



Metal Nanoparticles Decorated on Carbon Nanotube Surfaces as Fillers to Improve Thermal Conductivity of Stable Phase Change Composite Materials

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Abstract: The composite phase change materials (CPCM) are prepared by using porous silicon carbide foam as the carrier, N-octadecane (C18) as the phase change material, and metal nanoparticles decorated on carbon nanotube surfaces (M-NPs@CNTs) as fillers. It is a new type of shape and performance stable C18/M-NPs@CNTs/SF CPCM with better performance. The thermal conductivity of the C18/M-NPs/CNT/silicon carbide foam (SF) composite is higher than that of pure C18. When the thermal filler is AgNPs@CNTs, the thermal conductivity of CPCM is improved by 666% compared with C18. The results of thermogravimetric and differential thermal analysis indicate good structural stability and chemical stability. C18/1wt%AgNPs/CNT/SF has the highest thermal conductivity and heat storage capacity, and the best overall performance in the process of thermal energy storage and release. The silver nanoparticles The well-dispersed thermal fillers (M-NPs@CNTs) form excellent heat conduction path and improve the thermal performance of the system. The SF is an excellent thermal conductive carrier materials and its porous structures are attributed to the adsorption of phase change materials and structural stability of CPCM. The application of SF both improves the thermal conductivity and electrical resistivity of CPCM and decreases its leakage during phase change. The application of solid-liquid CPCM can be enlarged in thermal management field.

Keywords: Thermal Conductive Filler, Metal Nanoparticles Decoration, Porous Silicon Carbide, Phase Change Materials, Thermal Conductivity

1. Introduction

Porous silicon carbide foam (SF) has special uniform three-dimensional network structure, the porosity is from 60% to 98% and the pore size is in the range of micrometers/mm. It usually consists of a large number of solid pillars, forming a network of interconnected voids that allow working fluid to pass through. This complex disordered structure makes the material have a larger specific surface area and excellent flow and mixing ability, so this brings the potential of fluid stability and heat transfer enhancement. These characteristics make SF suitable for thermal energy storage [1-2]. The SF has become a research hotspot in the field of porous materials due to its

good mechanical strength, high temperature resistance, oxidation resistance, acid and alkali corrosion resistance, low thermal expansion coefficient, high thermal conductivity, high hardness, thermal shock resistance and semiconductor characteristics [3-5].

Thermal energy storage (TES) technology can improve energy efficiency by solving the contradiction between space and time energy demand and supply mismatch. TES can be achieved in three different ways such as chemical reaction, sensible heat and latent heat storage [6]. Latent heat storage relies on the phase change enthalpy of the PCM to store and release a large amount of heat in a small temperature range, which is better than chemical reactions and sensible heat storage [7, 8]. The solid-liquid phase transition has been

widely studied and applied due to its high thermal energy storage capacity and chemical stability [9, 10]. However, leakage during phase change and low thermal conductivity limit their application. Using SF as carriers can avoid the leakage. Which also have the following advantages: (1) low pressure drop ideal for low contact time operations [11], (2) improving mass transport and heat transfer due to uniform dispersion of PCM, (3) capability to pre-shape the foam to match reactor configurations [12], (4) high thermal conductivity, low thermal expansion coefficient and chemical inertness at high temperatures.

Adding high thermal conductivity materials into PCM can improve the thermal conductivity of PCM [13-18]. The metals in the form of particle [19], foam [20], matrix [21], fin [22] and so on have been extensively studied to increase thermal conductivity of PCM. Carbon-based materials such as graphite block [23], expanded graphite [24], carbon fibers [25], oxidizing graphene (GO) and carbon nanotubes (CNTs) [26] have been used as thermal fillers, indicating that GO and CNTs can largely improve the thermal conductivity of composites. However, these metals and carbon-based materials are good electric conductors, which can reduce the insulating property of the composite PCMs. As carriers, SF with higher thermal conductivity [27], higher electrical resistivity [28] and thermal energy storage and release performance [29] can improve the insulating property and at the same can improve the thermal conductivity just like the thermal fillers.

Our previous work [30] shows that the carbon materials

decorated by metal particles (M-NPs/CNTs) are excellent thermal fillers. This work innovatively prepared the composite phase change materials (CPCM) by using porous silicon carbide foam (SF) as the carrier, N-octadecane (C18) as the phase change material, and three kinds of thermal fillers including carbon nanotubes decorated by silver nanoparticles, cobalt nanoparticles, or nickel nanoparticles. The latent heat of CPCM is up to 190.3 J/g. M-NPs/CNTs greatly improve the thermal conductivity of CPCM. In short, the further addition of composite thermal fillers to composite materials is a meaningful attempt to obtain CPCM with high thermal conductivity. In addition, studying the effect of SF as a carrier on the properties of CPCM has important practical application value.

2. Experiments

2.1. Materials

The purity of multi-walled carbon nanotubes is above 98%. The CPCM selected for the experiments is C18 ($\text{CH}_3(\text{CH}_2)_{16}\text{CH}_3$) with a phase change temperature of 28°C. The SF used is from Suzhou JST Foam Metal Co., Ltd. The porosity, pore density and size are 85%, 80PPI and 2cm*2cm*7mm, respectively. The silver acetate, cobalt acetate, and nickel acetate are applied to decorate metal nanoparticles on carbon nanotube surfaces. Carbon nanotubes decorated with metal nanoparticles are used as additives to improve the thermal conductivity of CPCM.

Table 1. Compositions of CPCM.

Samples	C18 (g)	SiC (g)	NiNPs@CNTs (g)	CoNPs@CNTs (g)	AgNPs@CNTs (g)
C0	6.6	2.349	0	0	0
C1	6.6	2.226	CNTs0.66	0	0
C2	6	1.730	0.06	0	0
C3	6	1.657	0.3	0	0
C4	6	1.717	0.6	0	0
C5	6	1.723	0	0.06	0
C6	6	1.800	0	0.3	0
C7	6	1.830	0	0.6	0
C8	6	1.973	0	0	0.06
C9	6	1.926	0	0	0.3
C10	6	1.968	0	0	0.6

2.2. Preparation of CPCM

The melt infiltration method and the vacuum impregnation method are combined to prepare the C18/M-NPs@CNTs/SF composite materials. Specific steps are as follows. Put a certain proportion of phase change material C18 at the bottom of beaker, then a certain amount of M-NPs@CNTs composite thermal filler or pure carbon nanotubes is put into the beaker. The beaker is kept at temperature of 70°C with magnetic stirrer. The C18 is gradually melted and evenly mixed with the M-NPs@CNTs composite thermal filler, and then the SF is placed in the heating beaker for 10 minutes. When the C18 is completely melted, SF must be completely immersed in the liquid C18. The beaker is placed in a vacuum drying oven for 10 minutes, taken out and cooled to room temperature.

2.3. Thermal Analysis of CPCM

The thermal properties (such as melting temperature, latent heat of melting or solidifying) of the porous silicon carbide-based composite thermal conductive material and thermal treated samples were measured by a differential scanning calorimetry (DSC, DSC³⁺, METTLER TOLEDO). Briefly, about 5 mg samples was sealed in an aluminum pan and placed inside the DSC chamber with an empty aluminum pan as a reference under continuously purged nitrogen gas with a flow rate of 40 ml/min at heating rate of 10°C/min from 0 to 50°C, and perform 50 thermal cycle experiments on the sample to test its thermal stability.

The thermal stability of the samples thermally treated at different temperatures were investigated by a

thermogravimetric analyzer (TGA, DSC³⁺, METTLER TOLEDO) scanning from 30 to 600°C at 10°C/min heating rate under a constant nitrogen stream rate of 40 ml/min.

2.4. Thermal Conductivity Measurements

The thermal conductivity of the prepared CPCM samples was tested by using a thermal conductivity meter (HotDisk TPS2200, Sweden). Each sample is tested three times to get the average value of thermal conductivity.

3. Results and Discussions

3.1. Microstructure Analysis

The morphology of M-NPs@CNTs, SF and SF based CPCM is shown in Figure 1. The image shows that M-NPs@CNTs and C18 are well immersed in SF. The metal particles are decorated on the surface of the carbon nanotubes, and the composite material with SF as the carrier can effectively control the leakage of the PCM.

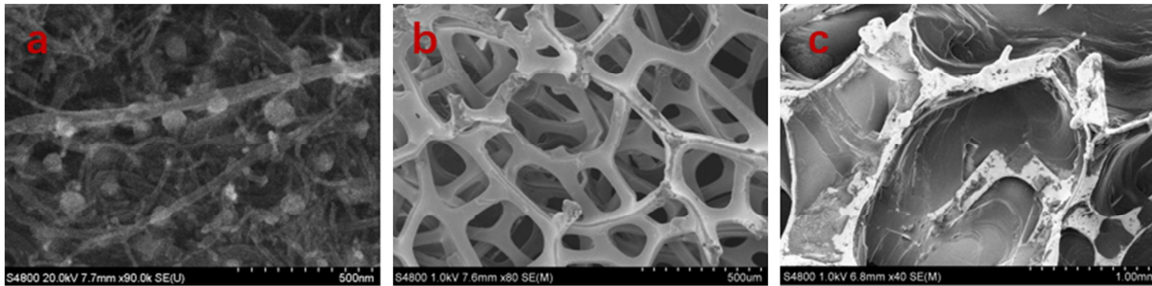


Figure 1. Image of M-NPs@CNTs (a), SF (b), and SF based CPCM (c).

3.2. Thermal Storage Properties Analysis

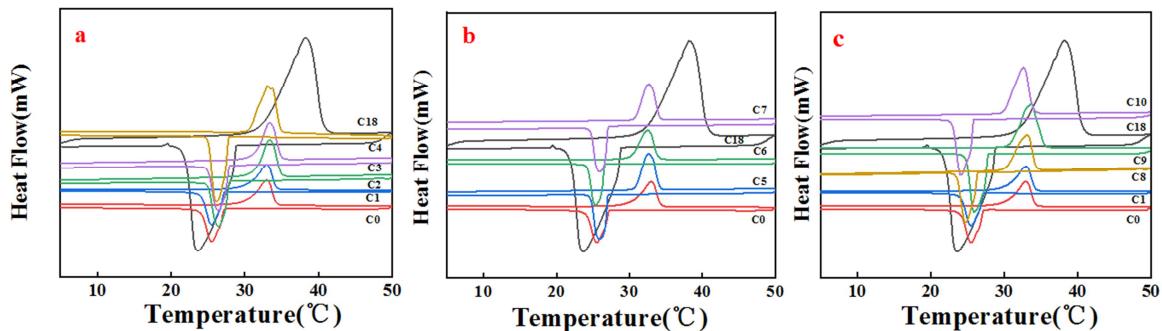


Figure 2. DSC curve of C18 and CPCM samples.

Figure 2 shows the differential scanning calorimetry (DSC) test curves of C18 and CPCM samples during melting and solidification. It can be observed that during the melting and solidification process, CPCM has only one peak, which is similar to C18. The phase change behavior of the matrix PCM C18 will not be changed by the addition of M-NPs@CNTs. The melting temperature and solidification temperature of CPCM are smaller than pure C18. Compared with pure C18, the melting peak temperature of CPCM filled with M-NPs@CNTs thermal filler is slightly lower, from 38.17°C to about 33°C. The added M-NPs@CNTs with high thermal conductivity makes the thermal response characteristics of CPCM more sensitive.

The latent heat of phase change is one of the most important parameters for evaluating PCM. The larger the value, the better the heat storage performance of the PCM will be under the same temperature rising and falling conditions. When the addition of M-NPs@CNTs is 1wt%, the latent heat of phase change of CPCM is greater than that (77.8 J/g) of C18/SF without thermal fillers, but keeping increase the content of M-NPs@CNTs it will become smaller. This is because M-NPs@CNTs occupies the position of C18

in the pores, resulting in less adsorption of C18. In addition, after M-NPs@CNTs is combined with C18, part of C18 wraps the surface of M-NPs@CNTs. The adsorption of NPs@CNTs on C18 leads to a decrease in crystallization performance, so the heat transfer performance of the PCM in the system decreases, and the latent heat value of CPCM decreases. The phase change latent heat of CPCM filled with 1wt% AgNPs@CNTs is the highest, which is 190.31 J/g, and is only 15% lower than pure C18.

3.3. Thermal Conductivity of CPCM

Thermal conductivity is another one of the important properties of CPCMs, because it is closely related to the thermal performance of the applied CPCM. Figure 3 shows the thermal conductivity of samples with different mass fractions of M-NPs@CNTs. It can be seen that M-NPs@CNTs/SF can act as a thermally conductive networks to enhance thermal conductivity. When the mass fractions of AgNPs@CNTs are 1wt%, 5wt%, and 10wt%, respectively, the thermal conductivity of C18/M-NPs@CNTs/SF composites are 2.23 W/(m·K), 2.38 W/(m·K), and 2.68 W/(m·K). The thermal conductivity of CPCM filled with 10wt% AgNPs@CNTs is up to 2.68W/(m·K),

which is 666% higher than pure C18, and 60.5% higher than C18/SF without M-NPs@CNTs. The thermal conductivity of C18/M-NPs@CNTs/SF CPCM increases with the increase of the mass fraction of M-NPs@CNTs. Because that the well-dispersed thermal fillers can form an excellent heat conduction path with the increase of the mass fraction of M-NPs@CNTs.

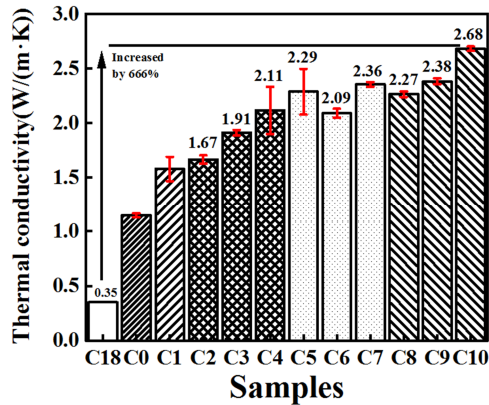


Figure 3. Thermal conductivity of C18 and CPCM samples.

The addition of M-NPs@CNTs with high thermal conductivity improves the thermal conductivity of the entire system. When the thermal filler is AgNPs@CNTs, the thermal conductivity of CPCM is greater than that of CPCM filled with the other two kinds of thermal fillers. This is because the thermal conductivity of AgNPs is slightly greater than that of the other two kinds of metal nanoparticles decorated on the carbon nanotube surfaces. When C18 in the CPCM undergoes melting phase change behavior, the M-NPs@CNTs with high thermal conductivity and large specific surface area promote the energy transmission, accelerate its melting rate, and enhance the heat transfer performance. When C18 in CPCM undergoes solidification behavior, after adding M-NPs/CNTs, it has a certain aggregation effect on C18, which accelerates the nucleation rate of C18. So the melting efficiency and solidification efficiency are both improved and strengthened. The heat transfer performance of the composite material is improved.

3.4. Thermal Stability Analysis

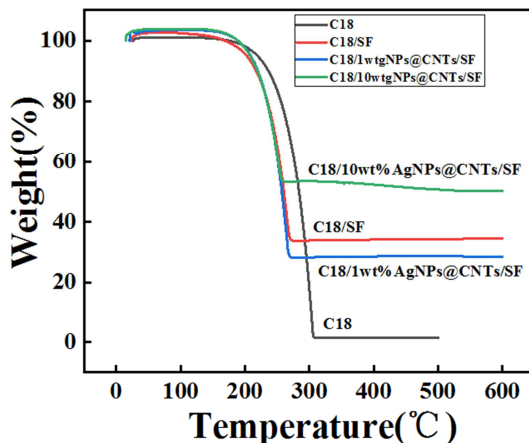


Figure 4. Thermogravimetric diagram of C18 and CPCM samples.

The thermogravimetric curve of the composite material and pure C18 is shown in Figure 4. It can be seen that C18 has only experienced a weight loss process, and the mass changes rapidly, with almost 100% weight loss at 162.2°C. All samples start to decompose at about 234°C, and there is only one first-level decomposition process due to the decomposition of C18. The loading rates of C18/SF, C18/1wt%AgNPs@CNTs/SF, and C18/10wt%AgNPs@CNTs/SF are 68.22%, 74.86% and 52.12%, respectively. The complete decomposition temperature of the sample increases with the increase of C18 loading. C18 is completely decomposed at about 300°C, and the final decomposition temperature (288°C) of C18/1wt%AgNPs@CNTs/SF is higher than C18/SIC (286°C) and C18/10wt%AgNPs@CNTs/SF (250°C). The results show that C18/1wt%AgNPs@CNTs/SF is more stable. During the entire pyrolysis process, when the temperature is lower than 170°C, there is no significant weight loss of C18 and CPCM samples, indicating that the CPCM have excellent thermal stability when temperatures is below 170°C.

3.5. Recyclability Analysis

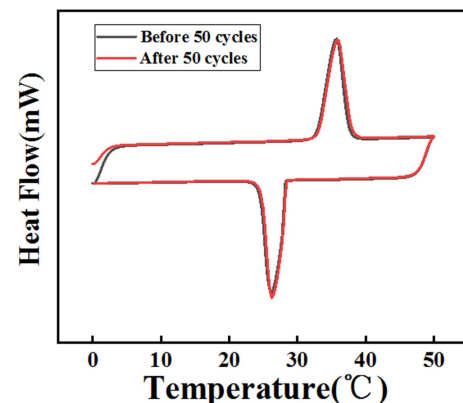


Figure 5. DSC curves of one CPCM sample before and after 50 thermal cycles.

The solid-liquid phase transition cycle test of the CPCM was measured by DSC. Figure 5 shows the DSC curve results of one CPCM sample before and after 50 thermal cycles. It can be seen that after 50 cycles, no significant changes were found in the DSC curve. The melting and solidification temperature of CPCM sample is also basically unchanged. The fluctuation of the phase transition temperature is only about 0.1°C, and the fluctuation of the latent heat value of the phase transition is less than 1%, that is almost unchanged. The changes of temperature and phase change latent heat value are all within the acceptable ranges, and the prepared CPCM has reliable thermal stability and can be used for multiple cycles without affecting its overall performance.

4. Conclusion

A new type of shape and performance stable C18/M-NPs@CNTs/SF CPCM with better heat storage performance was successfully prepared. There are differences

in thermal performance of CPCM filled with different M-NPs/CNTs in terms of thermal energy storage. Good thermal fillers can more effectively improve the thermal conductivity of the CPCM. Porous silicon carbide foam is an excellent thermal conductive carrier materials, it can improve the thermal conductivity and electrical resistivity of CPCM and decrease its leakage during phase change. Porous silicon carbide foam can be well used in thermal energy storage systems. The application of the prepared solid-liquid CPCM can be enlarged in thermal management field.

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