Journal of Thermal Analysis and Calorimetry, Vol. 87 (2007) 2, 369–373

STUDY OF A PCM BASED ENERGY STORAGE SYSTEM CONTAINING Ag NANOPARTICLES

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In this paper, organic phase change material (PCM)/Ag nanoparticles composite materials were prepared and characterized for the first time. The effect of Ag nanoparticles on the thermal conductivity of PCM was investigated. 1-tetradecanol (TD) was selected as a PCM. A series of nano-Ag-TD composite materials in aqueous solution were in-situ synthesized and characterized by means of thermal conductivity evaluation method, TG-DSC, IR, XRD and TEM. The results showed that the thermal conductivity of the composite material was enhanced as the loading of Ag nanoparticles increased. The composite materials still had relatively large phase change enthalpy. Their phase change enthalpy could be correlated linearly with the loading of TD, but their phase change temperature was a little bite lower than that of pure TD. The thermal stability of the composite materials was close to that of pure TD. It appeared that there was no strong interaction between the Ag nanoparticles and the TD. Furthermore, the experiment results indicated that the Ag nanoparticles dispersed uniformly in the materials, occurred in the forms of pure metal.

Keywords: *Ag nanoparticles, composite materials, DSC, energy storage, phase change materials, TG-DTG, thermal conductivity*

Introduction

Phase change materials (PCMs) are very important for thermal protection and optimal utilization of energy. It is one of the most efficient ways of storing thermal energy. It provides much higher storage density, with a smaller temperature difference between storing and releasing heat. Furthermore, there are a lot of phase change materials that melt and solidify at a wide range of temperatures, making them attractive in a number of applications. As a result, PCMs have been a main topic in research for the last 20 years [1–3].

Because almost all of the PCMs possess the unacceptable low thermal conductivity, thermal conduct enhancement is required for PCMs application. Various methods were proposed to enhance the thermal conductivity of PCMs: 1) hollow aluminum plate with channels or compartments filled with PCM [4]; 2) fillers dispersed in PCM with high conductivity such as: fins [5], carbon fibers [6–8], 3) PCM embedded in a high conductivity material matrix structure [9–11].

Due to their small size, nanoparticles exhibit novel material properties, which largely differ from the bulk properties [12]. Nano-sized metal particles show particular thermal, electronic, magnetic and optical properties. The heat transfer of nanoparticles is favored as the size decreases because the ratio of surface to volume increased [13]. The thermal conductivity of nanoparticles has been a hot field in recent years [14–18].

Nanoparticles can drastically enhance the thermal conductivity of nanofluids at very low volume fractions [16, 19, 20]. The phase change properties of one PCM can be affected by adding a new kind of element into it [21]. But to our best knowledge, so far there is not any PCM dispersed with metal nanoparticles has been reported. Therefore, in a proof-of-principle experiment, we prepare organic PCM 1-tetradecanol (TD)/Ag nanoparticles composite materials, and study the effects of doped Ag nanoparticles on the performance of PCM of TD.

Experimental

Sample preparation

The reagents used in the experiment were of analytical grade. The composite materials were prepared according to the reference [22] with some modifications depicted as follows: A certain amount of $AgNO_3$ and $NH_3{\cdot}H_2O$ were solved in 200 mL deionized water. To this solution, an ethanol solution containing certain amount of TD was added to form a white emulsion (solution A). A certain amount of H_2O_2 was added into 100 mL deionized water (solution B). Solutions A and B were mixed under the

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1388–6150/$20.00

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condition of ice water bath with vigorous stirring. Pale yellow materials were formed immediately. The product was obtained after filtration, washed with deionized water and dried in vacuum.

Methods

Differential thermal analysis was carried out on a DSC141 differential scanning calorimeter (Setaram, France) in the temperature range of –30 to 70°C with the heating rate of 10 K min^{-1}. The masses of the samples were about 4–9 mg. The instrument was calibrated using In (99.999%), Sn (99.999%), Pb (99.999%), Al (99.999%). Thermogravimetry (TG) measurement were carried out on Setsys 16/18 thermogravimetry analyzer (Setaram, France) from room temperature to 400°C with the heating rate of 10 K min^{-1} and N_2 as purge gas with flow rate of 30 mL min^{-1}. The masses of samples were about 10–20 mg. The instrument was calibrated using $CaC_2O_4 \cdot H_2O$.

IR spectra were recorded on a Bruker EQUINOX 55 FT-IR spectrometer using KBr pellet (400~4000 cm^{-1}). Powder X-ray diffraction (XRD) experiments were carried out on a Rigaku D/max-γb X-ray diffractometer with monochromatic detector. CuK_α radiation was used, with a power setting of 50 kV and 200 mA, and a scan rate of 5° min^{-1}. TEM experiments were performed with a Jeol JEM-2000EX transmission electron microscope (120 kV).

In order to compare the thermal conductivity of the composite materials with that of the pure TD, the thermal conductivity performance of samples was evaluated by the procedures as follows: A thermocouple (type J) was fixed at the center of a copper box which has the inner void of 6×6×10 mm^3. The samples were melted and then poured into the box and stirred gently to remove air. After the samples were solidified, the box was sealed. The thermocouple was connected to a PC via a data acquisition apparatus (Agilent 34970A). The temperature of the center of the box was recorded at the sampling rate of once per second. The box was first immersed in ice-water until its temperature reached stable. Then the box was moved to a water bath with the temperature of 33°C. The temperature change of the box was recorded until it reached stable. The thermal conductivity was evaluated by comparing the speed of temperature rising.

Results and discussion

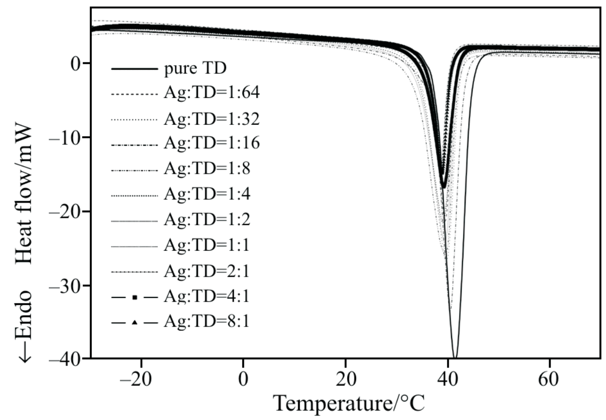

Fig. 1 DSC curves of the composites materials when heating at the first time

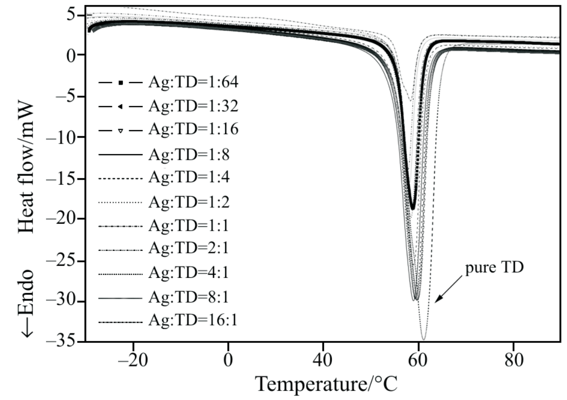

Fig. 2 DSC curves of the composites materials when heating at the second time

Figures 1 and 2 show the DSC curves of the composite materials at the 1st and the 2nd heating scans. The shapes of all the DSC curves were alike. It means that there was no transformation of TD occurred during the procedure of preparation. From the DSC curves it could be seen that the melting point (*m.p.*) of the composite materials was a little bite lower than pure TD. The phase change enthalpy of the composite materials and the pure TD in the 1st and 2nd heating and the 1st cooling scans are shown in Table 1. It is clear that the composite materials still had relatively large phase change enthalpy. There was no variety of melting enthalpy occurred between the 1st and 2nd heating cycles, indicating the composite materials might have good thermal stability under extended cycling in the temperature range of –30 to 70°C.

The original and derivatives of the thermogravimetric curves of the composite materials are presented in Figs 3 and 4 and the data are shown in Table 1. The results demonstrate that the thermal degradation of all composites and TD proceeded by a one step process with a maximum decomposition temperature (Table 1). From the results of FTIR and XRD studies (show below) we will know that there were only TD and Ag in the composite materials. All the TD of each material decomposed at temperature higher than the maximum decomposition temperature of the material, so the load-

Table 1 DSC and TG-DTG data of the composite materials and pure TD

Sample	TD:Ag	TD/(Ag+TD)*	$\Delta H_{\text{heating1}}$/ J g^{-1}	$\Delta H_{\text{heating2}}$/ J g^{-1}	$\Delta H_{\text{cooling}}$/ J g^{-1}	$\Delta H_S/\Delta H_{TD}$**	Mass loss/ %	MDT***/ °C
TD			234.2	228.1	–225.9		100	256.37
1	64:1	0.98	216.5	218.7	–217.5	0.94	96.522	255.08
2	32:1	0.97	201.7	203.3	–205.5	0.88	–	–
3	16:1	0.94	204.7	203.3	–205.4	0.88	92.774	260.45
4	8:1	0.89	186.9	180.3	–183.1	0.79	–	–
5	4:1	0.80	172.8	172.5	–173.9	0.75	81.701	258.93
6	2:1	0.67	155.2	152.5	–156.2	0.67	–	–
7	1:1	0.50	119.4	121.8	–122.2	0.52	54.626	263.69
8	1:2	0.33	80.1	81.0	–82.5	0.35	–	–
9	1:4	0.20	55.5	54.7	–54.8	0.22	24.476	237.03
10	1:8	0.11	32.7	33.6	–33.8	0.14	–	–
11	1:16	0.06	17.0	–	–17.1	0.07	7.696	215.12

*TD/(Ag+TD) – mass of TD divided by the whole mass of Ag and TD in raw materials,
**$\Delta H_S/\Delta H_{TD}$=[$(\Delta H_{\text{heating1}}+\Delta H_{\text{heating2}})_{\text{sample}}/2$]$)/[(\Delta H_{\text{heating1}}+\Delta H_{\text{heating2}})_{TD}/2)$], ***MDT – maximum decomposition temperature.

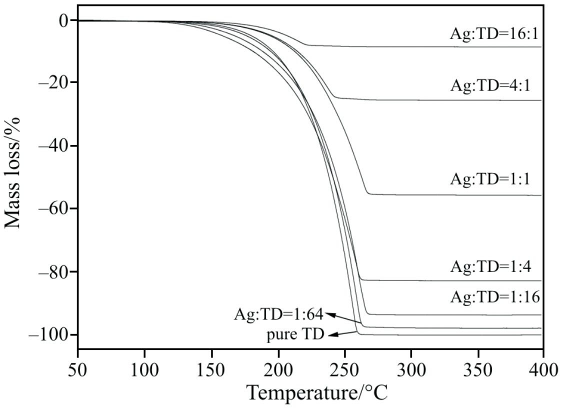

Fig. 3 TG curves of the composite materials

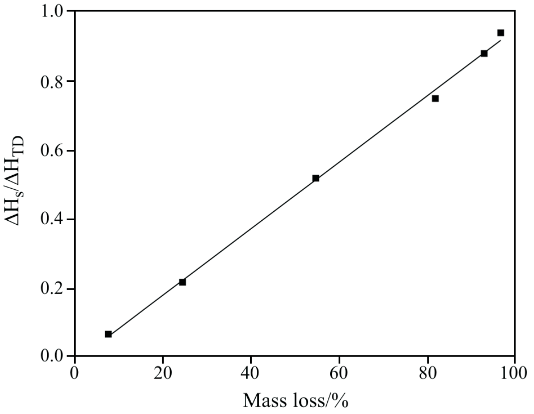

Fig. 5 The relation between mass loss and $\Delta H_S/\Delta H_{TD}$ of the samples

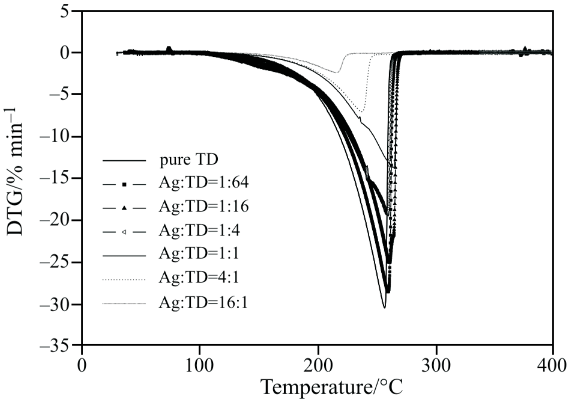

Fig. 4 DTG curves of the composite materials

ing of Ag in the product could be obtained according to the results of the TG [23]. The relation between the mass loss and $\Delta H_S/\Delta H_{TD}$ of the samples is illustrated in Fig. 5. The figure indicates that the phase change enthalpy of the composite materials can be correlated linearly with the loading of TD in the concentration range of our experiment.

Figure 6 shows the IR spectra of the composite materials and pure TD. Obviously, these IR spectra are similar. The absorption bands in each spectrum were at the same site: the broad band in the range of 3200–3500 cm^{-1} was assigned to the stretching vibration of hydroxyl group of the alcohol. The ν_{CH} and δ_{CH} absorption bands were exhibited at 2917, 2846 and 1465, 721 cm^{-1}, respectively. The stretching vibration of C–O of primary alcohol could be seen at 1062 cm^{-1}. This result demonstrates that there was no strong interaction between the Ag nanoparticles and TD. Besides, there was no absorbance near 530 cm^{-1} [24], indicating that Ag in the composite material was in the form of pure silver.

XRD patterns of the composite materials are presented in Fig. 7. The peaks were assigned to the diffraction of (111), (200), (220), (311) and (222) planes of silver respectively, according to the

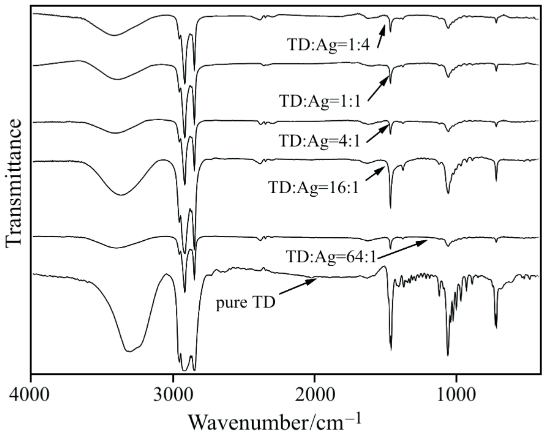

Fig. 6 IR spectrum of the composite materials and pure 1-tetradecanol

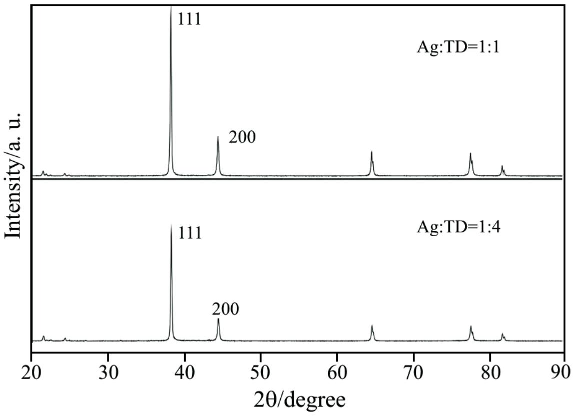

Fig. 7 XRD patterns of the composite materials

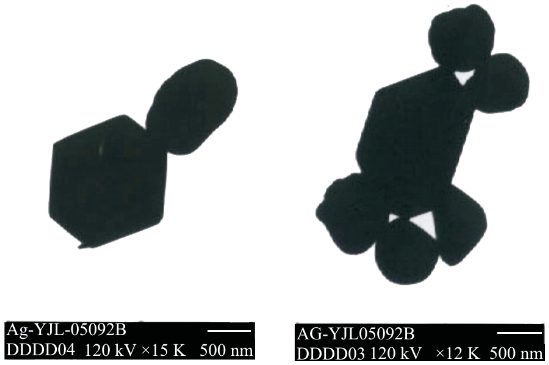

Fig. 8 TEM images of a typically composite material, Ag:TD=1:2

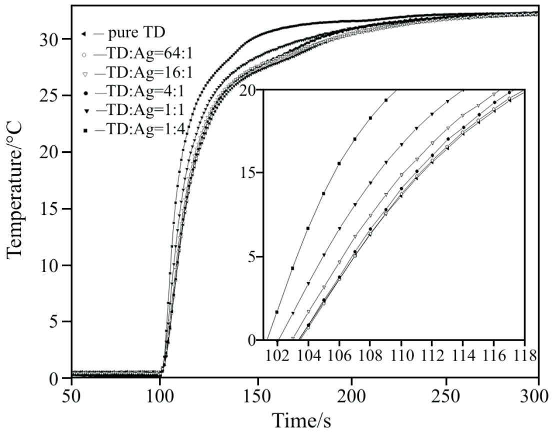

Fig. 9 Temperature change of TD and composite materials from 0 to 33°C. The insert is the enlarging of the figure in selected range of coordinate

literature (PCPDF No. 040783). There was no other peak found, indicating that only silver existed in the composite material. This result agrees with the result of the IR experiment. Interestingly, the intensity ratio of (111) to (200) was about 4.2, much larger than literature (the intensity ratio of (111) to (200) peaks was 100:40, PCPDF No. 040783). It indicates that the product had the structure with a preferential [111] orientation. The TEM images (Fig. 8) of Ag nanoparticles of a typical composite material, whose ratio of Ag to TD was 1:2, shows that the particle size of Ag particles is about 500 nm and the nanoparticles are multi-shapes. There was no agglomerate observed. This is because that TD has the weak ability to prevent the Ag nanoparticles to reunite and the nanoparticles disperse uniformly in the material.

The temperature change of the samples is depicted in Fig. 9. When a material has a better thermal conductivity, its temperature change speed would be higher than others in the same condition of our experiment. The temperature rising curve of the material would be steeper and in the Fig. 9 it would be appeared at upper side. In the Fig. 9, the curve of the pure TD is at the lowest site, indicating that TD has the worst thermal conductivity compared with the composite materials. The curve of the composite with highest Ag loading is at the highest site, indicating that it has the best thermal conductivity. So in general, it is clearly that the thermal conductivity of the composite increases as the loading of Ag nanoparticles increasing.

Conclusions

Ag nanoparticles-TD composite PCMs were in-situ synthesized and characterized by means of thermal conductivity evaluation, IR, XRD, TEM, DSC and TG for the first time. The results demonstrated that the thermal conductivity of the composite increased with the increasing of the Ag nanoparticles loading. There was no existence of Ag_2O in the materials. The Ag nanoparticles with multi-shape dispersed uniformly in the material. There was no strong interaction between Ag particles and TD. The IR spectra also indicated there was no silver oxide in the materials. The composite materials still had relatively large phase change enthalpy which could be correlated linearly with the loading of TD. The thermal stability of the composite materials was close to TD and might have good long-term stability.

Acknowledgements

The authors gratefully acknowledge the National Nature Science Foundation of China for financial support to this work under Grant No. 20473091.

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Received: June 28, 2006
Accepted: August 9, 2006
OnlineFirst: December 18, 2006

DOI: 10.1007/s10973-006-7783-z