

EFFECTS OF MWNTS ON PHASE CHANGE ENTHALPY AND THERMAL CONDUCTIVITY OF A SOLID–LIQUID ORGANIC PCM

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The effects of multi-walled carbon nanotubes (MWNTs) on the phase change enthalpy (ΔH) and the thermal conductivity (κ) of a solid-liquid phase change materials (PCM), palmitic acid (PA), have been investigated. The results showed that both the ΔH and the κ of the composite were lower than that of PA when the loading of MWNTs was small. As the concentration of MWNTs in the composites increased, the ΔH of the composites was slightly improved and then decreased linearly. However, the κ of the composites was monotonously increased from the minimum value. When the loading of MWNTs increased to 5% and no surfactant was added, the κ of the composite was enhanced to be 26% higher than that of PA. The κ of the composite could be enhanced by CTAB instead of SDBS when the loading of MWNTs was small, as SDBS showed no obvious effect on the κ of the composites. Furthermore, the effects of surface modification of MWNTs on the ΔH and the κ of the composites have also been investigated.

Keywords: multi-walled carbon nanotubes, phase change enthalpy, solid–liquid phase change materials, thermal conductivity

Introduction

Phase change materials (PCMs) are materials used for latent heat energy storage [1–3]. It provides much higher storage density, with a smaller temperature difference between storing and releasing heat. Furthermore, there are lots of PCMs that melting and solidifying at a wide range of temperature, making them attractive in a number of application fields such as thermal energy storage [1], thermal protection [4] and heat transfer fluid [5]. The main drawback that hinders the application of PCMs is their low thermal conductivity (κ). Numerous methods have been proposed to enhance the κ of PCMs such as: hollow aluminum plate with channels or compartments filled with PCM [6]; high conductivity fillers such as fins [7] and carbon fibers [8, 9] dispersed in PCM; PCM embedded in a high conductivity material matrix structure [10, 11]. However, great efforts are still needed in this field.

Since its appearance, carbon nanotubes (CNTs) have been a hot topic [12–14]. Among its fantastic properties, ultra-high κ is very attractive for many scientists. CNTs have been employed as great thermal conductive filler candidate as soon as single-walled carbon nanotubes (SWNTs) with κ of about $6600 \text{ W m}^{-1} \text{ K}^{-1}$ [15] and multi-walled carbon nanotubes (MWNTs) with κ of about $3000 \text{ W m}^{-1} \text{ K}^{-1}$ [16] were reported. Yet the research was mainly focused in

which polymer or ceramic was used as matrix [17–19].

For PCMs κ enhancement, one should increase the κ as high as possible while sacrifice the phase change enthalpy (ΔH) as small as possible. As a result, CNTs are much more attractive than any other thermal conductive filler because of their ultrahigh κ and low density. Recently we have found that MWNTs could remarkably improve the κ of a form-stable PCM [20]. However, there is no report concerns the effects of CNTs on bulky solid-liquid PCM. In this paper, palmitic acid (PA) was selected as a solid–liquid PCM. The effects of MWNTs on the ΔH and the κ of the PCM were studied. The influences of surface modification of MWNTs and the adding of surfactants were also investigated.

Experimental

Materials

Two kinds of pristine MWNTs, marked as P-L-MWNTs and P-S-MWNTs, were obtained from Shenzhen Nanotech Port Co., Ltd. (Shenzhen, China). The outer diameter and the length of P-L-MWNTs were 10–30 nm and 5–15 μm , respectively, while that of P-S-MWNTs were 10–30 nm and 5–15 μm , respectively. All other reagents were of analytical grade and used as received.

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Surface oxidation of MWNTs by nitric acid

Pristine MWNTs were mixed with concentrate nitric acid in a round-bottom flask. The mixture was ultrasonicated for 5 min. The flask was moved into an oil bath and refluxed at 70°C for 24 h and then cooled to room temperature. Great amounts of deionized water were added to the mixture and the supernatant was decanted after the MWNTs were set down. This procedure was repeated for three times. Then the mixture was filtrated using a polycarbonate membrane filter with pore diameter of 45 μm and washed with deionized water till the filtrate was neutral. The filter cake was dispersed into a 5 M HCl solution in a round-bottom flask under the assistant of ultrasonication. The mixture was refluxed at 120°C for 16 h. Then the mixture was washed and filtrated as mentioned above. The filter cake was dried in a vacuum desiccator at 80°C for 24 h and then grinded for use. Two kinds of pristine MWNTs were all oxidized and marked as O-L-MWNTs for long MWNTs and O-S-MWNTs for short MWNTs, respectively.

Surface oxidation of MWNTs by mixed acid

The MWNTs were refluxed in mixed acid (H₂SO₄:HNO₃=3:1) at 70°C for 2 h. The detailed procedure was similar to treating the MWNTs by nitric acid except the concentrate nitric acid was replaced by mixed acid and did not reflux in HCl solution. Two kinds of pristine MWNTs were all treated and marked as M-L-MWNTs for long MWNTs and M-S-MWNTs for short MWNTs, respectively.

Preparation of composites

The composites were prepared as follows. MWNTs, PA and surfactants (cetyltrimethyl ammonium bromide (CTAB), sodium dodecylbenzene sulfonate (SDBS) or without surfactant) were mixed in capped test tubes. The mixtures were ultrasonicated at 80°C for 1 h. The composites were grinded after they were cooled to room temperature. The ingredients of the composites were listed in Tables 1 and 2.

Table 1 Raw materials ratio of P-L-MWNTs/PA composites

Composites	PA-P-L-N0.1	PA-P-L-N0.5	PA-P-L-N1	PA-P-L-N2	PA-P-L-N5
PA/g	2.0	2.0	2.0	2.0	2.0
P-L-MWNTs/g	0.002	0.01	0.02	0.04	0.1
Composites	PA-P-L-C0.1	PA-P-L-C0.5	PA-P-L-C1	PA-P-L-C2	PA-P-L-C5
PA/g	2.0	2.0	2.0	2.0	2.0
P-L-MWNTs/g	0.002	0.010	0.020	0.040	0.10
CTAB/g	0.10	0.10	0.10	0.10	0.10
Composites	PA-P-L-S0.1	PA-P-L-S0.5	PA-P-L-S1	PA-P-L-S2	PA-P-L-S5
PA/g	2.0	2.0	2.0	2.0	2.0
P-L-MWNTs/g	0.002	0.010	0.020	0.040	0.10
SDBS/g	0.10	0.10	0.10	0.10	0.10

Table 2 Raw materials ratio of different kinds of MWNTs/PA composites

MWNTs	O-L-MWNTs	M-L-MWNTs	P-S-MWNTs	O-S-MWNTs	M-S-MWNTs
Composites	PA-O-L-N5	PA-M-L-N5	PA-P-S-N5	PA-O-S-N5	PA-M-S-N5
PA/g	2.0	2.0	2.0	2.0	2.0
Composites	PA-O-L-C5	PA-M-L-C5	PA-P-S-C5	PA-O-S-C5	PA-M-S-C5
PA/g	2.0	2.0	2.0	2.0	2.0
CTAB/g	0.1	0.1	0.1	0.1	0.1
Composites	PA-O-L-S5	PA-M-L-S5	PA-P-S-S5	PA-O-S-S5	PA-M-S-S5
PaAg	2.0	2.0	2.0	2.0	2.0
SDBS/g	0.1	0.1	0.1	0.1	0.1

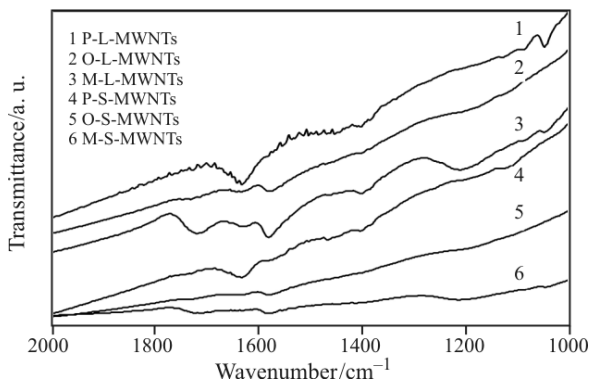


Fig. 1 FTIR spectra of untreated- and treated-MWNTs

Instrumental methods

IR spectra of the MWNTs were recorded on a BRUKER EQUINOX 55 FT-IR spectrometer using KBr pellet ($400\sim 4000\text{ cm}^{-1}$). Differential scanning calorimeter (DSC, DSC141 Setaram, France) was used to obtain the energy storage properties of the composites from 20 to 100°C with the heating rate of 10 K min^{-1} in nitrogen atmosphere. The masses of the composites were about 4–9 mg. For κ measurement, the grinded composites were pressed under 20 MPa to form two cylinders with the diameter of 13 mm. A Hot Disc thermal constant analyzer was used to obtain the κ of the composites at room temperature

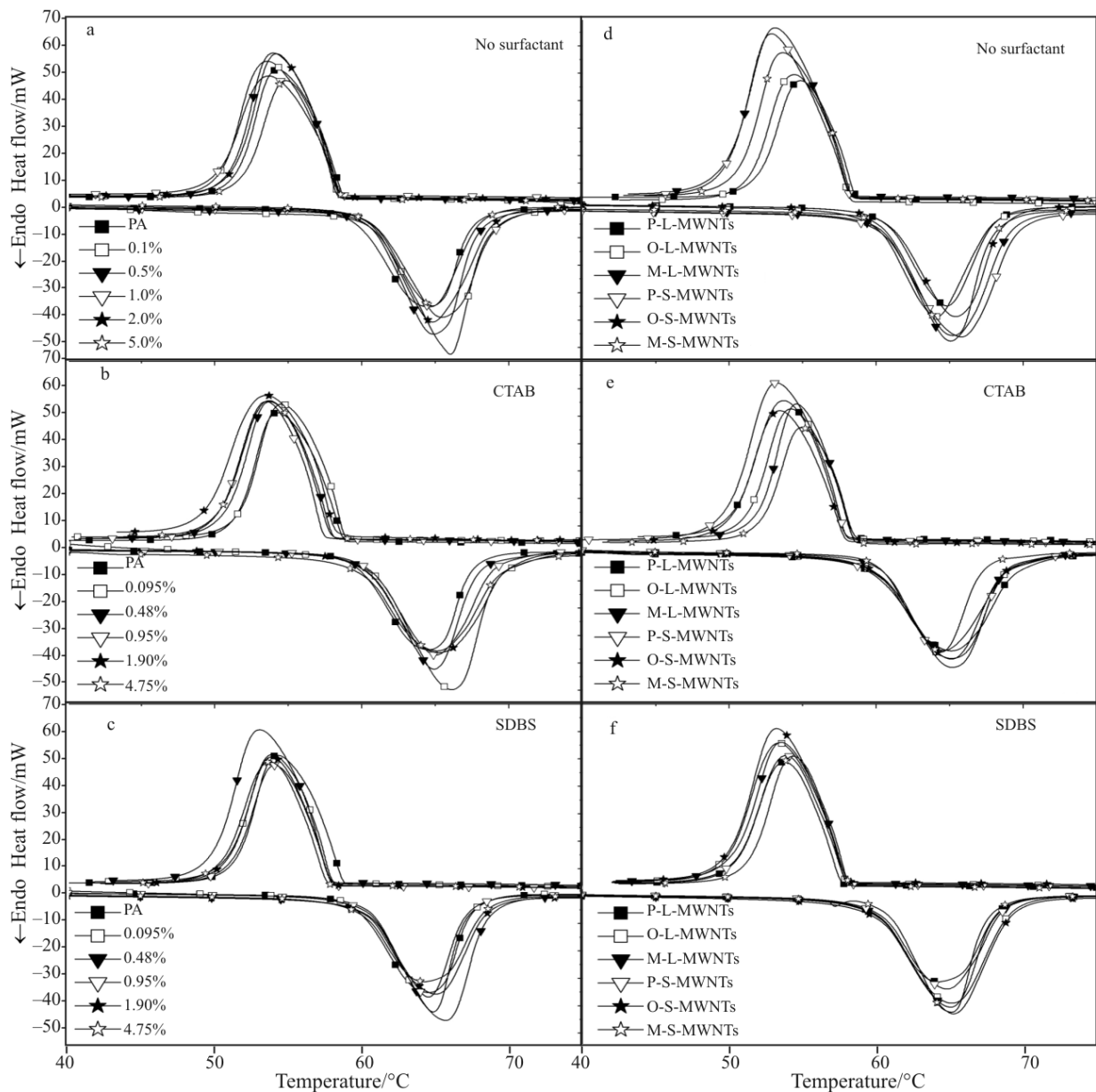


Fig. 2 DSC curves of 6 groups of composites. a, b and c – P-L-MWNTs/TD composites with different surfactants. d, e and f – different-MWNTs/TD composites with different surfactants

with a sensor diameter of 2.001 mm. The sensor was sandwiched by two cylinders and fixed by a clamp.

Results and discussion

The surface of the MWNTs could be modified and activated by the oxidation of concentrate nitric acid or mixed acid [21, 22]. The IR spectra of the pristine and the treated MWNTs in the wavenumber range of 2000–1000 cm^{-1} are depicted in Fig. 1. In order to eliminate the catalyst, the MWNTs have been purified by producer. As a result, on the spectra of pristine MWNTs, there exist weak peaks corresponding to the absorption of –O–H and –C=O groups. After the MWNTs were oxidized by acid, some new peaks are appeared. The stretching vibration of C=O can be seen clearly at 1720 cm^{-1} . The absorption band near 1200 cm^{-1} could be ascribed to the C–O vibration of carboxyl or phenolic group, while the band near 1400 cm^{-1} could be ascribed to the O–H bending distortion vibration in the same group [23, 24]. The peak at 1580 cm^{-1} is caused by the stretching vibration of activated C=C double bond on the MWNTs surface [25]. Obviously, the surface of the MWNTs has been successfully modified by the oxidation of concentrate acid. Furthermore, from the IR spectra, it is clearly that the absorption intensity of the MWNTs treated by mixed acid is stronger than that of the MWNTs treated by nitric acid, indicating that the surface of MWNTs treated by mixed acid is more activated than that of MWNTs treated by nitric acid. This is in consistent with the oxidation ability of these two kinds of acids.

The DSC curves of the composites are listed in Fig. 2. From the DSC curve of PA, it could be obtained that the melting and freezing point of PA is 59.48 and 58.78°C, respectively. The ΔH of melting and freezing is 200.3 and –201.9 J K^{-1} , respectively. The figure also shows that the DSC curves of all composites are similar to that of PA and the onset point of melting and freezing has no significant variation, indicating that the phase change characteristics of PA are not affected by the adding of MWNTs and surfactants, no matter what kinds of MWNTs and surfactants were added.

From the DSC curves, the ΔH of all composites during melting could be obtained. Figure 3a shows the relationship between the ΔH of the composites and the loading of MWNTs. The figure shows that at low MWNTs content, the ΔH of composites would decrease drastically comparing to that of PA as the MWNTs content is increased. After the loading of MWNTs reached an extent, the ΔH of the composites would increase abruptly to form a peak in the curve. Then the ΔH of composites would decrease linearly as

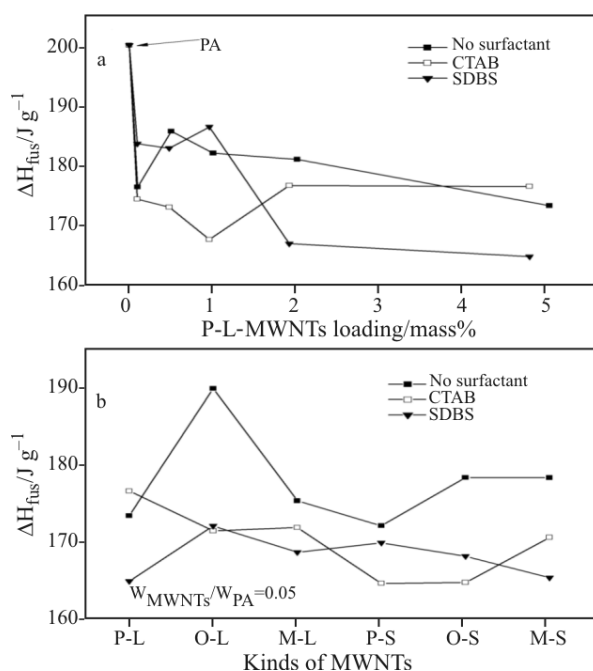


Fig. 3 Relation between the heat storage capacity of the composites and the loading of a – P-L-MWNTs, b – the kinds of the MWNTs

the MWNTs content is increased. It has been reported that the –COOH group of fatty acid could bond with active groups such as –COOH and –OH groups on the surface of CNTs, forming a layer of fatty acid on the surface of CNTs [22]. Besides, the hydrophobic part of PA could absorb onto the CNTs surface [26, 27]. Obviously, when its loading is low, the MWNTs could be dispersed more uniformly and separately in the PA matrix, so that a single CNT could absorb large amounts of PA molecules. As a result, lots of PA molecules would lose the phase change properties. This is why the ΔH of the composites would drop drastically at low MWNTs content. As its content in the composites is increased, the MWNTs would agglomerate more and more, hence the percentage of MWNTs to absorb PA molecules would decrease. When the MWNTs loadings reached such an extent that great part of MWNTs in the composites are agglomerated and loss the absorbability, the ΔH of the composites would increase to a peak point. Further increase of MWNTs content could not affect the agglomeration of MWNTs, so that the ΔH would decrease linearly.

The MWNTs content where the peak point of ΔH appeared could be affected by surfactant. It can be acquired from Fig. 3a that when no surfactant is added, the peak point appeared at MWNTs content of 0.5%; when SDBS is added, the peak appeared at MWNTs content of 1%; however, when CTAB is added, the peak appeared at MWNTs content of 2%. This result might be caused by the fact that CTAB is

cationic surfactant while SDBS is anionic surfactant and more detailed work on the cause of these differences is undertaken.

The effects of surface modification of MWNTs on the ΔH of the composites are described in Fig. 3b when the loading of MWNTs is fixed at 5%. It could be seen from the figure that in general, the surface properties of the MWNTs have no significant effect on the ΔH of the composites. However, the ΔH of PA-O-L-N5 is abnormally much larger than other composites in which no surfactant was added. The reason is that since the oxidizability of concentrate HNO_3 is weaker than mixed acid and the long CNTs are more difficult to be oxidized than short CNTs, there are relatively fewer active groups on the O-L-MWNTs surface than other acid treated MWNTs. Consequently, the interactions existed between PA and O-L-MWNTs would be weaker than that of PA and other acid treated MWNTs. Besides, the slightly oxidized MWNTs would be more inclined to agglomerate than none-oxidized MWNTs. Thus there is more PA in PA-O-L-N5 than in other composites could melt and freeze; hence the ΔH of PA-O-L-N5 is larger than other composites. The figure also shows that when surfactants were added, the ΔH of the composites is lower than the composites without surfactants. This is caused by that the adding of surfactant would decrease the containing of PA in the composites.

Figure 4a shows the effects of the MWNTs content on the κ of the composites. The κ of PA is $0.318 \text{ W m}^{-1} \text{ K}^{-1}$. However, at low MWNTs containing, the κ of the composites is lower than that of pure PA and there exists a minimum value. When MWNTs loading is 0.1% (to PA), the κ of three kinds of composites is $0.316 \text{ W m}^{-1} \text{ K}^{-1}$ (PA-P-L-N0.1), $0.310 \text{ W m}^{-1} \text{ K}^{-1}$ (PA-P-L-C0.1) and $0.281 \text{ W m}^{-1} \text{ K}^{-1}$ (PA-P-L-S0.1), respectively. The κ of PA-P-L-N0.5 is further decreased to be only $0.306 \text{ W m}^{-1} \text{ K}^{-1}$. It has been reported that the main hindrance to apply CNTs as thermal conductive filler is its high interface thermal resistivity [28]. At low MWNTs content, the thermal conductive network has not been formed. The high interface thermal resistivity between MWNTs and matrix would make the κ of the composites lower than pure matrix. When surfactant is added, the surfactant would be absorbed on the surface of MWNTs, so that another interface would be formed between MWNTs and matrix, results in an even lower κ . Only after the containing of MWNTs exceeds the minimum value, would the κ of the composites increase linearly as the MWNTs content is increased. It means that the thermal conductive network has been formed. The thermal conductive network becomes compact more and more as the

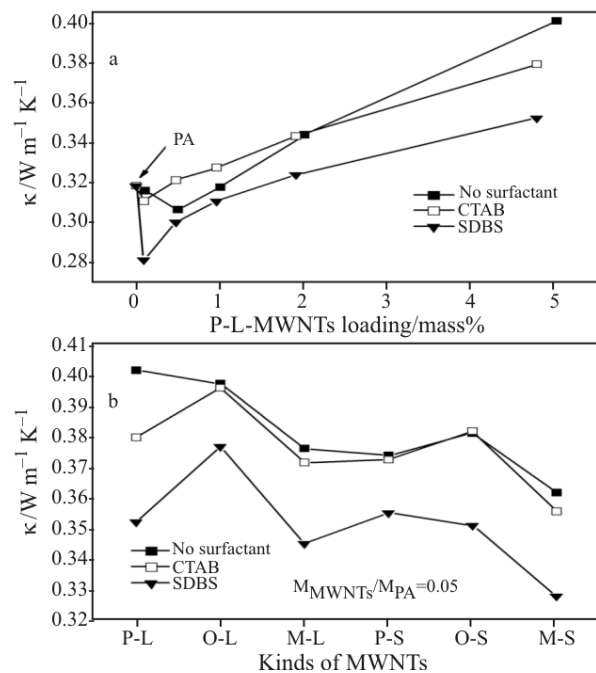


Fig. 4 Relation between the thermal conductivity (κ) of the composites and the loading of a – P-L-MWNTs and b – the kinds of the MWNTs

MWNTs content increased, results in more and more higher κ . When the loading of MWNTs is increased to 5% (to PA), the κ of the composites are $0.402 \text{ W m}^{-1} \text{ K}^{-1}$ (PA-P-L-N5), $0.380 \text{ W m}^{-1} \text{ K}^{-1}$ (PA-P-L-C5) and $0.352 \text{ W m}^{-1} \text{ K}^{-1}$ (PA-P-L-S5), respectively, which are 26.3% (PA-P-L-N5), 19.4% (PA-P-L-C5) and 10.74% (PA-P-L-S5) higher than that of PA, respectively, indicating that MWNTs can largely enhance the κ of PA.

Also could be seen from the data is that when large amount of MWNTs are applied to enhance the κ of the PCM, surfactant has no positive effect. However, at low MWNTs content, the κ of the composites containing CTAB is higher than that of composites without surfactant. This is because that the dispersing of the MWNTs plays a key role in the κ enhancement and CTAB has the ability to disperse MWNTs more separately when the MWNTs content is low.

The effects of surface modification and the length of MWNTs on the κ of the composites are shown in Fig. 4b. Obviously, long MWNTs have stronger ability to enhance the κ of the composites. Besides, the composites containing MWNTs oxidized by nitric acid possess higher κ than other composites under the same surfactant environment except PA-P-L-N5, indicating that slightly oxidized MWNTs could be dispersed in PA more separately by the help of surfactant. PA-P-L-N5 possess the highest κ in all composites is because that the intrinsic κ of

MWNTs could be weakened even if it was just slightly functionalized [29]. The figure also shows that because CTAB has the ability to disperse MWNTs more separately in the matrix, the κ of the composites containing CTAB is close to that of composites without surfactant and is much higher than that of composites containing SDBS. The difference in MWNTs dispersibility of CTAB and SDBS might come from the differences in the properties of CTAB and SDBS.

Conclusions

MWNTs/PA composites were prepared and the effects of MWNTs on the ΔH and the κ of the solid–liquid PCM, PA, were studied. The results showed that both ΔH and κ of the composite were lower than that of PA when the MWNTs content was low. As the loading of MWNTs in the composites increased, the ΔH of the composites was slightly improved and then decreased linearly. However, the κ of the composites was monotonously improved to be higher than that of PA. When the loading of MWNTs increased to 5% and no surfactant was added, the κ of the composite was enhanced to be 26% higher than that of PA, indicating that MWNTs could greatly enhance the κ of the liquid–solid PCM. The κ of the composite could be enhanced by CTAB instead of SDBS when the loading of MWNTs was small. The surface properties of the MWNTs had no significant effect on the ΔH of the composites. But nitric acid treated MWNTs and long MWNTs bore stronger κ enhancement ability than mixed acid treated MWNTs and short MWNTs, respectively. Furthermore, the κ of composites containing CTAB was close to that of composites without surfactant though the MWNTs content in the former was lower than in the latter, indicating that CTAB possessed the ability to disperse the MWNTs more uniformly and separately in PA.

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