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ORIGINAL CONTRIBUTION

Thermal conductivity of microPCMs-filled epoxy matrix composites

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Abstract Microencapsulated phase change materials (microPCMs) have been widely applied in solid matrix as thermal-storage or temperature-controlling functional composites. The thermal conductivity of these microPCMs/matrix composites is an important property need to be considered. In this study, a series of microPCMs have been fabricated using the in situ polymerization with various core/shell ratio and average diameter; the thermal conductivity of microPCMs/epoxy composites were investigated in details. The results show that the microPCMs have smooth surface and regular global shape with compact methanol–melamine–formaldehyde shell. The shell thickness does not greatly influence the phase change behaviors of PCM. Moreover, smaller microPCMs embedded in epoxy can improve the thermal transmission ability of composites. The effect of thermal conductivity of composites can be improved with higher volume fraction (10–30%) of microPCMs; and smaller size microPCMs with the same content of PCM may also enhance the thermal transmission area in matrix. Modeling analysis of relative thermal conductivity indicates that mixing higher thermal conductivity additive in PCM or matrix is an appropriate method to improve the thermal conductivity of microPCMs/matrix composites.

Keywords Microcapsules · Phase change materials · Thermal conductivity · Epoxy · Composites

Introduction

Phase change materials (PCMs) have been widely used to store thermal energy in aerospace, solar energy utilization, energy-saving building, and heat exchanger domains. They can take advantage of latent heat during phase change at a fixed temperature [1–4]. The thermal energy storage by PCMs can resolve the time mismatch between the energy supply and the consumption of energy, and play the role in switching peak load and increasing efficiency of energy utilization. Ordinary solid–liquid PCMs are inexpensive and owe large latent heat, but they need containers to avoid extra thermal resistance and leakage [5]. The technology of microencapsulation of PCMs (microPCMs) has supplied a proper way to enlarge the utility fields of the PCMs with advantages, including protecting the PCM against the influences of the outside environment, increasing the heat transfer area, and withstand changes in volume [6]. MicroPCMs has the particle size from less than 1 μm to more than 1,000 μm [7–10]. A survey of literature shows that a number of studies have been carried out on microPCMs using different inorganics, natural or synthetic polymers as microcapsule shell materials. MicroPCMs have been widely applied in solid matrix as smart temperature-regulation composites, such as fibers, construction materials, and functional packaging materials [11–13]. The core

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materials in microPCMs are usually organic solid–liquid materials such as paraffin (C_nH_{2n+2}) and fatty acids ($CH_3(CH_2)_{2n}COOH$) [14–16].

In practical application, the thermal conductivity of these microPCMs/matrix composites is an important property need to be considered. Although lots of studies have been carried out, we still have little knowledge about the thermal conductivity of these microPCMs/matrix composites. It is well known that the thermal conductivity of microPCMs is related to the material composition, structure, and state. Therefore, the thermal conductivity of these microPCMs/matrix composites is determined by the thermal conductibility of PCMs, shells, and matrix. The thermal conductibility of solid–liquid PCM in microcapsules tends to be lower than its desired value because all the components of the PCM are organic materials, which limits the thermal transmission. Introduction of higher thermal conductive materials in PCM is a logical solution to enhance the thermal conductivity of PCM. The insertion of metal fins, foams, wools into the PCM has long been practiced [17, 18]. As the polymeric shell of microPCMs is tiny membrane, it may have negative impact on thermal transmission of the encapsulated PCMs. For example, silica encapsulation process has been applied to enhance the thermal conductivity and performance of microPCMs [19]. Thermal transmission of microPCMs/matrix composites is also predominantly governed by the thermal conduction of matrix. As a result, many researches have been done to study this phenomenon in significantly diverse class of materials, which include inorganic substances (gypsum, clay, and concrete) and organic substances (polyolefin, polyurethane, and epoxy). Barmar [20] had investigated the thermal conductivity fibers containing microPCMs. Among these matrix materials, epoxy resin-based thermosets and their composites present a special class of materials which possess excellent mechanical properties. In our previous studies, we have successfully fabricated microPCMs/epoxy composites as functional temperature-controlling materials [21, 22]. However, epoxy is normally considered to be a poor thermal material due to its low thermal conductivity [23]. The issue of thermal transmission through epoxy networks becomes quite significant in situations when they are used as matrix of microPCMs to transmit the thermal inside or outside of PCMs. Carbon nanotubes and metal nanoparticles have been mixed in epoxy to solve this problem [24]. In order to improve or alter the thermal conduction in these systems, it is necessary to understand what modes and interactions govern the heat transmission in polymeric network.

The shape, size, volume fraction, and interphase of particles are factors which greatly dominate the mechanical properties of the particle-filled composites [25]. These factors also need to be considered in investigation of thermal conduction of these composites. Reports are available in the existing literature on experimental as well as numerical and analytical studies on thermal conductivity of some filled polymer composites [26–28]. A number of experimental and theoretical works have been devoted to investigation of the thermal conductivity (λ) of two-phase epoxy composites. In accordance with modern views, λ is expected to depend on the conductivity of the matrix material, the conductivity of the filler, the volume fraction of the filler, the boundary resistance, the aspect ratio, and the equivalent radius [29]. However, these studies are restricted to composites containing homogeneous single-component particles. Most of these studies were confined to the thermal behavior of neat polymers only and not to their composites. Little knowledge is available to the thermal conductivity of microPCMs/matrix composites. Pal [30] had developed new models to predict the relative thermal conductivity of concentrated three-component composites of core–shell particles. According to this model, the relative thermal conductivity is a function of five variables, that is core/shell ratio, shell/matrix ratio, volume fraction of particles, core–shell thermal conductivity, and shell–matrix thermal conductivity. In our previous studies [31], we reported the fabrication method of methanol-modified melamine formaldehyde (MMF) shell microPCMs containing paraffin. It was found that the particle size and volume fraction of microPCMs can affect the thermal properties of microPCMs/epoxy composites. Such composites cannot meet the stringent requirements of thermal stability and the necessary thermal conductivity with very high filler loading. This method will, at the same time, reduce the mechanical properties of composites.

In view of the above, the present work was undertaken to investigate experimentally and numerically the thermal conductivity of epoxy matrix composites filled with microPCMs. Paraffin was applied as the microPCM for its availability in a reasonable phase change temperature range and its large amount latent heat [31]. Moreover, paraffin has been found to exhibit many desirable characteristics, such as high heat of fusion, negligible supercooling, low vapor pressure in the melt, chemically inert and stable, self-nucleating, etc. Epoxy resin is an epoxy oligomer; it can form thermosetting plastics with three-dimensional cross-linked network solidified by hardener. The thermoset epoxy generally possesses excellent characteristics: heat, moisture and chemical resistance, toughness, electrical and mechanical resistance, etc., so epoxy resin can been chosen as a polymer matrix for PCM [32]. The thermal conductivity of microPCMs/epoxy was systematically tested based on the parameters of core/shell ratio, average diameter, and volume fraction of microPCMs embedded in epoxy matrix. Based on the experimental data, a semi-experiential model of thermal conductivity was applied to analyze the thermal conductivity of microPCMs/matrix composites. We believe that these results will be guides for the fabrication and application of the functional microPCMs/matrix composites.

Experimental

Materials

Paraffin (Tianjin Kemel Chemical Reagent Development Center, Tianjin, China) was used as the PCM material (core material). The shell material was prepolymer of melamine formaldehyde modified by methanol (MMF, solid content was 78.0%, Aonisite Chemical Trade Co., Ltd., Tianjin). Styrene maleic anhydride (SMA) copolymer (Scripset® 520, Hercules, USA) was applied as a dispersant. Organic diluent (butyl glycidyl ether), bisphenol-A epoxy resin (E-51), and curing agent (amine) were supplied by Tianjin Synthetic Material Research Institute (Tianjin, China).

Fabrication of microPCMs/epoxy composites

The fabrication methods of microPCMs and microPCMs/epoxy composite have been described in our previous reports [22, 31].

1. The encapsulation was carried out in a 500-ml three-neck round-bottomed flask. SMA (3.0 g) and 0.8 g sodium hydroxide (NaOH) were dissolved in 100 ml water (50 °C). The pH value was adjusted to 4–5 by acetic acid solution. Paraffin (10.0 g) was added to the aqueous SMA solution, and the mixture was emulsified mechanically under a vigorous stirring rate for 10 min using QSL high-speed dispersing machine (Shanghai Hongtai Ltd., Shanghai, China). The emulsion was dropped in a bottle, dipping in steady temperature flume with a stirring speed of 1,500 $\mathrm{r\,min^{-1}}$. Prepolymer (12.8 g) was dropped in this bottle with a rate of 0.25 $\mathrm{g\,min^{-1}}$. The shell formed after 2.5 h by heating slowly to temperature of 60 °C. Then, the temperature elevated to 75 °C. After polymerization for 1.5 h, temperature was dropped slowly at 2 °C $\mathrm{min^{-1}}$ to room temperature. The resultant microcapsules were filtered and washed with deionized water and dried in a vacuum oven.
2. MicroPCMs powder was mixed with 1.5 g organic diluent (butyl glycidyl ether) by ultrasonic vibration for 5 min. The power of ultrasonic devices was 40 W. The 10-g bisphenol-A epoxy resin was dropped in the mixture prepared, and then the mixture was mixed by the same ultrasonic vibration for 5 min. Amine curing agent (2.5 g) was added and ultrasonic vibrated for 5 min. At last, the mixture prepared was casted in the PTFE mold. After cured for 24 h at room temperature, the samples were demoulded out.

Optical and SEM morphologies

After the microPCMs fabrication, 1 ml of the colloidal solution was extracted and spread on a clean glass slide (1× 3 cm). Optical photographs of the microcapsules retained in emulsion were taken by an optical microscope (MiVnt image analysis system, China). The dried microPCMs and the interfacial morphologies of composites were adhered to the stages and the surface of samples was sprayed with gold. The surface morphologies were observed by using a FEI Nanosem 430 SEM (USA) at an accelerated voltage of 15 kV. After the composite was dried in room temperature, it was carefully cut to obtain the cross section by an ultramicrotome (RMCMT-7000, USA).

Differential scanning calorimetry measurements

The thermal analyses of microPCMs were measured by a PerkinElmer Diamond DSC (USA) at a heating rate of 5 °C $\mathrm{min^{-1}}$ among the range of 0–50 °C under nitrogen (N_2) atmosphere. Each sample was analyzed at least twice, and the average value was recorded.

Average diameters of microPCMs

The average diameters of microPCMs were measured using a partial diameter distribution machine (LA950 V2, Japan).

Thermal conductivity of composites

Unitherm™ Model 2022 (Anter Corp., USA) is used to measure thermal conductivity of a variety of materials. The tests are in accordance with ASTM E-1530 standard. A sample of the composite is held under a uniform compressive load between two polished surfaces, each controlled at a different temperature. The lower surface is part of a calibrated heat flow transducer. The heat flows from the upper surface, through the sample, to the lower surface, establishing an axial temperature gradient in the stack. After reaching thermal equilibrium, the temperature difference across the sample is measured along with the output from the heat flow transducer. These values and the sample thickness are then used to calculate the thermal conductivity. The temperature drop through the sample is measured with temperature sensors in the highly conductive metal surface layers on either side of the sample. For one-dimensional thermal conduction, the formula can be given as Eq. 1,

$$Q = \lambda A \frac{T_1 - T_2}{x} \tag{1}$$

where Q is the heat flux (W), λ is the thermal conductivity (W/(m K)), A is the cross section area (m^2), x is the thickness of the composite sample (m).

Results and discussion

Controlling of microPCMs structure

The fabrication process of microcapsules using melamine-formaldehyde (MF) and urea-formaldehyde (UF) resins as shell materials is usually defined as an in situ polymerization method. Emulsifying agent is used to absorb the shell materials on core droplets. The direct polymerization of a single monomer or prepolymer is carried out on the core particle surface. It has been proved that the MMF can be successfully applied to fabricate microPCMs using the in situ polymerization method [31]. The shell thickness, surface morphology, and average size of microPCMs can be controlled by regulating the core/shell ratio, prepolymer adding speed, and emulsion stirring rate [33].

Table 1 lists the structure properties of microPCMs (core/shell ratios of 2:1, 1:1, and 1:2) samples fabricated under emulsion stirring rates in range of 1,000–3,000 r min^{-1}. With the increasing of stirring rate, the average diameter decreased. This result accords to our previous report, which indicates that the average diameter is mainly determined by emulsion stirring rate [10]. The MMF shells applied in this study do not influence this rule. The MMF resin can crosslink forming thin shells with compact structure. The shell thickness is in the range of 0.97±0.22 to 1.89±0.10 μm. The shell thickness of microPCMs fabricated by various conditions is not changed too much. It means that the shell is a thin membrane which is not greatly affected by the core/shell ratios and emulsion stirring rates.

Figure 1a–d shows the optical morphologies of microPCMs in emulsion fabricated by emulsion stirring rates of 1,000, 2,000, 3,000, and 4,000 r min^{-1}, respectively. It is clear that the average diameter of microPCMs had decreased with the increasing of emulsion stirring rate. Being encapsulated by shell material, the core droplets are ultimately separated through the regulation of hydrolyzed SMA molecules. These microPCMs have regular globe shape with smooth surface. Figure 2a, b shows the SEM surface morphologies of dried microPCMs with core/shell ratio of 2:1 fabricated by 1,000 and 3,000 r min^{-1} emulsion stirring rates. Their average diameters are about 10 and 20 μm. The dried microPCMs still keep the regular global shape. There is no adhesion and impurity substance between microPCMs. The shells are compact without holes and cracks.

Table 1 Structure properties of microPCMs samples

Samples	Core/shell ratio	Emulsion speed (r min^{-1})	Shell thickness (μm)	Average diameter (μm)
M-1	2:1	1,000	1.02±0.50	20.20±5.70
M-2		2,000	0.97±0.22	14.67±5.82
M-3		3,000	0.97±0.32	8.30±2.40
M-4	1:1	1,000	1.51±0.44	22.54±2.10
M-5		2,000	1.67±0.50	15.67±5.82
M-6		3,000	1.80±0.24	8.46±1.31
M-7	1:2	1,000	1.89±0.10	23.12±3.11
M-8		2,000	1.88±0.41	16.25±2.17
M-9		3,000	1.80±0.22	12.51±2.11

DSC measurements

Differential scanning calorimetry (DSC) analysis was applied to supply information of heat transmission characters of microPCMs and microPCMs/epoxy composites. Figure 3 shows DSC curves of paraffin and typical microPCMs with core/shell ratio of 1:3 fabricated by emulsion rate of 1,000 r min^{-1}. The pure paraffin has the phase change temperature (T_p) of 24 °C similar to the reported result [34]. The microPCMs sample exhibits nearly the same phase change behaviors as pure paraffin. The reason of selection of this typical microPCMs sample is that it has the relative thicker shell (Table 1). It can be figured out that other microPCMs with less thickness than this sample will have the similar phase change character. The conclusion can be induced that the shell may not greatly influence the phase change behaviors of PCM.

It needs to be explained that the T_p of epoxy composites is the data only reflecting the phase change behaviors of encapsulated PCM. Epoxy is a resin with low thermal transmission ability. It is determined that the epoxy composite have higher thermal transmission ability with higher weight ratio of PCM. Therefore, we only compared the T_p values of composites containing 20 vol.% of microPCMs to understand the effect of structure of microPCMs (core/shell ratio and size) on the phase change behaviors. Figure 4 shows the SEM cross-section morphology of a microPCMs/epoxy composite sample. It can be seen that the microPCMs are dispersed in epoxy matrix homogeneously. The shells keep the integrate state without cracks. It indicates that the shell has enough thermal stability to resist the thermal impact during of epoxy cross-linkage. Figure 5 shows the phase change temperature (T_p) values of microPCMs/epoxy composites with 20 vol.% microPCMs. MicroPCMs samples were fabricated under various conditions of core/shell ratios and emulsion stirring rates. Higher emulsion stirring rate will make the microPCMs smaller. The embedded microPCMs with small

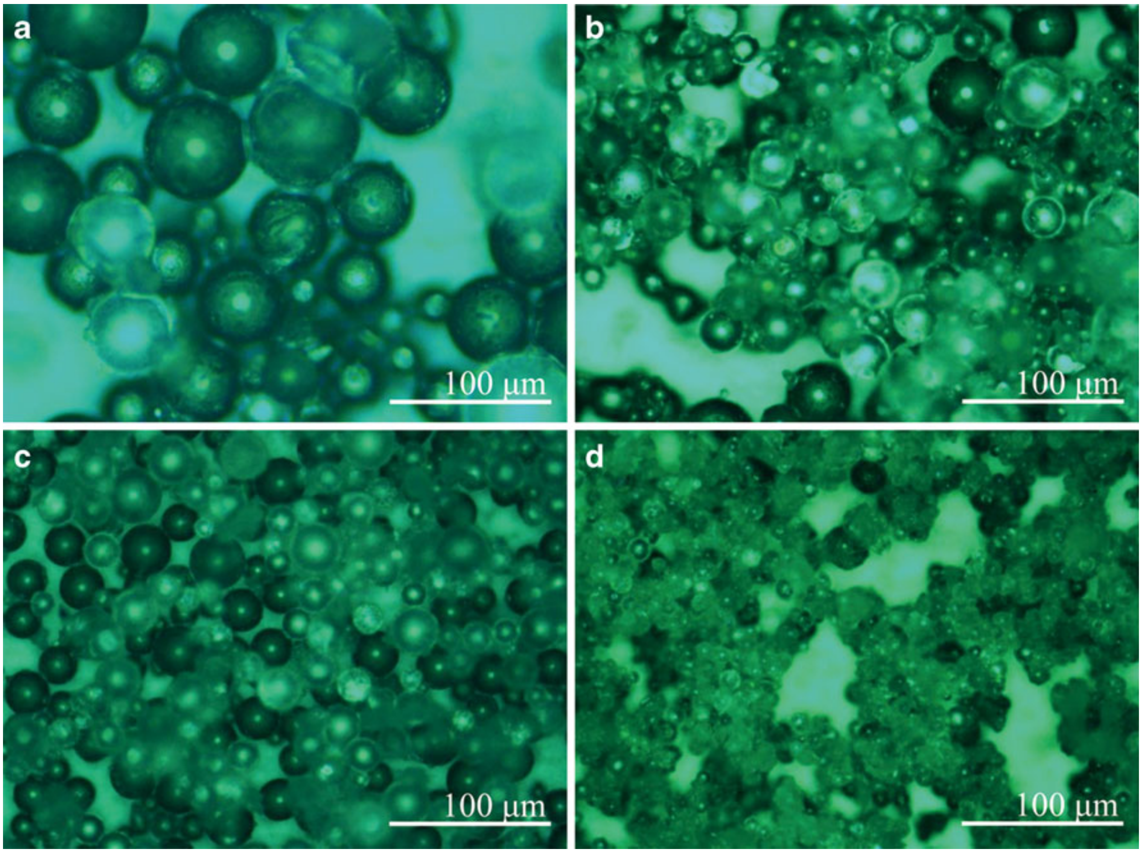

Fig. 1 Optical morphologies of microPCMs in emulsion

size (with the same core/shell ratio) will enhance the thermal transmission ability of the composites. The reason is that the smaller microPCMs in epoxy can improve the thermal transmission area. With the increasing of core/shell ratios of microPCMs (with the same emulsion stirring speed), the T_p value of microPCMs/epoxy composites has a variation from 27.5 to 30.5 °C.

Effective thermal conductivity of composites

In this paper, the core/shell ratio, size, and volume content of microPCMs are considered as the parameters affecting the effective thermal conductivity (λ_e) of microPCMs/epoxy composite. In Table 2, λ_e value of neat epoxy (sample E-0) is about 0.405 W/(m K) which is close to the reported data [35]. The λ_e value of composites filled with the same volume content of microPCMs (with the same core/shell ratio) has a little improvement with the decreasing of microPCM size. This phenomenon accords to the result in the DSC measurement. Smaller size microPCMs may enhance the thermal transmission area in matrix. The composite samples (EM-1, EM-2, and EM-3) have the λ_e value of 0.409, 0.409, and 0.410 W/(m K), respectively. It means that λ_e cannot be markedly improved only by adding smaller microPCMs.

On the other hand, the results show that the λ_e value of the composite increased with the increasing of filler volume fraction. For example, λ_e of EM-9 has increased to 0.565 W/(m K) with 30% volume fraction of microPCMs. When a material undergoes a phase change from solid to liquid or from liquid to gas, its thermal conductivity may change. In this study, more PCM in epoxy matrix will enhance the thermal transmission ability of composites, because substances can exhibit very different thermal conductivities along different microstructure and crystal axes.

Analysis of relative thermal conductivity

Many works have been carried out to investigate the thermal conductivity of particle-filled/epoxy composites. For example, Yung et al. [35] had studied the effects of contents on the thermal conductivity of hollow glass bead-filled epoxy composites: it is concluded that the properties of these composites are improved expect for the decrease in thermal conductivity. However, few literatures focus on the thermal conductivity of three-component composite materials containing core–shell microPCMs randomly distributed in a continuous matrix because of its complex phase change behavior and thermal transmission process. Figure 5 illus-

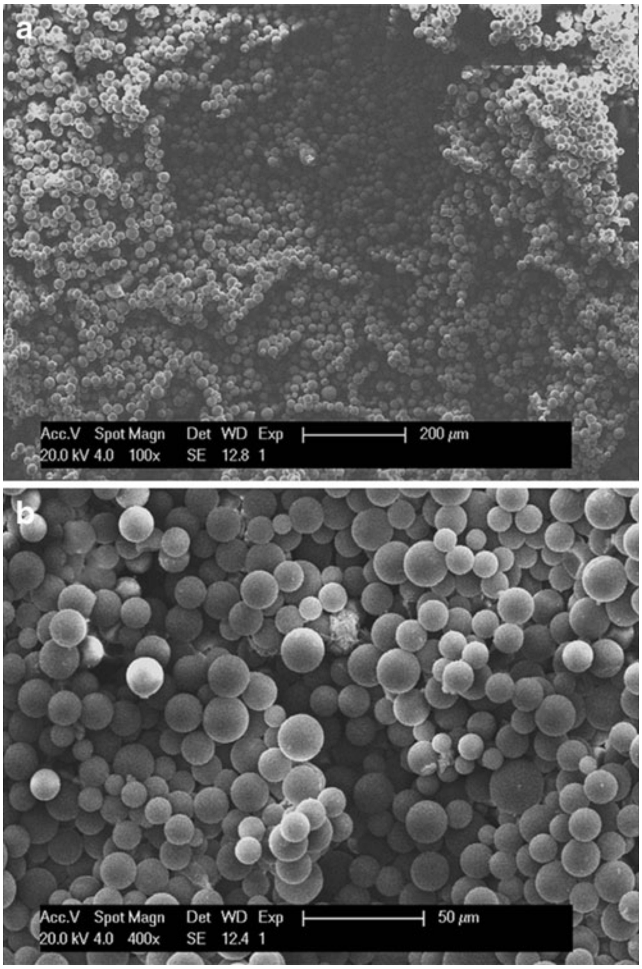

Fig. 2 SEM surface morphologies of dried microPCMs

trates the structure of core–shell particle embedded in matrix. According to the model derived by Felske [36], the relative thermal conductivity (K_r) of core–shell particle-filled/matrix composites is a function of five variables as Eq. 2

$$K_r = f(\delta, \lambda_{21}, \lambda_{32}, \phi, \phi_m) \tag{2}$$

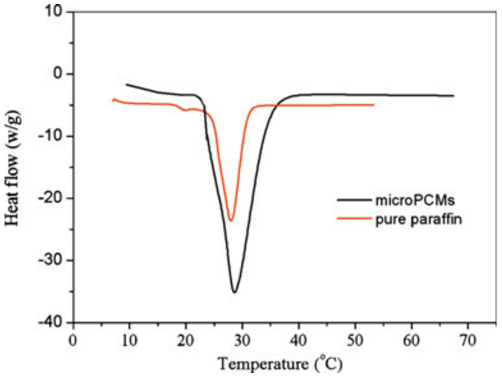

Fig. 3 DSC curves of paraffin and typical microPCMs with core/shell ratio of 1:3

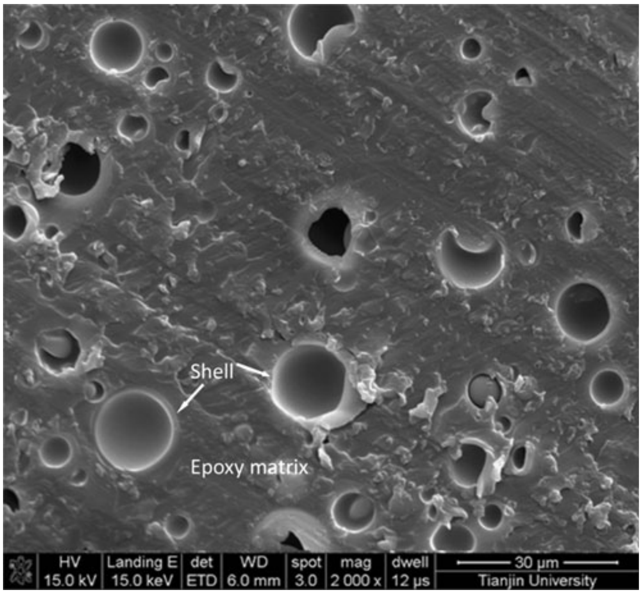

Fig. 4 SEM cross section of microPCM/epoxy composite

where δ is the ratio of shell-to-core radii ($\delta = R/r$), λ_{21} is the ratio of shell-to-matrix thermal conductivities, λ_{32} is the ratio of core-to-shell thermal conductivities, $\varnothing$ is the volume fraction of filler, and $\varnothing_m$ is the maximum packing volume fraction of filler (core–shell particles). Pal [30] had developed a new model describing the thermal data reasonably well for thermal conductivity of three-component composites of core–shell particles as Eq. 3, β is given as Eq. 4,

$$(K_r)^{1/3}\left[\frac{\beta - 1}{\beta - K_r}\right] = \left(1 - \frac{\phi}{\phi_m}\right)^{-\phi_m} \tag{3}$$

$$\beta = \frac{(2+\delta^3)\lambda_{31} - 2(1-\delta^3)\lambda_{21}}{(1+2\delta^3) - (1-\delta^3)\lambda_{32}} \tag{4}$$

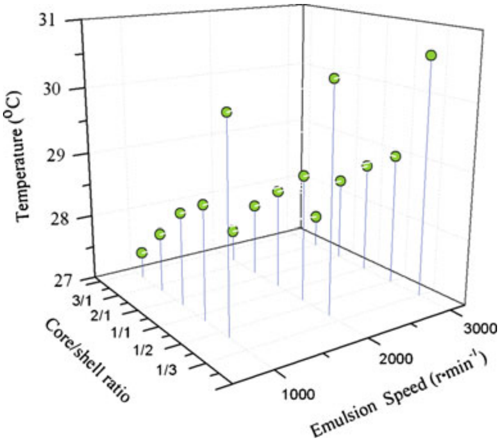

Fig. 5 Phase change temperature (T_p) of microPCMs/epoxy composites with various microPCMs contents

Table 2 Effective thermal conductivity (λ_e) of MicroPCMs/epoxy composite samples

MicroPCMs/epoxy composite samples	MicroPCMs volume contents	Embedded microPCMs samples	Effective thermal conductivity W/(m K)
E-0	0%	–	0.405
EM-1	10%	M-1	0.409
EM-2		M-2	0.409
EM-3		M-3	0.410
EM-4	20%	M-4	0.520
EM-5		M-5	0.525
EM-6		M-6	0.531
EM-7	30%	M-7	0.545
EM-8		M-8	0.562
EM-9		M-9	0.565

Based on this model, it was found that when core material is relative highly thermal conducing, K_r is greater than unity and is increasing with the increase in ∅ provided that $\lambda_{21}>1.0$. When λ_{21} is less than, but close to unity, the relative thermal conductivity of the composite is larger than unity. The relative thermal conductivity increases with the increase in λ_{21} for any given ∅ and δ (Fig. 6).

Because the shell of microPCMs is thin membrane in this study, the value of δ can be also considered as of $\delta \rightarrow 1$. The above Eqs. 4 and 3 can be simplified as Eqs. 5 and 6,

$$\beta = \lambda_{31} \tag{5}$$

$$(K_r)^{1/3}\left[\frac{\lambda_{31}-1}{\lambda_{31}-K_r}\right] = \left(1-\frac{\phi}{\phi_m}\right)^{-\phi_m} \tag{6}$$

From Eq. 6, we can deduce that there are two ways to improve the value of K_r. One way is that, if λ_{31} is a constant, K_r will increase with the increasing of ∅. However, it has been proved that with the increasing of ∅, the tensile strength (σ_c) of composite will decrease sharply [31]. Therefore, it is not a sensible option only increasing the K_r while losing the mechanical properties of microPCMs/epoxy composites. It is necessary in future work to find out the appropriate value of ∅ both considering the K_r and σ_c. It is well known that the properties of composites are strongly dependent on the interphase of the filler and matrix. The interphase region is comprised of polymer molecules that are bonded at the filler particles being restricted from dipole polarization. Higher microcapsules loading will bring more interface deficiency and destroy the mechanical properties of composites. At the same time, the interphase will also be the main factor that influences K_r when the volume fraction of microPCMs increases to a certain extent.

To increase the value of K_r, another way is to enhance the heat transmission ability of core material. Normally, the solid–liquid organic PCM has unacceptable low thermal conductivity, and hence, heat transfer enhancement technologies are required for thermal absorbing–releasing application. Higher thermal conductivity additive in PCM can help solve this problem. At the same time, this method is practicable for polymeric matrix to increase the value of λ_{31}.

Conclusion

The effects of core/shell ratio, average diameter, and volume fraction of embedded microPCMs on the thermal conductivity of epoxy composites were investigated in details. Based on the experimental data, semi-experiential model of thermal conductivity was discussed to supply ways to enhance the thermal conductivity of microPCMs/epoxy composites. The following conclusions can be drawn from this study: (1) The in situ polymerization method was applied successfully to fabricate a series of microPCMs with various average diameter by controlling the emulsion stirring rate. The shell thickness of microPCMs fabricated by various conditions is not change too much. (2) DSC measurements show that shell thickness do not greatly influence the phase change behaviors of PCM. Moreover, smaller microPCMs embedded in epoxy can improve the thermal transmission ability of composites. (3) The λ_e value of composites has been improved with higher volume fraction of microPCMs; and smaller size microPCMs with the same content of PCM may also enhance the thermal transmission area in matrix. (4) Modeling analysis of relative thermal conductivity shows that mixing higher thermal conductivity additive in PCM or matrix can help to

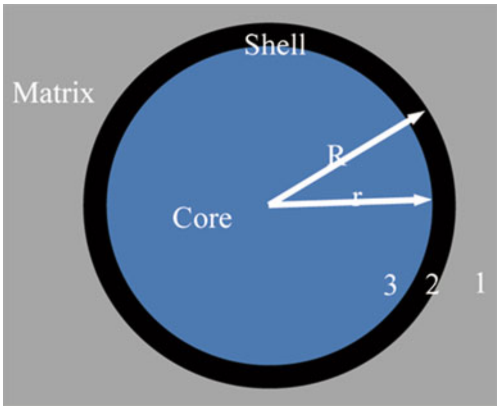

Fig. 6 Illustration of the structure for core–shell microPCMs embedded in epoxy matrix

improve the thermal conductivity of composites. The method is the optimal choice both considering the thermal conductivity and mechanical properties of composites.

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