

PW based phase change nanocomposites containing γ -Al₂O₃

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Abstract Phase change nanocomposites were prepared by dispersing γ -Al₂O₃ nanoparticles into melting paraffin wax (PW). Intensive sonication was used to make well dispersed and homogeneous composites. Differential scanning calorimetric (DSC) and transient short-hot-wire (SHW) method were employed to measure the thermal properties of the composites. The composites decreased the latent heat thermal energy storage capacity, L_s , and melting point, T_m , compared with those of the PW. Interestingly, the composites with low mass fraction of the nanoparticles, have higher latent heat capacity than the calculated latent heat capacity value. The thermal conductivity of the nanocomposites was enhanced and increased with the mass fraction of Al₂O₃ in both liquid state and solid state.

Keywords Phase change composites · Thermal properties · Paraffin wax · γ -Al₂O₃

Introduction

Paraffin wax (PW) with low melting temperature (T_m), high latent heat capacity (L_s) and small temperature variation from storage to retrieval is often used as phase change material (PCM) [1–5]. However, the low thermal conductivity as the major drawback limits its utility areas. It leads to decreasing

the rates of heat storage and retrieval during melting and solidification processes. To overcome the problem of low thermal conductivity, a wide range of investigations were carried out to enhance the thermal conductivity of PW [6, 7]. Aluminum and other metallic particles have been extensively used in energy-conversion applications due to their unusual energetic properties. Several studies proved that a small amount of metal or nonmetal nanoparticles could greatly increase the thermal conductivity of the based fluids or condense materials [8, 9]. In the past decade, nanofluids become one of the most attractive heat transfer media. Al₂O₃ nanoparticles were often used as additives in nanofluids because of the high thermal conductivity and cheap price among the metal oxide nanoparticles. Nanofluids containing Al₂O₃ in water were reported to have higher heat transfer enhancement than those containing CuO with same volume fraction [9, 10]. However, there is no significant theoretical or experimental study that deals with the addition of the Al₂O₃ nanoparticles on the thermal transport of the composites as PCMs.

In this paper, we present the investigation on a novel thermal performance enhanced PCM. Al₂O₃ nanoparticles are used as additives for tailoring the thermal properties of the matrix material, PW. Oleylamine is employed to treat the nanoparticles with poor dispersibility. The thermal conductivity of the prepared PCM nanocomposites is investigated and the mechanism of the thermal transport enhancement is further discussed.

Experimental

Preparation of the nanocomposites

PW (industrial grade) with melting temperature of 325–327 K was obtained from Sinopharm Chemical

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Reagent Co. Ltd. The PW was used without further purification. Al₂O₃ nanoparticles (99.9%) are obtained from Hangzhou Jingtian Nanotech. Co. Ltd. The density of the Al₂O₃ nanoparticles is 3.9 g/cm³. The average diameter of the particles is about 20 nm.

The Al₂O₃ powders were added into melting PW in a mixing container. Oleylamine was already dispersed in the PW. The mixture was subjected to intensive sonication to make well dispersed and homogeneous PW/Al₂O₃ composites. Al₂O₃ nanoparticles with mass fractions of 1–5 wt% were dispersed in PW to prepare the composites.

Characterization

Various analytical methods have been applied to characterize the Al₂O₃ nanoparticles. Transmission electron microscopy (TEM) pictures were taken on a JEOL 2100F high resolution TEM device. Scanning electron microscopy (SEM) observation was performed on a Hitachi S-4800 field emission SEM device. Fourier transformation infrared (FTIR) spectra were collected on a Bomem DA 8 spectrometer. X-ray diffraction (XRD) patterns were recorded on a D8-Advance diffractometer using Cu K α X-ray at 40 kV and 100 mA.

Thermal properties including melting temperature (T_m) and latent heat capacity (L_s) of pure PW and PW/Al₂O₃ composites were measured using a differential scanning calorimetric (DSC) instrument (Diamond DSC, Perkin Elmer, USA). The DSC measurements were performed at a heating rate of 5 K min⁻¹ and in a temperature range of 273–348 K.

Thermal conductivities (k) of the pure PW and the PW/Al₂O₃ composites were measured by a transient short-hot-wire (SHW) method. The detailed measurement principle and procedure have been described elsewhere [11–13]. Briefly a platinum wire with a diameter of 70 μ m 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. The uncertainty of this measurement is estimated to be less than $\pm 1.0\%$. For thermal conductivity measurements, the PCM sample was melted and poured into a stainless steel cylinder container. A platinum wire and a thermocouple were immersed in the PCM to record and test the temperature of the PCM before a waterproof lid covered the container. The container was put into a water bath with a temperature of 288 K. When the thermocouple in the PCM showed the temperature vibration less than 0.1 K for 10 min it was taken for the hot wire probe in an isotropic medium. The hot wire probe was subjected at time $t = 0$ to a step change in the electrical current applied to the wire. The temperature of the water bath was increased every 10 K from 288 to 318 K while increased

every 5 K from 328 to 338 K. At every temperature, three measurements were conducted and the average value was taken as the result.

Results and discussion

Analysis of the Al₂O₃ nanoparticles

The SEM and TEM images of the used Al₂O₃ nanoparticles were shown in Fig. 1. In these figures, the Al₂O₃ nanoparticles are turned to be spherical and club-shaped. The diameter of the particles is fairly uniform and the average diameter of the particles is 20 nm. Figure 2 presents the FTIR spectrum of Al₂O₃ nanoparticles. In Fig. 2, there is transmission band centered at about 3400 cm⁻¹, characteristic of hydrogen bonded –O–H of the adsorbed water. The band at 1384 cm⁻¹ is corresponding to the phonon lengthways stretching band of Al₂O₃ [14, 15], while the band at 500–1000 cm⁻¹ can be interpreted to the bending stretching band of Al–O [16]. The transmission band at 1639 cm⁻¹ is the characteristic of the bending stretching of the adsorbed H₂O, while the bands at 2852 and 2923 cm⁻¹ are the characteristics of the adsorbed CO₂. Figure 3 shows the XRD pattern of the Al₂O₃ nanoparticles. The broad bands at 30°–40° and strong bands at 46° and 67° mean that the structure of the sample is γ -phase.

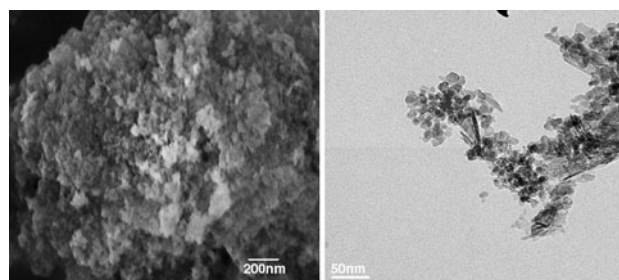


Fig. 1 SEM (left) and TEM (right) image of Al₂O₃ particles

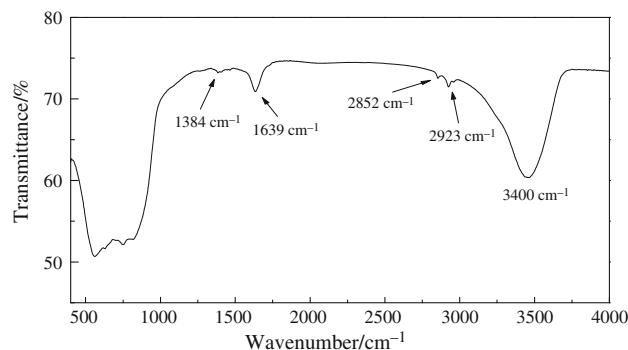


Fig. 2 FTIR spectrum of Al₂O₃ nanoparticles

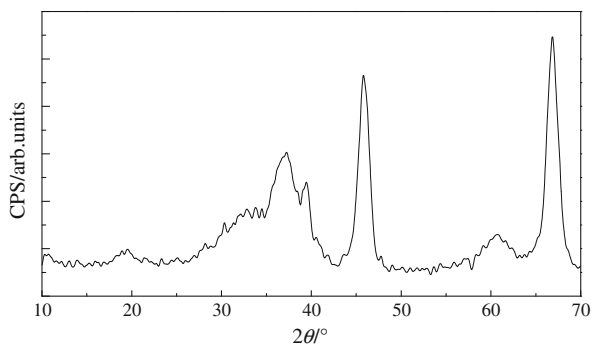


Fig. 3 XRD pattern of Al₂O₃ nanoparticles

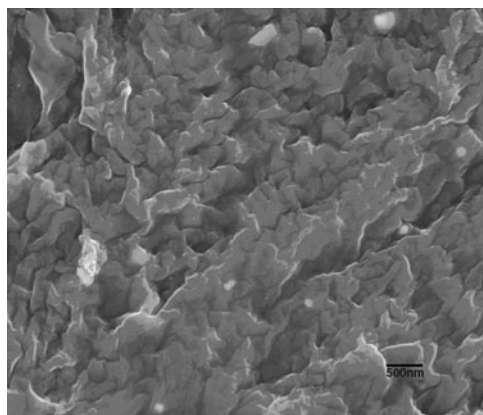


Fig. 4 SEM image of the composite with Al₂O₃ mass fraction of 5%

Compatibility of the composites

In order to see how the dispersity of the Al₂O₃ particles in the PW matrix, the SEM image of the composite was given in Fig. 4. The mass fraction of the selected sample is 5%. It is observed that the composite is homogeneous and the Al₂O₃ particles are separated individually in PW.

Melting temperature and latent heat capacity

The phase change temperature and latent heat capacity of the PW and the composites were measured to investigate the influence of the Al₂O₃ nanoparticles addition on the thermal properties of the composites. Table 1 presents the result of the DSC analysis including the solid–solid phase

change temperature (T_{s-s}), melting temperature (T_m), latent heat capacity of solid–solid phase change (L_{s-s}) and of solid–liquid phase change (L_s). The data of calculated latent heat capacity (Cal. L_{s-s} and Cal. L_s) are obtained by multiplying the value of the latent heat capacity (L_{s-s} and L_s) of the pure PW with the mass ratio of the PW in the composites. It is seen from Table 1 that the phase change temperature both T_{s-s} and T_m shift to a lower temperature due to the addition of Al₂O₃ into PW, except the composite with Al₂O₃ mass fraction of 1%. All the composites decrease the latent heat capacity L_s , compared with the PW. The composite with Al₂O₃ mass fraction of 1% increases L_{s-s} by 2.2 J g⁻¹, compared with pure PW. Interestingly, the data of L_{s-s} for the composites, with Al₂O₃ mass fraction of 1 and 2%, are higher than the Cal. L_{s-s} by 2.5 and 0.3 J g⁻¹ while the composite with Al₂O₃ mass fraction of 5% is lower than the Cal. L_{s-s} . The data of L_s of all the composites are lower than that of the PW and their Cal. L_s . This might be caused by the interaction between the PW molecules and the Al₂O₃ particles [17]. The PW increases its volume with the increasing of the temperature, that is, the matrix structure of the PW turns expanded when temperature rising. However, the interactions between the PW molecules and the Al₂O₃ particles are stronger than those between the PW molecules at T_{s-s} but weaker at T_m .

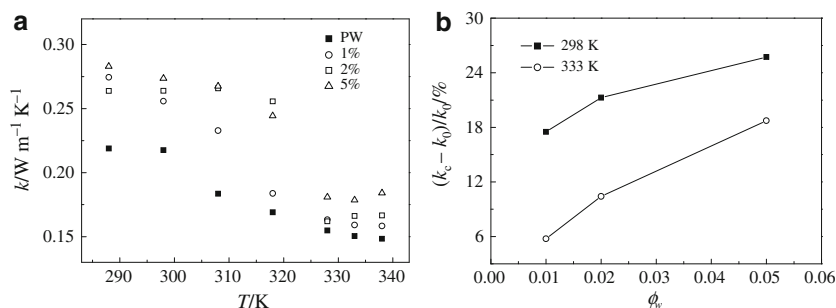
Thermal conductivity improvement

Thermal conductivity is one of the most important properties of PCMs. Thermal conductivity enhancement is expected in the composites with Al₂O₃ particles addition since Al₂O₃ have high thermal conductivity. To investigate the effect of Al₂O₃ particles on the thermal conductivity of phase change composites containing Al₂O₃, PW based composites at different Al₂O₃ loadings were prepared and their thermal conductivities were measured by the SHW method. Figure 5a shows the temperature dependent thermal conductivity of the PW and the composites. The thermal conductivities of the composites are higher than those of the PW at the same temperature. Interestingly, the thermal conductivities of the PW and the composites decrease with an increase in the temperature at the solid state. The thermal conductivities of the composites increase with the Al₂O₃ particles in the composites in the

Table 1 The phase change temperature and latent heat capacity of PCMs

PCMs	T_{s-s}/K	T_m/K	$L_{s-s}/J\ g^{-1}$	$L_s/J\ g^{-1}$	Cal. $L_{s-s}/J\ g^{-1}$	Cal. $L_s/J\ g^{-1}$
PW	303.2	321.2	31.4	142.2		
With 1% Al ₂ O ₃	302.4	321.3	33.6	136.1	31.1	140.8
With 2% Al ₂ O ₃	302.6	321.0	31.0	136.3	30.7	139.4
With 5% Al ₂ O ₃	299.9	319.3	29.2	134.1	29.8	135.1

Fig. 5 Temperature dependent k (a) and k enhancement as a function of Al_2O_3 (b) of PCMs



solid state at the same temperature except for the composite with 2% Al_2O_3 particles at 318 K higher than that with 5% Al_2O_3 particles and 288 K lower than that with 1% Al_2O_3 particles. The highest thermal conductivity of the composites is $0.28 \text{ W m}^{-1} \text{ K}^{-1}$ of the composite with 5% Al_2O_3 particles at 288 K in the solid state and $0.19 \text{ W m}^{-1} \text{ K}^{-1}$ in the liquid state. The thermal conductivity of the composite with Al_2O_3 mass fraction of 5% is higher than PW by about $0.07 \text{ W m}^{-1} \text{ K}^{-1}$ in the solid state at 288 K and $0.05 \text{ W m}^{-1} \text{ K}^{-1}$ in the liquid state at 338 K, respectively. We calculated the thermal conductivity enhancement ratios of the PW/ Al_2O_3 composites in order to show clearly the effect for the thermal transfer with adding Al_2O_3 particles to PW. Figure 5b shows the thermal conductivity enhancements as functions of Al_2O_3 mass fraction of the nanocomposites at 298 and 333 K. k_c and k_0 represent the thermal conductivities of composites and pure PW, respectively. $(k_c - k_0)/k_0$ is the thermal conductivity enhancement ratio of the nanocomposites. It is shown in the figure, thermal conductivity enhancement of the nanocomposite increases with an increase of Al_2O_3 mass fraction at both 298 and 333 K. At 298 K, the slope of the line through the point Al_2O_3 mass fraction of 1 and 2% is larger than that through 2 and 5%, as well as at 333 K. This indicates that there is not a simple relationship between the thermal conductivity enhancement and the mass fraction of the additives in the PW/ Al_2O_3 composites.

It is very complicated that how the factors would influence the composite on the thermal conductivity. The contributions of the thermal conductivity enhancement of a composite include the thermal conductivity of materials in the composite and the interaction between them. Thermal conductivity enhancement was expected for composite containing nanoparticles with high thermal conductivity. However, our experimental results indicated that the enhancement ratios of the thermal conductivity of the composite are much lower than the value predicted by effective medium theory [18]. This disappointing thermal performance can be attributed to two main reasons. One is the lower intrinsic matrix conductivity after treatment, possibly due to scattering of heat carrying phonons by interactions with the surroundings or from defects. The other is the thermal contact resistance at

the nanoparticle surfaces [19, 20]. Fu and Mai [21] reported the thermal conductivity of the composites increased almost linearly with carbon fiber content. When the additive thermal conductivity is high, the composite thermal conductivity increases significantly with the increase of mean fiber aspect ratio. While the fiber thermal conductivity is low, the composite thermal conductivity increases slowly with the increase of the additive ratio. As particulate composite, the Al_2O_3 particles in the organic matrix can be regarded as a special case of short fiber composites with short fibers a low aspect ratio and random orientation.

Conclusions

We prepared a series of stable, homogeneous, and thermal performance enhanced heat storage nanocomposite PCMs consisting of PW and $\gamma\text{-Al}_2\text{O}_3$ nanoparticles. DSC analysis revealed that the PW/ Al_2O_3 composites have reduced both melting point and latent heat capacity with an increase in the mass fraction of Al_2O_3 nanoparticles. Due to the interaction of the Al_2O_3 nanoparticles and the PW molecules during phase change process, the composites with low mass fraction of the nanoparticles have higher latent heat capacity compared to the calculated value. PW/ Al_2O_3 composites have enhanced thermal conductivities compared to the pure PW, with the enhancement ratios increasing with the mass fraction of Al_2O_3 nanoparticles.

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