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Thermal properties of the graphite/*n*-docosane composite PCM

Min Li · Zhishen Wu

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Abstract Graphite/*n*-docosane composite phase change materials (PCM) were prepared. 4, 10, and 16% graphite were added into *n*-docosane in order to study the effect of the amount of graphite to the thermal properties of the composite PCM. The structure of the composite PCM was characterized using scanning electron microscopy. The thermal properties of the composite PCM were determined using thermal constant analysis, heat storage/release curve, differential scanning calorimetry, and thermogravimetry analysis. The results revealed that the heat storage/release rate and the thermal conductivity increased with an increase in the amount of graphite, whereas the latent heat of the composite PCM decreased with the increase in the amount of graphite.

Keywords Graphite · Phase change material (PCM) · Thermal properties

Introduction

Thermal energy storage is gaining an increasing interest because it can prompt effective use of solar energy and waste heat. The most common way for thermal energy storage is to utilize the sensible heat change. The advantage of sensible heat storage is the simplicity; however, large volumes are required and the energy is released at varying temperature. Latent heat storage with phase change material (PCM) has higher storage density and constant temperature during phase change compared to the sensible heat change. Therefore, latent heat storage with PCM is an effective way for heat storage [1–5].

Traditional PCM that have been studied and used in applications are alkanes, paraffin wax, fatty acid, and salt hydrates [6–10]. Alkanes have a large heat of fusion per unit weight and are non-corrosive and chemical stable. They are suitable for latent heat storage. However, alkanes undergo a reversible solid to liquid phase change at the transition temperature and usually have to be encapsulated to contain the liquid phase. In addition, alkanes have a low conductivity, which hinders the transfer of the latent heat of PCM [11, 12].

The additives such as fins, carbon fibers, carbon nanotubes, carbon foams, and graphite could increase the thermal conductivity [13–20]. Graphite has advantages include porous, high surface energy, and strong absorbability. Moreover, graphite has excellent thermal conduction performance. It is a good thermal conductivity improvement material.

The heat transfer rate of the paraffin/graphite composite PCM was obviously higher than that of the pure paraffin owing to the combination with the expanded graphite [21]. Ping Zhang [22] found that when the mass fraction of 5% graphite replaced the equiponderant intumescent flame retardant, the thermal conductivities of the composite PCM increased as 82.14%. Xia [23] performed an experiment study on thermal conductivity improvement of PCM. The result showed that an addition of 10 wt% expanded graphite results in a more than 10-fold increase in the thermal conductivity compared to that of the pure paraffin. Ahmet Sari [24] studied the amount of the effect of expanded graphite on the thermal conductivity of paraffin.

M. Li (✉)
Jiangsu Key Laboratory for Construction Materials, Southeast University, Nanjing 211189, China
e-mail: limin.li@163.com

M. Li · Z. Wu
International Institute for Urban System Engineering, Southeast University, Nanjing 210096, China

Thermal conductivity of the pure paraffin and the composite PCMs including 2, 4, 7, and 10 wt% EG was measured as 0.22, 0.40, 0.52, 0.68, and 0.82 W/m K. Lafdi [16] proposed a numerical study to investigate and predict the thermal performance of graphite foams infiltrated with phase change materials. The results showed that the average value of the output power of the new energy storage system has been increased by more than eight times. Some studies investigated the heat storage enhancement of exfoliated graphite nanoplatelets to paraffin [25, 26]. Andrew Mills [27] increased the thermal conductivity of paraffin wax by two orders of magnitude by impregnating porous graphite matrices with the paraffin.

Although investigations have been carried out on some PCM/graphite composites, data still lack in the effect of graphite on the thermal properties of PCM. The microstructure, pore distribution, and size distribution of graphite may influence the performance of the composite PCM. Further studies are necessary on the thermal properties prior to the application of PCM/graphite composite.

This study reports on the thermal properties of graphite/*n*-docosane composite PCM. The influences of the amount of graphite on the thermal conductivity, latent heat capacity, heat release, and storage rate of *n*-docosane are investigated. The structure of graphite/*n*-docosane composite PCM is characterized.

Experimental

Materials

Graphite (EXP-P) and *n*-docosane was supplied by Kanto Chemical Co., Ltd. The melting point of *n*-docosane is 42–44 °C, and the density of *n*-docosane is 0.9 g/ml at 20 °C. The apparent density of graphite is 0.06 g/cm^3.

Preparation of the graphite/*n*-docosane composite PCM

The graphite/*n*-docosane composite PCM was prepared by melting method. 10 g of *n*-docosane was put into a beaker, that is, in a water bath at 55 °C. 0.4, 1, and 1.6 g of graphite was added into the beaker after *n*-docosane is melted. The mixture was stirred for 30 min at 500 rpm and then dispersed by ultrasound for 30 min at 55 °C. The mixture was cooled to the room temperature and ground. Then, the graphite/*n*-docosane composite PCMs were obtained.

Characterization of the graphite/*n*-docosane composite PCM

The size distribution of the graphite was measured by Laser Particle Sizer Analyser (Winner 2000, Jinan Winner Instrument Co., Ltd.). The heat storage/release rate of the graphite/*n*-docosane composite PCM was measured with Multi-channel Temperature Recorder (TP0008U, ShangHai Ruiqin Electronic Co., Ltd.). The temperature change range was from 26 to 54 °C. The scheme of the measurement system is shown in our former work [28]. The thermal conductivity of the graphite/*n*-docosane composite PCM was tested using Thermal Constant Analysers (1500TPS, Hot Disk Inc. Sweden). The microstructure of graphite and the graphite/*n*-docosane composite PCM was observed with a SEM (JSM-6700F, JEOL, Japan) at the acceleration voltage of 20 kV under low vacuum. The thermal stability was characterized by TG analysis (209F1 Iris, Netzsch Instrument Inc., Germany) from 0 to 100 °C. The latent heat and phase change temperature were measured with Differential Scanning Calorimetry (DSC200F3, Netzsch Instrument Inc., Germany) at the heating rates of 5 K/min in a nitrogen atmosphere from 0 to 100 °C.

Results and discussion

Morphology of the graphite/*n*-docosane composite PCM

The size distribution of graphite is shown in Fig. 1. The Granularity parameters of the graphite are presented in Table 1.

The average particle size of the graphite is 52.13 μm. The morphologies of the graphite with different magnifications are shown in Fig. 2. Figure 2 shows that particles of the graphite are composed by many lamellars. Some micro-cracks are detected in the microstructure of the graphite. After the lamellars are exfoliated by the external force, they can compound with paraffin to form the composite PCM. The morphology of the graphite/*n*-docosane

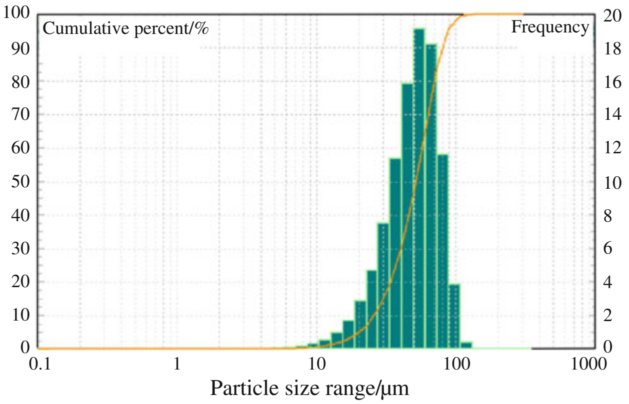


Fig. 1 The size distribution of graphite

Table 1 Granularity parameters of the graphite

Granularity parameters	D10/μm	D50/μm	D90/μm	D_{av}/μm
Value	25.72	51.27	80.87	52.13

Annotation D10, D50, and D90 mean the corresponding particle size when the cumulative distribution percentage reaches 10, 50, and 90%, respectively. D_{av} means the average particle size in the cumulative distribution of size

composite PCM with 10% graphite is presented in Fig. 3. It can be seen that the surface of *n*-docosane is covered with paraffin. The elements' content in Fig. 3a are measured by energy-dispersive spectroscopy analysis. The results are shown in Fig 3b. There are two kinds of elements in the graphite. The main element is carbon and its content is 97.09%. The other element is oxygen and the content is 2.91%.

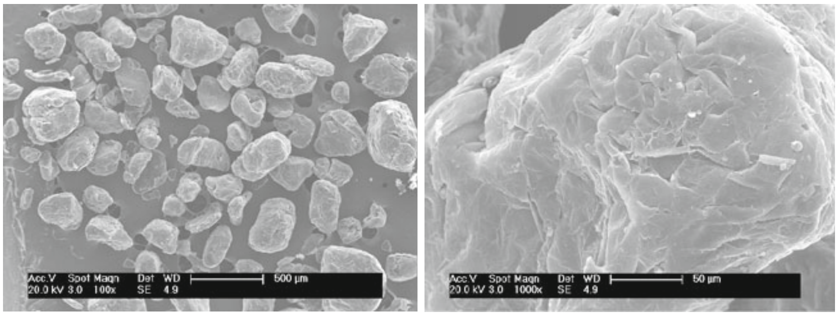
The heat storage/release rate of the graphite/*n*-docosane composite PCM

The heat storage curve and heat release curve of the graphite/*n*-docosane composite PCM are shown in Fig. 4. The amounts of graphite in the composite PCM are 4, 10, and 16%.

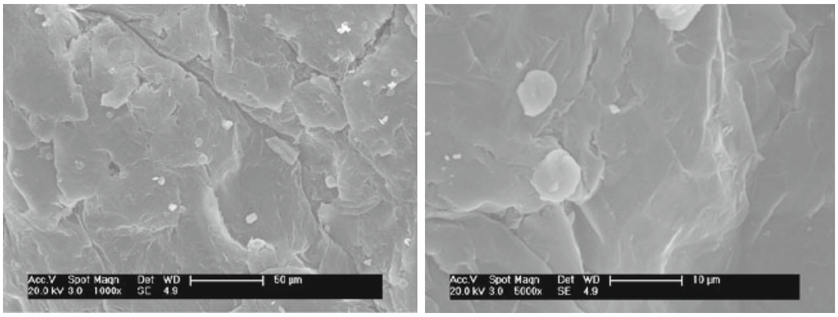
It is clear from Fig. 4 that the heat storage/release rate increases with an increase in the amount of graphite before the samples arrive the objective temperature. We compared the heat storage/release rate of *n*-docosane and the composite PCM in Table 2. The heat storage/release rate is calculated by the ratio of the elevated temperature and the desired time. The time range is from 26 to 50 °C.

Table 2 shows that graphite can improve the heat storage/release rate of *n*-docosane remarkably. When 16% graphite is added into *n*-docosane, the heat storage rate increase from 0.027 to 0.233 °C/s and the increase percentage is 763.0%.

Fig. 2 Morphology of the expanded graphite

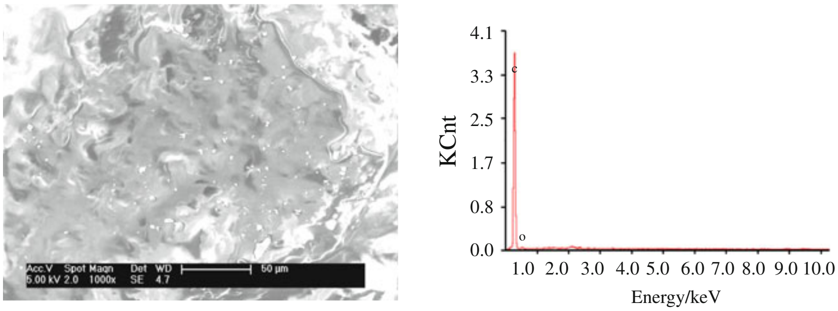


(a) magnification × 100 **(b)** magnification × 1000



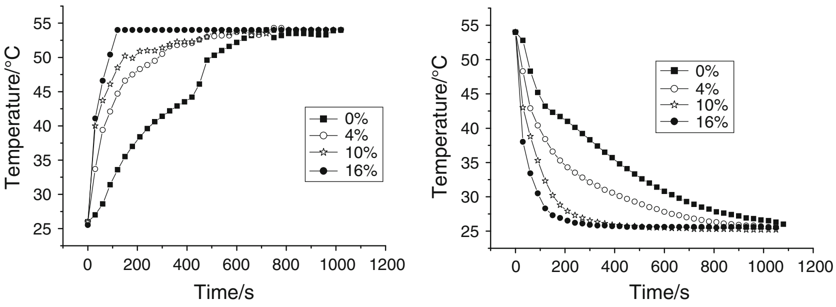
(c) magnification × 1000 **(d)** magnification × 5000

Fig. 3 Morphology of the graphite/*n*-docosane composite PCM with 10% graphite



(a) Morphology **(b)** Element content

Fig. 4 The heat storage/release curves of the composite PCM



(a) Heat storage **(b)** Heat release

Table 2 The heat storage/release rate of *n*-docosane and the composite PCM

Samples	*n*-Docosane	4% graphite/*n*-docosane	10% graphite/*n*-docosane	16% graphite/*n*-docosane
Heat storage rate (°C/s)	0.027	0.035	0.037	0.233
Heat release rate (°C/s)	0.026	0.032	0.075	0.098

The heat release rate increase from 0.026 to 0.098 °C/s, and the increase percentage is 276.9%. The increase in the amount of graphite will cause the decrease in the mass percentage of *n*-docosane in the composite PCM. Therefore, the heat storage density of the composite PCM per unit weight will be decreased.

Thermal parameters of the graphite/*n*-docosane composite PCM

Heat conductivity, thermal diffusivity, and specific heat of the composite PCM are measured to compare the thermal properties of the composite PCM and *n*-docosane. The results are presented in Table 3.

Table 3 indicates that the thermal conductivity of the composite PCM is higher than that of *n*-docosane. The thermal conductivity of the composite PCM is increased with the increase in the graphite. The increase percentages of the composite PCM are 81.5, 148.8, and 264.4% when the amount of graphite is 4, 10, and 16%, respectively. The results show that graphite can improve the thermal conductivity of *n*-docosane remarkably. The more the mount of graphite is, the greater the thermal conductivity of the composite PCM is. This result is in accordance with the results from the heat storage/release curves. Table 3 also shows that the composite PCM has higher specific heat than *n*-docosane. The composite PCM with 16% graphite has both higher thermal conductivity and higher thermal diffusivity than *n*-docosane.

Table 3 Thermal parameters of the graphite/*n*-docosane composite PCM

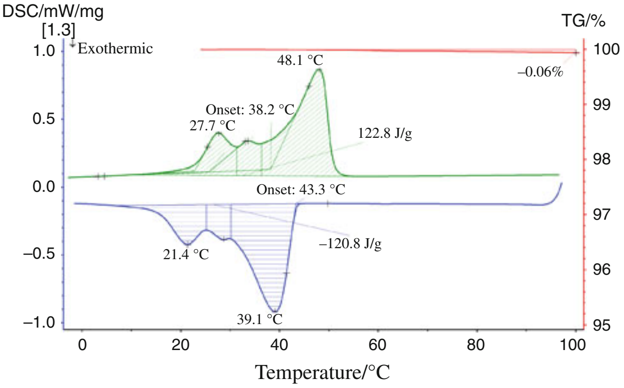
Samples	Thermal constants		
	Thermal conductivity (W/m K)	Thermal diffusivity (mm^2/s)	Specific heat (MJ/m^3 K)
n-Docosane	0.205	0.139	1.468
4% graphite/*n*-docosane	0.372	0.154	2.424
10% graphite/*n*-docosane	0.510	0.110	4.871
16% graphite/*n*-docosane	0.747	0.165	4.539

DSC/TG analysis of the graphite/*n*-docosane composite PCM

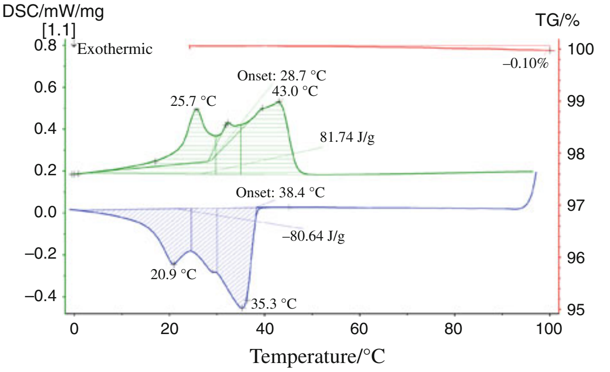
The graphite/*n*-docosane composite PCM was analyzed by using DSC and TG analysis method. The results are shown in Fig. 5.

It can be seen form Fig. 5 that there are two great peaks which are corresponding to the solid–solid phase change and the solid–liquid phase change. The main peak is the solid–liquid phase change phase. Figure 5 indicates that the peak temperatures in the heat storage process are different from those in the heat release process. It means that the freezing point is lower than the melting point of the composite PCM. In addition, the latent heat in the heat storage process and the heat in the heat release process are different slightly. This reflects the difference of the phase change process between melting and freezing. The peak temperature and phase change temperature are marked in Fig. 5. The latent heats of the composite PCMs are calculated based on the DSC curves, and the results are given in Table 4.

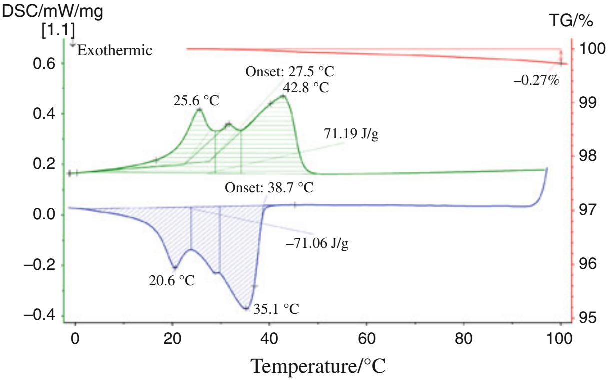
Table 4 shows that the peak temperatures and phase change temperature of the composite PCM are lower than that of *n*-docosane for both solid–solid peak and the solid–liquid peak in the heat storage process. The exception is that the peak temperature of the 4% graphite/*n*-docosane is slightly higher than that of *n*-docosane. The reason is that the surface of the composite PCM is covered with



(a) 4% graphite/*n*–docosane



(b) 10% graphite/*n*–docosane



(c) 16% graphite/*n*–docosane

Fig. 5 DSC/TG curves of the graphite/*n*-docosane composite PCM

n-docosane, and interfaces are formed in the composite PCM. These interfaces affect the phase change process. It can be seen from Table 4 that the latent heat of the composite PCM decreases with the increase in the amount of graphite. It illustrates that the latent heat of the composite PCM is decreased although the addition of graphite is an effective way to improve the thermal conductivity of PCM. TG curves in Fig. 5 show that the thermogravimetry loss is little when the composite PCMs are heated from 0 to 100 °C. The thermogravimetry loss is mainly induced by the water or the impurity in graphite. Moreover, the

Table 4 Characteristic temperature and latent heat of the composite PCM

Samples	Properties							
	Solid–solid peak temperature/°C		Solid–liquid peak temperature/°C		Solid–solid phase change temperature/°C		Latent heat/J/g	
	Heat release	Heat storage	Heat release	Heat storage	Heat release	Heat storage	Heat release	Heat storage
n-Docosane (cited from [27])	–	30.1	–	47.9	–	40.2	–	124.49
4% graphite/*n*-docosane	21.4	27.7	39.1	48.1	43.3	38.2	120.8	122.8
10% graphite/*n*-docosane	20.9	25.7	35.3	43.0	38.4	28.7	80.64	81.74
16% graphite/*n*-docosane	20.6	25.6	35.1	42.8	38.7	27.5	71.06	71.19

thermogravimetry loss of the composite PCMs increase with the increase in the amount of graphite. Therefore, the optimum amount of the graphite should be determined by considering synthetically the thermal conductivity, latent heat, and thermal stability.

Conclusions

Different amounts of graphite are used to improve the thermal conductivity of PCM. The structure and the thermal properties are characterized, and the following conclusions are drawn.

(1) The graphite is composed by many lamellars. The microstructure of the prepared composite PCM shows that graphite is covered *n*-docosane.
(2) The heat storage/release rate increases with an increase in the amount of graphite. When 16% graphite is added into *n*-docosane, the heat storage and release rate are increased 763.0 and 276.9%, respectively.
(3) The thermal conductivity of the composite PCM is increased with the increase in the amount of graphite. The thermal conductivity of the composite PCM with 16% graphite is increased 264.4%.
(4) The peak temperature, latent heat, and the thermal stability of the composite PCM decreases with the increase in the amount of graphite. The phase change temperature of the composite PCM is lower than that of *n*-docosane.

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