Effects of expanded graphite and nano-AlNon the thermal conductivity and specific heat capacity of phase change materials

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ABSTRACT

Latent heat energy storage technology (LHES) has the advantages of high heat storage density, stable phase change temperature and easy process control. The development of high-performance phase change materials is crucial to the use of thermal energy storage. In this study, physisorption is used to create a variety of paraffin wax (PA) based composite phase change materials (PCMs), employing expanded graphite (EG) and aluminum nitride (AIN) nanoparticles as fillers. The thermal conductivity of composite samples at 25 °C is measured based on the principle of steady-state heat flow method. Thermal characterization of the composite PCM by differential scanning calorimetry (DSC) showes the effect of EG and nano-AIN on the specific heat capacity of paraffin. The thermal conductivities of the prepared PCMs are 6.4-11.8 times that of PA. This is a guiding meaning for the preparation of composite PCMs with high specific heat and thermal conductivity.

Keywords: composite phase change materials, specific heat capacity, thermal conductivity.

1. INTRODUCTION

Excessive usage of fossil fuels releases a considerable quantity of waste heat into the environment, resulting in energy overload operation [1]. Thermal energy storage (TES) has gained a lot of interests for fulfilling the demand of future energy system. PCMs have low cost and high energy storage capacity, LHES using PCMs as heat storage media has become an increasingly essential technology in many engineering fields [2].

As an organic solid-liquid phase change material, PA has been widely studied because of its high latent heat, wide melting temperature, excellent chemical stability and low cost [3]. However, the low thermal conductivity, generally below 0.4 W·m⁻¹·k⁻¹, is a major drawback of paraffin leading to poor heat storage/retrieval efficiency, which limits its utilization as an energy storage material [4]. Therefore, various methods have been proposed to improve the thermal conductivity of PCM, such as filling high-conductivity particles into PCM, inserting fibrous

materials, incorporating the heat pipes or porous medias into PCM [5].

Compared with other materials, porous expanded graphite has the advantages of high thermal conductivity, simple preparation, and low cost, which can significantly improve the thermal conductivity of PCM and reduce the material production cost. In addition, many studies have added highly thermally conductive nanoparticles to PCM to improve the heat transfer performance of PCM. Several investigations have been conducted to increase the thermal conductivity of paraffin using various Nanoscale materials [7]. Teng and Yu prepared nano-enhanced PCMs by mixing paraffin with Al₂O₃, TiO₂, SiO₂ and ZnO particles, respectively. The results showed that, TiO2doped paraffin has better thermal conductivity and heat storage performance among the four kinds of composite PCMs [8]. Therefore, in this study, EG and nano-AlN particles are selected to improve the thermal conductivity of PCM

However, the magnitude of the latent heat of PCM depends mainly on the high mass fraction of phase changeable material. Filling with highly conductive particles in order to improve the thermal conductivity of PCM will reduce the proportion of phase changeable materials in PCMs, further reducing the latent heat of PCMs, which is very detrimental to the utilisation of PCM. Noteworthy, a remarkable increase in heat capacity was firstly observed in 2009 when Nelson et al. [8] added a small amount nanoparticles in paraffin-based oil. Sarmad I. Ibrahim et al. [9] added nano-TiO₂ and MgO and a 50% mixture to Iraqi paraffin and the best improvement in specific heat capacity was obtained when mixed nanoparticles were added. The addition of nanoparticles not only affects the thermal conductivity of the material but also the specific heat capacity of the material, if the presence of nanoparticles increases the specific heat capacity of the PCM it will compensate for the decrease in the thermal storage capacity of the PCM. Therefore, in this work, the specific heat capacity of PCM is measured to further investigate the effect of AIN nanoparticles on the specific heat capacity of PCM.

In this paper, PA is used as the thermal storage material and different contents of EG and nano-AIN are added in PA to investigate the effects of EG and nano-AIN. Three kinds of composite PCM (EG/PA, AIN/PA and EG/PA/AIN) with different mass fraction are prepared by physical adsorption method. In order to evaluate their potential applications, the thermophysical properties of the materials including thermal conductivity and specific heat capacity are measured. In particular, the specific heat and thermal conductivity of materials are compared, and the effect of the mass fraction of AIN on the specific heat capacity of the materials is also investigated.

2. EXPERIMENTAL

2.1 Materials

In this research, expandable graphite (80 mesh, 99% purity) is purchased from Shanghai Daoguan Rubber & Plastic Hardware Co., China. Paraffin wax (melting point: 58-60 °C, latent heat: 177.7 J/g, thermal conductivity: 0.350 W·m⁻¹·k⁻¹) is purchased from Nanjing Jingyou Biotechnology Co., China. Nano aluminum nitride (40 nm) is purchased from Hebei Keze Metal Material Co., China.

2.2 Preparation of the EG

The raw expandable graphite is put into a muffle furnace, following with a subsequent heat treatment at 680-700°C for 15 min, and the EG is obtained. The apparences of expanded graphite is prepared is significantly different from that of the original expanded graphite. The shape becomes loose worm-like, and the surface has a loose porous structure as shown in Fig. 1.



Fig. 1 (a) EG sheet, (b) EG sheet

2.3 Preparation of the composite PCMs

The composite PCMs are prepared through traditional physical adsorption method. Firstly, the solid PA is placed in a thermostat water bath at a constant temperature of 80 °C and completely melte after 30 min. Secondly, the AIN nanoparticles are manually stirred into liquid PA. Due to the density difference, it is founded that the extra nano-AIN particles would be deposited in the lower area of the vessel. Therefore, during the preparation of PA/AIN composites, ultrasonic vibration is

employed to uniformly distribute the nanoparticles. Furthermore, using ultrasonic vibration could speed up the dispersion of nanoparticles in liquid paraffin wax and be conductive to the exclusion of air in liquid during the preparation process. The mixture is then transferred to a stirrer with a beaker, prepared to 80 °C in a water bath, stirred, and the desired amount of EG is added in stage. After adding the graphite, stirring is continued for 30 min to ensure the expanded graphite to absorb all of the paraffin. Fig. 2 (a) and (b) show the powder and block sample of EG/PA/AIN composite PCM.



Fig. 2 EG/PA/ALN composite PCM. (a)Powder sample. (b)Block sample

The procedure of making EG/PA composites is identical to that of making EG/PA/AIN composites, except that nanoparticles are not incorporated. Similarly, AIN/PA PCMs are prepared according to the above method.

The mass fractions of the composite PCMs are shown in Table 1 $\,$

Table 1

Mass fractions of each component in different samples.

Samples	EG(wt.%)	PA(wt.%)	AlN(wt.%)
SO	0	100	0
S1	0	98	2
S2	0	94	6
S3	7	93	0
S4	7	90	3
S5	8	92	0
S6	8	90	2
S7	9	91	0
S8	9	90	1

3. CHARACTERIZATION

3.1 Thermal conductivity

A test device based on the principle of the steady heat flow method is used to measure the thermal conductivity of composite samples at 25°C, and the experimental test system is shown in Fig. 3. The thermal conductivity of the material is obtained by measuring and calculating the temperature gradient of the sample at steady state [10]. The thermal conductivity is identified using the Fourier's law.



Fig. 3 Physical diagram of the experimental test

3.2 Differential scanning calorimetry

Specific heat capacities are measured by differential scanning calorimetry (DSC, Q2000 Instruments, TA Inc., USA). In this paper, the trilinear method is used for the specific heat measurement of materials, which is defined as the specific heat analysis of three heat flow curves with identical temperature programs. The specific heat capacity of the unknown sample can be calculated by comparing the DSC curves of the standard sample with known specific heat capacity and the sample to be measured with unknown specific heat capacity. Sapphire is used as the standard sample in the experiment.

The measurement procedure is isothermal at 10 °C for 10 min, ramped up to 90 °C at a heating rate of 5 °C/min, and isothermal at 90 °C for 10 min.

4. RECULTS AND DISCUSSION

4.1 Thermal conductivities of composite PCMs



Fig. 4 Thermal conductivities of PA and PCMs

Fig. 4 shows the thermal conductivity of different samples. The thermal conductivity of pure PA is 0.35, which is a very low value for practical applications. When

EG and nano-AIN are added, the thermal conductivity of the composite PCM is significantly increased.

As shown in Fig. 5, the ratio of $\lambda_{PCM}/\lambda_{PA}$ is used to represent the increment of thermal conductivity for composite PCM compared to PA. The thermal conductivities of composite PCMs are 6.4-11.8 times that of PA.

Comparing the thermal conductivities of EG/PA PCMs (S3, S5, S7) and EG/AIN/PA PCMs (S4, S6, S8), it can be found that the presence of nano-AIN can further enhance the heat transfer capability of the PCMs at the same EG content. The thermal conductivity of PCM with added AIN nanoparticles increases linearly with increasing the amount of nanoparticles compared to PCM without AIN nanoparticles. The thermal conductivity increases by 5.5%, 6.1% and 7.8% when the mass fraction of AIN nanoparticles is 1%, 2% and 3%, respectively.



Fig. 5 Ratio of thermal conductivity of PCMs to PA

When the percentage of total fillers is 10%, the higher the mass fraction of EG, the higher the thermal conductivity of PCM. The thermal conductivity of S8 is 41.8% higher than that of S4. This is because the nano-AlN is scattered in the matrix material as particles with a diameter of 40 nm. The microscopic structure is not favourable to the creation of heat conduction routes. However, EG has a worm-like porosity structure macroscopically, and the higher the EG concentration, the easier it is to form more thermal conduction channels in the composite. As a result, when the overall filler content is the same, raising the fraction of EG is more favourable to improving the thermal conductivity of the PCMs than raising the fraction of nano-AlN.

4.2 Specific heat capacities of composite PCMs

The variation of the specific heat capacities of PA and PCM with temperature are shown in Fig. 6. In solid

and liquid states, the specific heat capacities of all PCMs increase slowly with increasing temperature. The specific heat capacities of all PCMs in liquid state is higher than that in solid state.

By comparing the specific heat capacities of S3, S5 and S7 it can be found that the effect of EG content on the specific heat capacities of the composites is irregular. The average specific heat capacity of the composites increases at first and then decreases with the increase of EG. This is because PA can be adsorbed in the pores of EG by capillary action, and when the content of EG is low, the dispersion of EG in PA leads to an increase in the specific heat of the composite. When the content of EG exceeds 8%, its thermal conductivity in PA is higher due to the staggered distribution of EG, and the specific heat of the PCM decreases again.



Comparing the specific heat capacities of PA and PA/ALN PCMs (S1, S2) it can be found that when the content of ALN nanoparticles is 2%, the specific heat capacity of the composite is similar to that of paraffin wax. However, when the mass fraction of AlN nanoparticles in ALN/PA PCMs is 6%, the specific heat capacity of ALN/PA PCM increases by 16.07% compared to that of PA. A possible explanation is based on the expectation that the specific heat of the nanoparticles will be accompanied by an abnormal increase. The existence of a great interfacial thermal resistance between PA and nano-AlN may increase the thermal storage potential of the PCMs. This interfacial thermal resistance (known as Kapitza resistance) is due to the high surface area per unit mass [11].

As shown in Fig 6, comparing the specific heat capacities of EG/PA PCMs (S3, S5, S7) and EG/PA/ALN PCMs (S4, S6, S8). The specific heat capacity of the material with 1% and 2% nano-AIN decreases by 8.69% and 13.95%, respectively. But the specific heat capacity

of the material increases by 10.93% with 3% nano-AIN. From the above analysis, it can be seen that when the proportion of total fillers is 10%, the higher the mass proportion of nano-AIN (greater than 3%), the more conducive to improving the specific heat capacity of PCMs.

The theoretical value of the specific heat capacity of the composite can be calculated by equation (1).

$$C_P = \phi_{PA} C_{P,PA} + \phi_{EG} C_{P,EG+} \phi_{ALN} C_{P,ALN} \tag{1}$$

where C_P (J·g⁻¹·K⁻¹) is the specific heat, \emptyset is the volume fraction. Subscripts PA, EG and ALN denote paraffin, expanded graphite and nano-AlN, respectively. Fig. 7 shows the experimental and calculated values of specific heat capacity of PCMs at 85 °C.



Fig. 7 Experimental and calculated values of specific heat capacity of PCMs

The specific heat capacities of EG and AIN are both around 0.7. According to the mixing law, under the thermodynamic equilibrium condition, the addition of EG and nano-AIN will lead to the decrease of specific heat of the PCM. The more filler content, the more obvious the decrease of specific heat of the composite. But it is worth noting that the experimental values of specific heat capacities of S1, S2, S3, S4, and S5 are higher than their theoretical values.

The specific heat capacities of S2, S3, S4 and S5 in the materials prepared in this work are higher than that of PA. The increase in specific heat capacity increases the sensible heat storage capacity, which compensates for the decrease in latent heat of the composites due to the addition of thermally conductive fillers.

CONCIUSIONS

In this paper, PCMs of different compositions are obtained by adding EG and nano-AIN to PA, and the thermal conductivities and specific heat capacities of the prepared samples are experimentally investigated. The main conclusions are as follows:

(1) The thermal conductivities of the prepared PCMs are 6.4-11.8 times that of PA, and the thermal conductivity of PCMs rises as the EG and nano-AIN content increases. At the same EG content, the presence of nano-AIN can further enhance the heat transfer ability of the composite phase change materials.

(2) The specific heat capacities of the materials containing 1% and 2% nano-AIN decreased by 8.69% and 13.95%, respectively. However, the specific heat capacity of the material with 3% nano-AIN increased by 10.93%. When the total filler ratio is 10%, the higher the mass proportion of nano-AIN (greater than 3%), the more favorable it is to increase the specific heat capacity of PCM.

(3) The mechanism of the effect of nanoparticles and EG on the specific heat of phase change materials is still unclear, and further theoretical research and experimental verification are needed in this regard.

ACKNOWLEDGEMENT

This work was supported by the National Key Research and Development Program of the 13th Five-Year Plan of China (No. 2019YFB1501805).

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