

Preparation and characterization of flame retardant phase change materials by microencapsulated paraffin and diethyl ethylphosphonate with poly(methacrylic acid-co-ethyl methacrylate) shell

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ABSTRACT: Microcapsules containing paraffin and diethyl ethylphosphonate (DEEP) flame retardant with uncrosslinked and cross-linked poly (methacrylic acid-co-ethyl methacrylate) (P(MAA-co-EMA)) shell were fabricated by suspension-like polymerization. The surface morphologies of the microencapsulated phase change materials (microPCMs) were studied by scanning electron microscopy. The thermal properties and thermal stabilities of the microPCMs were investigated by differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA). The flame retarding performances of the microcapsule-treated foams were calculated by using an oxygen index instrument. The DSC results showed that the crosslinking of the polymer shell led to an increase in the melting enthalpies of the microcapsule by more than 15%. The crosslinked P(MAA-co-EMA) microcapsules with DEEP and without DEEP have melting enthalpies of 67.2 and 102.9 J/g, respectively. The TGA results indicated that the thermal resistant temperature of the cross-linked microcapsules with DEEP was up to 171°C, which was higher than that of its uncrosslinked counterpart by ~20°C. The incorporation of DEEP into the microPCM increased the limiting oxygen index value of the microcapsule-treated foams by over 5%. Thermal images showed that both microcapsule-treated foams with and without DEEP possessed favorably temperature-regulated properties. As a result, the microPCMs with paraffin and DEEP as core and P(MAA-co-EMA) as shell have good thermal energy storage and thermal regulation potentials, such as thermal-regulated foams heat insulation materials. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 41880.

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INTRODUCTION

Phase change materials (PCMs) are attractive materials for thermal regulation and thermal energy storage since they allow storage and release of high quantities of thermal energy per unit mass at approximately constant temperature.^{1–3} A variety of PCMs including paraffin, poly ethylene glycols, fatty acid, eutectic materials, salt mixtures and salt hydrates, metals, and their alloys have so far been investigated for different applications.^{4–7} As a typical organic PCM, paraffin exhibits some merits with respect to other PCMs, such as chemically inert and stable, high heat of fusion, lack of phase segregation, supercooling or corrosion problems, and also, an adjustable transition zone.^{3,4,8} However, the leakage of the melted bulk paraffin problem restricts their further applications. Microencapsulation of PCMs with polymer shells is considered to be one of the best ways to obtain PCMs confinement.^{9–12} Besides, microencapsulated PCMs (microPCMs) have some another advantages of lowering

the volume change of the PCMs, increasing the heat-transfer area, and decreasing the interaction between the PCMs and the matrix materials.^{8,13,14} These features make them more functional than the conventional PCMs in the application of thermal insulation materials, which is very useful in the heat-insulating application, such as footwear, clothing, automotive interiors, and medical product.^{15–18} Therefore, the integration of microPCMs into conventional insulating foams to improve their thermal performance has drawn considerable attention.^{15–18}

Polymer shells of the microcapsules play a key role in adjusting the performance of microPCMs, such as morphologies, phase change properties, and thermal stabilities. Microencapsulation of PCMs with copolymer shells had attracted increasingly interests since the properties of the copolymer shells can be regulated by modification of their macromolecular compositions.^{9–12} Methacrylic acid (MAA) is one kind of commercially available carboxylic acid. Because of its water-soluble characteristic, MAA

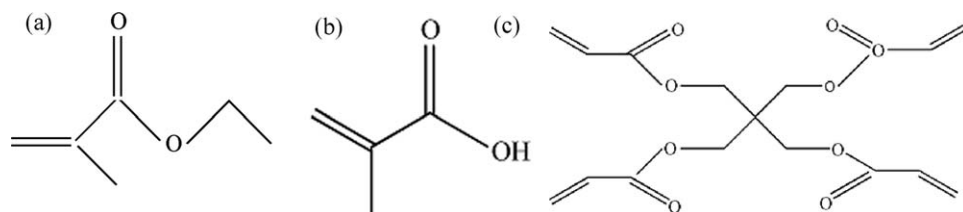


Figure 1. Chemical structures of the monomers used in this study: (a) EMA; (b) MAA; (c) PETRA.

as the constituent in the polymer shell can produce a great polarity gap between the monomers and the paraffin, thus providing a strong driving force for phase separation during suspension polymerization process.⁹ Shan *et al.*¹⁰ synthesized *n*-octadecane-containing microcapsules by copolymerization methylmethacrylate (MMA) with methacrylic acid (MAA) as shell. Sánchez *et al.*⁹ studied microencapsulation of PRS paraffin with P(MMA-*co*-MAA-*co*-methyl acrylate(MA)) terpolymer shells by a suspension-like polymerization. Additionally, Yang *et al.*¹¹ prepared tetradecane-containing microcapsules by *in situ* polymerization with polystyrene, PMMA, polyethyl methacrylate (PEMA) as encapsulation materials, respectively. Their study indicated that the softer shell, PEMA, might be favorable for the microencapsulation of PCMs. *n*-Octadecane was microencapsulated with p(butyl methacrylate-*co*-MAA) as shell in our previous work.¹² Nevertheless, microencapsulation of PCMs by copolymerization of EMA with MAA as shell is rarely reported. Additionally, though EMA-based polymers with lower glass transition temperature (T_g) have greater film-forming abilities as compared with MMA-based polymers, the films formed by them exhibit low Young's moduli.¹⁹ Crosslinking can provide a better mechanical strength of the shell of the microcapsule. Therefore, one of the major objective of this study was to prepare microPCMs by the uncrosslinked and crosslinked P(MAA-*co*-EMA) copolymer as shells and paraffin as core for thermal energy storage and thermal regulation. Pentaerythritol tetraacrylate (PETRA) was employed as the crosslinking agent. The chemical structures of EMA, MAA, and PETRA are shown in Figure 1. However, the chemical constitution of both polymer shells and paraffin are easily flammable,²⁰ so it is important to improve the fire resistance of the microPCMs. Although, halogen-containing flame retardants possess excellent retardant performance, the combustion of them may cause inevitable severe environmental impact since they give rise to toxic and dense smoke.²¹ As a halogen-free flame retardants, phosphorus-containing flame retardants has become a popular green substitute for conventional flame retardant additives for polymers since they are quite effective in enhancing the flame resistance of polymers and do not generate toxic smokes.^{22–24} In addition, Gao *et al.*²¹ incorporated phosphorus-containing flame retardant into rigid polyisocyanurate-polyurethane (PIR) foams to improve their flame resistance. They found that incorporation of phosphorus-containing flame retardant into PIR foam can significantly decrease the smoke production rate and rate of smoke release of PIR foam. Nevertheless, little information is available on the incorporation of phosphorus-containing flame retardants into microPCMs. Hence, the other objective of this study was to prepare microPCMs incorporated diethyl ethyl-

phosphonate (DEEP), a strong fire retardant with a wide liquidus temperature range (-83 to 198°C),²⁵ to improve fire resistant of the microPCM. Subsequently, the microPCMs with and without flame retardants were integrated into polystyrene foams to improve their temperature-regulation and fire resistance performance. And the morphologies, phase change properties and thermal stabilities of the microcapsules, as well as the temperature-regulation and fire resistant performance of the microcapsule-treated polystyrene foams were also investigated.

EXPERIMENTAL

Materials

Methacrylic acid (MAA, C.R., Sinopharm Chemical Reagent, Ltd.) and ethyl methacrylate (EMA, C.R., Tianjin Damao Chemistry Reagent) were employed as monomers. Paraffin (99 wt %, Alfa) and diethyl ethylphosphonate (DEEP, C.R., Sinopharm Chemical Reagent) were used as core materials. Pentaerythritol tetraacrylate (PETRA, 80 wt %, Xinlimei Technology) was employed as a crosslinking agent. 2,2'-Azobisisobutyronitrile (AIBN, A.R., Sinopharm Chemical Reagent) was used as an initiator. Sodium salt of styrene-maleic anhydride polymer (SMA, Shanghai Leather Chemical Works) was selected as a suspension stabilizer. Styrene-butadiene latex (49–51 wt %, BASF) was utilized as a binder.

Preparation of Microcapsules

Microcapsules containing paraffin were prepared by a suspension-like polymerization method, which was described in detail in Ref. 26. The reaction medium involves two phases, i.e., a continuous phase and a discontinuous phase. The continuous phase containing water and small amount of suspension stabilizer was transferred to the glass reactor with mild agitation. The discontinuous phase consisting monomers, crosslink agent, paraffin, and initiator was added into the continuous phase. Next, the discontinuous phase was added into the continuous phase and was maintained for 15 min under vigorous agitation (1000 rpm) and a constant temperature of 35°C to form a stable oil-in-water emulsion. The polymerization process was allowed to continue under vigorous agitation (540 rpm) and a constant temperature of 85°C . The microencapsulation of paraffin and DEEP as core materials was conducted in a similar manner. Except, DEEP was also added into the mixture of monomers, PETRA, paraffin, and AIBN to form the discontinuous phase. Once obtained, the microcapsule particles were separated by centrifugation and filtration, and then repeatedly washed with 30 wt % ethanol solution at about 60°C . Finally, the samples were dried at 60°C for 48 h. The recipes varying

Table I. Recipes for Varies Type of Monomers and Core Materials

Sample	MAA (g)	EMA (g)	PETRA (g)	Paraffin (g)	DEEP (g)
1	4	3	-	10	-
2	4	3	3	10	-
3	4	3	-	6	4
4	4	3	3	6	4

with the type of monomer and core material are presented in Table I.

Characterization of Microcapsules

The morphologies of the microcapsules were observed by using a HITACHI SU1510 scanning electron microscope (SEM). More than 200 microcapsules were measured on the SEM micrographs to determine the diameters of the microcapsules.

Phase change temperatures and phase change enthalpies of the microcapsules were determined by using a differential scanning calorimetry (DSC, TA, Q2000). These measurements were carried out at a scanning rate of $\pm 5^\circ\text{C min}^{-1}$ in the temperature range from 0 to 50°C under a nitrogen atmosphere flow of 50 mL min^{-1} . Each sample was placed in a sealed aluminum crucible of $40\ \mu\text{L}$ prior to the measurement. The content of paraffin within the microPCMs was calculated by the following formula:

$$\text{Paraffin content of} = \frac{(\Delta H_{m,\text{microPCMs}} + \Delta H_{c,\text{microPCMs}})}{(\Delta H_{m,\text{PCMs}} + \Delta H_{c,\text{PCMs}})} \quad (1)$$

where $\Delta H_{m,\text{microPCMs}}$ and $\Delta H_{c,\text{microPCMs}}$ are melting enthalpy and crystallization enthalpy of microPCMs, respectively; $\Delta H_{m,\text{PCMs}}$ and $\Delta H_{c,\text{PCMs}}$ are melting enthalpy and crystallization enthalpy of PCMs, respectively.²⁷

The mass loss of paraffin and microPCMs with increasing temperature was examined with a thermalgravimetric analysis (TGA, TA, Q500) in a nitrogen atmosphere (flow rate was 50 mL min^{-1}). The heating rate was $10^\circ\text{C min}^{-1}$ from 50 to 500°C .

Application of the Microcapsules to the Foams

The microcapsules were incorporated to polystyrene foams by a coating method. The crosslinked paraffin/P(MAA-co-EA) microcapsule with and without DEEP were mixed with a 240 g/L styrene-butadiene latex binder solution in distilled water. The foam samples were impregnated into this solution at 10 rpm rotating speed at a condition of ambient air and temperature. Then, the foams were dried in an oven at 70°C for 1 h. The concentration of the microcapsules was maintained 50 g/L in the solution.

Evaluation of the Microcapsule-Treated Foams

To investigate the temperature-regulated performances of the microcapsule-treated foams, heating-up experiments were

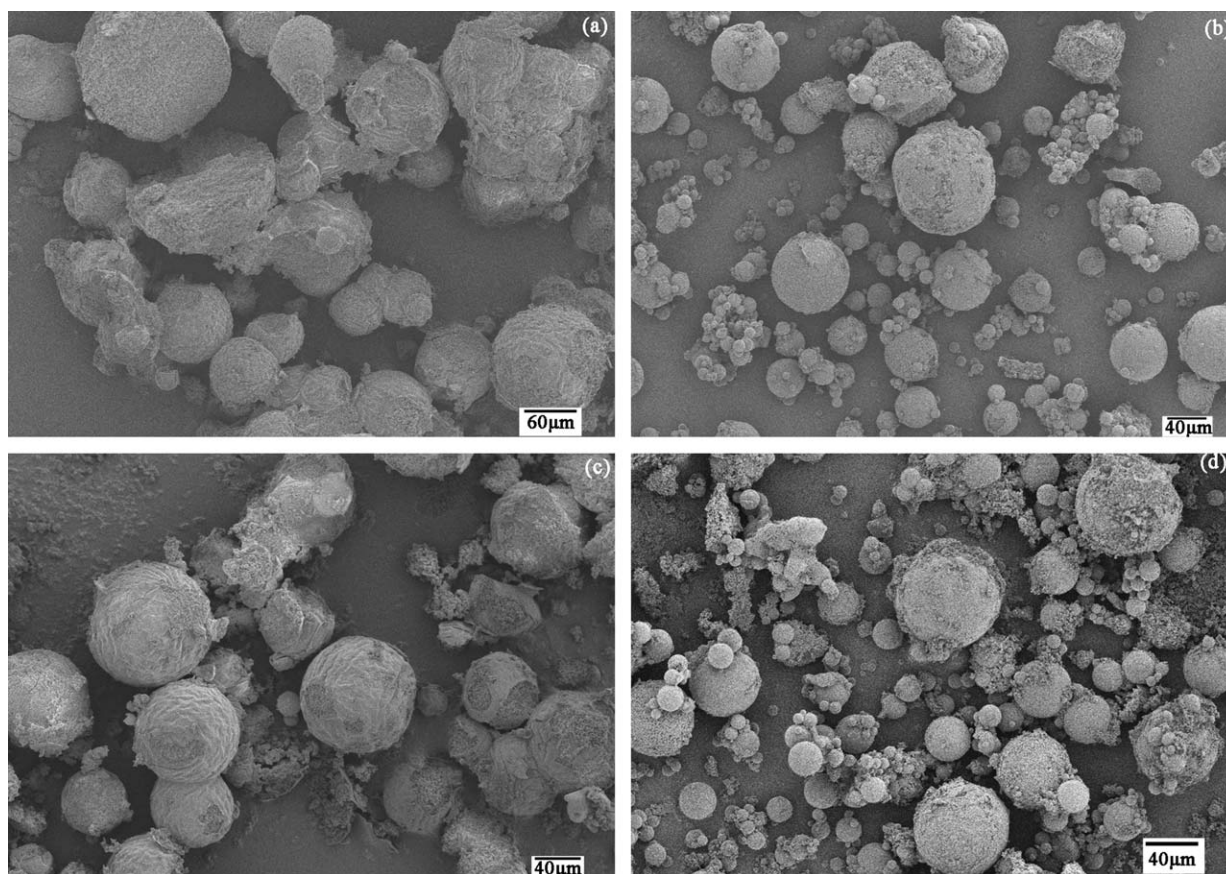


Figure 2. SEM micrographs of microcapsules: (a) uncrosslinked paraffin/P(MAA-co-EMA); (b) crosslinked paraffin/P(MAA-co-EMA); (c) uncrosslinked paraffin-DEEP/P(MAA-co-EMA); (d) crosslinked paraffin-DEEP/P(MAA-co-EMA).

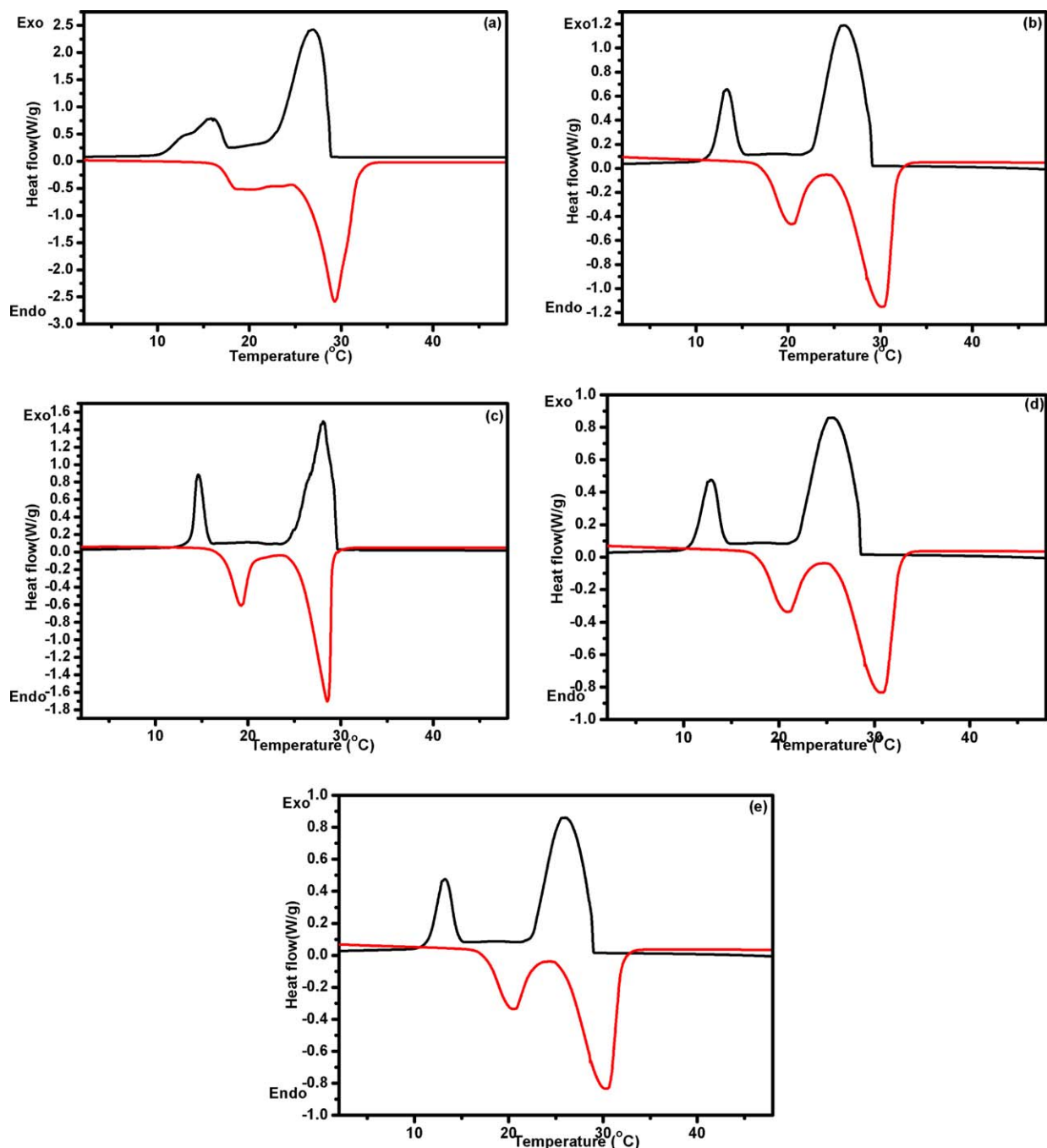


Figure 3. DSC curves of microcapsules: (a) paraffin; (b) uncrosslinked paraffin/P(MAA-*co*-EMA); (c) crosslinked paraffin/P(MAA-*co*-EMA); (d) uncrosslinked paraffin-DEEP/P(MAA-*co*-EMA); (e) crosslinked paraffin-DEEP/P(MAA-*co*-EMA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

carried out on three foams according to Refs. [28,29]. Foam-b, Foam-c contained crosslinked paraffin-DEEP/P(MAA-*co*-EMA) microcapsule and crosslinked paraffin/P(MAA-*co*-EMA) microcapsule, respectively, whilst Foam-a is a raw foam board employed as a reference. Each piece of foams was about 1.0 g with a dimension of $30 \times 30 \times 30 \text{ mm}^3$. All the foams were placed in a refrigerator to cool to 15°C , and then put into a thermostatic bath maintaining a constant temperature of 40°C .

The temperature distributions of the surface of the foams were determined by using an infrared thermography (FLIR, T400). The surface of the foams was observed from a distance of 30 cm between the lens of the infrared thermography and the foam at an ambient temperature of 25°C . Images of the surface of all foams with increasing temperature were taken at different times from 18 to 40°C , which were downloaded by FLIR ResearcherIR software.

Table II. Thermal Properties of MicroPCMs with Different Recipes

Sample	T_{om} (°C)	T_{pm} (°C)	ΔH_m (J/g)	T_{oc} (°C)	T_{pc} (°C)	ΔH_c (J/g)	Paraffin content (wt %)
1	28.6	30.7	89.0	26.2	25.6	89.3	54.2
2	28.6	29.3	102.9	27.4	26.3	103.2	62.6
3	26.1	29.1	48.0	28.0	27.1	47.6	29.0
4	25.7	28.7	67.2	28.4	27.5	66.6	40.7
Paraffin	26.3	29.3	166.0	28.8	27.5	163.1	100

T_{om} , melting onset temperature; T_{pm} , melting peak temperature.

T_{em} , melting endset temperature; ΔH_m , melting enthalpy.

T_{oc} , crystallization onset temperature; T_{pc} , crystallization peak temperature.

T_{ec} , crystallization endset temperature; ΔH_c , crystallization enthalpy.

The limiting oxygen index (LOI) test is generally used as an effective method for comparing and rating the fire behavior of materials.³⁰ Hence, the LOI test was selected to evaluate the flame retarding performance of the treated foams with paraffin-DEEP microcapsules. The LOI values were calculated by using an oxygen index instrument (LFY-605, Shandong Textile Science Research Institute) according to Ref. 30.

RESULTS AND DISCUSSION

Morphologies of Microcapsules

The morphologies of the microcapsule particles obtained in each case were investigated with SEM shown in Figure 2. All microPCMs particles have spherical profiles. However, the uncrosslinked microPCMs exhibit distinctly different morphologies with respect to the crosslinked ones. There were many wrinkles on the surface of the uncrosslinked microPCMs particles; however, no wrinkle could be observed on the surface of the crosslinked microPCMs particles. Furthermore, many damaged shells could be observed on the surface of the uncrosslinked microPCMs particles. Nevertheless, in the case of the crosslinked microPCMs particles, there were plenty of small polymer particles adhering to some big polymer particles, and few of these microPCMs particles cracked. This seems to suggest that crosslinking can increase the mechanical strength of the microPCMs. The higher mechanical strength of the crosslinked microPCMs can resist the particle shells shrinkage brought about the difference in density between the copolymer shell and the shell forming monomers,³¹ and also resist external pressure resulting from post-treatment of the samples, such as centrifugation.

Phase Change Properties and Thermal Stabilities of Microcapsules

The heating and cooling thermograms of pure paraffin and the microcapsules with various monomers and core materials are shown in Figure 3. The DSC curve of paraffin and all the microcapsules had two phase change peaks on both cooling and heating processes. The main peak corresponds to solid-liquid phase change of the paraffin, while the minor peak represents solid-solid phase transition of the paraffin. The uncrosslinked paraffin microcapsules, the crosslinked paraffin microcapsules, the uncrosslinked paraffin-DEEP microcapsules and the crosslinked paraffin-DEEP microcapsules melt at 28.6, 28.6, 26.1,

and 25.7°C, respectively, and crystallized at 26.2, 27.4, 28.0, and 28.4°C, respectively, while pure paraffin has a melting point of 26.3°C and a crystallization point of 28.8°C. It was found that the melting points and crystallization points of all microPCMs decreased or increased slightly in comparison with those of pure *n*-octadecane. These results are consistent with earlier

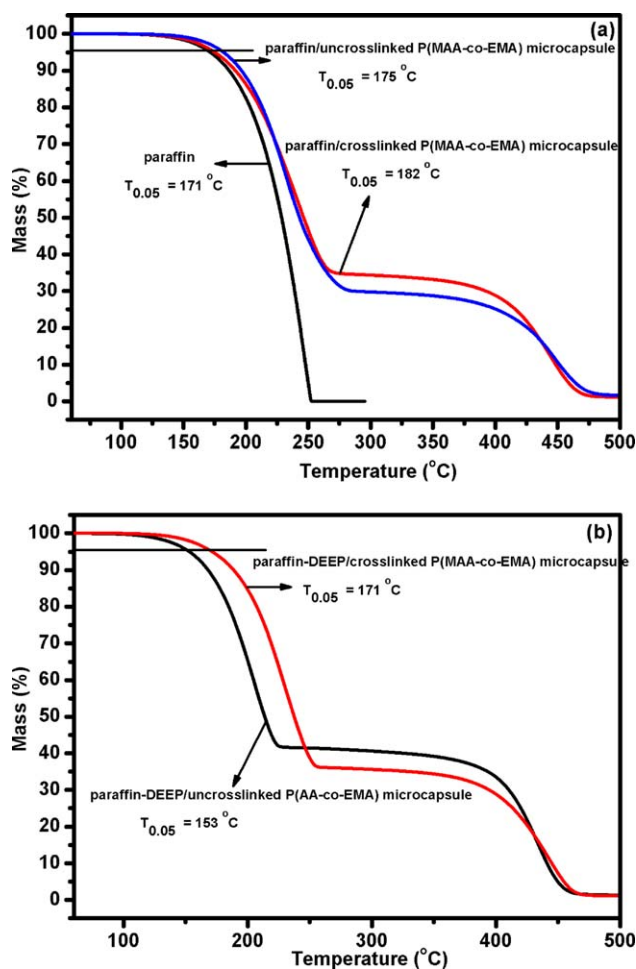


Figure 4. TGA curves of paraffin and microcapsules: (a) paraffin and microcapsule with uncrosslinked paraffin/P(MAA-*co*-EMA); (b) microcapsule with crosslinked paraffin-DEEP/P(MAA-*co*-EMA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

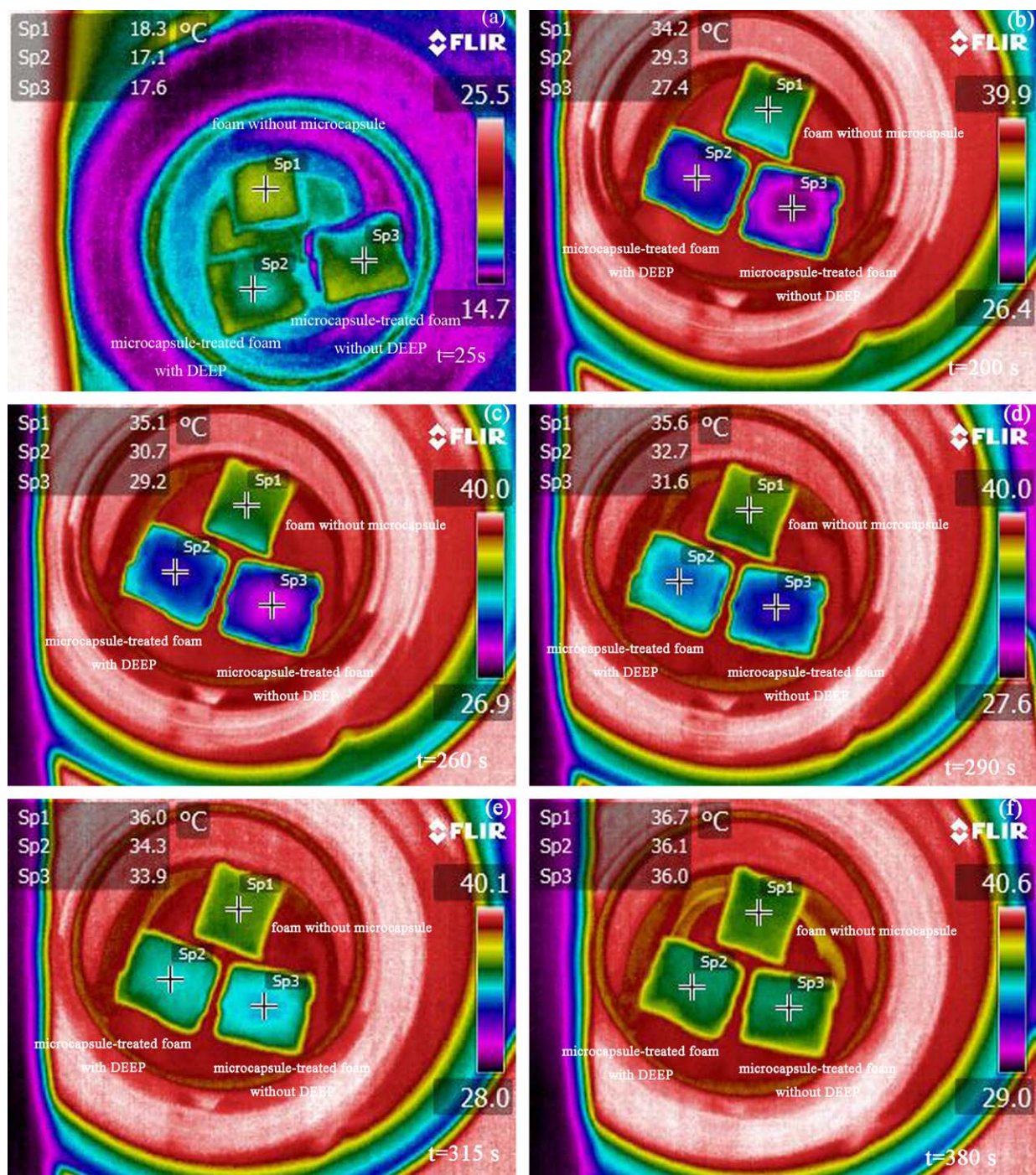


Figure 5. Thermal images of foams heated at different times: (a) $t = 25$ s; (b) $t = 200$ s; (c) $t = 260$ s; (d) $t = 290$ s; (e) $t = 315$ s; (f) $t = 380$ s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

findings,^{12,26,31,32} indicating that the low thermal conductivity of the polymer can slow down heat transferring through the microPCMs.

The phase change enthalpy and the percentage of PCM in microcapsules is the key factor for microPCMs. It determines directly energy storage efficiency of microPCMs.³² The phase change enthalpies corresponding to solid–liquid transition (melting and freezing) of the microcapsules and the content of

PCMs in the microcapsules are given in Table II. It was found that the paraffin content of the crosslinked microPCMs without and with DEEP were significantly increased by about 8 and 12% as compared with their uncrosslinked counterparts. This is consistent with the result obtained from the morphologies analysis, indicating that the crosslinking of the polymer shell can provide a greater mechanical strength of the polymer shell, which could lead to an increase of paraffin content, thus to an

Table III. Surface Temperature at the Center of the Foams with the Heating Time

Heat-up time (s)	$T_{\text{foam-a}}$ (°C)	$T_{\text{foam-b}}$ (°C)	$T_{\text{foam-c}}$ (°C)
25	18.3	17.1	17.6
200	34.2	29.3	27.4
260	35.1	30.7	29.2
290	35.6	32.7	31.6
315	36.0	34.3	33.9
380	36.7	36.1	36.0

$T_{\text{foam-a}}$, foam without microcapsule; $T_{\text{foam-b}}$, microcapsule-treated foam with DEEP; $T_{\text{foam-c}}$, microcapsule-treated foam without DEEP.

enhancement of the heat capacity of microPCMs.^{31,33} The cross-linked paraffin/P(MAA-co-EMA) microcapsule has the highest phase change enthalpies of melting (102.9 J/g) and crystallization (103.2 J/g) as well as the highest paraffin content (62.6 wt %). Apparently, the melting enthalpy of this microcapsules was slightly higher than that (94.8 J/g) of P(MMA-co-MA-co-MAA)/paraffin microcapsule prepared by Sánchez *et al.*⁹ and that (99.0 J/g) of P(MMA-co-AA)/paraffin microcapsule fabricated by Xu *et al.*,³⁴ and similar to that of (101.0 J/g) of the paraffin wax phase in PMMA microcapsules fabricated by Ma *et al.*,³⁵ and that (101.6 J/g) of paraffin/P(BMA-co-MAA) microcapsule prepared in our previous work.¹² Moreover, the paraffin content of this microcapsule was comparable to those (60.0–70.0 wt %) of the above microPCMs prepared by other acrylic resin as shell.^{9,12,34,35} However, the paraffin content of the microPCMs was decreased by around 12% when DEEP was introduced to the core materials since the DEEP loadings occupied a fraction of the interior space of the microcapsules.

Figure 4 presents the TGA curves of paraffin and microcapsules. It is clear that the temperature at 5% mass loss ($T_{0.05}$) of both the uncrosslinked and crosslinked microcapsules were more or less higher than that of the raw paraffin. This result indicates that the copolymer shell can prohibit the paraffin from losing mass too quickly with increasing temperature.^{36,37} In addition, it can be found that $T_{0.05}$ of the crosslinked paraffin microcapsules was increased by 7°C as compared with the uncrosslinked paraffin microcapsules. Furthermore, in the case of the core containing paraffin and DEEP, the $T_{0.05}$ of the crosslinked microcapsules was remarkably enhanced by 18°C in comparison with their uncrosslinked counterpart. This result is in accordance with the contrast analysis of PCM content. This suggests that crosslinking may also result in a higher mechanical strength of the copolymer shell and, hence in a greater thermal stabilities of microPCMs.^{31,33} Nevertheless, the $T_{0.05}$ of the microcapsule containing paraffin and DEEP was lower than the microcapsule containing paraffin by 22 and 11°C for the crosslinked one and for the uncrosslinked one, respectively. This is possibly due to DEEP evaporation before boiling point (198°C),²⁵ leading to a rapid loss of paraffin-DEEP microcapsules in contrast with paraffin microcapsules.

Temperature-Regulated Property of Microcapsule-Treated Foams

Thermal images of the surface temperature distribution of foams without and with microcapsules in means of infrared thermography are presented in Figure 5, and the surface temperature at the center of the foams with the heating time is given in Table III. The zero time was taken when the foams were placed in a thermostatic bath. Thermal images showed that both microcapsule-treated foams with and without DEEP undergo a less distinct heating effect than the raw foam without microcapsules. Thermoregulatory effect observed for the microcapsule-treated foam without DEEP with respect to the raw foam was roughly 7°C, 6°C, 4°C, 2°C after 200 s, 260 s, 290 s, and 315 s, respectively. Similarly, the thermoregulatory effects for the microcapsule-treated foam without DEEP in contact with the raw foam of about 5°C, 4°C, 3°C, and 2°C after 200 s, 260 s, 290 s and 315 s, respectively, were observed. These results indicated that both the microcapsule-foams with and without DEEP possessed temperature-regulated properties, which is due to the amount of heat absorbed by paraffin in its melting process with increasing temperature. Besides, due to the higher heat capacity of the microcapsule-foam without DEEP as against the microcapsule-foam with DEEP, the microcapsule-foam without DEEP exhibits a better temperature-regulated property with regard to the microcapsule-foam with DEEP.

Flammability of Microcapsule-Treated Foams

The calculated LOI values of the treated foams with the microcapsules are presented in Table IV. As seen from Table IV, microcapsule-treated foams with DEEP increased the LOI value by 9% and 6% for the crosslinked microcapsule-treated foam without DEEP and the uncrosslinked microcapsule-treated foam without DEEP, respectively. Furthermore, it was found that the LOI value of the microcapsule-treated foams with DEEP was higher than that (17%) of the form-stable PCM blend as composed by paraffin and ethylene-propylene-diene-terpolymer rubber (EPDM).³⁰ These seem to suggest that the incorporation of DEEP flame retardant could improve the fire resistance of the PCM-treated materials. The enhanced LOI value is positively due to the DEEP loadings. And the improved fire resistance of the paraffin-DEEP microcapsule-treated foams can be explained by the fire suppression mechanism of phosphorous-containing fire retardant. On the one hand, the thermal decomposition of DEEP is an endothermic process with water vapor release, which can smother the flames by diluting the amount of oxygen in the surrounding air and reducing the ambient temperature.^{34,35} On the other hand, the decomposition procedure of DEEP can form a cohesive and impact char layer, which can act as an excellent insulator and effectively inhibit the underlying flammable component

Table IV. LOI Values of Foams with Different Type of Microcapsules

Sample	LOI (%)
Foam with uncrosslinked paraffin microcapsule	17
Foam with crosslinked paraffin microcapsule	17
Foam with uncrosslinked paraffin-DEEP microcapsule	23
Foam with crosslinked paraffin-DEEP microcapsule	26

contacting with oxygen and heat directly. Additionally, the decomposition procedure of phosphorous-containing fire retardant can also function in the vapor phase through an H radical capture mechanism to slow down the combustion rate.^{21,38} Besides, the LOI value of the crosslinked microPCMs as shells was modestly enhanced by 3% when compared with the uncrosslinked microPCMs. This result accords with the conclusion obtained in the evaluation of PCM content and thermal stability. This suggests that an increased DEEP content is possibly obtained when crosslinking was introduced to the shell.

CONCLUSIONS

Microcapsules containing paraffin and diethyl ethylphosphonate (DEEP) flame retardant with uncrosslinked and crosslinked poly (methacrylic acid-co-ethyl methacrylate) (P(MAA-co-EMA)) shells were fabricated by a suspension-like polymerization. The DSC results showed that the crosslinking of the polymer shell led to an increase in the melting enthalpy of the microcapsules by more than 15%. The crosslinked P(MAA-co-EMA) microcapsule with DEEP and without DEEP have melting enthalpies of 67.2 and 102.9 J/g, respectively. The TGA results indicated that the thermal resistant temperature of the crosslinked microcapsules with DEEP was up to 171°C, which was higher than that of its uncrosslinked counterpart by ~20°C. The incorporation of DEEP into the microPCM increased the LOI value of the microcapsule-treated foams by over 5%. Thermal images showed that both microcapsule-treated foams with and without DEEP possessed favorably temperature-regulated properties. As a result, the microPCMs with paraffin and DEEP as core and P(MAA-co-EMA) as shell have good thermal energy storage and thermal regulation potentials, such as thermal-regulated foams heat insulation materials.

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