

Preparation, characterization, and thermal stability of double-composition shell microencapsulated phase change material by interfacial polymerization

Shaofeng Lu¹ · Tianwei Shen¹ · Jianwei Xing¹ · Qingwen Song¹ · Cheng Xin¹

Received: 18 October 2016 / Revised: 30 July 2017 / Accepted: 24 August 2017 / Published online: 31 August 2017
© Springer-Verlag GmbH Germany 2017

Abstract Polyurea/polyurethane double-composition shell microcapsules with *n*-octadecane as the main core material were prepared by interfacial polymerization. The outer polyurea shell was formed by the polymerization of toluene-2,4-diisocyanate (TDI) and diethylene triamine (DETA), and the inner polyurethane shell was formed by the polymerization of TDI and polypropylene glycol 2000 (PPG2000). The phase change property, chemical structure, surface morphology, and thermal stability of microcapsules were investigated by differential scanning calorimetry (DSC), FTIR, SEM, TEM, and thermal gravimetric analysis. The results show that the melting temperature and melting enthalpies of double-composition shell microcapsules were 28.6 °C and 143 J g⁻¹, respectively, and only one exothermic peak for *n*-octadecane and three peaks for microcapsules were observed in the DSC cooling curve. The prepared microcapsules with the average diameter 3 ~ 5 μm had a smooth and compact surface. The thermal stabilities and compactness of the microcapsules with double-composition shells were greatly improved compared to those of the microcapsules with single-composition shells.

Keywords Microcapsules · Polyurea · Polyurethane · Phase change material · *n*-Octadecane · Interfacial polymerization

Introduction

Microcapsules are small particles which contain functional material or core material with a polymer shell. Due to the protection

of the shell, the core materials of microcapsules cannot be easily affected by the outside environment [1]. The protection ability of the polymeric wall depends on the wall-forming materials, microencapsulation methods, and physical and chemical conditions in the process [2]. Microencapsulated phase change materials (MicroPCMs) are a kind of microcapsules with PCMs as core material, which can absorb, store, and release large amounts of latent heat over a certain temperature range when experiencing a phase transition [3–5], and have been employed in many fields such as solar and nuclear heat storage systems, building energy-saving textile fibers, and systems of industrial waste heat recovery [6–8].

During the phase change stage, PCMs can absorb or release a large amount of latent heat, but in fact the temperature of the material is constant. Fiber and textiles incorporated with the PCMs may establish a microclimate in the temperature ranges of the melting points of the employed PCMs, and so may meet the requirement for comfort. As a desirable organic PCMs, *n*-octadecane is universally applied to thermal-regulating fiber and textiles due to its appropriate phase change temperature range of 23 ~ 28 °C which is comfortable for the human body as well as its high latent heat of around 230 J/g [9].

Polyurea shell, due to the formaldehyde-free property, is widely used as shell materials of MicroPCMs. But, its applications suffering from poor thermal stability and compactness and low core contents are greatly limited. Therefore, how to improve the thermal stability and compactness of polyurea MicroPCMs has attracted more and more attention [10–12]. It was reported that improving the preparation process, such as decreasing the core/shell ratio and higher stirring speed, is helpful to enhance the thermal stability and compactness of MicroPCMs, but the effect is limited [13–15]. The existing literatures are mainly focused on single-composition shell MicroPCMs [16–18], and the single polyurea shell synthesized by diisocyanate and diamine in the aqueous phase shows

✉ Shaofeng Lu
lsf622@163.com

¹ College of Textile & Material, Xi'an Polytechnic University, Xi'an, China

obvious permeability and poor thermal stability. Su prepared double-shell microcapsules by addition of the melamine-formaldehyde (MF) prepolymer in two steps [19, 20], and the thermo-gravimetric analysis (TGA) results indicated that the thermal stability of the double-shell microcapsules was better than that of the single-shell microcapsules. However, there may exist ineluctable remnant formaldehyde when MF resins are selected as shell materials; as is known, formaldehyde is harmful to environment and health. To cover the shortage of single polyurea shell, polyurea/polyurethane double-composition shell microcapsules were prepared in this paper. The outer polyurea shell was formed by the polymerization of toluene-2,4-diisocyanate (TDI) and diethylene triamine (DETA) and the inner polyurethane shell was formed by the reaction between the unreacted or residual isocyanate and polypropylene glycol 2000 (PPG2000) in the inner surface of the polyurea shell. The formation of polyurethane shell can ameliorate or even repair the defects of polyurea shell and improve the thermal stability and compactness of the formed MicroPCMs and contribute to the wide use of double-composition shell MicroPCMs in the fields, such as of textiles, buildings, and functional thermal fluids.

Experimental

Materials

PPG2000 and *n*-octadecane were obtained from Sinopharm Chemical Reagent Co. LTD (China). Cyclohexane was obtained from Xi'an Sanpu Chemical Factory (China). DETA was obtained from Shantou Xilong Chemical Factory (China). TDI was obtained from Chengdu United Chemical & Pharmaceutical Co. LTD (China). Styrene maleic anhydride copolymer (PSMA) was obtained from Hercules (USA). All of these chemicals were of reagent grade and used without further purification.

Preparation of microcapsules

Five grams of TDI, 22.5 g of *n*-octadecane, 7.5 g of cyclohexane, and 1 g of PPG2000 were mixed well at 33 °C and used as the oil phase. 1.5 g of PSMA was used as emulsifier and dissolved in 200 ml of distilled water, and then the pH value was adjusted to 8 by adding 0.1 mol l⁻¹ of NaOH aqueous solution. This PSMA solution was used as an aqueous phase. Then, the oil materials and the aqueous emulsifier solution were put in a 500-ml beaker. The oil-in-water emulsion was

formed by stirring the mixture at 6000 rpm for 8 min using a high-shear mechanical stirrer consisting of a mesh plate encasing the stirrer blades. Then, 2 g of DETA dissolved in 20 ml of distilled water was added gradually to the emulsion, stirring at 800 rpm to initiate the interfacial polymerization, and the reaction was continued for 30 min at 33 °C (the reaction of TDI with DETA is shown in Scheme 1). The bath temperature was then raised to 70 °C to promote the reaction between TDI and PPG2000, and the reaction was continued for another 180 min (the reaction of TDI with PPG2000 is shown in Scheme 2). Thereafter, a dose of 1 g of DETA was dissolved in 20 ml of distilled water which was added to the aforementioned system, and the reaction was continued for 45 min. After that, the so-formed microcapsules were filtered and washed thoroughly in distilled water at 60 °C to remove the residual monomers and core material. The microcapsules were filtered again and then dried at 40 °C for 12 h in an oven.

Characterization of microcapsules

FTIR spectra

Infrared spectra of microcapsules were obtained by using a Nicolet 5700 Fourier transform infrared spectrophotometer.

Surface characterization

The surface morphologies of the microcapsules were examined by using a KYKY-2008B scanning electron microscope (SEM) and a JEM-3010 transmission electron microscope (TEM).

Differential scanning calorimetry curve

The phase change behaviors of the microcapsules were measured by using a TA Q100 differential scanning calorimetry (DSC) attached with an intracooler. The samples were scanned at a rate of 5 °C min⁻¹ in nitrogen (N₂) atmosphere.

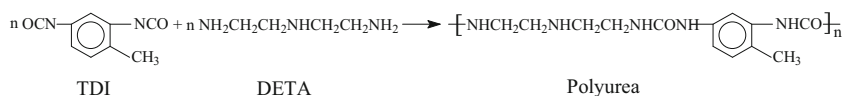
Distribution of particle size

The microcapsule size distribution was performed using a Malvern MS2000 laser particle size analyzer.

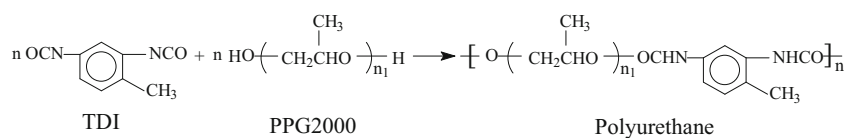
Thermal gravimetric analysis

The thermal gravimetric curves of the microcapsules were obtained by using a TA Q500 Thermogravimetric Analyzer at a heating rate of 10 °C min⁻¹ under a N₂ atmosphere.

Scheme 1 The formation of outer polyurea shell



Scheme 2 The formation of inner polyurethane shell



Results and discussion

FTIR spectra of the microcapsules

The FTIR spectra of the single-composition shell (the dosage of PPG2000 is 0 g) and double-composition shell MicroPCMs are illustrated in Fig. 1.

The FTIR spectrum of pure TDI, with the transmission bands at 2260 cm^{-1} , in Fig. 1a, was assigned to the stretching vibration of the N=C=O groups. As shown in Fig. 1b and c, the spectra reveal the bands at 3307 and 1545 cm^{-1} , which were assigned as stretching vibration and bending vibration of N-H groups, respectively, and the peaks at 1656 cm^{-1} were attributed to the stretching vibration of the C=O group. However, the peak at 2260 cm^{-1} disappeared, and this suggests that N=C=O was completely eliminated by the reaction. The absorptions at 2953 , 2912 , and 2846 cm^{-1} indicate the stretching vibration of C-H in methyl and methylene, while Fig. 1b shows two new absorption bands at 1116 and 1010 cm^{-1} which were assigned to the stretching vibration of ether bond and framework vibration of poly-oxypopylene, respectively. The FTIR spectra confirm that the shell structure of the single-composition shell microcapsules was polyurea and the shell structure of the double-composition shell microcapsules consisted of polyurea and polyurethane.

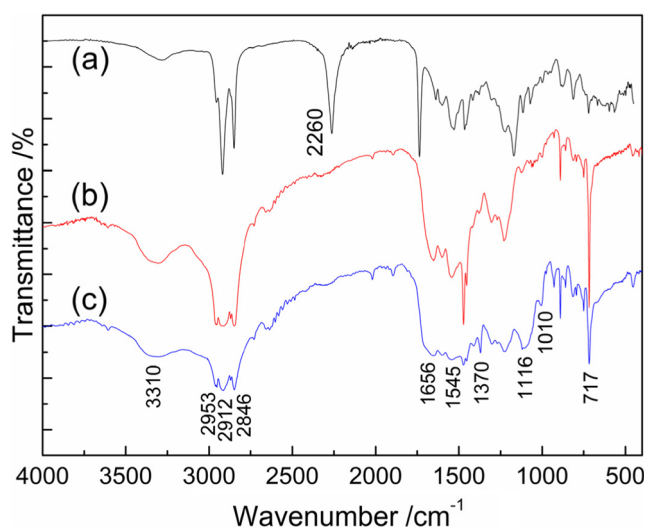


Fig. 1 FTIR spectra of **a** TDI, **b** single-composition shell MicroPCMs, and **c** double-composition shell MicroPCMs

Differential scanning calorimetry measurement of the microcapsules

The DSC melting and cooling curves of *n*-octadecane and the related MicroPCMs are shown in Fig. 2 and summarized in Table 1.

In Fig. 2 and Table 1, the enthalpies of the melted *n*-octadecane and the enthalpies of *n*-octadecane crystal are 232 and 231 J g^{-1} , respectively. The enthalpies of the microcapsules containing both liquid and solid PCMs are about $230 \sim 240 \text{ J g}^{-1}$ and the enthalpies of double-composition shell microcapsules are higher than those of single-composition shell microcapsules. These data indicate that the prepared MicroPCMs have an obviously latent heat storage performance, and the encapsulation efficiency of double-composition shell MicroPCMs is higher than that of single-composition shell MicroPCMs. Since larger latent heat change allows more heat to be absorbed or released during the phase change, the MicroPCMs can stay in the phase change temperature range for a longer period. The melting curve of microencapsulated *n*-octadecane was similar to that of the bulk *n*-octadecane, and the peak melting temperatures of *n*-octadecane and the microcapsules were approximately $28.0 \text{ }^\circ\text{C}$. In contrast, the cooling curves of the MicroPCMs were different from those of pure *n*-octadecane, and only one exothermic peak for *n*-octadecane and three peaks for single-composition shell and double-composition shell

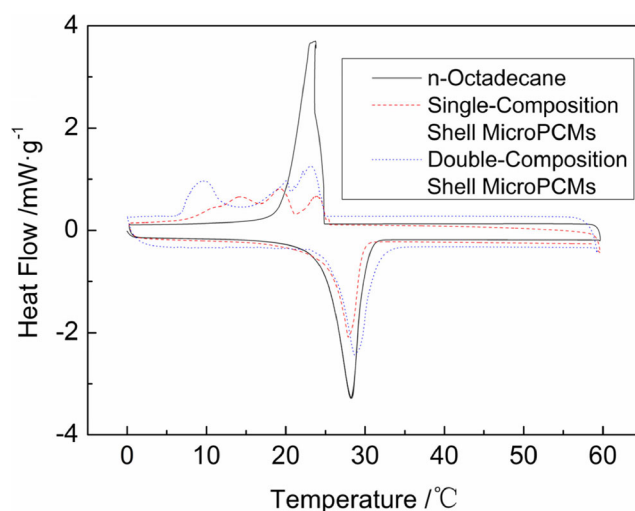


Fig. 2 DSC curves of *n*-octadecane, single-composition shell MicroPCMs, and double-composition shell MicroPCMs

Table 1 Phase change properties of *n*-octadecane and MicroPCMs

PCM/MicroPCMs	T_m (°C)	ΔH_m (J g ⁻¹)	T_c (°C)			ΔH_c (J g ⁻¹)
			α	β	γ	
<i>n</i> -Octadecane	28.2	232	23.6	–	–	231
Single-composition shell	27.9	133	24.0	19.3	14.1	130
Double-composition shell	28.6	143	23.2	19.9	9.7	141

microcapsules were observed in the DSC cooling curves. The sole exothermic peak in the DSC cooling curve of *n*-octadecane is attributed to the heterogeneous nucleation of the liquid-crystal transition [21]. Kraack found that multiple crystallization peaks appeared because of the change of the crystallization mechanism [22]. The peak alpha corresponds to the heterogeneously nucleated liquid-rotator transition, the peak beta is attributed to rotator-crystal transition, and the peak gamma is attributed to the homogeneously nucleated liquid-crystal transition. The multiple peaks in the DSC cooling curves denoted that the latent heat of MicroPCMs would be released at a wider temperature range or at a lower temperature.

Surface morphology of microcapsules

The prepared microcapsules were dried in an oven at 40 °C for 12 h, and their morphologies are shown in Fig. 3.

It can be seen from Fig. 3 that most of the microcapsules are spheres with a smooth and compact surface, and the

average diameter of the microcapsules was 3 ~ 5 μm. The dosage of *n*-octadecane has a great influence on the morphology of the prepared MicroPCMs. When the dosage of *n*-octadecane is 32.5 g, serious adhesion occurs between the particles of single-composition shell MicroPCMs (Fig. 3c), but the adhesion between the particles of double-composition shell MicroPCMs is lighter (Fig. 3f). This may suggest that when PPG2000 was employed, the as-prepared double-composition shell was more compact that can effectively prevent the leakage of the core material. It can also be seen from Fig. 3 that there were some dimples on the surface of single-composition shell MicroPCMs, and the main reason was low shell strength or poor encapsulation effect. However, the dimples in double-composition shell microcapsules can be ignored. The shell strength or compactness of the double-composition shell microcapsules with PPG2000 was higher than that of single-composition shell microcapsules.

Moreover, the core shell structures of the prepared microcapsules were further investigated by TEM, and demonstrated by the micrographs in Fig. 4. The light polymeric shell was

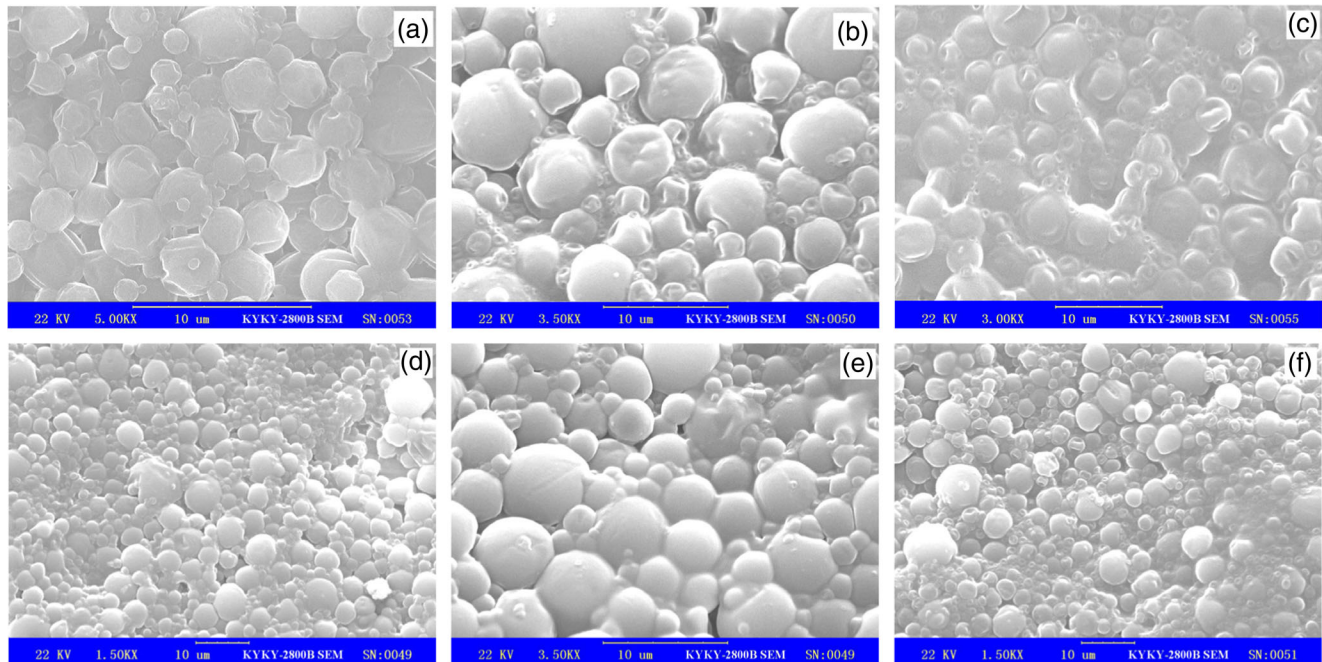
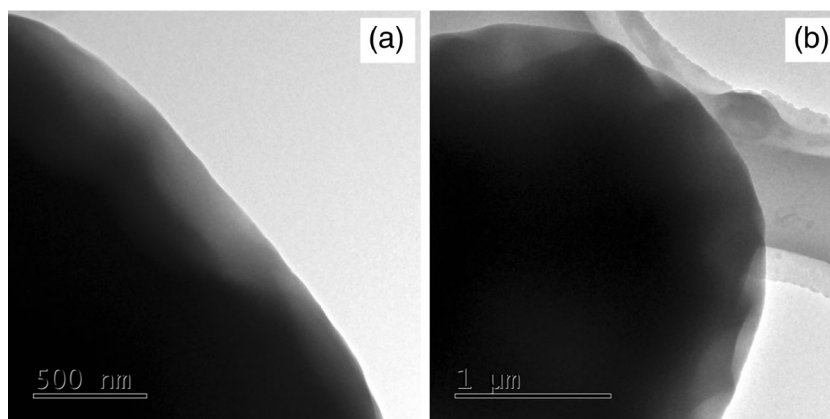


Fig. 3 SEM photograph of single-composition shell MicroPCMs and double-composition shell MicroPCMs with different dosages of *n*-octadecane (a 12.5 g, single-shell; b 22.5 g, single-shell; c 32.5 g, single-shell; d 12.5 g, double-shell; e 22.5 g, double-shell; f 32.5 g, double-shell)

Fig. 4 TEM photographs of **a** single-composition shell MicroPCMs and **b** double-composition shell MicroPCMs



clearly different from the dark *n*-octadecane core, and this result confirms that the *n*-octadecane core was well encapsulated by the polymeric shell.

Particle size and size distribution

In Fig. 5a, the particle diameter distribution and cumulative distribution of the single-composition shell MicroPCMs were shown, and those of the double-composition shell MicroPCMs were shown in Fig. 5b.

As shown in Fig. 5, the average particle diameters of the single-composition shell and double-composition shell were 5.2 and 4.6 μm , respectively. The results indicate that the particle size of the double-composition shell microcapsules was smaller than that of single-composition shell microcapsules. Because PPG2000 is a kind of nonionic surfactant, when a small amount of PPG2000 was added 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 [12]. The diameter distribution of most of the double-composition shell microcapsules was in a narrow range.

Thermal stability of MicroPCMs

Thermal stability and compactness are important performances of MicroPCMs. However, the traditional single polyurea shell synthesized by diisocyanate and diamine in the aqueous phase shows obvious permeability and poor thermal stability. In order to solve the defect problem, polyurea/polyurethane double-composition shell microcapsules were prepared in this paper. The outer polyurea shell was firstly formed by the reaction of TDI and DETA on the oil-aqueous interface under 30 $^{\circ}\text{C}$. Then, the bath temperature was elevated to 70 $^{\circ}\text{C}$ to accelerate the reaction between the unreacted isocyanate and PPG2000 in the inner surface of the polyurea shell, and the inner polyurethane shell was formed. The formation of the inner polyurethane shell can ameliorate or even repair the defects of the polyurea shell. Furthermore, the two shells can be connected by isocyanate groups and can effectively reduce the permeability of the polyurea shell. Thus, the prepared double-composition shell MicroPCMs were more compact and can effectively avoid the leakage of core material.

Figure 6 shows the TGA curves of *n*-octadecane and the single-composition shell and double-composition shell microcapsules.

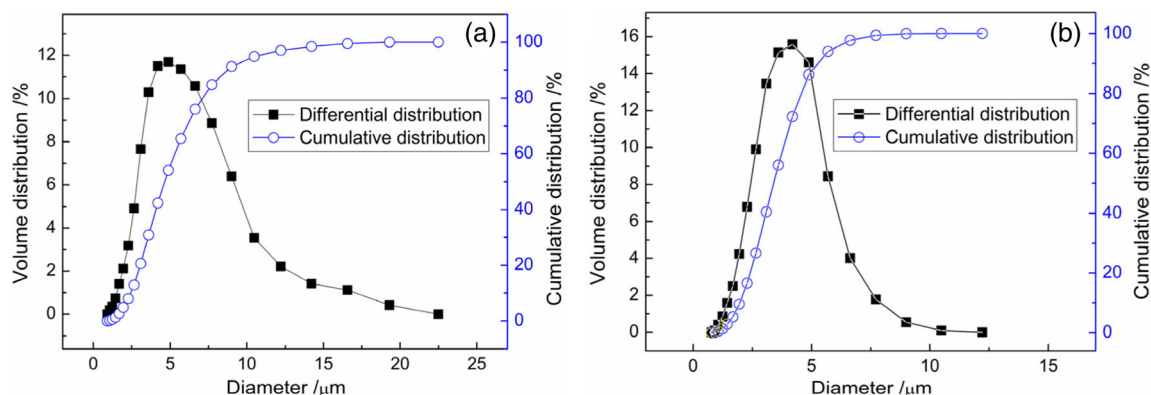


Fig. 5 Particle size and size distribution of **a** single-composition shell MicroPCMs and **b** double-composition shell MicroPCMs

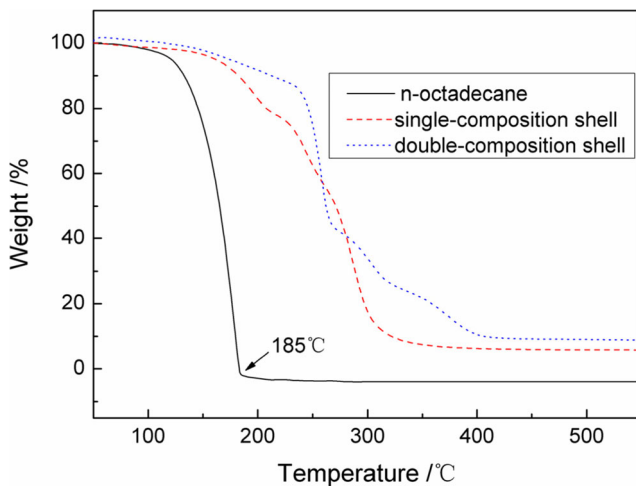


Fig. 6 TGA curves of *n*-octadecane and prepared MicroPCMs

According to Fig. 6, it can be seen that pure *n*-octadecane completely lost its weight at 185 °C, whereas the weight retention rate of the prepared MicroPCMs was around 93% at 185 °C. The results indicate that, after microencapsulation, the polymer shell significantly protected the core material from leakage and greatly improved the thermal stability. When the shell materials for the microcapsule were different, the changes of the weight loss of the microcapsule were also different. When the temperature rises to 250 °C, the weight retention rate of single-composition shell microcapsule was 62% and the weight retention rate of double-composition shell microcapsule was 75%. This indicates that the shell material of double-composition shell microcapsule can protect the core material well even at a higher temperature than the boiling point of the core material. The thermal stability of the double-composition shell microcapsules with the incorporation of PPG2000 has been greatly improved compared to that of single-composition shell microcapsule.

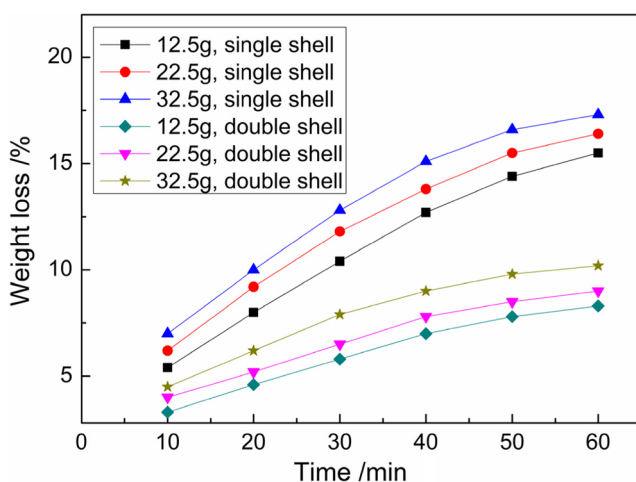


Fig. 7 The effect of *n*-octadecane dosage on compactness of prepared single-composition shell and double-composition shell MicroPCMs

The microcapsules on a tissue paper were dried at 120 °C for 1 h. The net weights of microcapsules before and after drying were measured and the compactness of microcapsules can be estimated. The weight losses of the MicroPCMs with different dosages of *n*-octadecane measured in different time intervals are shown in Fig. 7.

It can be seen from Fig. 7 that, along with drying, the weight loss increases continuously and it was caused by the leakage of core material at high temperature. With the increase of the dosage of *n*-octadecane, the weight loss of the microcapsule was also increased. With the same *n*-octadecane dosage, the weight loss of the double-composition shell microcapsules was much less than that of the single-composition shell microcapsules. The results indicate that single-composition shell microcapsule had poor compactness, while double-composition shell microcapsules with the incorporation of PPG2000 had good compactness, and only a small amount of PCM leaks after the drying. Therefore, the thermal stability of the prepared double-composition shell microcapsules was better than that of single-composition shell microcapsules.

Conclusions

The microcapsules using polyurea/polyurethane as the double-composition shell were prepared by interfacial polymerization, and the chemical structure, the phase change property, and the thermal stability of the microcapsules were investigated, respectively. FTIR results confirm that the shell structure of the single-composition shell microcapsules was polyurea, and that of the double-composition shell microcapsules was polyurea together with polyurethane. According to DSC analysis, the microcapsules had obvious latent heat and the melting point of the microencapsulated *n*-octadecane was the same as that of the bulk. Multiple peaks that occurred in the DSC cooling curves were attributed to liquid-rotator, rotator-crystal, and liquid-crystal transitions. The particle size of the double-composition shell microcapsules was smaller than that of the single-composition shell microcapsules. The prepared double-composition shell microcapsules had higher thermal stability and compactness than the single-composition shell microcapsules.

Acknowledgements This study was funded by the National Natural Science Foundation of China (51403169) and Shaanxi Provincial Key Laboratory Scientific Research Project (15JS029). This study was also funded by the Science and Technology Guidance Project of China National Textile and Apparel Council (2016034).

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Pascu O, Garcia-Valls R, Giamberini M (2008) Interfacial polymerization of an epoxy resin and carboxylic acids for the synthesis of microcapsules. *Polym Int* 57:995–1006
2. Chao DY (1993) The role of surfactants in synthesizing polyurea microcapsule. *J Appl Polym Sci* 47:645–651
3. Bishop JRP, Nelson G, Lamb J (1998) Microencapsulation in yeast cells. *J Microencapsul* 15:761–773
4. Song QW, Li Y, Xing JW, Hu JY, Marcus Y (2007) Thermal stability of composite phase change material microcapsules incorporated with silver nano-particles. *Polymer* 48:3317–3323
5. Xing S, Yang JS, Huang YL, Zheng Q, Zeng JC (2015) Preparation and characterization of a novel microcapsule-type latent curing agent for epoxy resin. *Mater Des* 85:661–670
6. Li W, Zong JW, Huang R, Wang JP, Wang N, Han N, Zhang XX (2016) Design, controlled fabrication and characterization of narrow-disperse macrocapsules containing Micro/NanoPCMs. *Mater Des* 99:225–234
7. Chen C, Wang L, Huang Y (2009) Crosslinking of the electrospun polyethylene glycol/cellulose acetate composite fibers as shape-stabilized phase change materials. *Mater Lett* 63:569–571
8. Chen Z, Fang GY (2011) Preparation and heat transfer characteristics of microencapsulated phase change material slurry: a review. *Renew Sust Energ Rev* 15:4624–4632
9. Zhang H, Sun S, Wang X, Wu D (2011) Fabrication of microencapsulated phase change materials based on n-octadecane core and silica shell through interfacial polycondensation. *Colloids Surf A Physicochem Eng Asp* 389:104–117
10. Siddhan P, Jassal M, Agrawal AK (2007) Core content and stability of n-octadecane-containing polyurea microcapsules produced by interfacial polymerization. *J Appl Polym Sci* 106:786–792
11. Su JF, Wang LX, Ren L, Huang Z, Meng XW (2006) Preparation and characterization of polyurethane microcapsules containing n-octadecane with styrene-maleic anhydride as a surfactant by interfacial polycondensation. *J Appl Polym Sci* 102:4996–5006
12. Lu SF, Xing JW, Zhang ZH, Jia GP (2011) Preparation and characterization of polyurea/polyurethane double-shell microcapsules containing butyl stearate through interfacial polymerization. *J Appl Polym Sci* 121:3377–3385
13. Han PJ, Lu LX, Qiu XL, Tang YL, Wang J (2015) Preparation and characterization of macrocapsules containing microencapsulated PCMs (phase change materials) for thermal energy storage. *Energy* 91: 531–539
14. Fan YF, Zhang XX, Wu SZ, Wang XC (2005) Thermal stability and permeability of microencapsulated n-octadecane and cyclohexane. *Thermochim Acta* 429:25–29
15. Lu SF, Xing JW, Wu Q (2013) Preparation and characterization of high stability polyurea MicroPCMs using a two-step method of adding DETA by interfacial polymerization. *J Fiber Bioeng Inform* 6:185–194
16. You M, Zhang XX, Li W, Wang XC (2008) Effects of MicroPCMs on the fabrication of MicroPCMs/polyurethane composite foams. *Thermochim Acta* 472:20–24
17. Chen L, Xu L, Shang H, Zhang Z (2009) Microencapsulation of butyl stearate as a phase change material by interfacial polycondensation in a polyurea system. *Energy Convers Manag* 50:723–729
18. Li W, Zhang XX, Wang XC, Tang GY, Shi HF (2012) Fabrication and morphological characterization of microencapsulated phase change materials (MicroPCMs) and macrocapsules containing MicroPCMs for thermal energy storage. *Energy* 38:249–254
19. Su JF, Wang LX, Ren L, Huang Z (2007) Mechanical properties and thermal stability of double-shell thermal-energy-storage microcapsules. *J Appl Polym Sci* 103:1295–1302
20. Su JF, Wang L, Ren L (2005) Preparation and characterization of double-mf shell microPCMs used in building materials. *J Appl Polym Sci* 97(5):1755–1762
21. Oliver MJ, Calvert PD (1975) Homogeneous nucleation of n-alkanes measured by differential scanning calorimetry. *J Cryst Growth* 30:343–351
22. Kraack H, Sirota EB, Deutsch M (2000) Measurements of homogeneous nucleation in normal-alkanes. *J Chem Phys* 112:6873–6885