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Thermal properties of paraffin based composites containing multi-walled carbon nanotubes

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ABSTRACT

Heat storage nanocomposites consisting of paraffin wax (PW) and multi-walled carbon nanotubes (MWNTs) have been prepared and their thermal properties have been investigated. Differential scanning calorimetric (DSC) results revealed that the melting point of a nanocomposite shifted to a lower temperature compared with the base material, with increasing the mass fraction of MWNTs, ϕ_w. With the addition of MWNTs, the latent heat capacity was reduced. The enhancement ratios in thermal conductivities of nanocomposites increase both in liquid state and in solid state with the increasing with ϕ_w when compared to the pure PW. For the composite with a mass fraction of 2.0%, the thermal conductivity enhancement ratios reach 35.0% and 40.0% in solid and in liquid states, respectively.

1. Introduction

The energy sources and the demands do not always match each other, especially in solar heating applications because solar radiation is a time dependent energy source with an intermittent characteristic. Thermal energy storage (TES) has always been one of the critical factors in residential solar space heating and cooling applications [1–5]. Of various TES methods, latent heat thermal energy storage (LHTES) using phase change materials (PCMs) represents a promising and attractive option for use [6–10]. Due to the high storage density and small temperature variation from storage to retrieval, paraffin waxes and fatty acids have been applied as PCMs for thermal energy storage in solar heating and cooling applications [11–17]. In spite of their desirable properties of the original materials, low thermal conductivities are their major drawback. It leads to decreasing the rates of heat storage and retrieval during melting and solidification processes. The low thermal conductivities in turn limit their utility areas. To overcome the low thermal conductivity problem, a wide range of investigations were carried out to enhance the thermal conductivity of the organic PCMs. The often used method is to disperse solid particles with high thermal conductivity, such as carbon nanofibers, metal particles and so on, or to insert metal matrix into the organic PCMs [18–20]. However, such types of heat transfer promoters considerably increase the weight and volume of LHTES systems. Carbon nanotubes (CNTs) with their light weight and high thermal conductivity have shown tremendous potential for heat transfer applications [21–24]. The high intrinsic thermal conductivity of CNTs suggests many heat transfer enhancement applications.

Recently, some studies were carried out to disperse CNTs into organic PCMs to enhance the thermal conductivity of the base materials [25–28]. However, the previous used CNTs without surface treatment always separate out from the composites during phase change. Moreover, most of the previous literatures only provided the thermal conductivity of the materials at room temperature. Especially, the information of thermal properties of a composite PCM at its phase change temperature is very useful for TES applications. The relationship between temperature and the thermal conductivity of the material is an important parameter for selecting PCMs. Furthermore, the studies regarding the relationship between the thermal conductivities of nanocomposite PW/MWNTs and temperature especially near its melting point is limited in literature.

In the present work, a novel nanocomposite PCM was prepared by dispersing MWNTs into PW. The energy storage properties of the nanocomposite PCM were determined by DSC analysis. In addition, the relationship between thermal conductivity of the PCM and temperature was investigated at temperature range, 15–65 °C.

2. Experimental

2.1. Materials

Paraffin wax (industrial grade) with melting temperature of 52–54 °C was obtained from Sinopharm Chemical Reagent Co. Ltd.

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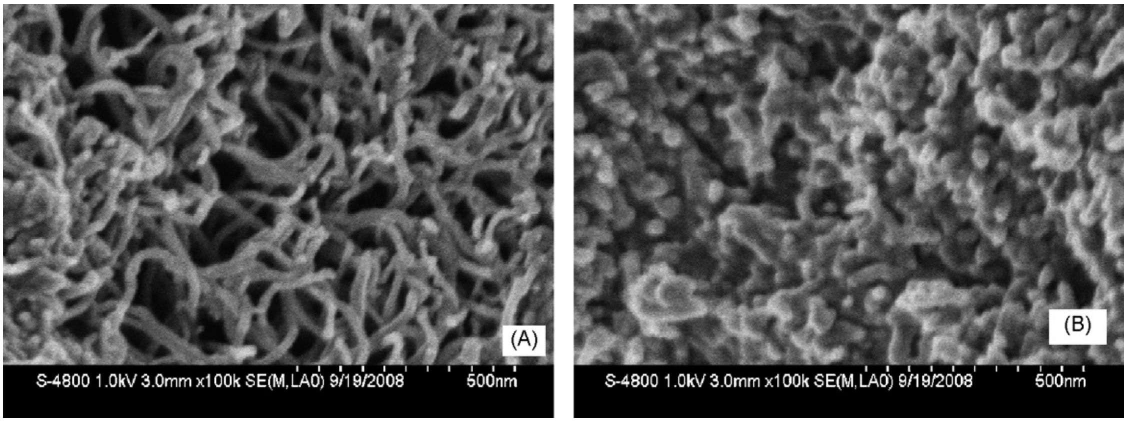

Fig. 1. SEM images of pristine CNTs (A) and ball milled CNTs (B).

The PW was used without further purification. Multiwall carbon nanotubes (MWNTs) were supplied by Chendu Organic Chemicals Co. Ltd., Chinese Academy of Sciences. The purity of the MWNTs was 95%. The average diameter, average length, and specific surface area of the MWNTs were 30 nm, 50 μm, and 60 m^2/g, respectively.

2.2. Preparation of the nanocomposites

Ball milling was employed to cut the MWNTs in order to enhance their dispersibility in PW. Fig. 1 shows the pristine CNTs (A) and CNTs treated by ball milling for 720 min (B). The treated MWNTs look short in Fig. 1 and they have better dispersibility in the organic solvent, compared with the untreated ones. The treated MWNT powders were added into melting PW in a mixing container. The mixture was subjected to intensive sonication to prepare well dispersed and homogeneous PW/MWNT composites.

2.3. Methods

The solid samples were observed by scanning electron microscope (SEM, S-4800, Japan). Thermal properties including melting temperature (T_m) and latent heat capacity (L_s) of pure PW and PW/MWNT composites were measured using a differential scanning calorimetric (DSC) instrument (Diamond DSC, PerkinElmer, USA). The DSC measurements were performed at a heating rate of 5 K/min and in a temperature range of 0–75 °C.

Thermal conductivities (k) of the pure PW and the PW/MWNT composites were measured by a transient short-hot-wire method. The detailed measurement principal and procedure have been described elsewhere [29,30]. Briefly a platinum wire with a diameter of 70 μm was used for the hot wire, and it served as both a heating unit and as an electrical resistance thermometer. Initially the platinum wire immersed in media was kept at equilibrium with the surroundings. When a regulation voltage was supplied to initiate the measurement, the electrical resistance of the wire changed proportionally with the rise in temperature. The thermal conductivity was calculated from the slope of the rise in the wire's temperature against the logarithmic time interval. The uncertainty of this measurement is estimated to be within ±1.0%.

3. Results and discussion

3.1. Compatibitity of MWNTs with PW

In order to test the stability of the PW/MWNT, the composites were put into an oven and kept 70 °C. After 96 h the composites were taken out of the oven to cool down to room temperature. The treated samples were cut and taken photos to see if there was any delamination. Four samples were prepared and the mass fractions (ϕ_w) were 0.2%, 0.5%, 1.0%, and 2.0%, respectively.

Fig. 2 shows the SEM images of the pure PW and the composite with 0.2 wt.% MWNTs after kept at 70 °C for 96 h. It is observed that the PW/MWNT composite is very homogenous. No delamination has been observed in other three samples after kept at 70 °C for 96 h.

3.2. Melting temperature and latent heat capacity

DSC analysis was conducted to investigate the influence of MWNT addition on the thermal properties including the melting

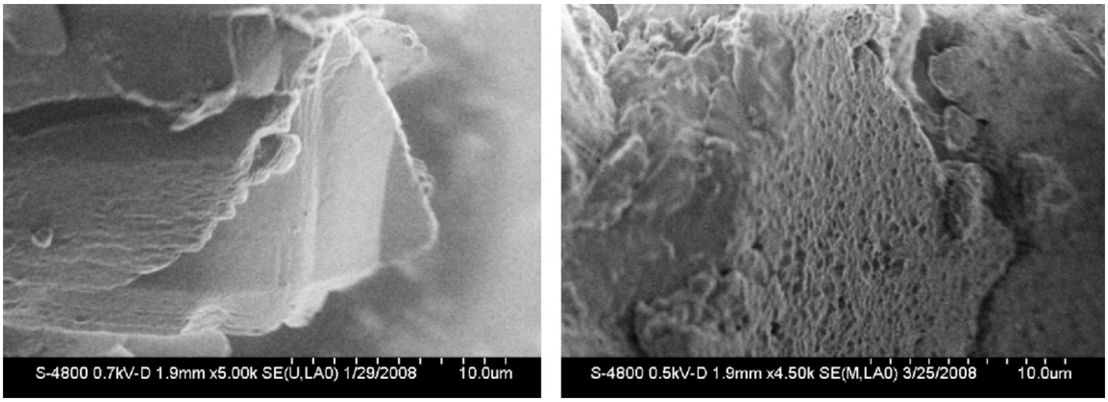

Fig. 2. SEM images of pure PW (left) and the composite with 0.2 wt.% MWNTs (right).

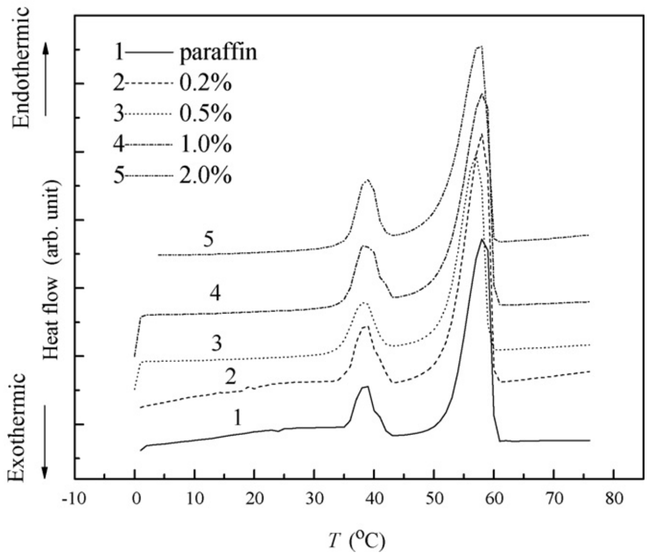

Fig. 3. DSC curves of the pure PW and the composites.

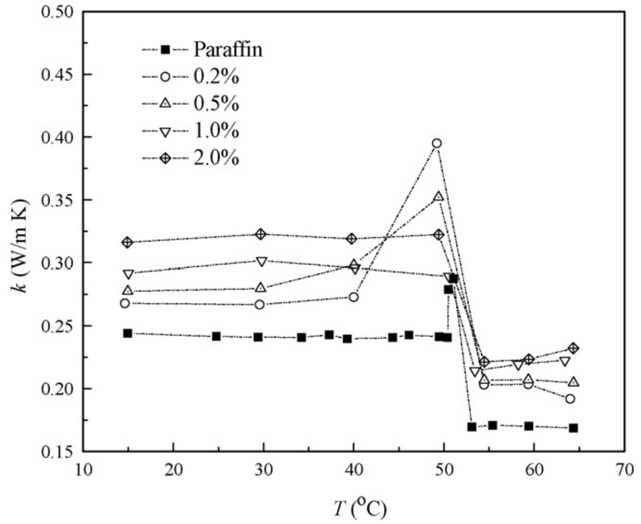

Fig. 4. Dependence of the thermal conductivity of pure PW and composites on the temperature.

temperatures and the latent heat storage capacities. Fig. 3 presents the DSC thermograms of PW/MWNT composites. The left small peak on each DSC curve is the solid-solid phase change peaks and the main peaks represent solid-liquid phase change (melting) [31]. It is seen from Fig. 3 that the phase change peaks shift to a lower temperature due to the addition of MWNTs into PW. With an increase in the mass fraction of MWNTs, the phase change temperature is decreased. Thermal properties of PW and PW/MWNT composites depending on the CNT loadings are summarized in Table 1. It is represented in Table 1 that the melting temperatures of the composites with 0.2, 0.5, 1.0 and 2.0 wt.% MWNTs are lower than that of pure PW by 0.04, 0.35, 0.57 and 1.06 K, respectively. According to the theory of mixtures, the latent heat capacity of PW/MWNT composites is equal to the values calculated by multiplying the latent heat value of pure PW. However, the latent capacity of every composite is higher than the calculated latent capacity. The latent capacities of composites with 0.2, 0.5, 1.0 and 2.0 wt.% MWNTs are higher than the calculated latent capacities of the composites by 0.4, 0.6, 1.3 and 1.8 kJ/kg, respectively. The latent heat capacity discrepancy increases with an increase in the mass fraction of MWNTs. This phenomenon is ascribed to the interaction between the PW molecules and the MWNTs. Shadab et al. performed experimental and theoretical investigation on the latent heat of PCM composites consisting of wax and CNTs. They demonstrated that the latent heat of the nanocomposites could be enhanced to a value even higher than that of the pure wax. They further concluded that the very great intermolecular attraction in the nanocomposite accounted for this enhancement [32]. Here in our experiments, because the average diameter of the used MWNTs is relatively large (30 nm) and the surface area is relatively small, the latent heat enhancement is less considerable compared to those reported in Ref. [32].

Table 1
Melting temperature (T_m) and latent heat capacity (L_s) of PW and PW/MWNT composite PCMs.

PCMs	T_m (°C)	L_s (kJ/kg)	Cal. L_s (kJ/kg)
Pure PW	53.0	165.3	
$\phi_w = 0.2$	52.9	165.4	165.0
$\phi_w = 0.5$	52.7	165.1	164.5
$\phi_w = 1.0$	52.5	164.9	163.6
$\phi_w = 2.0$	52.0	163.8	162.0

3.3. Thermal conductivity improvement

Phase change materials are used in the environment with temperature variation for thermal energy storage. The rate of energy storage and release is highly depended on the thermal conductivity of the PCMs at both solid and liquid states. Therefore, it is important to know how the thermal conductivity of the PCMs changes with temperatures. The thermal conductivity of the nanocomposite PCM is also crucial nearby its melting point.

Fig. 4 presents the temperature depended thermal conductivities of the nanocomposites. For every sample at a fixed temperature, the thermal conductivity has been measured three times. The average value for these three measurements was used in this article. It is shown in Fig. 4 that the thermal conductivity curves of the PW/MWNT composites are over that of the pure PW. At the same time, the thermal conductivities of the PW/MWNT composites increase with the mass ratios of MWNTs. Furthermore, thermal conductivity of PW and the PW/MWNT composites is weakly depended on the temperature when the temperature is lower than 45 °C or higher than 55 °C. However, the thermal properties of PW and the composites break near the melting point. Because of the breakage of the orderly solid structure into disorderly liquid structure, the thermal conductivities of PW and PW/MWNT composites suddenly fall down when the PCMs turn into liquid state. Interestingly, the thermal conductivities of PW and PW/MWNT composites suddenly increase near the melting point in solid state. As phase change materials, high thermal conductivity close to the phase change temperature is desirable for TES application. The reason for this abnormal increase is unclear and the molecular dynamic simulation is currently underway to clarify it.

Fig. 5 shows the temperature dependent thermal conductivity enhancement ratio of PW/MWNT composites, $(k_c - k_0)/k_0$. The thermal conductivity enhancement of the composite with 0.2 wt.% MWNTs is more than 10.0% in every measured temperature. For the composite with 0.2 wt.% MWNTs, the thermal conductivity enhancement in the liquid state is larger than that in the solid state. In our experiments the composite with 2.0 wt.% MWNTs has the largest thermal conductivity enhancement which is about 35.0% and 40.0% in solid state at 30 °C and in liquid state at 65 °C, respectively. It is observed that the higher thermal conductivity is turned out in the composite with more MWNT addition.

The contributions of the thermal conductivity enhancements of the composites include MWNTs, PW and the interaction between

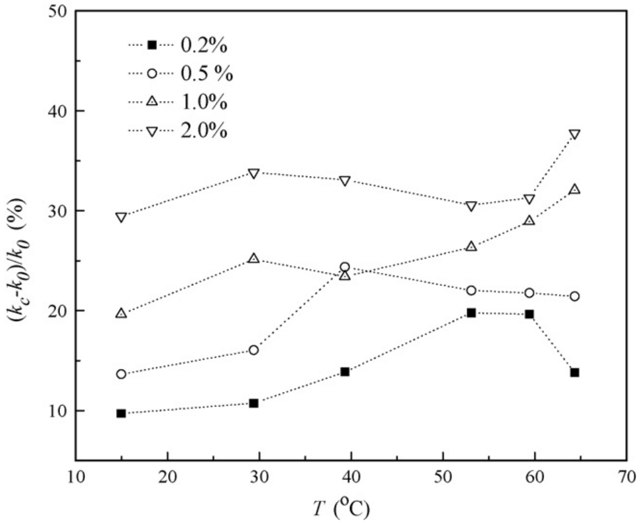

Fig. 5. Thermal conductivity enhancement ratio as a function of the temperature.

them. As CNTs have very high thermal conductivity, the composites are expected to have considerable higher thermal conductivity than that of the pure PW. However, the thermal resistance at the interface between MWNTs and PW cannot be ignored. On the other hand, the properties of the interface between MWNTs and PW are different when PW is in different states. They might change with temperature even in the same state. Recent studies of thermal contact resistance have shown that tube-matrix and tube-tube contact resistances are both very high [33,34]. Since MWNTs have much higher thermal conductivity than the pure PW, thermal conductivity of the PW/MWNT composites is highly depended on how MWNTs transfer heat to PW. Both the heat transfer through the carbon nanotube network and the thermal resistance between two adjacent carbon nanotubes can affect the thermal conductivity of the composite. Additionally, there is often a poor heat transfer between the organic matrix and the MWNTs and the heat flows essentially through the matrix. Therefore the experiment data of the thermal conductivity of composites often deviate from the predicted values by a traditional theory [33]. The mechanism of the thermal conductivity enhancement caused by the MWNT addition needs further investigation.

4. Conclusions

In this study, the stable and homogeneous nanocomposites consisting of PW and MWNTs were prepared as novel PCMs. The PW/MWNT composites showed no lamination after settled for 96 h at liquid state. DSC analysis was used to reveal that the melting points and heat capacities of PW/MWNT composites were reduced with increasing the mass fraction of MWNTs. Due to the interaction of the MWNTs and the PW molecules during melting process, the composites have higher latent heat capacity compared to the calculated value. PW/MWNT composites have enhanced thermal conductivities compared to the pure PW, with the enhancement ratios increasing with the mass fraction of MWNTs. The thermal conductivity of the PW/MWNT nanocomposites was raised with increasing the mass fraction of MWNTs when compared to that of pure PW. The thermal conductivity of the PW/MWNT composites changes slightly with temperature at temperatures which are far from the melting point and they suddenly increase as the temperature was raised from 45 °C to its melting point of the nanocomposite PCM. Compared with the pure PW, the thermal conductivity enhancement ratio of the nanocomposite including 2.0 wt.% MWNTs is determined to be about 35.0% and 45.0% in solid and liquid states, respectively.

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