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Polyurethane foam containing microencapsulated phase-change materials with styrene–divinybenzene co-polymer shells

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Abstract Polyurethane (PU) foam containing phase change materials is a kind of new heat-insulating material which can store and release heat energy. The microencapsulated *n*-octadecane (MicroPCMs) with a styrene (St)–divinybenzene (DVB) co-polymer shell was synthesized by means of suspension-like polymerization. The surface morphology, diameter, enthalpy, and thermal stability were investigated by using scanning electronic microscope (SEM), differential scanning calorimeter (DSC), and TGA. The average diameter of the microcapsules is about 80 µm. The enthalpy of the microcapsule is about 126 J/g. PU foams containing MicroPCMs were fabricated by adding the MicroPCMs in reactants. MicroPCMs are evenly inserted inside the foam and the enthalpy of the foam rises with the increase of the content of microcapsules. The enthalpy is about 24 J/g for the foam containing 26.8 wt% MicroPCMs.

Introduction

Microcapsules are tiny particles that contain active agent or core material surrounded by a coating or shell [1]. MicroPCMs have attracted more and more attention since 1980s, as they are regarded as renewable and clean energy storage materials [2, 3]. From then on, MicroPCMs have been wildly used in coolants, fibers, fabrics, and coatings [4–8].

The attempt of using MicroPCMs in polyurethane (PU) foams to improve their thermal performance was developed in 1990s [9]. This technology relates generally to the field of foamed heat insulation materials. The foam containing MicroPCMs is very useful in the heat-insulating application, such as footwear, clothing, automotive interiors, and medical product [10, 11]; however, there is little information available about the composition. MicroPCMs with melamine–formaldehyde co-polymer shells have been applied in fabrication of heat-insulated PU foams in our previous research [12]. The process of fabrication was complex because of the defoaming action of MicroPCMs with melamine–formaldehyde co-polymer shells [13] and the rapid increase of the mixture viscosity. The change of the viscosity is probably caused by the reaction between isocyanate and the hydroxyl groups on the surface of melamine–formaldehyde shells. In this study, MicroPCMs with a styrene (St)–divinybenzene (DVB) co-polymer shells were added in foaming system directly and PU foams containing MicroPCMs were prepared.

Experimental

Materials

Styrene (purity 98 wt%, Tianjin Chemical Reagent Factory) and divinybenzene (purity about 80 wt%, Chengdu Kelong Chemical Reagent Factory) were used as shell-forming monomers. *n*-Octadecane (95 wt%, Union Lab. Supplies Limited, Hong Kong) was used as core material. 2, 2′-azobisisobutyronitrile (AIBN, analytical pure) was purchased from Tianjin Kermel Chemical Reagent Co., Ltd. and was used as an initiator. Polyvinyl alcohol 1750 (PVA, purity 99 wt%, Tianjin Kermel Chemical Reagent Co., Ltd.) and

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polyvinylpyrrolidone (PVP, purity 95 wt%, Tianjin Kermel Chemical Reagent Co., Ltd.) were used as stabilizer.

High elasticity polyurethane foam mixed materials, YB-5181 (Stuff A: mixture of polyether polyol, foaming agent and so on), YB-6280 (Stuff B: isocyanate) were purchased from Jiangyin YOBO Chemical Industry Co. Ltd., Jiangsu province. The producer proposed weight radio was: Stuff A:Stuff B = 100:33; stuff temperature: 20–25 °C; mold temperature: 65 ± 5 °C.

Dibutyltin dilaurate (DBTL, chemical pure) was purchased from Tianjin Chemical Reagent Factory and was used as catalysts of foaming.

Fabrication of MicroPCMs

Styrene was washed with sodium hydroxide to remove the inhibitor and calcium chloride as the desiccant to keep for 24 h.

Microencapsulation was carried out in a three-neck-flask of 500-ml with predetermined stirring rate, a water thermostat bath and a nitrogen gas inlet tube. Figure 1 shows the preparation process of MicroPCMs.

The synthesis process involves two phases: a discontinuous phase and a continuous phase (Table 1). A discontinuous phase was obtained by mixing *n*-octadecane, St, DVB, and AIBN. One gram of PVA and 1.4 g of PVP were dissolved in 237.6 g of distilled water to form a continuous phase. The discontinuous phase was added to the continuous phase when the continuous phase was heated to 55 °C. The mixture was emulsified with a stirring rate of 1,400 rpm for about 10 min. Then the temperature was risen to 80 °C, the reaction was begun and continued with a stirring rate of 800 rpm for 5 h. The resultant microcapsules were washed with hot water and filtered to remove impurities, and then dried in an oven at about 50 °C until the mass was constant.

Fabrication of PU foams containing MicroPCMs

The predetermined masses of Stuff A, MicroPCMs, and DBTL were added in a beaker and mixed vigorously with strong stirring to obtain a formulated mixture. The predetermined masses of Stuff B were then added in the same beaker and strong stirring was applied for 5–10 s. The obtained mixture was left undisturbed for about 1 min allowing the formation and growth of the foam. Then it was immediately moved into an oven and kept at 60 °C for about 10 min.

Table 1 Recipe for the preparation of MicroPCMs

Continuous phase			Discontinuous phase			
PVA (g)	PVP (g)	H_2O (g)	St (g)	DVB (g)	*n*-Octadecane (g)	AIBN (g)
1.0	1.4	237.6	27.2	2.8	24–45	0.7

Characterization of MicroPCMs and foams

The surface morphologies of MicroPCMs and foams were obtained by using a scanning electronic microscope (SEM, Quanta-200). The specimens were coated with gold.

The thermal properties of MicroPCMs and foams were measured using a differential scanning calorimeter (DSC, Perkin-Elmer, DSC7) at a rate of ±5 °C/min in a nitrogen atmosphere. The content of *n*-octadecane in the microcapsule can be calculated approximately according to the measured enthalpies,

$$x = \frac{|\Delta H|}{|\Delta H_0|} \times 100\% \quad (1)$$

where, $|\Delta H|$ is the enthalpies of MicroPCMs; $|\Delta H_0|$ is the melting enthalpy of *n*-octadecane, and here it is about 222 J/g measured by DSC.

The thermal stabilities of MicroPCMs and foams were investigated by using a thermogravimetric analyzer (NETZSCH STA 409 PC/PG TG-DT) at a scanning rate of 10 °C/min in the range of 25–600 °C under a nitrogen atmosphere.

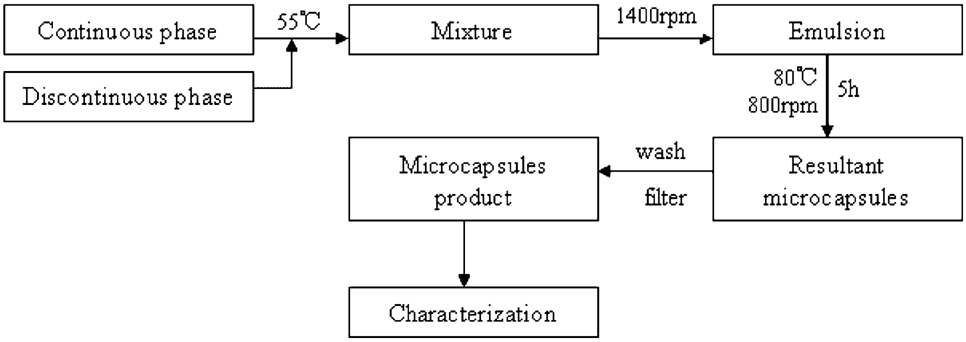

Fig. 1 Preparation process of microcapsules

Results and discussion

Effects of monomer/n-octadecane mass ratios on the enthalpy of MicroPCMs

In order to explore the effects of monomer/*n*-octadecane mass ratio on the enthalpy of MicroPCMs, a series of experiments using different monomer/*n*-octadecane mass ratios in the range from 5:4 to 2:3 were carried out (Table 2). *n*-Octadecane could be well encapsulated when the ratio of St to DVB was about 10:1 [14], and the ratio was controlled at about 9.7:1 in our experiment.

Figure 2 shows DSC curves of MicroPCMs with different monomers/*n*-octadecane mass ratios. The heat absorbing and evolving properties of MicroPCMs are listed in Table 3. The results show that MicroPCMs have endothermic peak and exothermic peak in the process of heating and cooling in the range of 5–40 °C compared to pure St–DVB co-polymer, respectively. Furthermore, it can be seen that, when the monomers/*n*-octadecane mass ratio of 1:1 is used, the enthalpy of MicroPCMs is the highest among all and the content of *n*-octadecane is about 56.8 wt%. The enthalpy of MicroPCMs would decrease when the monomers/*n*-octadecane mass ratio was less than 1:1. The fact could be a consequence of a shortage of co-polymer that could not completely cover *n*-octadecane.

Table 2 Different monomer/*n*-octadecane mass ratios

St (g)	DVB (g)	*n*-Octadecane (g)	AIBN (g)	Monomer:*n*-octadecane mass ratio
27.2	2.8	0	0.7	1:0
27.2	2.8	24	0.7	5:4
27.2	2.8	30	0.7	1:1
27.2	2.8	37.5	0.7	4:5
27.2	2.8	45	0.7	2:3

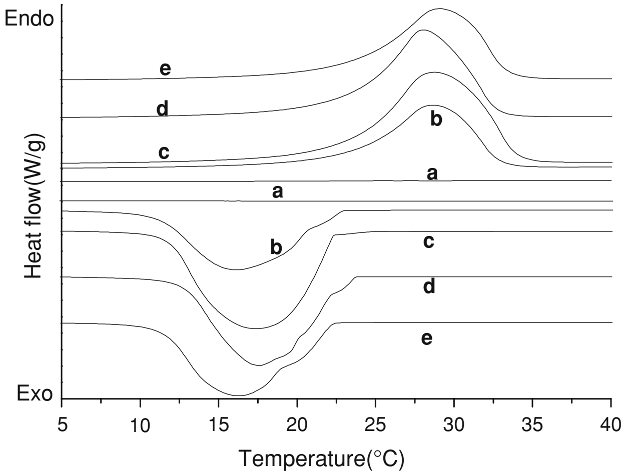

Fig. 2 DSC curves of MicroPCMs with different monomers/*n*-octadecane mass ratios: (a) 1:0; (b) 5:4; (c) 1:1; (d) 4:5; (e) 2:3

Characterization of MicroPCMs

Scanning electronic microscope micrographs of MicroPCMs synthesized with monomers/*n*-octadecane of mass ratio 1:1 are shown in Fig. 3. The average diameter of MicroPCMs is about 80 μm, which could be adequate for the application in foams [9]. The sizes of MicroPCMs are affected by the stirring rate in emulsion and reaction process, the viscosity of liquid medium in the suspension process, etc., and the results have been reported elsewhere [15, 16]. It can be seen from SEM micrographs that majority of MicroPCMs show large concaves.

The reason can be explained by the production of reserved expansion space in the process of MicroPCMs preparation [17]. First, the density of monomer was smaller than that of St–DVB co-polymer and the expansion space would produce in the process of reaction because of the density change. Second, *n*-octadecane would shrink from melting state to crystal state in the cooling process. Therefore, these large concaves are mainly attributed to the shrinkage of the expansion space (Fig. 4).

Differential scanning calorimeter (DSC) curves of St–DVB co-polymer, *n*-octadecane, and MicroPCMs are presented in Fig. 5. MicroPCMs have endothermic peak and exothermic peak in the process of heating and cooling compared to pure St–DVB co-polymer. DSC cooling curve of MicroPCMs also illustrated the supercooling phenomenon, which was attributed to the decrease of nucleation with the diameters reduction of MicroPCMs [18].

Figure 6 shows TG diagrams of St–DVB co-polymer and MicroPCMs. Obviously, the weight-loss of pure St–DVB co-polymer at the temperature of about 395 °C was caused by the decomposition of molecular chains. There was no weight-loss of MicroPCMs before 230 °C and the weight-loss at the temperature of about 230 °C was caused by the diffusion of core materials out of the shell, which was resulted by the expansion of *n*-octadecane [19]. The existence of the expansion space of MicroPCMs led to a higher thermal resistant temperature compared to MicroPCMs with a melamine–formaldehyde co-polymer shell at about 160 °C [20]. It can be seen from the characterization of MicroPCMs that *n*-octadecane had been well encapsulated by St–DVB co-polymer.

Morphology of PU foams

In the process of PU foam formation, the use of filler can influence the surface tension and viscidity of foaming

Table 3 Heat properties of MicroPCMs with different monomers/*n*-octadecane mass ratios

Monomer/*n*-octadecane mass ratio	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	ΔH_a (°C)	*n*-Octadecane content (wt%)
1:0	–	0	–	0	0	–
0:1	31	222	21	222	222	–
5:4	29	80	16	82	81	36.5
1:1	29	125	16	127	126	56.8
4:5	28	108	18	109	109	48.7
2:3	29	95	16	95	95	42.8

T_m Melting point; ΔH_m Melting enthalpy; T_c Crystallization point; ΔH_c Crystallization enthalpy; $\Delta H_a = (|\Delta H_m| + |\Delta H_c|)/2$

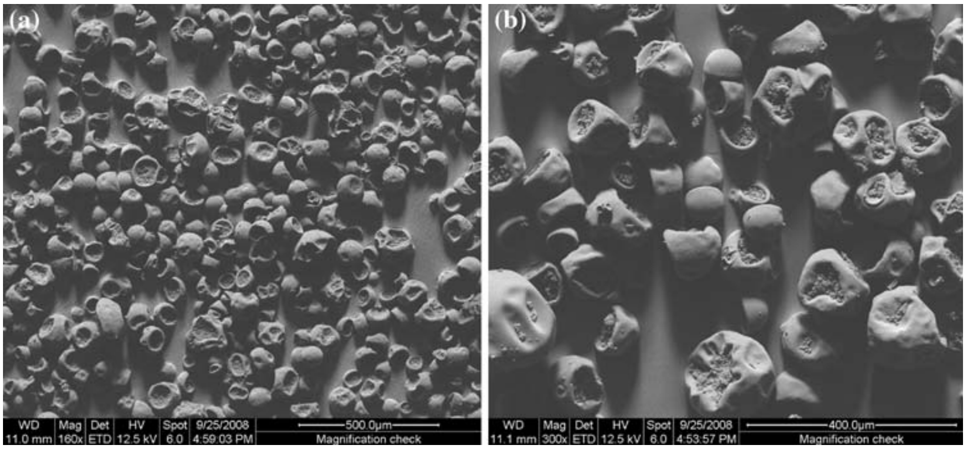

Fig. 3 SEM micrographs of MicroPCMs: **a**160×; **b** 300×

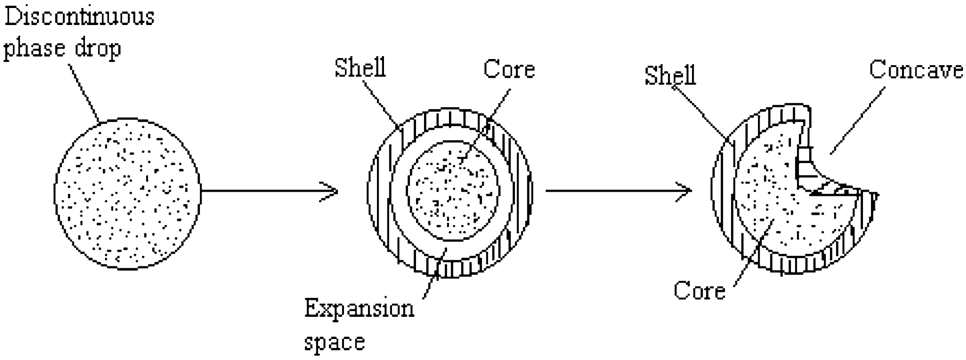

Fig. 4 Process of concave production

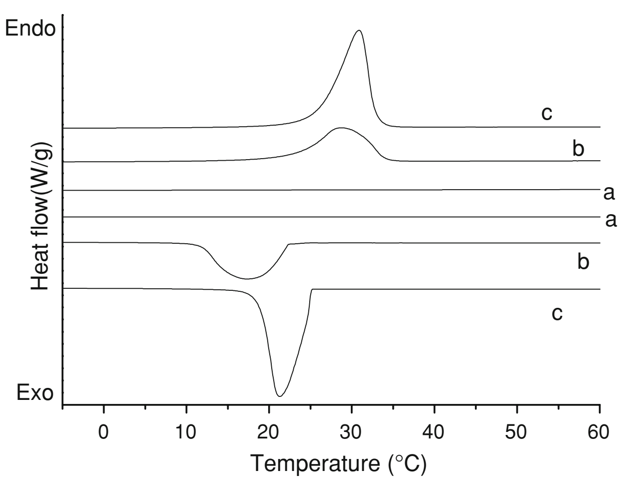

Fig. 5 DSC curves of samples: (a) St–DVB co-polymer; (b) MicroPCMs; (c) *n*-Octadecane

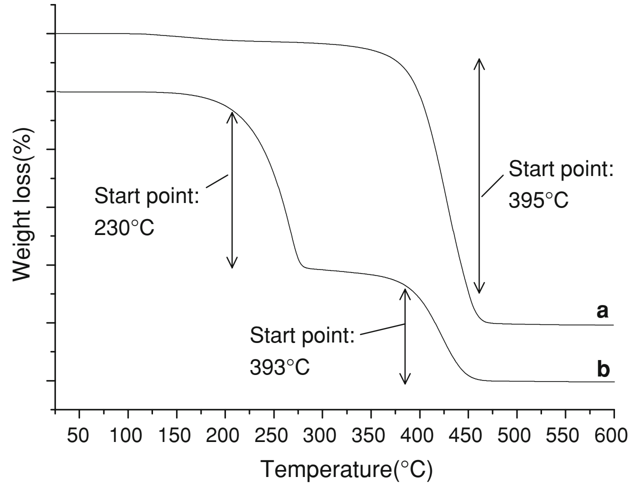

Fig. 6 TG curves of samples: (a) St–DVB co-polymer; (b) MicroPCMs

Table 4 Foaming formulation after adjusting the content of additives

Stuff A (wt%)	Stuff B (wt%)	MicroPCMs (wt%)	DBTL (wt%)	Appearance of foams
75.19	24.81	0	0	Excellent
69.93	23.07	7.00	0	Excellent
65.27	21.54	13.06	0.13	Excellent
60.49	21.17	18.16	0.18	Excellent
57.01	19.95	22.81	0.23	Excellent
53.65	19.31	26.82	0.22	Excellent

system and further cause negative effect on the foam process [21]. Increasing the content of organic stannum not only reduces the surface tension but also increases the rate of gelling reaction [22]. In this study, DBTL was used to control the quality of foams. The content of Stuff B has to be increased when adding MicroPCMs in the foaming system. In order to improve the quality of the foams, the contents of additives were adjusted. The composition and appearance of PU foams containing MicroPCMs are listed in Table 4.

MicroPCMs with a shell of St–DVB co-polymer were added in foaming system directly without heat-treatment compared to MicroPCMs with a melamine–formaldehyde co-polymer shell [13]. The reason is that the composition of discontinuous phase is simple and the additives in discontinuous phase have no negative influence on foaming system. Meanwhile, the hydrophobic shell (St–DVB co-polymer) can reduce the viscosity of foaming system, which is a benefit for the improvement of MicroPCMs content. However, the viscosity of foaming system was too high to fabricate foams when the content of MicroPCMs was higher than 26.82 wt%. In contrast, the highest content of MicroPCMs with melamine–formaldehyde shell in PU foam is only 12.59 wt% [13].

Scanning electronic microscope (SEM) micrographs of PU foam are presented in Fig. 7. Microcapsules were evenly inserted inside the foam matrix and were well compatible with polyurethane matrix.

Figure 8 shows SEM micrographs of PU foam cell structure. When MicroPCMs are added into the foaming system, the cell diameter is generally smaller than that without MicroPCMs, which is induced by the "nucleation" function and accords the rule that general added powder filling will reduce the cell diameter.

Heat absorbing and evolving properties of PU foams containing MicroPCMs

Figure 9 shows DSC curves of PU foam with various contents of MicroPCMs. Compared to pure PU foam, the foam containing MicroPCMs has endothermic peak and exothermic peak in the process of heating and cooling in the range of 5–40 °C. The heat absorbing and evolving properties of the foams are listed in Table 5. The higher the MicroPCMs content, the higher is the heat storage and thermo-regulated ability of foam. The measured average enthalpy is lower than the calculated value, which is probably caused by the poor thermal conductivity of the foam [10]. This phenomenon has been observed in MicroPCMs/polypropylene blend chips [5].

Thermal stability of PU foams containing MicroPCMs

TG curves of the foam with various contents of MicroPCMs are presented in Fig. 10. The obvious weight-loss of pure PU foams was at about 250 and 370 °C. The weight-loss at about 250 °C was caused by the decomposition of nitrogenous groups, and the weight-loss at about 370 °C was caused by further decomposition of groups and rupture of molecular chain. The foams containing MicroPCMs also have obvious weight-loss at about 250 and 370 °C. However, the inflection at about 160 °C occurred and the weight-loss was about 9 and 13 wt% when the content of MicroPCMs was 18.14 and 22.81 wt%, respectively. The

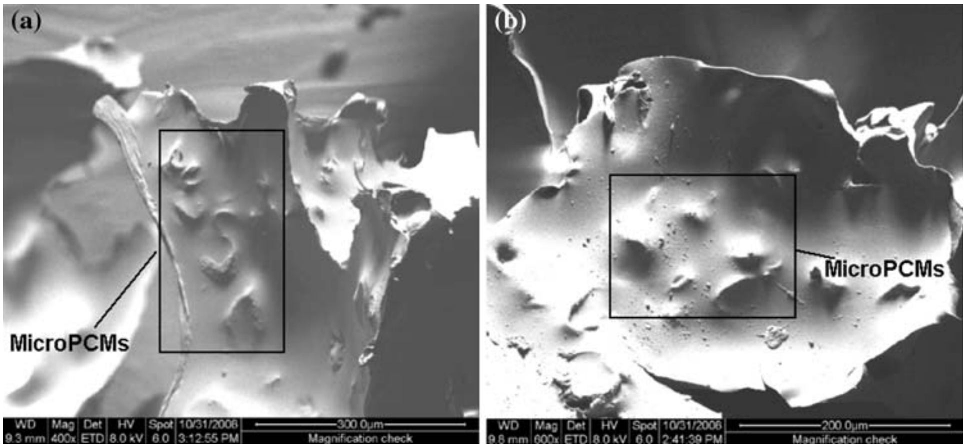

Fig. 7 SEM micrographs of PU foam containing MicroPCMs: **a** 400×; **b** 600×

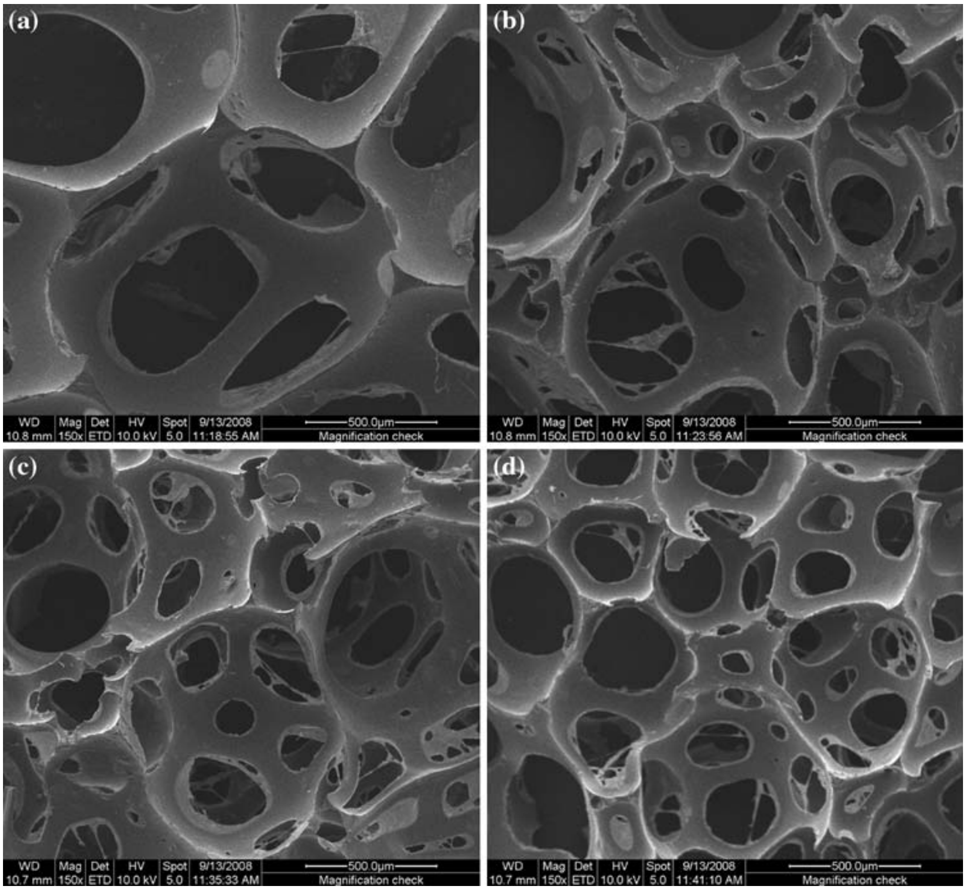

Fig. 8 SEM micrographs of PU foams with different MicroPCMs contents: **a** 0 wt%; **b** 13.06 wt%; **c** 22.81 wt%; **d** 26.82 wt%

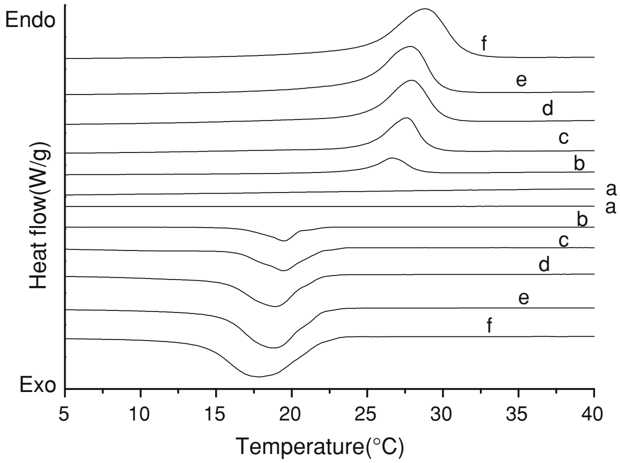

Fig. 9 DSC curves of PU foam with various contents of MicroPCMs: (a) 0 wt%; (b) 7.00 wt%; (c) 13.06 wt%; (d) 18.14 wt%; (e) 22.81 wt%; (f) 26.82 wt%

Table 5 Heat absorbing and evolving properties of PU foam containing MicroPCMs

MicroPCMs content (wt%)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	ΔH_a (J/g)	ΔH (J/g)
0 (Pure PU foam)	–	0	–	0	0	–
100 (MicroPCMs)	28	123	17	123	123.0	–
7.00	26	4	19	4	4.0	8.61
13.06	27	12	19	11	11.5	16.06
18.14	28	16	19	15	15.5	22.31
22.81	27	20	19	20	20.0	28.06
26.82	28	24	18	24	24.0	32.99

T_m Melting point; T_c Crystallization point; ΔH_m Melting enthalpy; ΔH_c Crystallization enthalpy; $\Delta H_a = (|\Delta H_m| + |\Delta H_c|)/2$; ΔH Calculated enthalpy from the composition of the foam

weight-loss was caused by *n*-octadecane leaking out of the shell at about 160 °C. It can be seen from the characterization of MicroPCMs that the thermal resistant temperature of MicroPCMs is about 230 °C, which is higher than 160 °C. It can be explained that the concaves of some MicroPCMs cannot expand with the expansion of *n*-octadecane from melting state to crystal state. The concaves of MicroPCMs are full of polyurethane matrix, which is equal to the elimination of expansion space.

Conclusions

MicroPCMs with a shell of styrene–divinybenzene copolymer can be added in foaming system directly without

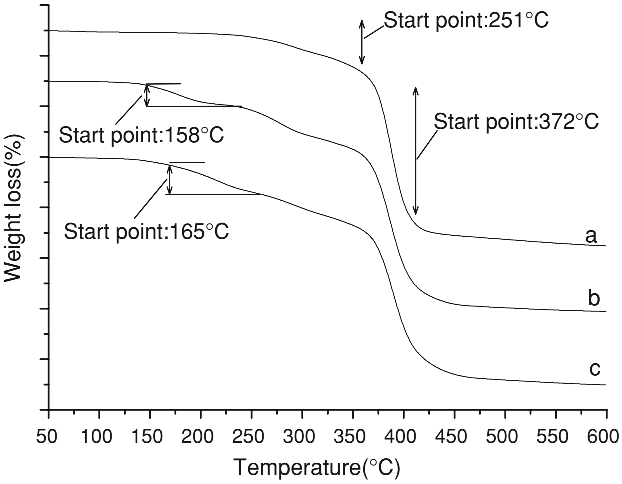

Fig. 10 TG curves of PU foams with various contents of MicroPCMs: (a) 0 wt%; (b) 18.14 wt%; (c) 22.81 wt%

heat-treatment. The content of additives was adjusted to improve the quality of foam when MicroPCMs were added in the reactants. MicroPCMs were evenly inserted inside the foam matrix and compatible well with polyurethane. The enthalpy of PU foam containing 26.82 wt% MicroPCMs is about 24 J/g. Qualified PU foam cannot be fabricated when the content of MicroPCMs is higher than 26.82 wt%. The thermal resistant temperature of MicroPCMs with styrene–divinybenzene co-polymer shells will decrease when MicroPCMs are added in foaming system. The foam can be used below 160 °C. How to decrease the viscosity of foaming system and enhance the content of MicroPCMs needs to further research.

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