The investigation of thermal conductivity and energy storage properties of graphite/paraffin composites

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Abstract Phase change materials (PCM) have been extensively scrutinized for their widely application in thermal energy storage (TES). Paraffin was considered to be one of the most prospective PCMs with perfect properties. However, lower thermal conductivity hinders the further application. In this letter, we experimentally investigate the thermal conductivity and energy storage of composites consisting of paraffin and micron-size graphite flakes (MSGFs). The results strongly suggested that the thermal conductivity enhances enormously with increasing the mass fraction of the MSGFs. The formation of heat flow network is the key factor for high thermal conductivity in this case. Meanwhile, compared to that of the thermal conductivity, the latent heat capacity, the melting temperature, and the freezing temperature of the composites present negligible change with increasing the concentration of the MSGFs. The paraffin-based composites have great potential for energy storage application with optimal fraction of the MSGFs.

Keywords Thermal conductivity · Paraffin · MSGFs · Heat network · Latent heat capacity

Introduction

Thermal energy storage (TES) is utilized in energy recovery and conservation processes and for solar thermal systems [1–3]. Of various TES methods, latent heat thermal energy storage (LHTES) is one of the most efficient methods due to its high storage density and small temperature difference between storing and releasing heat [4, 5]. Several phase change materials (PCMs) including organic materials (e.g., paraffin and fatty acids/esters), and inorganic materials (e.g., salt hydrates and metal), have been used for LHTES materials [4]. Among the PCMs proposed, paraffin has been considered most valuable due to desirable characteristics, including large latent heat capacity, negligible super cooling, low vapor pressure in melt, good thermal and chemical stability, and self-nucleating behavior [1, 6]. However, the main drawbacks that hinder the further application of paraffin are its low thermal conductivity (0.21–0.24 W/mK). Some methods have been used to enhance heat transfer properties in these PCMs, including impregnations of porous materials [7, 8], dispersion of high thermal conductivity particles in the PCM [9–11], and placing metal structure in PCM [12]. Of the methods, adding high thermal conductivity material into paraffin is a widely used technique to enhance thermal conductivity of matrix [13]. The additives with high thermal conductivity are including ceramic particle [14], metallic particle [9], and carbon material [15]. Carbon nanotube is a good choice to obtain high thermal conductivity enhancement [16]; however, some weakness of difficulty to dispersion and high cost restrict its further application. Graphite is another carbon allotrope with high thermal conductivity, lower cost than that of nanotubes and has been used to fill in paraffin to enhance thermal conductivity [17, 18]. However, most researches focus on high concentration additive of graphite, which badly weakens other properties, such as latent heat capacity [18, 19]. Moreover, the mechanisms of thermal conductivity of composites remain unclear.

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In this article, we experimentally explored the thermal transport and the heat storage properties of the paraffin-based composites by dispersing MSGFs with high thermal conductivity. The results strongly show the thermal conductivity of composites increases evidently with increasing the concentration of the MSGFs. Moreover, the thermal conductivity of the composites increases sharply when the concentration is above 1wt%, which indicates a lower fraction threshold for thermal conductivity of the composites. The other properties such as the latent heat capacity show negligible effect with additive of the MSGFs.

Materials and experiments

The natural graphite used was purchased from (Qingdao Graphite Co., Ltd. China) with about diameter of 200 μm and thermal conductivity of 2000 W/mK. The paraffins were supplied by (Shanghai Specimen and Model factory of China) with melting point of 54–56 °C and thermal conductivity of 0.21–0.24 W/mK at 25 °C. The composites were prepared by two-step method. First, the natural graphite was processed to the MSGFs. The pristine graphite has not been well suited to intercalation by monomers without an oxidation process. The well-known method of the oxidation of the natural graphite was conducted by Hummer [20], which immerse the natural graphite flakes into a mixture of H_2SO_4, $NaNO_3$, and $KMnO_4$ to obtain graphite intercalation compounds. Here, we followed Hummer's method and obtained intercalated graphite. Microwave was used to expand graphite and formed into multi-layer with bigger spaces [21] and easy to separate the natural graphite layers to several layer or monolayer, so-called graphene [22, 23]. Second, the expanded graphite was mixed with melting paraffin at 70 °C and stirred quickly with magnetic bar. After fully mixed, the high energetic ultrasound [24] was used to exfoliate graphite layer to form a uniform dispersion. The optical images of solid composites are shown in inset of Fig. 1d.

The microstructures of samples were investigated by scanning electron microscope (SEM, TEOL JSM-6490LA, Japan) with sputtered with gold. The phase change temperatures and the latent heat were measured using differential scanning calorimeter (TA-Instruments, Q200, America) with using Nitrogen and a temperature rising rate of 5 °C/min. The form-stable composites before and after thermal cycling test were characterized by Fourier Transformation Infrared (FTIR, Bruker TENSON 27, Japan) spectrometer with the wavenumber range 4000–400 cm^{-1}.

The thermal conductivity of the composites both in liquid and in solid state was measured using the commercial hot disk method (Hot Disk, TPS2500, Sweden). We

Fig. 1 Scanning electron microscope of natural graphite (**a**), treated graphite flake (**b**), pure paraffin (**c**), treated graphite/paraffin composite (1 wt%) **d**. The *inset* in (**d**) is optical image of solid composites after 1000 recycling
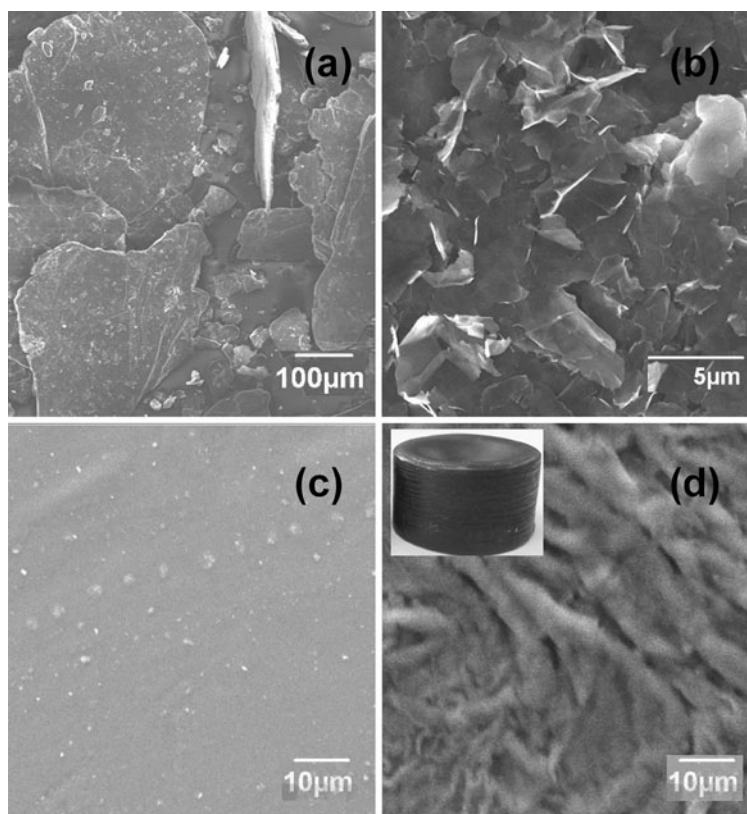
have used this method in the past [14]. In this method, the TPS element behaves both as temperature sensor and heat source. A constant current is supplied to the sensor and the temperature gradient is calculated from the variation in the sensor resistance with time. The systematic uncertainty of this equipment experimentally calibrated to be less 3% which is same with instrument description. A thermal bath with 1.5 °C accuracy was used to control temperature and the temperature range of the bath can be changed between 25 and 80 °C. Thermal conductivity value for a given temperature was the same within 0.32% during the heating and cooling cycle. Average data of the cooling and heating are presented.

Results and discussions

Morphology of the graphite and the composites

The morphology of samples is shown in Fig. 1. The diameters of natural graphite and treated graphite flake are about 200 and 5 μm, respectively. Apparently, the process of expanding and exfoliation decreases the diameter and thickness of graphite according to Fig. 1a and b. The body density of graphite decreases, so the flakes are easy to float in liquid paraffin to form the uniform suspension. Figure 1d shows the surface structure of composites. Basically, the surface structure changed evidently with additive of MSGFs, and the color of composites deepens compared to matrix. We did not obtain clearer images of the composites with bigger magnification for equipment limitation. The inset of Fig. 1d also shows the optical image of composite after 1000 recycling and no evident sedimentation appears.

Chemical stability of composites

The Infrared spectral of the graphite/paraffin composites before and after recycling is shown in Fig. 2. The two patterns of before and after 1000 time recycles remain almost no change both in curve shape and absorbed frequency. The results indicate that the chemical band information does not vary with the repeated melting and freezing cycles. Therefore, the composites are believed to be stable chemically even thought 1000 times cycles.

Thermal conductivity of the composites

Figure 3 shows the thermal conductivity ratio of defined as k/k_0, where k and k_0 are the thermal conductivity of the composites and the base media at room temperature, respectively, as a function of mass fraction of the MSGFs along with the predictions of the Maxwell-Garnet (MG)
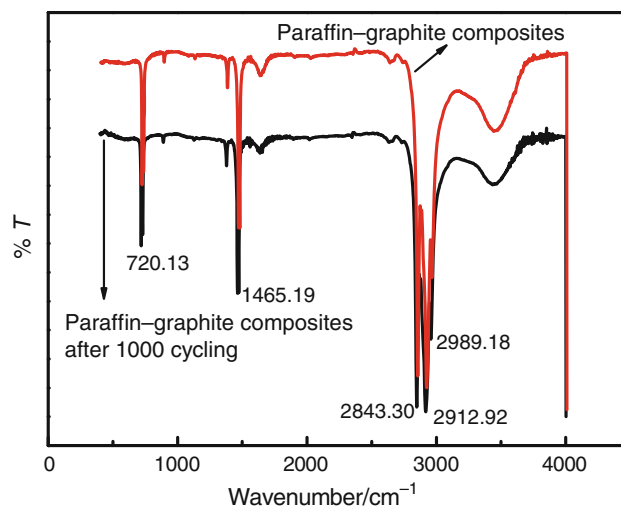

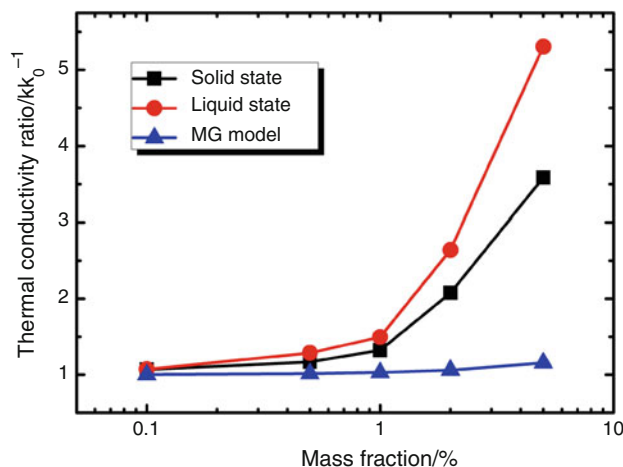Fig. 2 Infrared spectral of graphite/paraffin composites (1 wt%) before and after recycling

Fig. 3 Thermal conductivity ratio of the composites as a function of MSGFs mass fraction

model without considering interfacial thermal resistance [25] as shown in Eq. 1.

$$k/k_0 = \frac{k_p + 2k_0 + 2\varphi_p(k_p - k_0)}{k_p + 2k_0 - \varphi_p(k_p - k_0)} \quad (1)$$

where k, k_0 are thermal conductivities of the composites and pure paraffin, respectively, and φ_p is the mass fraction of the MSGFs in the composite, and k_p is constant value as large as 2000 W/m•K [26]. The thermal conductivity ratio of the composites shows the same trends for the composites both in the solid state and liquid state. The thermal conductivity ratio of the composites increases with increasing the mass fraction of the MSGFs. Moreover, the thermal conductivity ratio of the composites both in the solid state and the liquid state are much higher than the predictions of MG model. The most interesting is that the thermal conductivity shows

a typical non-linear increase with increasing the fraction of the MSGFs. The thermal conductivity ratio of the composites with 0.1, 0.5, 1, 2, 5 wt% MSGFs are 1.07, 1.28, 1.49, 2.64, and 5.30, respectively, in the liquid state. The thermal conductivity ratio increases sharply once the MSGFs fraction overpasses 1 wt%. The results suggest that a heat network of percolated MSGFs starts forming above 1 wt%. The SEM image of composite shown in Fig. 1d verifies the network structure with some bundlers. As to Gao et al. [27] studies on nanofluids, the results show that clustering is the key role in enhancing thermal conductivity. When heat dissipates in the composites, the heat carries transport in two ways: scattering in the base matrix and conducting through in plane MSGFs and base matrix alternately. The MSGFs used have characterized to be several layers and micrometer diameters, so the aspect ratio of a flake can reaches to 100 to 1000 and prone to overlap and cluster. Once clustering, the effective length of heat carries transporting in MSGFs increases and the thermal conductivity increases. As to Fig. 3, the thermal conductivity ratio in the solid state presents lower than that of in the liquid state. The results are found to be line with reported literatures [28]. As to Gao et al. [27] experimental investigation on nanofluids, the thermal conductivity of the solid state composites presents higher than that of the liquid state for the particle cluster formation during the freezing of crystalline hexadecane. But in hog fat, the different trend is presented, the thermal conductivity in solid state is almost familiar or a little lower than that of the liquid state. In this case, paraffin is same with hog fat, which is mixture of homolog and behaves amorphous state. The molecular structure of paraffin is no evident change during the solidification of paraffin. We could not explain clearly this trend so far, and we will clarify in our next research paper.

The thermal conductivity of the pure paraffin and the composites as a function of temperature is shown in Fig. 4. The results indicate that the temperature dependence thermal conductivity of the pure paraffin and the composites are familiar, which all show almost no temperature dependence when the environment temperature is far from phase change temperature even in the liquid state and the solid state.

Heat storage properties of composites

Figure 5 presents the DSC thermograms of the pure paraffin and the composites with different mass fraction MSGFs. The left small peak of 30–40 °C on each curve behaves solid–solid phase transition of paraffin. The main peak of 50–60 °C represents solid–liquid phase change of paraffin (melting and freezing point). The value of the melting temperature (T_m), the freezing temperature (T_m), the melting latent heat (H_{Lm}), and the freezing latent heat (H_{Lm}) also list in Table 1. The melting temperature of
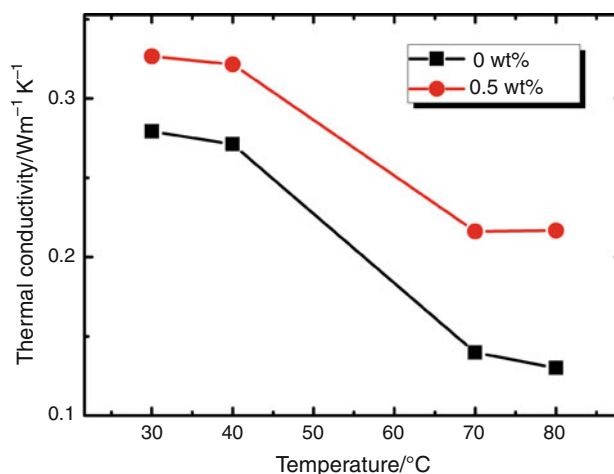

Fig. 4 Temperature dependence thermal conductivity ratio of the pure paraffin and the paraffin based composites with 0.5 wt% MSGFs
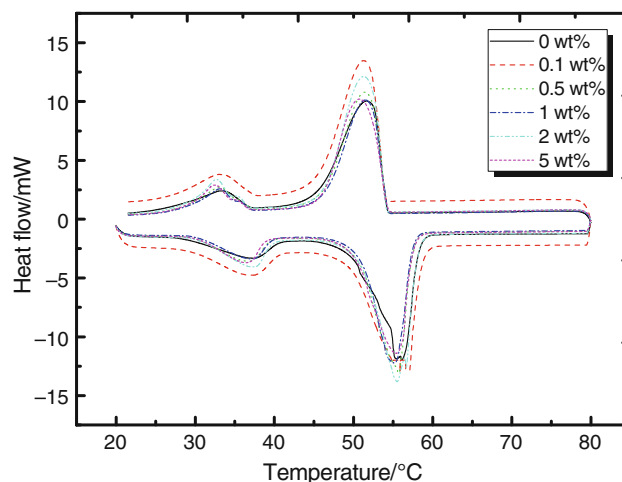

Fig. 5 DSC curve of the pure paraffin wax and the paraffin based composites with different fraction MSGFs

composites with 0.1, 0.5, 1, 2, and 5 wt% are lower than that of pure paraffin wax by deceasing of 2.8, 5.7, 7.1, 7.4, and 8.1%, respectively. The latent heat capacity of composites with 0.1, 0.5, 1, 2, and 5 wt% are lower than that of pure paraffin wax by 1.7, 5.2, 9.1, 10.6, 22%, respectively. Compared to thermal conductivity ratio with same mass fraction MSGFs shown in Fig. 3, the phase change temperatures and latent heat capacity presents negligible decrease with increasing the mass fraction of MSGFs within 5 wt%. With the increasing of thermal conductivity of the composites, the melting and solidification time decrease evidently as shown in Fig. 6. The solidification time of pure paraffin, composite with 1wt% MSGFs, and 5wt% MSGFs are 250, 500, and 700 s, respectively. Obviously, the solidification time are reduced by 250 and 450 s, respectively, for 1 and 5% mass fraction of MSGFs compared with pure paraffin. For application, the

Table 1 The phase change temperature (melting and freezing point) and the latent heat capacity of the PCM composites

PCMs/wt%	$T_m/°C$	$T_f/°C$	H_{Lm}/kJ kg^{-1}	H_{Lf}/kJ kg^{-1}
0	53.94	54.19	187.6	174.9
0.1	52.43	54.09	184.3	171.8
0.5	50.95	54.06	177.9	171.7
1	50.29	53.94	171.4	164.7
2	50.20	53.09	169.3	163.5
5	49.83	51.17	150.3	147.1
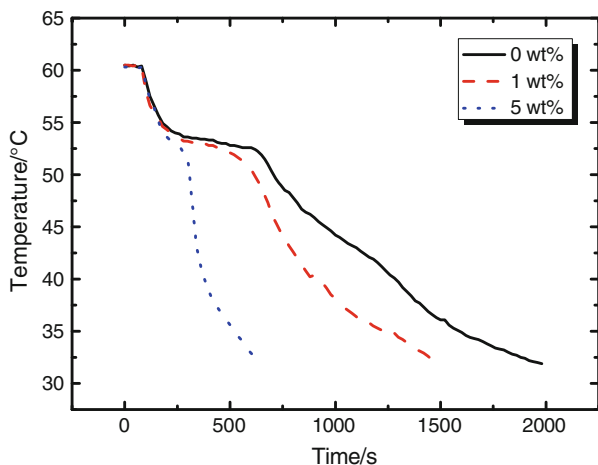
Fig. 6 Heat discharging (freezing) temperature curves of pure paraffin and composites

concentration of 1 wt% is preferred with enormous enhancement in thermal conductivity and negligible decrease in heat storage properties.

Conclusions

In conclusion, we investigated the thermal conductivity and heat storage properties of the composites with the paraffin and the MSGFs. The results indicate that the thermal conductivity of composites with paraffin and MSGFs behaves the non-linear increase with increasing mass concentration of MSGFs. The formation of graphite clustering appears to be the key contributor to the thermal conductivity enhancement. While the heat storage properties present negligible changes compared to that of thermal conductivity. Our study has provided a strategy for achieving paraffin PCM systems with high thermal conductivity and good heat storage properties by additive of a small mount micron-size graphite flakes.

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