Effects of MicroPCMs on the fabrication of MicroPCMs/polyurethane composite foams

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ARTICLE INFO

ABSTRACT

Polyurethane (PU) composite foam containing microencapsulated phase change materials (MicroPCMs) was fabricated by adding heat-treated microencapsulated *n*-octadecane in reactants. The microcapsules are evenly inserted inside the foam. The composite foam absorbs heat energy at approximately 31 °C, and releases heat energy at approximately 28 °C. The enthalpy of the foam rises with the increase of the content of MicroPCMs. It is above 12 J/g for the foam containing 12.59 wt% MicroPCMs. The addition of MicroPCMs has no significant influence to the thermal stability of polyurethane foam.

1. Introduction

Phase change materials (PCMs) can absorb or release latent heat while the temperatures of the materials are kept constant in the process of phase change [1]. Microcapsules are tiny particles that the core materials are surrounded by a coating or shell [2]. The diameters of the microcapsules are usually in the range of 1–1000 μm. The core materials of the microcapsules can be drugs, enzymes, dyes, fragrant oils, water, or salts, etc. Microencapsulated phase change materials (MicroPCMs) have been widely studied since the late 1970s [1,3] and have also been widely applied to fibers and fabrics [4–7], heat transfer [8], solar and nuclear heat storage systems [1], packed bed heat exchangers [9], etc.

The attempt of applying MicroPCMs in polyurethane foam to improve their thermal performance was developed in 1990s [10]. The foam containing MicroPCMs can improve the heat-insulating ability [11]. This technology relates generally to the field of foamed heat insulation materials and more particularly to heat insulation materials for use in a variety of applications such as footwear, clothing, automotive interiors [12], and medical product [13]. However, the fabrication of this kind of foam has not been reported in detail. In this study, the effects of heat-treated MicroPCMs on the fabrication of MicroPCMs/PU composite foam was investigated.

2. Experimental

2.1. Materials

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 ratio: Stuff A: Stuff B = 100:33. Stuff temperature: 20–25 °C. Mold temperature: 65 ± 5 °C.

Dibutyltin dilaurate (DBTL) and chemical pure (C.P.) were purchased from Tianjin Chemical Reagent Factory and were used as catalysts; calcium carbonate ($CaCO_3$) and analytical reagent (A.R.), the diameters were lower than 37 μm, were purchased from Tianjin Chemical Reagent Factory; Calcium sulfate anhydrous ($CaSO_4$) and C.P., the diameters were lower than 37 μm, were purchased from Tianjin Chemical Reagent Factory; Hollow glass microsphere (HGM) was purchased from Qinhuangdao Municipal Glass Microsphere Factory.

2.2. Fabrication of microcapsules

Microencapsulated *n*-octadecane was fabricated by *in situ* polymerization using melamine-formaldehyde copolymers as shell and *n*-octadecane as core material. The fabrication process

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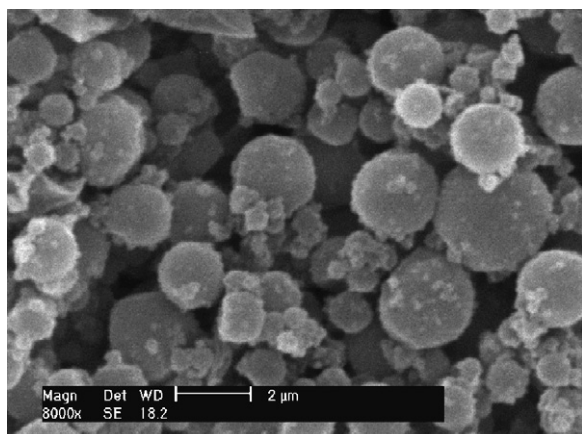*E-mail address:* zhangpolyu@yahoo.com.cn (X.X. Zhang).

Fig. 1. SEM micrograph of MicroPCMs.

was reported elsewhere [14]. Fig. 1 shows the morphology of MicroPCMs. The diameter of MicroPCMs is in the range of 1–5 μm. The *n*-octadecane content in MicroPCMs is approximately 65 wt% [14]; the melting enthalpy and crystallizing enthalpy of MicroPCMs are 143 and 144 J/g, respectively.

2.3. Fabrication of MicroPCMs/PU composite foam

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 into the same beaker and strong stirring was applied during 5–10 s. The resulted mixture was left undisturbed for about 1 min allowing the formation and growth of the foam. Then it was immediately moved and kept in an oven at 60 °C.

2.4. Characterization of MicroPCMs and foam

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

The effects of heat-treated temperature on thermal stability of MicroPCMs have been reported previously [15]. When the temperature is higher than 160 °C, some of the microcapsules were destroyed. When the temperature is lower than 110 °C, the water and formaldehyde were not totally removed. Therefore, MicroPCMs were heat-treated in an oven at 110, 120, 130, 140, 150 and 160 °C for 30 min, respectively. The thermal properties of MicroPCMs and the foam were measured using a differential scanning calorimetry (DSC, PerkinElmer, DSC-7) at a heating or cooling rate of 10 °C/min in the range of 0–100 °C under a nitrogen atmosphere.

The thermal stability of the foam were obtained by using a thermogravimetric analyzer (NETZSCH STA 409 PC/PG TG-DT) at

a scanning rate of 10 °C/min in the temperature range of 25–600 °C under a nitrogen atmosphere.

3. Results and discussion

3.1. Effects of fillers on the fabrication of composite foam

In order to study the effects of fillers on the fabrication of polyurethane foam, four types of fillers were added in the reactants, respectively. The results are shown in Table 1.

When $CaCO_3$, $CaSO_4$, and HGM were used as fillers, PU composite foams were fabricated easily. The effects of these fillers on the fabrication of the foams are negligible. By contrast, MicroPCMs have defoaming function to the reaction system even though the content of MicroPCMs is lower than that of the filler. Such a phenomenon can be explained by a plenty of additives, such as formaldehyde, emulsifier defoamer, etc. being used in the fabrication of MicroPCMs. The additives might be remained in MicroPCMs and had negative influence on the foaming system.

3.2. Effects of heat treatment of MicroPCMs on the fabrication of composite foam

SEM micrographs of the heat-treated MicroPCMs at various temperatures are shown in Fig. 2. When the heat-treatment temperature is 110–130 °C, the change of the morphology is not very significant. After heating to 140 °C, core materials of a small number of MicroPCMs diffuse out of shell due to the expansion of *n*-octadecane [15,16]. Some of the shells of heat-treated samples at 150 and 160 °C shrink corresponding to MicroPCMs losing *n*-octadecane in the core. Cross-linking was formed during the heat treatment process. In addition, water and formaldehyde were eliminated from the reaction of hydroxymethyl groups. The elimination of water and formaldehyde is helpful for the fabrication of the foams containing MicroPCMs.

The phase change properties of heat-treated MicroPCMs are listed in Fig. 3. The melting enthalpies are 142, 136, 100, and 93 J/g for heat-treated MicroPCMs at 130, 140, 150, and 160 °C, respectively; and the crystallizing enthalpies are 144, 133, 106, and 97 J/g, respectively. The enthalpy remains unchanged when MicroPCMs were heat-treated at a temperature below 130 °C. So the heat-treatment condition was selected at 130 °C for 30 min.

The heat-treated MicroPCMs at 110, 120, 130, 140, 150 and 160 °C for 30 min were used as fillers in the fabrication of composite foams, respectively. The compositions of the composite foams using heat-treated MicroPCMs at various temperatures for 30 min as fillers are listed in Table 2.

The appearance of the foam is excellent when using heat-treated MicroPCMs at 130–160 °C. MicroPCMs of being heat-treated at 110 and 120 °C make the diameter of the foam cell increase significantly. It can be explained that water and formaldehyde were not fully eliminated from MicroPCMs at 110 and 120 °C. They act as vesicant in some extent.

Table 1
Effects of various types of fillers on the appearance of foam

Type of filler	Stuff A (wt%)	Stuff B (wt%)	DBTL (wt%)	Filler (wt%)	Appearance of foam
$CaCO_3$	67.42	22.25	0.22	10.11	Excellent[*]
$CaSO_4$	67.42	22.25	0.22	10.11	Excellent
HGM	67.42	22.25	0.22	10.11	Excellent
MicroPCMs	69.77	23.03	0.22	6.98	Collapse

[*] Excellent: The cells in the foam are as uniform as that without fillers.
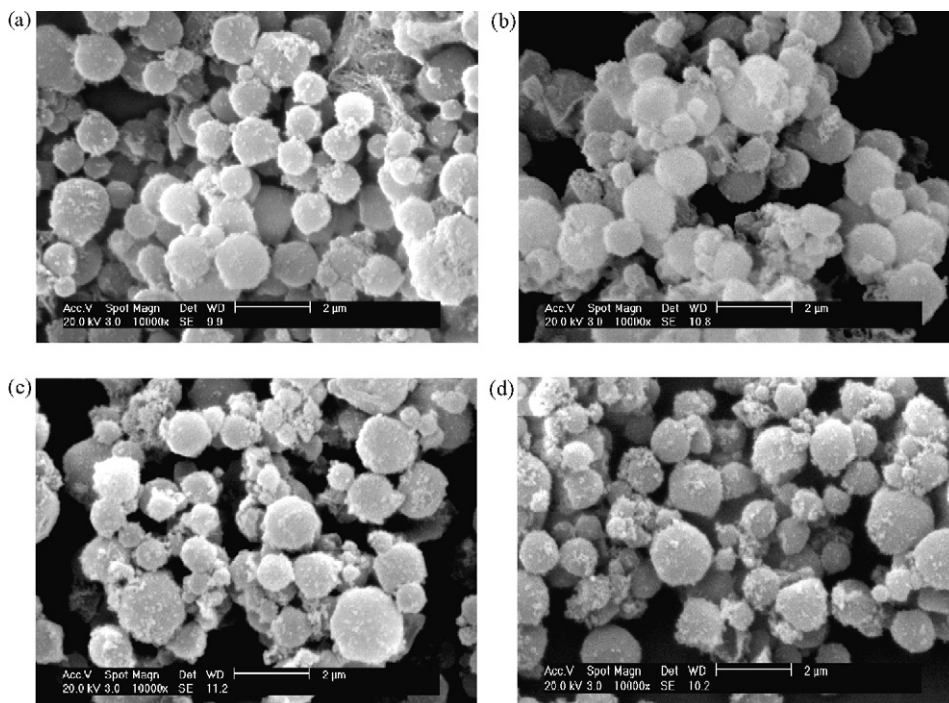
Fig. 2. SEM micrographs of heat-treated microcapsules: (a) 130 °C; (b) 140 °C; (c) 150 °C; and (d) 160 °C.
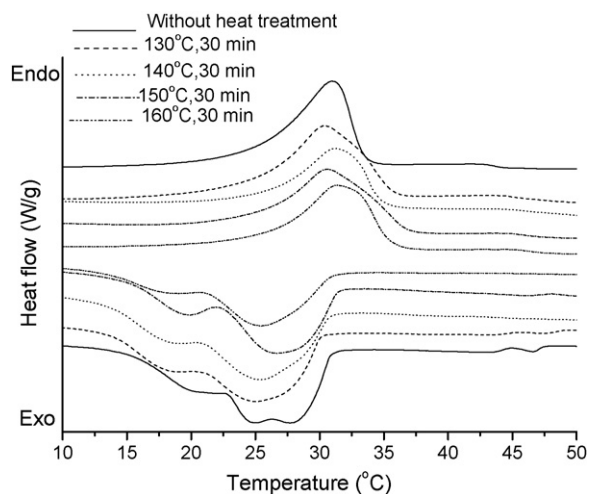
Fig. 3. DSC curves of heat-treated MicroPCMs at various temperatures.

3.3. Effect of organic stannum and isocyanate on the fabrication of composite foam

In the process of polyurethane foam formation, the use of filler can influence the surface tension and viscidity of foaming system and further cause negative effect on the foam product [17]. Increasing the content of organic stannum not only reduces the surface tension but also increases the rate of gelling reaction [18]. DBTL was used to control the quality of the foam in this study. Effect of DBTL on foaming is listed in Table 3.

The appearance of the foam can be improved by increasing the content of DBTL. At a higher content of DBTL the closed-cell rate will enhance and the foam will shrink, however.

The effects of Stuff B on foaming are listed in Table 4. The shell of MicroPCMs contains plenty of hydroxyl groups, and the ability of water absorption. So the content of Stuff B has to be increased when adding MicroPCMs in the foaming system.

In order to improve the quality of the foam, the contents of additives were adjusted. The composition and appearance of the composite foams are listed in Table 5.

The viscosity of foaming system was too high to fabricate foam when the content of MicroPCMs was greater than 12.59 wt%. Such a limitation is probably caused by the existence of the hydroxymethyl groups of melamine-formaldehyde shell. How to enhance the content of MicroPCMs needs further research.

3.4. Heat absorbing and evolving properties of MicroPCMs/PU composite foams

SEM micrograph of the composite foam is presented in Fig. 4. MicroPCMs are evenly inserted inside the foam and

Table 2
Foaming formulation

Stuff A (wt%)	Stuff B (wt%)	DBTL (wt%)	Heat-treated MicroPCMs (wt%)	Appearance of foam
65.98	23.75	0.36	9.91 (110 °C for 30 min)	Big cell
65.99	23.75	0.36	9.91 (120 °C for 30 min)	Big cell
65.99	23.75	0.36	9.91 (130 °C for 30 min)	Excellent
65.99	23.75	0.36	9.91 (140 °C for 30 min)	Excellent
65.99	23.75	0.36	9.91 (150 °C for 30 min)	Excellent
65.99	23.75	0.36	9.91 (160 °C for 30 min)	Excellent

Table 3
Effect of DBTL on foaming

Stuff A (wt%)	Stuff B (wt%)	DBTL (wt%)	Heat-treated MicroPCMs (wt%)	Appearance of foam
69.93	23.08	0.00	6.99	Collapse
69.88	23.06	0.08	6.99	Collapse
69.82	23.04	0.15	6.98	Split
69.77	23.03	0.22	6.98	Excellent
69.67	22.99	0.37	6.97	Shrinking

Table 4
Effect of Stuff B on foaming

Stuff A (wt%)	Stuff B (wt%)	Heat-treated MicroPCMs (wt%)	DBTL (wt%)	Appearance of foam
67.32	22.21	10.10	0.37	Big cell
65.98	23.76	9.90	0.36	Excellent
64.29	25.72	9.64	0.35	Shrinking

Table 5
Foaming formulation after adjusting the content of additives

Stuff A (wt%)	Stuff B (wt%)	Heat-treated MicroPCMs (wt%)	DBTL (wt%)	Appearance of foam
75.19	24.81	0.00	0.00	Excellent
72.30	23.86	3.61	0.23	Excellent
71.27	23.52	4.99	0.22	Excellent
69.77	23.03	6.98	0.22	Excellent
68.24	23.20	8.18	0.38	Excellent
65.99	23.75	9.90	0.36	Excellent
64.25	24.41	10.92	0.42	Excellent
62.95	23.92	12.59	0.54	Excellent
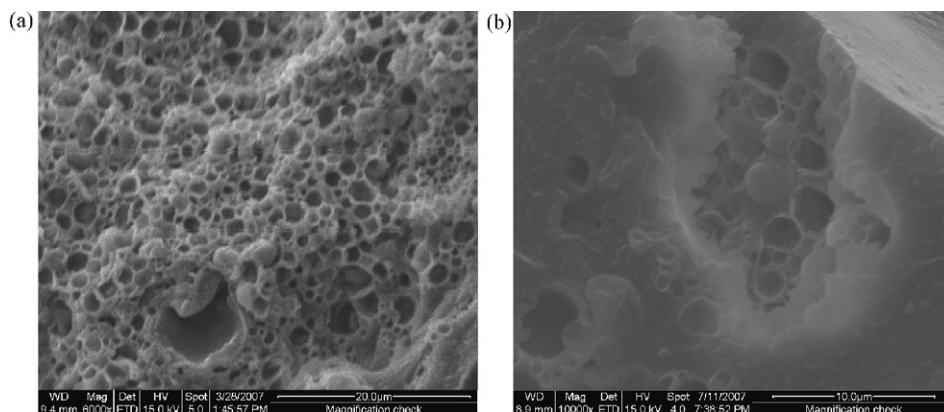
Fig. 4. SEM micrograph of MicroPCMs/PU composite foam: (a) 6000×; (b) 10,000×.

compatible well with polyurethane. The microcapsules are intact.

Fig. 5 illustrates DSC curves of PU foam with various contents of MicroPCMs. The heat absorbing and evolving properties of these foams are listed in Table 6. Compared to the pure PU foam, MicroPCMs/PU composite foam has endothermic peak and exothermic peak in the process of heating and cooling in the range of 20–40 °C, respectively [11]. The higher the MicroPCMs content in the composite foam, the higher is the heat storage ability of the foam. The measured average enthalpy is lower than the calculated value, which is probably caused by the poor thermal conductivity of the foam [11]. Such a phenomenon has been observed in MicroPCMs/polypropylene blend chips [7].

Table 6
Heat absorbing and evolving properties of MicroPCMs/PU composite foams

MicroPCMs (wt%)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	ΔH_a (J/g)	ΔH (J/g)
6.98	31	5	28	6	6	9
9.90	30	10	28	8	9	14
12.59	31	16	29	12	14	19

[*]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.
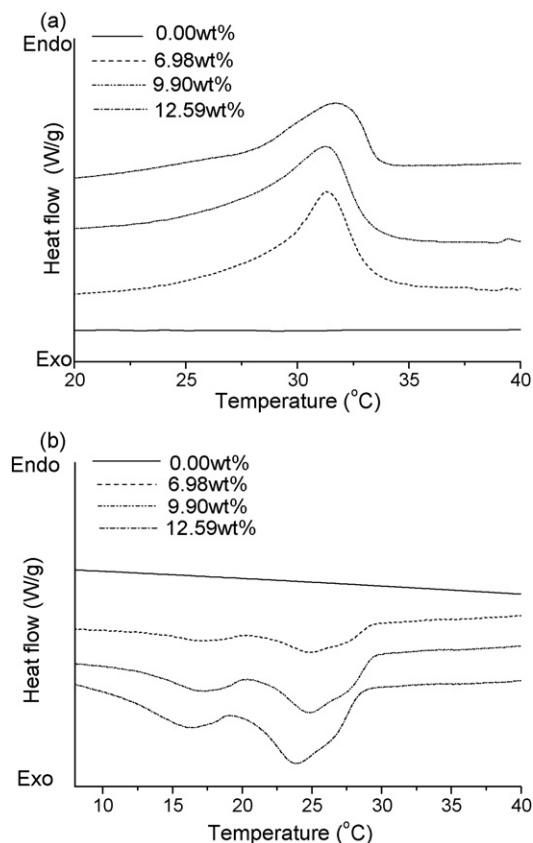
Fig. 5. DSC heating curves (a) and cooling curves (b) of PU foam with various contents of MicroPCMs.

3.5. Thermal stabilities of MicroPCMs/PU composite foams

Fig. 6 shows TG curves of the foam with various contents of MicroPCMs. The obvious weight-loss of PU foam was at 253, 251, 252 and 254 °C when the content of MicroPCMs was 0.00, 6.98,
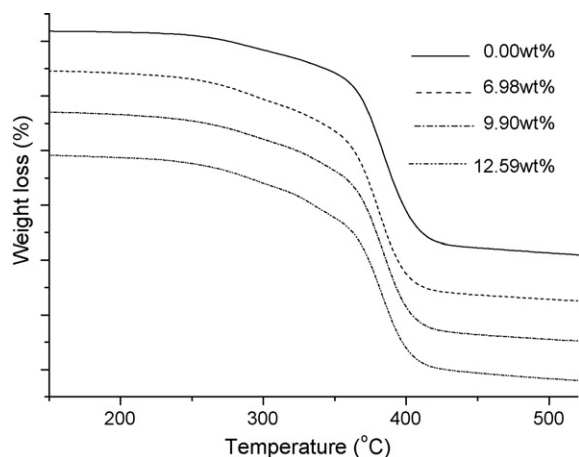
9.90 and 12.59 wt%, respectively. The weight-loss was less than 1.0% before 250 °C. The weight-loss of the PU foam at the temperature of about 250 °C was caused by the decomposition of nitrogenous groups. The weight-loss of MicroPCMs/PU composite foam is higher than pure PU foam at about 250 °C, which is 8.2%, 11.2%, 11.4% and 11.8% for the sample with the content of MicroPCMs being 0.00, 6.98, 9.90 and 12.59 wt%, respectively. The weight-loss was caused by the n-octadecane leaking out of the shell at temperature of about 200 °C. The inflexion near 365 °C in the TG curves of PU foam was caused by further decomposition of groups and rupture of molecular bond. The result shows that, MicroPCMs have no significant influence to the thermal stability of PU foam.

4. Conclusions

The heat-treated MicroPCMs at 130 °C for 30 min were more suitable for the fabrication of MicroPCMs/PU composite foam. The content of additives was adjusted to improve the quality of foam when MicroPCMs were added in the reactants. MicroPCMs are compatible well with polyurethane. The enthalpy of MicroPCMs/PU composite foam containing 12.59 wt% MicroPCMs is above 12 J/g. MicroPCMs have no significant influence to the thermal stability of polyurethane foam. Qualified MicroPCMs/PU composite foam cannot be fabricated when the content of MicroPCMs is higher than 12.59 wt%. Such a limitation is probably caused by the existence of the hydroxymethyl groups of melamine-formaldehyde shell. How to enhance the content of MicroPCMs needs further research.

Acknowledgments

References

[1] P.B.L. Chaurasia, Res. Ind. 26 (1981) 159.
[2] S. Benita, Microencapsulation: Methods and Industrial Applications, Marcel Dekker Inc., New York, 1996, pp. 1–2.
[3] D.P. Colvin, Advances in heat and mass transfer in biotechnology, ASME HTD-Vol. 363/BED 44 (1999) 199.
[4] D.C. Hittle, T.L. André, ASHRAS Trans. Res. 180 (2002) 175.
[5] Y.G. Bryant, D.P. Colvin, US Patent 5,366,801 (1994).
[6] J. Kim, G. Cho, Text. Res. J. 72 (2002) 1093.
[7] X.X. Zhang, X.C. Wang, X.M. Tao, K.L. Yick, J. Mater. Sci. 40 (2005) 3729.
[8] S.K. Roy, S. Sengupta, Int. Comm. Heat Mass Transfer 18 (1986) 495.
[9] M.N.A. Hawlader, M.S. Uddin, H.J. Zhu, Int. J. Energy Res. 26 (2006) 195.
[10] Y.G. Bryant, D.P. Colvin, US Patent 5,499,460 (1996).
[11] M.L. Nuckols, Ocean Eng. 26 (1999) 547.
[12] B. Pause, Int. Text. Tech. March (2002) 24.
[13] B. Pause, Med. Text. September (1999) 23.
[14] X.X. Zhang, Y.F. Fan, X.M. Tao, K.L. Yick, Mater. Chem. Phys. 88 (2004) 300.
[15] X.X. Zhang, X.M. Tao, K.L. Yick, X.C. Wang, Colloid Polym. Sci. 88 (2004) 330.
[16] X.X. Zhang, X.M. Tao, K.L. Yick, Y.F. Fan, J. Appl. Polym. Sci. 97 (2005) 390.
[17] R.D. Wu, X.L. Tong, J.K. Zhang, G.B. Liu, China Elastomerics March (2005) 5.
[18] X. Wang, H.Y. Ge, China Plast. Ind. May (2004) 20.

Fig. 6. TG curves of PU foams with various contents of MicroPCMs. (The curves were vertically shifted.)