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THERMAL CONDUCTIVITY ENHANCEMENT OF MWNTS ON THE PANI/TETRADECANOL FORM-STABLE PCM

J. L. Zeng[1,2], *Y. Y. Liu*[1, 2], *Z. X. Cao*[1,2], *J. Zhang*[1,2], *Z. H. Zhang*[1,2], *L. X. Sun*[1,*] *and F. Xu*[1]

[1]Materials and Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,
Dalian 116023, P. R. China
[2]Graduate School of the Chinese Academy of Sciences, Beijing 100049, P. R. China

We prepared PANI/tetradecanol/MWNTs composites via in-situ polymerization. DSC results indicated that the composites are good form-stable phase change materials (PCMs) with large phase change enthalpy of 115 J g^{-1}. The MWNTs were randomly dispersed in the composites and significantly enhanced the thermal conductivity of the PCMs from 0.33 to 0.43 W m^{-1} K^{-1}. The form-stable PCMs won’t liquefy even it is heated at 80°C, so that the MWNTs were fixed in the composite and the phase separation of the MWNTs from PANI/tetradecanol/MWNTs composites won’t occur.

Keywords: *carbon nanotubes, form-stable phase change materials, polyaniline, thermal conductivity*

Introduction

Organic phase change materials (PCMs) are a kind of very important latent heat energy storage materials [1] and can be applied in lots of fields such as thermal energy storage [1], thermal protection [2] and heat transfer fluid [3], but their thermal conductivity is so low that limits their application. Numerous methods [4, 5] have been proposed to enhance their thermal conductivity but great efforts are still needed in this field. Carbon nanotubes (CNTs) possess wonderful thermal conductivity. Ultra-high thermal conductivity of single-walled carbon nanotubes (SWNTs) (~6600 W m^{-1} K^{-1}) [6] and multi-walled carbon nanotubes (MWNTs) (3000 W m^{-1} K^{-1}) [7] has been reported. The incredible high thermal conductivity of CNTs has induced great interest to apply it as thermal conductive filler [8–10]. But it was mainly focused on the field in which polymer or ceramic was used as matrix. To the best of our knowledge, though PCM/CNTs thermal interface materials were investigated [11], no bulky PCM/CNTs system has been reported because of the difficulty of maintaining the uniformity of CNTs dispersed in melted PCM.

One feasible way to solve this problem might be dispersing the CNTs into form-stable PCMs. A form-stable PCM would keep its shape even it is heated to beyond the melting point of the solid-liquid PCM, which is dispersed in the supporting material [12]. When the CNTs are dispersed into it, the aggregation and the precipitation of CNTs would be negligible due to the existence of supporting material. We have found that PCM containing polyaniline (PANI) results in a new kind of form-stable PCM. Here we apply 1-Tetradecanol (TD) as PCM and PANI as supporting material, a series of form-stable PCM/MWNTs composites were prepared and the effect of the MWNTs on the thermal conductivity of the form-stable PCM was investigated.

Experimental

Materials

The MWNTs with outer diameter of 10–30 nm and length of 5–15 μm were obtained from Shenzhen Nanotech Port Co., Ltd (Shenzhen, China). Aniline was redistilled under reduced pressure. All other reagents were of analytical grade and used as received.

Preparation of the composites

Aniline (1.0 g), concentrated HCl (1 mL) and cetyltrimethyl ammonium bromide (CTAB) (0.03 g) were dissolved in 90 mL water. Different amounts of MWNTs (0.01, 0.02, 0.05 and 0.1 g) were added to the solution and ultrasonicated for 1 h. Then 1.0 g TD was added to the above solution and the mixture was vigorously stirred for 2 h in a 50°C water bath to form an emulsion. The water bath was cooled to room temperature and replaced by an ice-water bath while the stirring continued. After the temperature of the mixture was cooled to 0–5°C, 10 mL of water solution containing 2.3 g ammonium persulfate was poured into it. The mixture was stirred

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* Author for correspondence: lxsun@dicp.ac.cn

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

vigorously overnight and naturally warmed to room temperature. The mixture was left to precipitate the solid materials. The supernate and the solid material floating on the surface were decanted. The precipitation was mixed with water and left stand still again. This procedure was repeated till the supernate was nearly colorless. After the mixture was filtered and washed with water till the filtrate was totally colorless, the residue was collected and dried in a vacuum desiccator. In order to study the effect of the MWNTs, a composite without MWNTs was prepared following the method mentioned above except no MWNTs was added and without ultrasonication. PANI was also prepared following the method except no MWNTs and TD were added and without ultrasonication.

Methods

The samples were sputtered with gold and then the surface morphology of the composites was investigated by scanning electron microscope (SEM, JEOL/EO JSM-6360).

Differential scanning calorimeter (DSC, DSC141 SETARAM, France) was used to obtain the energy storage properties of the composites from –10 to 80°C with the heating rate of 10 K min^{-1} in nitrogen atmosphere. Thermogravimetry/derivative thermogravimetry (TG/DTG) measurements were performed on a Setsys16/18 thermogravimetry analyzer (SETARAM, France) from room temperature to 650°C with the heating rate of 10 K min^{-1} and air as carrier gas.

For thermal conductivity, the grinded samples were pressured under 2 MPa to form two cylinders with the diameter of 13 mm. A Hot Disc thermal constant analyzer was used to obtain the thermal conductivity of the samples at room temperature with a sensor diameter of 2.001 mm. The sensor was sandwiched by the two cylinders and fixed by a clamp.

Results and discussions

The morphologies of the composites with different loadings of MWNTs obtained by SEM are depicted in Fig. 1. The MWNTs are randomly dispersed in the composites. Figure 1a shows that the MWNTs are wrapped by a layer of composite. There are some bulky composites that without MWNTs in it can be observed. As the loadings of MWNTs increased, the isolated bulky composites decreased (shown in Fig. 1b and c). The network formed by the MWNTs can be seen clearly. When the loading of MWNTs increased to 0.1 g, attaining 5% (mass/mass) of the composite, the MWNTs were very hard to separate into individual nanotube. So that agglomerate of MWNTs would exist. The aniline and the liquefied TD would penetrate into the agglomerate and retained in it. When the oxidant was added, the composite would be formed inside the agglomerate of MWNTs. As a result, bulky composite with MWNTs buried in it and the tips of the MWNTs throwing out the particles could be obtained, just like those shown in Fig. 1d.

The composites were heated to the temperature of 80°C, which is much higher than the melting point of TD, the samples could maintain its shape and no liquid could be found. This means that the composites are form-stable PCMs.

Figure 2 shows the DSC curves of the composites and pure TD. The melting point of TD obtained from the DSC curve is about 35°C. Owing to the introducing of PANI and MWNTs, the onset temperature of the phase change of the composites is in the range of 33–34°C, which is a little bit lower than that of pure

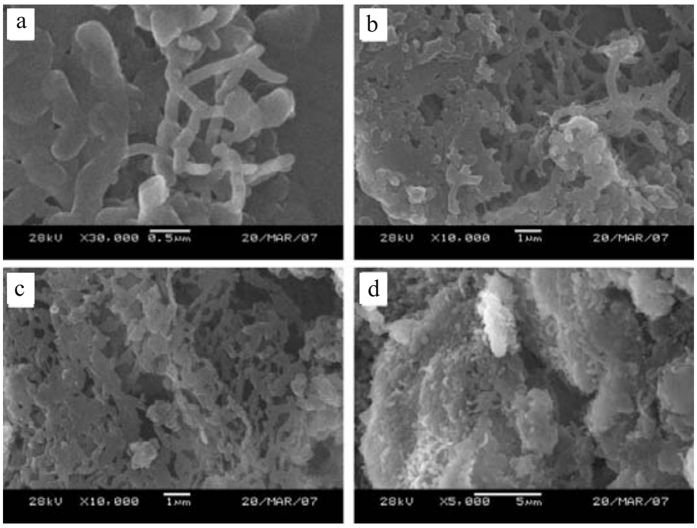

Fig. 1 The SEM images of the composites with different loadings of MWNTs. a – 0.01 g; b – 0.02 g; c – 0.05 g; d – 0.1 g

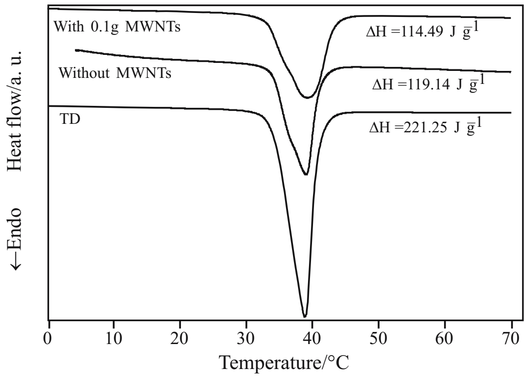

Fig. 2 DSC curves of the composites and TD

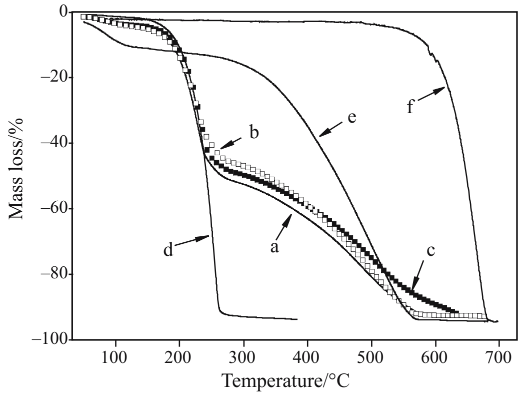

Fig. 3 TG curves of the composites and TD. a – composite without MWNTs; b – composite with 0.01 g MWNTs; c – composite with 0.1 g MWNTs; d – TD, e – PANI, f – MWNTs

TD. The peak temperature of the endothermic peak of the composites is also lower than that of pure TD. However, in general, the phase change properties of the composites are very similar to that of pure TD, which can be seen from Fig. 2. This result indicates that the ability of the composites to store latent heat energy is solely obtained from the phase change property of pure TD. The mean phase change enthalpy (Δ*H*) of the composites with MWNTs obtained by the DSC experiments is about (113±5%) J g^{-1}. The Δ*H* of the composite with MWNTs is close to that of the composite without MWNTs (119 J g^{-1}), indicating that the loadings of MWNTs has no apparent effect on the Δ*H* of the composites in the presented system. By comparing the Δ*H* of the composites and that of TD (221 J g^{-1}), we can know that the mass fractions of TD in the composites are close to 50%, agree with the mass fraction of TD in the raw materials, indicating that the present method is a feasible way to prepare the composites.

The TG curves of the composites, PANI and the MWNTs, along with the TD, are shown in Fig. 3. It can be seen that the TD is totally lost at the temperature range of 210–260°C. The PANI shows a three-step decomposition procedure. The mass loss under 110°C could be ascribed to the release of moisture and doped HCl from the surface of PANI [13]. The mass loss at the temperature range of 170–260 and 300–550°C are caused by the further release of doped-HCl from the backbone of the PANI and the decomposition of the PANI chain [13], respectively. The TG curves of the composites with loadings of 0.02 and 0.05 g MWNTs are omitted for clarity, but they are very close to the curves of the composites with loadings of 0.01 and 0.1 g MWNTs. The thermal degradation characteristics of the composite are very similar no matter whether there is MWNTs in it or not. The composites also experienced a three-step degradation procedure. The first step is caused by the loss of moisture and doped-HCl of PANI. The second step takes place at the temperature range from 200 to 250°C. This temperature range is slightly lower than that of the degradation of TD. The ratio of mass loss is approximately equal to the mass fractions of TD in the composites. Thus we can conclude that the second step of thermal degradation of the composite is mainly caused by the loss of TD. PANI also releases doped-HCl, although is very little, from the backbone of the PANI in this temperature range. This might be the cause of the lowering of the starting temperature of the second step of thermal degradation. After the TD and the doped-HCl are lost, the PANI chains start to decompose and are fully lost at 550°C (curves a and b). The MWNTs start to be lost when the temperature beyond 550°C (curve f). As a result, the decomposition of the composite with 0.1 g MWNTs won't terminate until the temperature attain 650°C (curve c).

The thermal conductivities of the composites are revealed in Fig. 4. It can be seen that the thermal conductivity of the composites improves significantly as the loadings of MWNTs increases. For composite without MWNTs in it, the thermal conductivity is 0.33 W m^{-1} K^{-1}. As the loading of MWNTs in the raw materials increases to 0.05 g (~2.5%), the thermal conductivity of the composite is enhanced to be 0.37 W m^{-1} K^{-1}. When 0.1 g (~5%) of MWNTs is

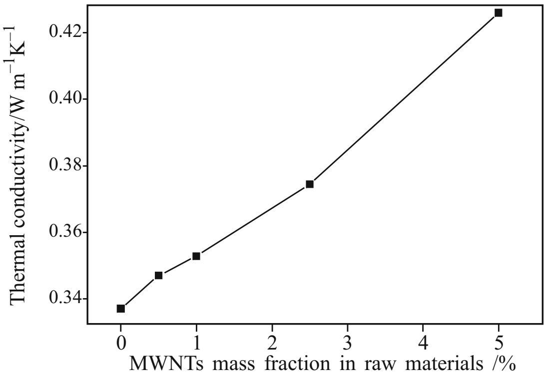

Fig. 4 Effects of MWNTs on the thermal conductivity of the composites

added to the reaction mixture, a thermal conductivity of 0.43 W m^{-1} K^{-1} (about 30% of enhancement) is obtained. This result shows that the thermal conductivity of the form-stable PCMs is significantly enhanced by adding MWNTs into it. Due to the small interface thermal conductance of CNTs [14], the improvement of the thermal conductivity is not as good as we have anticipated. The form-stable PCMs will not collapse when they are heated to a temperature beyond the melting point of the PCM, the MWNTs thus are fixed in the composites. Therefore, the precipitation and re-aggregation of MWNTs, which are the main hindrances of the composing of MWNTs with PCM, won't occur. Further improvement of the thermal conductivity of the form-stable PCMs/CNTs composites should be focused on chemically treating the CNTs as it can improve the interface thermal conductance [15], applying aligned CNTs as it can completely make use of the intrinsic thermal conductivity of CNTs [16] and more uniformly dispersing the CNTs in the PCM matrix.

Conclusions

In summary, we have successfully prepared PANI/TD/MWNTs composites via in-situ polymerization. DSC experiments show that the composites have large phase change enthalpy and thus can be applied as good form-stable PCMs with high latent heat energy storage ability. The thermal stability of the composites is close to that of pure TD. The MWNTs are randomly dispersed in the composites and the thermal conductivity of the PCMs is significantly enhanced. As the form-stable PCMs won't liquefy even they are heated to a temperature which beyonds their phase change temperature, the MWNTs won't precipitate and re-aggregate and thus the mixture might possess a good long-term stability of thermal conductivity.

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References

1 M. M. Farid, A. M. Khudhair, S. A. K. Razack and S. Al-Hallaj, Energy Convers. Manage., 45 (2004) 1597.
2 S. V. Garimella, Microelectron. J., 37 (2006) 1165.
3 J. L. Alvarado, C. Marsh, C. Sohn, M. Vilceus, V. Hock, G. Phetteplace and T. Newell, J. Therm. Anal. Cal., 86 (2006) 505.
4 A. Elgafy and K. Lafdi, Carbon, 43 (2005) 3067.
5 J. L. Zeng, L. X. Sun, F. Xu, Z. C. Tan, Z. H. Zhang, J. Zhang and T. Zhang, J. Therm. Anal. Cal., 87 (2007) 369.
6 S. Berber, Y. K. Kwon and D. Tománek, Phys. Rev. Lett., 84 (2000) 4613.
7 P. Kim, L. Shi, A. Majumdar and P. L. McEuen, Phys. Rev. Lett., 87 (2001) 215502.
8 H. Fukushima, L. T. Drzal, B. P. Rook and M. J. Rich, J. Therm. Anal. Cal., 86 (2006) 235.
9 H. Huang, C. H. Liu, Y. Wu and S. S. Fan, Adv. Mater., 17 (2005) 1652.
10 E. T. Thostenson and T. W. Chou, Carbon, 44 (2006) 3022.
11 J. Xu and T. S. Fisher, Int. J. Heat Mass Transf., 49 (2006) 1658.
12 H. Ye and X. S. Ge, Sol. Energy Mater. Sol. Cells, 64 (2000) 37.
13 X. M. Sui, Y. Chu, S. X. Xing, M. Yu and C. Z. Liu, Colloid Surf. A: Physicochem. Eng. Asp., 251 (2004) 103.
14 S. T. Huxtable, D. G. Cahill, S. Shenogin, L. P. Xue, R. Ozisik, P. Barone, M. Usrey, M. S. Strano, G. Siddons, M. Shim and P. Keblinski, Nat. Mater., 2 (2003) 731.
15 C. H. Liu and S. S. Fan, Appl. Phys. Lett., 86 (2005) 123106.
16 A. Bagchi and S. Nomura, Compos. Sci. Technol., 66 (2006) 1703.

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