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Preparation and thermal properties of expanded graphite/paraffin/organic montmorillonite composite phase change material

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Abstract Expanded graphite (EG)/paraffin/organic montmorillonite (OMMT) composite phase change material (PCM) was prepared by using melt intercalation method. The microstructure of EG/paraffin/OMMT is observed by scanning electron microscope (SEM). The thermal properties are investigated by differential scanning calorimetry (DSC). The mass loss of EG/paraffin/OMMT after 50 heating cycles was measured for investigating the influence of EG and OMMT on the thermal properties of paraffin. The results show that EG and OMMT have the ability of adsorption and shape-stability. The melting point EG/paraffin/OMMT is decreased slightly with an addition of paraffin and the latent heat of EG/paraffin/OMMT is determined by the mass ratio of paraffin. The heat transfer efficiency of EG/paraffin/OMMT is strengthened and the heating time is decreased to one-sixth of that of paraffin by addition of EG and OMMT. The thermal stability of EG/paraffin/OMMT is improved by addition of OMMT.

Keywords Expanded graphite · Paraffin · Organic montmorillonite · Phase change material · Thermal property

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Introduction

The energy deficiency and environmental pollution during the energy utilization prompt the utilization of clean energy, such as solar, wind, and cheap power. The energy storage technology with phase change material (PCM) is one of the methods to enhance the energy-saving efficiency. PCMs have unique thermal property. It can absorb (or release) heat from (or to) the environment during phase transition to save energy [1–3].

Organic PCM has the disadvantage of low thermal conductivity and can flow during the heat storage process. These disadvantages restrict its utilization in heat storage fields. These disadvantages may be overcome by compounding organic PCM and inorganic material [4]. Expanded graphite (EG) have special pore structure, large specific surface area, and high thermal conductivity. Some studies showed that the heat transfer effect of paraffin can be enhanced obviously by addition of EG [5–7]. Stratified silicate has special layer structure. Organic materials can be inserted into the layers of stratified silicate to prepare composite material. The stratified silicate acts as a supporting material. It improves the thermal stability and shaping stability [8, 9]. Moreover, the compatibility of composite material an organic material is also improved.

Some researchers prepared composite PCM by using molten intercalation method. It is found that the organic PCM is sealed in the interlaminations and the prepared composite PCM has good energy storage performance [10–12].

The composite PCMs in the investigated references are mainly binary composite PCMs that are compounded by organic and inorganic materials. The thermal conductivity and the thermal stability of the binary composite PCMs have not been improved greatly. In this study, EG/paraffin/

organic montmorillonite (OMMT) composite PCM were prepared by using molten intercalation method. And the influence mechanism of EG and OMMT on thermal properties of EG/paraffin/OMMT was studied.

Experimental

Materials

Expandable graphite is supplied by Qingdao graphite Co., Ltd, China. Paraffin is supplied by KANTO Chemical Co., Inc., China. Na-Montmorillonite is supplied by Xinyang Bentonite Factory, China. The physical properties of EG, paraffin, and OMMT are given in Table 1. The pictures of EG, paraffin, and OMMT are given in Fig. 1.

Preparation of EG

Firstly, the expandable graphite is dried in a vacuum oven at 60 °C for 10 h. Then, a steel crucible containing with 5 g of the EG is put into a muffle furnace at 900 °C for 60 s. The expansion of the expandable graphite occurs and EG is obtained.

Table 1 The physical properties of EG, paraffin and OMMT

Materials	Physical properties				
	Particle size/μm	Expansion ratio/ mL g^{-1}	Thermal conductivity/ W m^{-1} K^{-1}	Melting point/°C	Latent heat/ J g^{-1}
EG	270	300	125.3	–	–
Paraffin	–	–	0.2	41–44	128.5
OMMT	15	20	0.35	–	–

Preparation of the OMMT

Na-montmorillonite is put into 100 mL deionized water, and stirred until smooth. Then the reaction temperature is adjusted to 60 °C, and cetyl trimethyl ammonium bromide (CTAB) is added. After 2 h, the solution is cooled down to the room temperature. The production was washed with deionized water until there is no precipitation in the filtered liquid. The OMMT was dried for 36 h at 100 °C and then grounded into powder.

Preparation of EG/paraffin/OMMT

OMMT is added into EG and mixed for 30 min with magnetic blender and EG/OMMT is obtain. The prepared EG/OMMT and paraffin are mixed in a constant temperature water-bath at 70 °C. The EG/paraffin/OMMT is obtained after being cooled and then is grounded into powder. Figure 1 gives the pictures of EG/paraffin/OMMT.

Characterization

The microstructures of EG/paraffin, OMMT/paraffin, and EG/paraffin/OMMT are observed by a scanning electron microscope (SEM) (Hitachi E1010). The melt point and latent heat of EG/paraffin/OMMT are measured by a differential scanning calorimeter (Pyris1TGA, USA, Perkin-Elmer) in N_2 atmosphere at the raising rate of

Fig. 1 Pictures of EG, paraffin, OMMT and EG/paraffin/OMMT

temperature is 0.5 °C/min. The heat storage and release properties are tested by multiple temperature recorder (TP9008U, Shanghai Ruiqin electronics Co., Ltd, China).

Results and discussion

Morphology analysis of EG/paraffin/OMMT

Figure 2 shows morphologies of EG/paraffin, OMMT/paraffin, EG/OMMT, and EG/paraffin/OMMT. From Fig. 2a and b, it can be seen that paraffin is compatible well with EG. Paraffin is absorbed uniformly and filled into pores of OMMT by capillary force, and the two phases combine closely. Figure 2c shows that EG and OMMT distribute uniformly. Figure 2d indicates that paraffin is absorbed into EG and OMMT uniformly and the microstructure is more compacter than that of EG/paraffin or OMMT/paraffin.

DSC analysis of EG/paraffin/OMMT

Figure 3 shows differential scanning calorimetry (DSC) curves of paraffin, OMMT/paraffin, EG/paraffin, and EG/paraffin/OMMT, respectively. There are three peaks in the DSC curve of paraffin (Fig. 3a). The left peak corresponds to the solid–solid phase change and the right main peak corresponds to the liquid–solid phase change. The middle peak corresponds to other alkanes in paraffin. The melting point of paraffin is 41.45 °C and the solid–solid phase transition temperature of paraffin is 22.08 °C. The latent heat of paraffin is 128.5 J g^{-1}. The melting point of composite PCMs change slightly with an addition of OMMT (Fig. 3b), EG (Fig. 3c), and EG/OMMT (Fig. 3d). However, the latent heat reduces with an addition of EG and OMMT. The optimum proportion is determined by adsorbing maximum amount of paraffin without leakage in the heating process. The results showed that the optimum proportion is 1:7 for EG/paraffin, 12:5 for OMMT/paraffin, 4:36:1 for EG/paraffin/OMMT. Figure 3c and d is almost the same. It can be explained that the layers of OMMT distributes in the structures of EG/paraffin. It does not affect the melting point and the he latent heat of EG/paraffin.

The value of latent heat can be calculated in accordance with formula (1) [13].

$$\Delta H_{PCM} = \Delta H \cdot \eta \quad (1)$$

where ΔH and ΔH_{PCM} are the latent heat of paraffin and the composite PCM, respectively; η is the mass fraction of paraffin in the composite PCM. Table 2 shows the experimental and calculated values of latent heat of composite PCM according to formula (1). It can be seen that the experimental values of the composite PCM are close to the calculated value.

Heat storage and release properties

Figure 4 shows the sketch of heat storage-release processes measurement. Paraffin, OMMT/paraffin (12:5), EG/paraffin (1:7), and EG/paraffin/OMMT (4:36:1) are put into four test tubes. Four thermocouple probes are inserted into the center of the four samples. Firstly, test tubes are put into the constant temperature water-bath at 10 °C. They are put

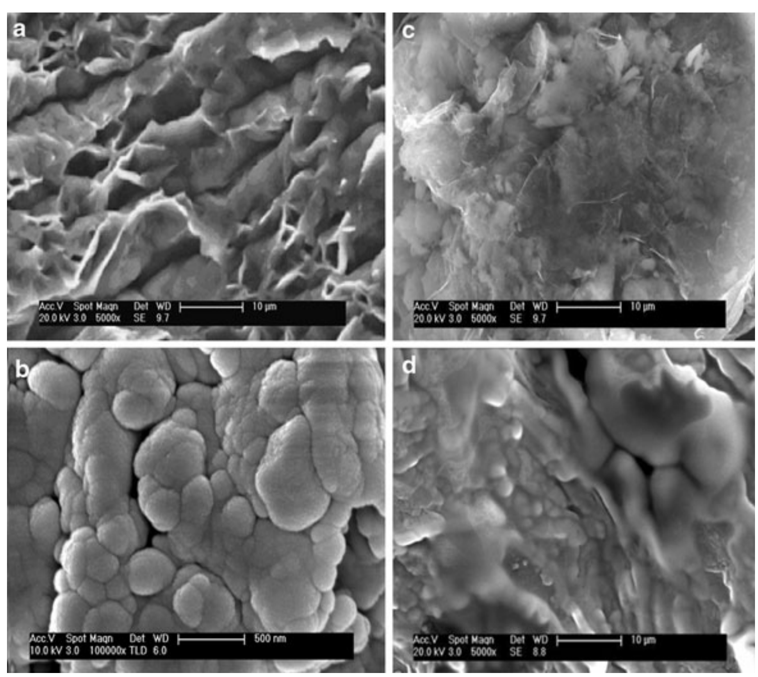

Fig. 2 SEM photographs of PCM: **a** EG/paraffin; **b** OMMT/paraffin; **c** EG/OMMT; **d** EG/paraffin/OMMT

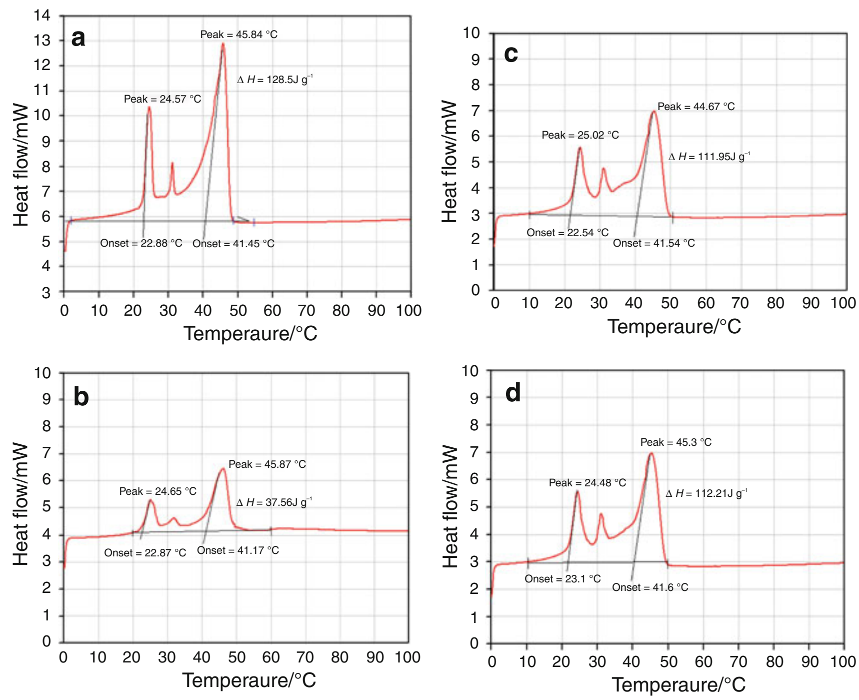

Fig. 3 DSC curves of PCM: **a** Paraffin; **b** OMMT/paraffin (12:5); **c** EG/paraffin (1:7); **d** EG/paraffin/OMMT (4:36:1)

Table 2 Experimental and calculated value of latent heat

Latent heat	Paraffin	OMMT/paraffin	EG/paraffin	EG/paraffin/OMMT
Experimental values of latent heat/J g^{-1}	128.5	37.56	111.95	112.21
Calculated values of latent heat/J g^{-1}	128.5	37.78	112.4	112.79
Mass ratio of paraffin η/%	100	29.4	87.5	87.78

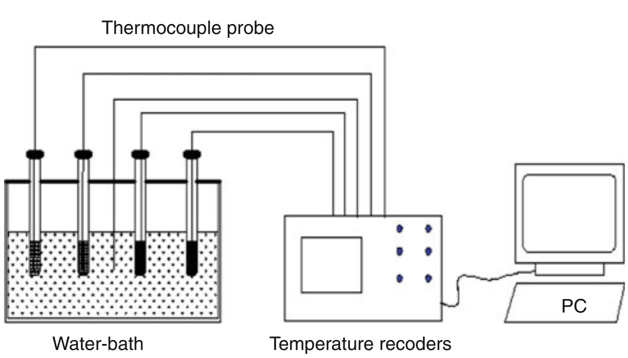

Fig. 4 Sketch of heat storage-release processes measurement

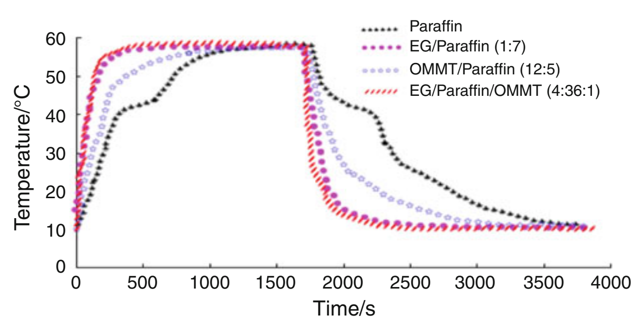

Fig. 5 Temperature–time curves for thermal storage and release

into the constant temperature water-bath at 60 °C quickly after the temperature of four samples is 10 °C. The heat storage process starts and the temperature are tested automatically every 5 s with data acquisition system. When the temperature of four samples reached 60 °C, the test tubes with samples are immediately put into the constant temperature water-bath at 10 °C. The heat release process starts and the temperature–time curves are tested.

Figure 5 shows the temperature–time curves of the heat storage and release processes. It takes 1800 s for paraffin to rise from 10 to 60 °C, and 1500 s for OMMT/paraffin. However, it only takes about 300 s for EG/paraffin and EG/paraffin/OMMT, which has been reduced to one-sixth of that for paraffin. The main reason is that EG has high thermal conductive and therefore can improve greatly the rate of heat storage and release and strengthen the heat transfer efficiency.

Thermal stability properties

The *mass* loss of the composite PCM after 50 times heating cycles is measured and the results are shown in Table 3.

Table 3 Mass loss of composite PCMs

Samples	EG/ paraffin (1:9)	EG/ paraffin (1:7)	EG/paraffin/ OMMT (4:36:1)
Initial mass/g	10	10	10
Quality after 50 times cycle/g	9.598	9.975	9.997
Mass losing percentage/%	−4.02	−0.25	−0.03

Table 3 shows that the *mass* loss of EG/paraffin (1:9) is greater than that of EG/paraffin (1:7) after 50 times heating cycles. With the addition of OMMT, the *mass* loss of EG/paraffin/OMMT is less than that of EG/paraffin. It indicates that the addition of OMMT can strengthens the thermal stability of EG/paraffin.

Conclusions

The EG/paraffin/OMMT composite PCM was prepared by using melt intercalation method and the thermal properties of it were analyzed. The following conclusions are drawn:

(1) Both EG and OMMT have the ability of adsorption and shape-stability. The EG/paraffin/OMMT composite PCM was prepared by absorption of paraffin into layer structures of EG and OMMT.
(2) The melting point of the prepared EG/paraffin/OMMT is 41.6 °C and the heat latent heat of it is 112.21 J g^{-1}. EG/paraffin/OMMT is suitable for being used as a PCM.
(3) The heating time of EG/paraffin/OMMT is decreased to one-sixth of that of paraffin by addition of EG. The thermal stability of EG/paraffin/OMMT is improved by the addition of OMMT.

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