3 FTIR spectra of (a) butyl stearate and (b) microPCMs.

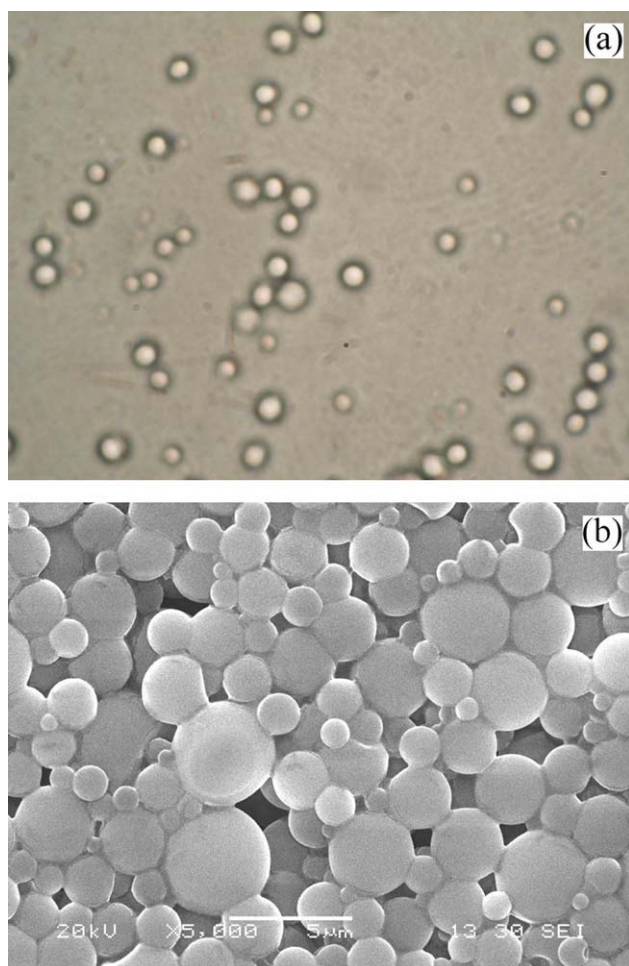


Figure 4 Surface morphology of Double-shell microPCMs of (a) optical photograph; (b) SEM photograph. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

observed in the slurry states. It can be clearly seen from Figure 4(b) that most of the microcapsules were spheres with a smooth and compact surface. The diameter of the microcapsules was found to be 1–5 μm .

DSC measurement of microcapsules

The DSC curves of butyl stearate and microPCMs (core-to-monomer ratio is 3, dosage of PPG2000 is 1 g) are plotted in Figure 5.

As is shown in Figure 5, for butyl stearate, the phase change temperature is 23.2°C, the phase change heat is 122 J/g, and for microcapsules, the phase change temperature is 24.1°C, the phase change heat is 85 J/g. So, the phase change temperature for microencapsulated butyl stearate slightly raises and the phase change heat decreases, which may be caused by the heat block of shell and the decrease of energy density in microcapsules. The

DSC results make it clear that the polymer shell of microcapsules does not influence the change properties of the PCM. Chen et al.¹⁹ microencapsulated butyl stearate through interfacial polymerization technique. It was found that when the core to monomer ratio is 3, the phase change temperature and phase change heat of the microPCMs were 29.3°C and 85.9 J/g, respectively. Xing et al.²⁰ microencapsulated butyl stearate through *in situ* polymerization technique, and the phase change temperature of the pure PCM and that of the microPCMs were, respectively, 22.1 and 21.7°C. With the change of temperature rise rate, the phase change temperature will appear great difference.²¹

Particle size and size distribution

Figure 6(a) shows the particle diameter size distribution and cumulative distribution of the single-shell microPCMs (core-to-monomer ratio is 3, dosage of PPG2000 is 0 g) and (b) the double-shell microPCMs

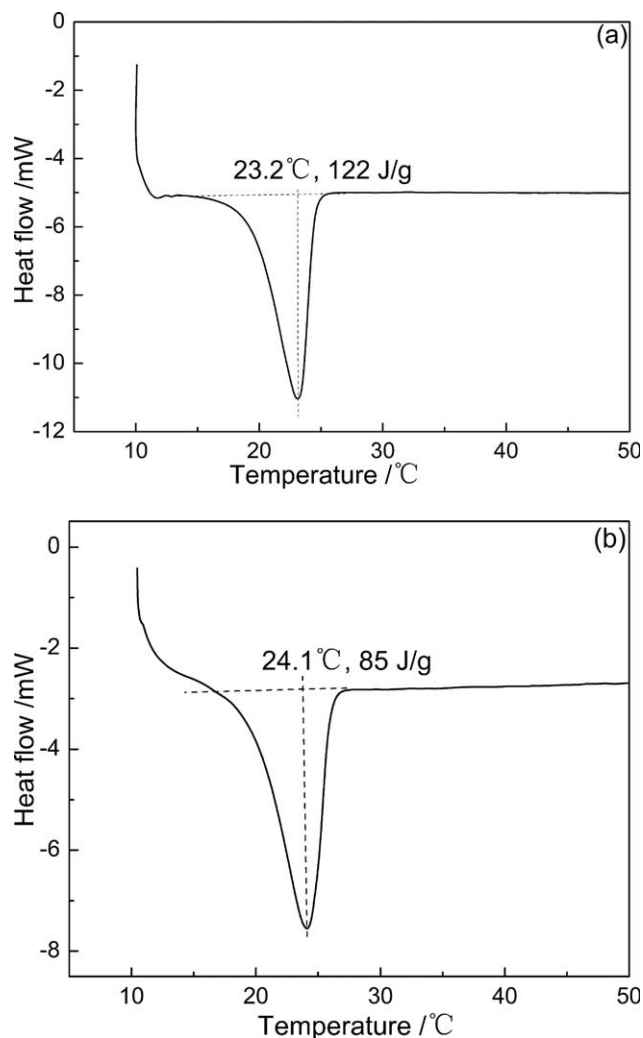


Figure 5 DSC curves of (a) butyl stearate and (b) double-shell microcapsules.

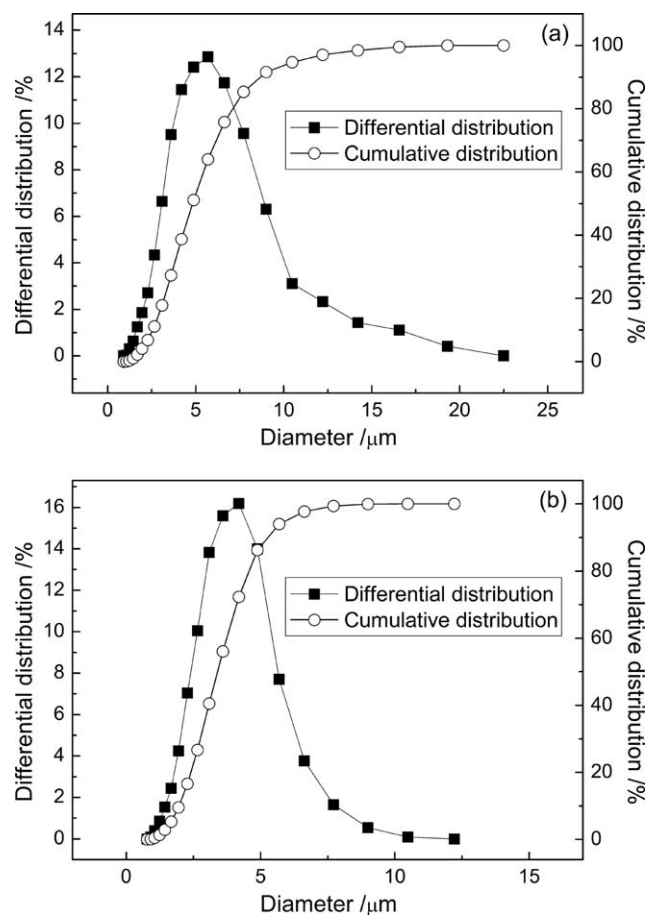


Figure 6 Particle size and size distribution of (a) single-shell microPCMs and (b) double-shell microPCMs.

(core-to-monomer ratio is 3, dosage of PPG2000 is 1 g).

As is shown in Figure 6(a), the average particle diameter size of the single-shell was 5.3 μm , and cumulative distribution was 100% at 19.31 μm . In contrast, in Figure 6(b), the average particle diameter size of the double-shell was 4.2 μm , and cumulative distribution was 100% at 10.48 μm . These results indicate that the particle size of the double-shell microcapsules was much smaller than that of single-shell microcapsules. Because PPG2000 is a kind of nonionic surfactant, when added small amount of PPG2000 to

the oil phase it can modify the surface tension of core material and make the small core material particles easy to emulsify. It is believed that the droplets of the core materials with modified surface tension became much more stable in the hydrophilic emulsion system. From Figure 6(b), it can also be seen that the diameter of most of the microcapsules was between 1 and 7 μm , so the prepared double-shell microcapsules were relatively small and uniform.

Stability of microPCMs

Stability to hot water wash

There is no leakage of butyl stearate, whereas the microcapsules are washed in 60°C hot water (higher than the melting point of butyl stearate, 23.2°C). This suggests that the shell of double-shell microcapsules has good stability to hot water washing.

Stability to ethanol wash

In the case of the core-to-monomer ratio being 3, microPCMs prepared with different dosage of PPG2000 were washed with ethanol at room temperature to test its solvent resistance. The results are given in Table II.

It can be seen from Table II that all samples have a drop of core content after being washed using ethanol. This can be explained that ethanol has good solubility to butyl stearate, and even the good encapsulation can hardly prevent the loss of core content. However, double-shell microPCMs formed with the addition of PPG2000 has more retention of core content than that of single-shell microPCMs without the usage of PPG2000, and with the increasing dose of PPG2000, the core content increases. So, double-shell microPCMs have better stability than single-shell microPCMs.

Stability to heat

Microcapsules (core-to-monomer ratio is 3, different dosage of PPG2000) were placed on kraft paper and

TABLE II
The Stability of Microcapsules with Different Dosage of PPG2000 to Ethanol^a

Dosage of PPG2000 (g)	Core content before ethanol wash (%)	Core content after ethanol wash (%)	Retention rate (%)
0	65.1 \pm 0.6	41.2 \pm 0.6	63.3
1.0	69.0 \pm 0.6	54.8 \pm 0.5	79.4
2.0	70.2 \pm 0.5	57.5 \pm 0.4	81.9

^a Values are shown as means \pm standard division of three experiments (error bars).

TABLE III
The Stability of Microcapsules with the Different Dosage of PPG2000 to Heat^a

Dosage of PPG2000 (g)	Weight of microcapsules before heat treatment (g)	Weight of microcapsules after heat treatment (g)	Retention rate (%)
0	2.15 \pm 0.12	1.38 \pm 0.15	64.19
1.0	2.11 \pm 0.15	1.78 \pm 0.21	84.36
2.0	2.23 \pm 0.08	1.98 \pm 0.18	88.79

^a Values are shown as means \pm standard division of three experiments (error bars).

heated at 120°C for 3 h to check the heat stability. The weights of microcapsules before and after heating were listed in Table III.

It can be seen from Table III that double-shell microcapsules have better heat stability than single-shell microcapsules, and with the increasing dosage of PPG2000, heat stability has obviously improved. This suggests that single-shell microcapsules have poor compactness, and the double-shell structure formed by the introduction of PPG2000 can largely improve the heat stability of microcapsules, which is caused by the better compactness of double-shell.

CONCLUSIONS

In this investigation, a series of double-shell microPCMs was prepared through interfacial polymerization, and butyl stearate and SMA were, respectively, used as core material and emulsifier. The outer shell is polyurea formed by the reaction between TDI and DETA, and the inner shell is PU formed by the reaction between TDI and PPG2000. Different core to monomer ratios and dosages of PPG2000 were investigated to increase the core content with improved encapsulation efficiency. High core content and high encapsulation efficiency were obtained when the core to monomer ratio was at 3–4, and the suitable addition of PPG2000 was 1 g. Both optical and SEM photographs show that the microPCMs have no agglomeration, and its surface is smooth and compact. DSC shows that the microPCMs have a phase change temperature for 24.1°C, which is close to that of pure PCM. This indicates that the polymer shell of the microcapsules does not significantly influence the thermal properties of the PCM. FTIR indicates that the polymer shell of microPCMs is polyurea and PU structure.

The double-shell microPCMs have a good stability property than that of single shell microPCMs.

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