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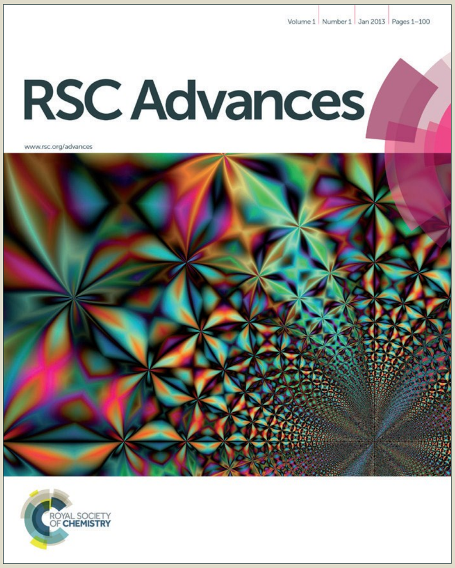

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1, 3: 2, 4-di-(3, 4-dimethyl) benzylidenesorbitolorganogelused as phase change materials: solvent effects on structure, leakage and thermal performance

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Abstract

Organogels used as shape-stable phase change materials were prepared by impregnating low molecular mass organogelator into organic phase change materials. 1, 3:2, 4-di-(3, 4-dimethyl) benzylidene sorbitol (DMDBS) was used as a supporting material and n-octadecane, ethyl palmitate, 1-octadecanol and 1-tetradecanol were used as phase change materials. The thermal properties, such as phase change temperature and latent heat, were investigated by a differential scanning calorimeter (DSC). The leakage and thermal storage performance of the composite phase change materials were also investigated in detail. Rheology measurements were used to demonstrate the true gel phase of the composite phase change materials. Fourier transformation infrared spectroscope (FTIR) and scanning electronic microscope (SEM) were used to determine the chemical structure and microstructure of the composites. The DSC results indicated that the composites exhibited acceptable thermal properties with high mass percentage of phase change material. Flory-Huggins parameters (χ) were calculated to estimate the interaction between the gelator and phase change materials. The results indicated that different χ resulted in different morphology of DMDBS, which led to different leakage and thermal storage performance of the prepared composites.

Keywords: organogels; phase change materials; three-dimensional network; Flory-Huggins parameters; interaction.

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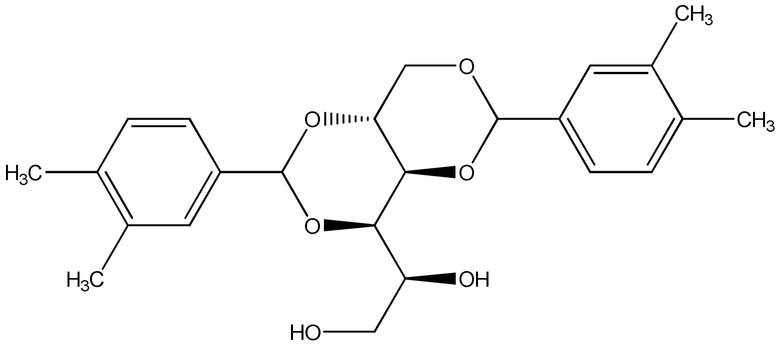
1. Introduction

The use of phase change materials (PCMs) for energy storage has received a great attention in recent years due to increasing energy consumption. PCMs can absorb or release large latent heat at their melting points as surrounding temperature increases and decreases [1]. PCMs are developed for various applications due to their different phase change intervals: materials that melt below 15 ^{o}C are used for keeping coolness in air-conditioning applications, while materials that melt above 90 ^{o}C are used to drop the temperature if there is a sudden increase in heat to avoid ignition. All other materials that melt between these two temperatures can be applied in solar heating and for heat load leveling applications [2]. Compared to inorganic PCMs, organic PCMs melt and freeze repeatedly without phase segregation and consequent degradation of their latent heat of fusion. However, they also have some undesirable properties, such as low thermal conductivities and need encapsulation for preventing leakage of melted PCM during phase change process, which results in extra thermal resistance and cost [3].

Much research has focused on the preparation of form-stable PCMs. Several methods have been used such as microencapsulation [4], adsorption by porous material [5] and the addition of a polymer as a supporting material [6]. Alkan et al. [7] successfully prepared PMMA microcapsules containing n-octacosane as core material. The composite PCMs exhibited desirable latent heats and good chemical stability. Yarin et al. [8] achieved the intercalation of different types of paraffins and their mixtures with triglycerides inside carbon nanotubes (CNTs). The nano-scale phase change materials (PCMs) obtained using this route can be tailored to process a relatively wide working temperature range, as well as a negligible thermal response time. Meng et al. [9] prepared fatty acid eutectic/polymethylmethacylate (PMMA) form-stable phase change material and the feasible maximum mass fraction of lauric acid-myristic acid eutectic was determined to be 70%. In our previous work, low molecular-weight organic gelator 1, 3:2, 4-di-(4-methyl) benzylidene sorbitol (MDBS) and 1, 3: 2, 4-di-(3, 4-dimethyl) benzylidene sorbitol (DMDBS) were used to prepare paraffin and 1-tetradecanol based gelatinous PCMs and showed lower leakage with high weight percentage of phase change materials.[10,11]In these gelatinous form-stabilized PCMs, the phase change material was well dispersed in the three-dimensional networks formed by gelators through intermolecular interactions such as hydrogen bonding and π-π interactions.

In molecular gels, solvent-gelator interactions play a key role in mediating organogel formation and ultimately determine the properties of the gel[12, 13]. Several groups have reported the effect of solvents on gel morphology and properties. Dasgupta[14] et al. reported that the supramolecular superstructure of an organogel can be significantly altered simply by adjusting with the solvent type. Wu[15] et al. proved that by varying the ratio of the mixed solvent, the gelation ability and thermal stability of the gel can be easily adjusted. Bielejewski[16] et al. found that the morphologies of xerogels were influenced by the nature of the solvent, and the polarity of the solvent influenced the thermal stability of the gel. In this work, DMDBS was used as the supporting material in different phase change materials such as n-octadecane, ethyl palmitate, 1-octadecanol and 1-tetradecanol. By investigating the self-assembly of a model gelator in different phase materials, we hope to gain a more detailed insight of the effects of phase change material on DMDBS morphology, macroscopic properties (leakage and thermal storage performance) of composite PCMs and study the interactions between DMDBS and phase change materials.



Scheme 1 Structure of DMDBS

2. Experiment

2.1 Materials

N-octadecane (99 wt%), ethyl palmitate (99 wt%), 1-octadecanol (99 wt%) and 1-tetradecanol (99 wt%) were obtained from Tianjin Guangfu Fine Chemical Research Institute. The n-hexane was obtained from Tianjin Jiangtian Chemical Technology Co., Ltd. 1,3:2,4-di-(3,4-dimethyl) benzylidene sorbitol (DMDBS) was provided by Yantai Zhichu Synthetic Chemistry Co., Ltd. All other compounds were analytical grade and used without further treatment.

2.2 Preparation of composite PCMs

To establish the relationship of DMDBS and the chosen PCMs, the composite PCMs were prepared by adding the desired amount of DMDBS to different melted pure PCMs, and the mixture was heated above the melting point of the gelator, about 275 ^{o}C. The composite PCM was obtained by slowly cooling to room temperature. Four kinds of composite PCMs using n-octadecane, ethyl palmitate, 1-octadecanol and 1-tetradecanol as phase change material were obtained, denoted as PCM-1, PCM-2, PCM-3 and PCM-4. The compositions of phase change material and DMDBS in the composites are listed in Table 1.

Table 1 The samples identification and compositions

Samples	Compositions
PCM-1	3% DMDBS+97% n-octadecane
PCM-2	3% DMDBS+97% ethyl palmitate
PCM-3	3% DMDBS+97% 1-octadecanol
PCM-4	3% DMDBS+97% 1-tetradecanol

2.3 Analysis methods

2.3.1 Characterization of composite PCMs

The structural analysis of the composites was carried out using a FTIR spectrophotometer. Rheology measurements were obtained on an AR 2000ex advanced rheometer (TA Instruments) using cone plate geometry in a Peltier plate. The frequency sweep experiment to obtain the storage modulus (G') and the loss modulus (G") was performed under a constant strain of 0.15%. The temperature for each sample was 30 °C higher than the melting temperature of corresponding pure phase change materials. The FTIR spectra were recorded on a TENSOR 27 instrument from 400 to 4000 $cm^{-1}$with a resolution of 2 cm^{-1} at room temperature using KBr pellets. The morphology and microstructure of the composite PCM and xerogel were observed using scanning electron microscopy (SEM S-4800, Hitachi, Japan). The xerogels were prepared as follows: the composite PCMs were added to the vigorous stirring n-hexane, and the white precipitate was filtered, washed with n-hexane, and then dried in vacuum for 24 h[17]. The white precipitate was dropped on the SEM plate and sputtered with Pt by sputtering. The physical thermal properties of the composite PCMs were investigated using differential scanning calorimeter (DSC 204 F1, NETZSCH, Germany) in an argon atmosphere. All experimental measurements were made at 5 °C/min constant heating rate.

2.3.2 Measurement of leakage

The leakage of composite PCMs was measured by the filter sheets-sandwich method which has been described previously[18]. The samples were kept at 30 °C above the melting temperature of each phase change material for 24 h. The sample was weighed before and after the annealing step and weights were given by M_1 and M_2, respectively. The leakage of the composite PCM was calculated using following equation:

$$\text{Leakage (wt\%)}=(M_1-M_2)/M_1 \qquad (1)$$

2.3.3 Thermal storage performance test

The composite PCMs and the pure phase change materials were placed into cylinders with diameters of 3.8 cm. The environment temperatures of the samples were from 10 to 40 °C for n-octadecane and ethyl palmitate, 30 to 70 °C for 1-octadecanol, 20 to 50 °C for 1-tetradecanol. The data were automatically monitored using a data acquisition/switch unit (TDAM 7034).

3. Results and discussion

3.1 Thermal properties of composite PCMs

The thermal properties of the composite PCMs, such as the melting and freezing points and the latent heats were measured by DSC. The theoretical enthalpies of the composite PCMs were calculated using following equations:

$$\Delta H_m^{calc} = W_{CM} \times \Delta H_{m,\,CM} \qquad (2)$$

$$\Delta H_f^{calc} = W_{CM} \times \Delta H_{f,\,CM} \qquad (3)$$

ΔH_m^{calc} and ΔH_f^{calc} represent the theoretical enthalpies of the composite PCMs during the melting and freezing process respectively. W_{CM} is the weight percentage of phase change material in the composite PCM, $\Delta H_{m,\,CM}$ and $\Delta H_{f,\,CM}$ are the melting and freezing enthalpies of pure phase change material respectively.

The DSC curves of all the samples show one endothermic peak on heating and two exothermic peaks on cooling. The endothermic peak is related to the solid-liquid transition. For the two exothermic peaks, the peak at higher temperature is related to the liquid-solid transition, and the peak at lower temperature may be attributed to a transition from a hexagonally packed solid phase to an orthorhombic ally packed solid phase (Fig. S 1-4). The phase change latent heat and temperature of pure phase change materials and composite PCMs are shown in Table 2. The enthalpy calculated from the total area under the peak by numerical integration is denoted as ΔH^{obs}. The melting and freezing points were determined from the onset temperature points of these curves. As can be seen from Table 2, during the heating process the phase change temperature of PCM-1, PCM-2, PCM-3 and PCM-4 are 25.0 ^{o}C, 22.0 ^{o}C, 55.8 ^{o}C and 35.7 ^{o}C and their latent heat values are determined to be 173.2 J/g, 145.8 J/g, 200.3J/g and 227.3J/g, respectively. In order to examine DMDBS whether degrades the latent heat performance of phase change materials, theoretical latent heat values of the composite PCMs were calculated as 196.0 J/g, 151.5J/g, 204.6 J/g and 231.5 J/g for PCM-1, PCM-2,PCM-3 and PCM-4. By comparison, it can be concluded that although the phase change enthalpies of phase change materials in PCM 1-4 change -11.6%, -3.7%, -2.1% and -1.8% respectively, the composite PCMs exhibit the acceptable heat capacities. It testifies DMDBS as the supporting material dose not influence the latent heat of phase change materials obviously. Similar results can also be observed in the freezing process of the composite PCMs.

Table 2 DSC data of the pure PCMs and composite PCMs

Sample	Melting			Solidifying		
	T_m (^oC)	ΔH_m^{obs}(J g^{-1})	ΔH_m^{cal}(J g^{-1})	T_f (^oC)	ΔH_f^{obs}(J g^{-1})	ΔH_f^{cal}(J g^{-1})
n-octadencane	25.1	202.1	202.1	25.3	205.2	205.2
PCM-1	25.0	173.2	196.0	25.0	173.8	199.0
Ethyl palmitate	22.0	155.6	156.2	18.0	147.8	147.8
PCM-2	22.0	145.8	151.5	17.9	139.0	143.4
1-octadecanol	56.0	210.9	210.9	56.0	205.4	205.4
PCM-3	55.8	200.3	204.6	55.7	196.0	199.2
1-tetradecanol	36.4	238.7	238.7	39.9	236.1	236.1
PCM-4	35.7	227.3	231.5	40.7	226.7	229.0

3.6 Rheological properties and FTIR analysis

The gelation of the four DMDBS-phase change materials systems at 30 ^oC higher than the corresponding phase change material (the temperature of leakage test) and their elasticity were probed by rheological experiments (Fig. S5). In the typical frequency sweep experiment, the variation of storage modulus G' and loss modulus G" is monitored under a constant strain of 0.15%. For all of the four samples, the G' and G" show a plateau region and the G' is greater than G", suggesting that it is the comportment expected of a true gel phase [19-21].

FTIR is an effective method to investigate a specific interaction in the composite PCMs. The FTIR spectra of the n-octadecane, DMDBS and the composite PCM-1 are shown in Fig. 1. Fig. 1a shows the spectrum of the n-octadecane. The peak at 2916 cm^{-1}signifies the symmetrical stretching vibration of its $–CH_3$ group and 2848 cm^{-1} represents the symmetrical stretching vibration of its $–CH_2$ group. The absorption peaks at around 1471 cm^{-1} belong to the deformation of $–CH_2$ and $–CH_3$, and the peak at 717 cm^{-1} represents the rocking vibration of $-CH_2$. Fig. 1c illustrates the spectrum of DMDBS. The peaks at 3278 and 3207 cm^{-1} signify the asymmetric stretching vibration of functional group of O-H. The peaks at around 2923-2854 cm^{-1} represents the stretching vibration of $-CH_2$ and $-CH_3$. The C-O and C-O-C stretching vibration can be seen at around 1100 cm^{-1}. The absorption bands at 857-769 cm^{-1} represent the bending vibration of C-H on the phenyl ring.

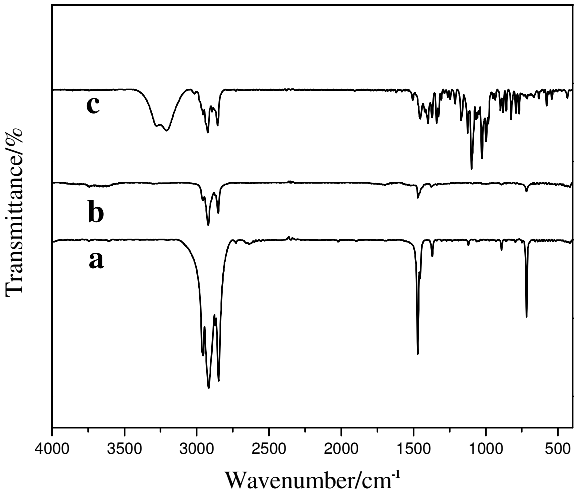


Fig. 1 FTIR spectra of (a) n-octadecane, (b) PCM-1, (c) DMDBS

As shown in Fig. 1b, the absorption peaks of n-octadecane at 2916, 2848, 1471 and 717 cm^{-1}also appear in the composite PCM-1 spectrum. It is also observed that there is no shift in the absorption peaks of PCM-1 composites when compared with the spectrum of n-octadecane. This result indicates that there is no chemical interaction between the functional groups of n-octadecane and DMDBS. The n-octadecane was easily retained in the networks of DMDBS by capillary and surface tension forces, and leakage of the melted n-octadecane from the composites could be prevented[22]. The similar observations were obtained in other composite PCMs (ethyl palmitate, 1-octadecanol and 1-tetradecanol, Fig. S6-8).

3.5 Morphology characterization of form-stable PCMs

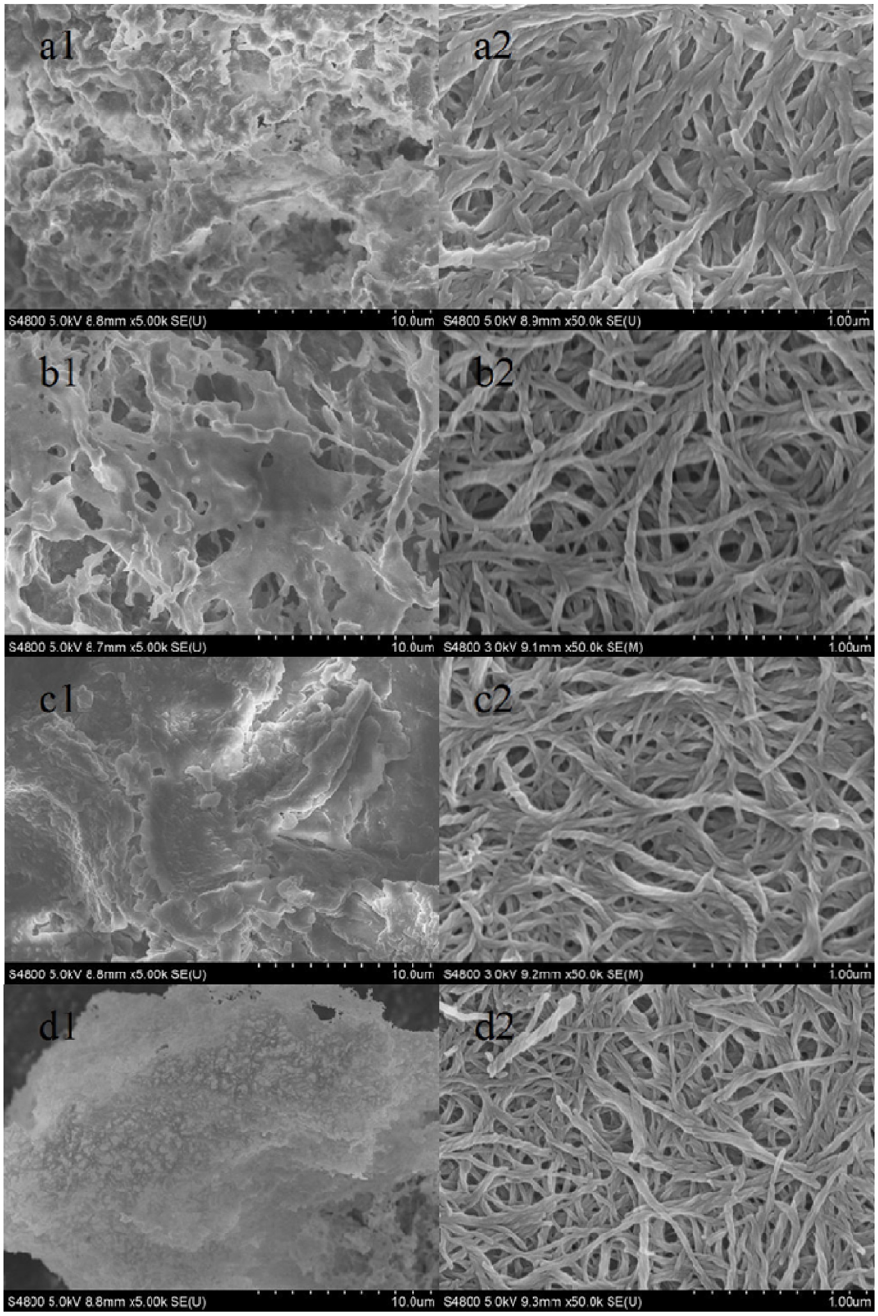


Fig. 2 SEM images of composite PCMs and DMDBS xerogels: (a1) PCM-1, (a2) DMDBS xerogel obtained from PCM-1; (b1) PCM-2, (b2) DMDBS xerogel obtained from PCM-2; (c1) PCM-3, (c2) DMDBS xerogel obtained from PCM-3; (d1) PCM-4, (d2) DMDBS xerogel obtained from PCM-4

Fig. 2 presents the morphologies of different form-stable PCMs and their xerogels. Fig. 2a1-d1 represents the morphologies of PCM-1, PCM-2, PCM-3 and PCM-4, respectively. The morphologies of the composites were slightly different as a result of the variation of phase change material type. There was no obvious demarcation between DMDBS and phase change material, indicating the phase change materials were dispersed in the networks of DMDBS. When the environmental temperature is above the melting point of phase change materials, DMDBS acting as a supporting material can effectively immobilize the liquid phase so as to prevent the leakage of the melted phase change materials. Fig. 3a2-d2 shows the xerogels prepared by removing phase change materials and the three-dimensional network could be clearly observed in these images, which is in good agreement with the theoretic inference.

By investigating the xerogels obtained from different composite PCMs, there are some slightly differences between the samples. As shown in Fig. 2a2-d2, the width of the fibrils were 0.34-0.52 μm for PCM-1, 0.17-0.32 μm for PCM-2, 0.18-0.28 μm for PCM-3 and 0.10-0.21 μm for PCM-4, respectively. It is also observed that the sample with thinner fibres has the denser networks. These results indicated that the self-assemble of DMDBS is affected by different phase change materials. Feng[23]has reported that the ability of immobilizing solvent of a gel was affected by the network formed by the gelator. So the different morphologies of DMDBS xerogels may lead to different leakage performances.

3.3 Leakage of phase change material from composite PCMs

The leakages of phase change material from the composite PCMs were measured at 30 ^{o}C higher than the melting point of the corresponding phase change material and the results are presented in Fig. 3. As shown in Fig. 3, the leakage of the phase change material decreased rapidly when the amount of DMDBS additive was 3 wt%. The leakages of PCM-1, PCM-2, PCM-3 and PCM-4 were 36.3%, 34.4%, 14.9% and 13.6%. The degree of the decrease for the four kind of composite PCMs was in the trend of PCM-1, PCM-2, PCM-3 and PCM-4. The obviously decrease of leakage is attributed to the three-dimensional network formed by DMDBS. As described previously, when the additive amount was 3 wt%, three-dimensional networks became thinner and denser in the trend of PCM-1, PCM-2, PCM-3 and PCM-4. In molecular gels, the networks formed by gelator immobilize the liquid component by surface tension and capillary forces [24].The denser three-dimensinal networks have more fibres, which would make the gels stronger and then more efficiency to prevent the flow of melted phase change material, which is the main reason for the leakage. So the sample which had denser networks would have a lower leakage. This distinction also existed in other additive amounts (Fig. 3). When the amount of additive exceed 7 wt%, there was only a slight decrease in leakage for all the composites. The probable reason is as the amount of DMDBS increased, the capillary forces of networks became stronger and when the amount was 7 wt%, the network was strong enough to immobilize most of the phase change material. So the leakage decreased a little when more DMDBS was added.

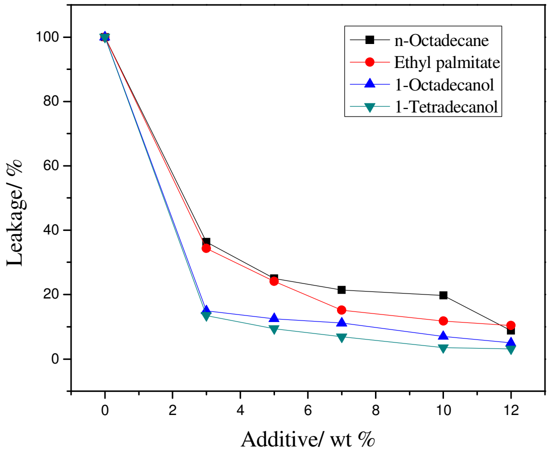


Fig. 3 Relationship between the leakage of the composite PCMs and the amount of DMDBS additive

3.4 Thermal storage performance of the composite PCMs

The thermal conductivity of composite PCMs was studied by comparing the heat storage and release curves of the pure phase change materials with corresponding composite PCMs (Fig. S9-12). Four couples of samples were tested; they were n-octadecane and PCM-1, ethyl palmitate and PCM-2, 1-octadecanol and PCM-3, 1-tetradecanol and PCM-4. As seen from the endothermic curves, the melting times for pure n-octadecane, ethyl palmitate, 1-octadecanol and 1-tetradecanol were 903, 490, 2544 and 1990s, respectively. When DMDBS was added, the melting time for

PCM-1, PCM-2, PCM-3 and PCM-4 were 1457, 1108, 5950 and 5461s. This result indicated that the heat transfer rate of composite PCMs is decreased in the melting process compared with that of corresponding pure phase change material. This is because in the case of heating, natural convection plays an important role in the heat transfer. As the phase change material undergoes phase transition in the network of solid DMDBS, natural convection is weakened. The weakening of natural convection overwhelmed the increase of conductivity, so the heat transfer rate in the heating process is reduced[25]. The extension of endothermic time is 61.4%, 126.1%, 133.9% and 174.4% for PCM-1, PCM-2, PCM-3, and PCM-4. The variation of endothermic time has a good correlation with the density of the networks, indicating that the denser networks formed in composite PCMs, the more effect on the weakening of natural convection. This disadvantage in heating process could be solved by adding a small quantity of exfoliated graphite, which has been reported in our previous work[10, 11]. In solidifying process, the cooling times were 1284, 2140, 1428 and 2199 s for the four pure phase change materials, and were changed to 858, 1865, 1089 and 2102 s for PCM-1, PCM-2, PCM-3, and PCM-4. This was attributed to the thermal conductivity of DMDBS is higher than that of phase change material and the heat transfer is enhanced in the conduction dominated solidification process.

Table 3 Endothermic and Exothermic time of pure PCMs and composite PCMs

Sample	Endothermic times^{-1}	Difference %	Exothermic time s^{-1}	Difference %
n-octadecane	903	61.4	1284	-33.2
PCM-1	1457		858	
Ethyl palmitate	490	126.1	2140	-12.9
PCM-2	1108		1865	
1-octadecanol	2544	133.9	1428	-23.7
PCM-3	5950		1089	
1-tetradecanol	1990	174.4	2199	-4.4
PCM-4	5461		2102	

Temperature acquisition range: n-octadecane: 23.1~29.7 °C for melt and 32.1~25.7 °C for solidification; ethyl palmitate: 21.3~27.6 °C for melt and 25.5~19.5 °C for solidification; 1-octadecanol: 47.8~59.6 °C for melt and 59.1~50.5 °C for solidification; 1-tetradecanol: 30.5~39.1 °C for melt and 38.4~31.2 °C for solidification;

3.7Solubility parameter analysis

In order to establish a method for estimating the effects of the interaction between gelator and phase change material on the leakage and thermal storage performance, we attempt to rationalize the thermal performance data by using solubility parameter analysis. Flory-Huggins parameter (χ) is used to propose the interaction between gelator and solvent[26, 27]. So we decided to consider Flory-Huggins parameter to discuss the DMDBS performance in the tested four phase change materials. The χ value could be estimated from the Hilderbrand solubility parameters of the solvent (δ_1) and gelator (δ_2) and the solvent molar volume (V_1) as shown in equation 2.

$$\chi_{12}=V_1\,(\delta_2-\delta_1)^2/RT \qquad (2)$$

The Hilderbrand solubility parameter of DMDBS and phase change material can be calculated according to the Fedors group contribution method (Table S1-5). These methods predict the cohesive energy with a mean accuracy of about 10%.

Table 4 Effects of χ on fiber diameter and thermal performance of composite PCMs

Sample	χ	Fiber diameter (μm)	Leakage/%	Endothermic difference%
PCM-1	10.14	0.34-0.52	36.30	61.35
PCM-2	7.81	0.17-0.32	34.36	126.12
PCM-3	4.45	0.18-0.28	14.91	133.88
PCM-4	3.09	0.10-0.21	13.55	174.42

The value of Flory-Huggins parameter of DMDBS in each phase change material was calculated as described above and a strong correlation between fiber diameters, leakage, extension of endothermic time and χ was found (Table 4). When χ decreased, the fiber diameter and leakage of corresponding composite PCM decreased gradually and the extension time of endothermic increased. Flory-Huggins parameter is a polymer-solvent interaction parameter, when the value of χ increases, the tendency toward dissolution decreases, which means the gelator-gelator interaction increases, so thick fibres would be formed in higher χ sample. The n-octadecane based composite has the highest χ value, indicating that the weakest interaction existed between DMDBS and n-octadecane. According to the experiment results, the loose three-dimensional networks with relative thick fibres were obtained in PCM-1, which had the weakest capillary force to immobilize the melted n-octadecane, resulted in higher leakage and lower extensive endothermic time. The minimum χ value of PCM-4 resulted in the densest networks of DMDBS, so it has the minimum leakage value and maximum extensive endothermic time. Similar conclusion could also be observed in PCM-2 and PCM-3 experimental results.

4. Conclusion

In conclusion, four gelatinous shape-stable phase change materials were successfully prepared and the morphology, leakage, thermal properties and thermal conductivity were investigated in detail. By introducing a low molecular mass organogelator into the PCM, most of the melted phase change material was immobilized in the three-dimensional network formed by DMDBS. It is encouraging that relatively low concentration of DMDBS addition had significant effect on reducing leakage. The heat transfer rates in composite PCMs were slower than pure phase change materials, which was caused by the weakened natural convection in these samples. Flory-Huggins parameters were calculated for the different composites. The results are helpful to understand the interactions between the gelator and phase change materials. The different composites have different interactions, which affect the self-assembly of the gelators to form three-dimensional networks, thus lead to different leakage and thermal conductivity performance. In terms of the applications of gelatinous soft materials, it is important to estimate the influence of the gelator-solvent interactions on aggregate structures which affect the structure, leakge and thermal conductivity of the materials.

Acknowledgements

We are grateful for the financial support of the National Natural Science Foundation of China (21276188).

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