Experimental study on the thermal performance of graphene and exfoliated graphite sheet for thermal energy storage phase change material

Xia Liu, Zhonghao Rao[*]

School of Electric Power Engineering, China University of Mining and Technology, Xuzhou 221116, China

ABSTRACT

In this paper, in order to enhance the thermal performance of paraffin in thermal energy storage, the graphene and exfoliated graphite sheet have been mixed with the paraffin to prepare composites. After the stability tests of dispersion, the scanning electron microscope (SEM), Fourier transform infrared spectroscope (FTIR), thermal conductivity analysis, differential scanning calorimeter (DSC) and thermogravimetric analyzer (TG) are applied to characterize the microstructure, chemical structure, thermal conductivity, enthalpy and stability of the materials, respectively. The results indicated that the thermal conductivity was able to be increased greatly with graphene or exfoliated graphite sheet. With the same mass fraction, the thermal conductivity of paraffin/graphene composite was greater than that of paraffin/exfoliated graphite sheet composite. Furthermore, when the mass fraction of graphene or exfoliated graphite sheet varied between 0–2.0 wt.%, the enthalpy of phase change material (PCM) composites rose firstly and then dropped down.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Phase change material (PCM) is able to be used in the thermal energy storage (TES), which has received great attention in recent years [1–4]. Besides, the temperature of PCM varies a little during the phase change process, including the melting process (heat absorbing) and solidification process (heat releasing). PCM can be classified into two major categories: inorganic PCM and organic PCM [5]. There are several kinds of inorganic PCM, including salts, salts hydrates, metals and alloys. Fatty acids/esters, polyalcohol and paraffin are treated as organic PCM [5]. However, resulting from the low thermal conductivity, most of the PCMs can't reach the demand of TES. Consequently, the thermal performance of PCM is necessary to be enhanced.

There are three methods to enhance the thermal conductivity of PCM: a. adopt enhanced heat transfer surface [6,7]; b. enhance the uniformity of the heat transfer process [8,9]; c. improve PCM thermal performance. The thermal properties of PCM are able to be enhanced by adding additives with high thermal conductivity, such as metal (e.g. nano-metal) [10–12], oxide class(e.g. titanium dioxide) [13,14] and graphite class (e.g. natural graphite) [15–17].

To enhance the thermal conductivity of shape-stabilized PCM effectively, Zhang et al. [18] have prepared nine kinds of composite PCM. They found that adding graphite could enhance the thermal properties mostly. Furthermore, when graphite content was 20 wt.%, the thermal conductivity was increased to 0.482 W m^{-1} K^{-1}, which was increased by as large as 221.4% [18]. In addition, with the same percentage of graphite (20 wt.%), the thermal conductivity of lithium nitrate composites has been increased by 426.53% [19]. Vitorino et al. [20] proved that the thermal properties of composites was approximately linear growth with graphite content.

Among the organic PCMs, the paraffin is of importance to TES since its excellent properties: large latent heat, no phase segregation, low cost, non-toxic and no corrosive [21–23]. Furthermore, no degradation of thermal properties was observed after several melting/solidification cycles [13]. However, the thermal conductivity of paraffin is low as well. In order to enhance the thermal performance of paraffin, two kinds of material with high thermal conductivity can be considered as additives, the graphene and exfoliated graphite sheet.

As one of the graphite, exfoliated graphite sheet and graphene have attracted more and more attentions due to their excellent thermal properties, Tao et al. [24] presented that graphene was the best material to enhance the thermal performance. When the graphene was 0.1 wt.%, 0.5 wt.%, 1.0 wt.%, 1.5 wt.%, 2.5 wt.%, the thermal conductivity has been enhanced by about

8.01%, 15.54%, 26.11%, 27.73%, respectively. Fan et al. [25] stated when the mass fraction of graphene was 3 wt.%, the thermal conductivity was 2 times higher. In Ref. [26], the thermal conductivity of palmitic acid/graphene nanoplatelets composite has been increased by 800% compared to that of original material. Furthermore, Silakhori et al. [27] proved that the thermal conductivity of palmitic acid/polypyrrole/graphene nanoplatelets form-stable PCM was 38.7% higher than that of palmitic acid particles and 34.3% higher than that of palmitic acid/polypyrrole form-stable PCM. Zeng et al. [28] added 7.87 wt.% of the exfoliated graphite sheet to the palmitic acid/polyaniline composite, and the thermal conductivity was 237.5% higher. Kalaitzidou et al. [29] reported that when the volume fraction of exfoliated graphite sheet was 25%, the thermal conductivity had reached 6 times of the raw material. Moreover, Xiang and Drzal [30] proved that the thermal conductivity was associated with the particle size of exfoliated graphite nanoplatelets.

The comparisons of thermal properties between paraffin/exfoliated graphite sheet composite and paraffin/graphene composite have been considered in this paper. The PCM composites are prepared in five kinds of mass ratio. The tests of morphology structure, chemical structure, latent heat and thermal conductivity were investigated in detail.

2. Experiments

2.1. Materials

The paraffin, which was purchased from Shanghai Joule wax Co., Ltd, China, was chosen as PCM. Two kinds of material with great thermal conductivity have been chosen as additives. One was the graphene ($3000–5000\,W\,m^{-1}\,K^{-1}$), which was obtained from Ninjing SCF Nanotech., Ltd, China (purity exceeding 99.5%). Another was the exfoliated graphite sheet ($300–400\,W\,m^{-1}\,K^{-1}$) by home-made, which was prepared from expanded graphite (EG). Furthermore, the EG was formed from the graphite powders (obtained from Qingdao Tianheda Graphite Co., Ltd, China) through microwave method. During the preparation of exfoliated graphite sheet, the absolute ethyl alcohol (C_2H_5OH, analytically pure, Shanghai Zhongqin Chemical reagent Co., Ltd, China) was used as solvent. The surfactant A (derived from Shanghai Lengfeng Chemical reagent Co., Ltd, China) and surfactant B (purchased from Tianjin kermel Chemical reagent co., Ltd, China) were applied to increase the stability of composites.

2.2. Preparations of the composites

In this paper, EG was used to form the exfoliated graphite sheet by ultrasonic oscillations, which was prepared from graphite powder through microwave method for 1 min. The EG was then added to the mixture of absolute ethyl alcohol and deionized water with the ratio of 3:2. After that, the solution was under ultrasonic vibration for 50 h. Finally, the filtration, washing, drying of solution were conducted to form exfoliated graphite sheet.

The preparation of paraffin/exfoliated graphite sheet composites were similar with that of paraffin/graphene composites. First of all, the paraffin was baked in the drying oven for 6 h. And then the paraffin was heated until completely melting (liquid phase) at thermostatic water bath. The melting state was kept for 30 min. Then the appropriate surfactant A, surfactant B and high-thermal-conductivity materials were added into the molten paraffin. Based on the work of Tao et al. [31], the effects of surfactant on enthalpy could not be ignored. In order to remove the effect during the comparisons, the ratio of paraffin, surfactant A and surfactant B was kept as 100: 3: 3. Then, the variation of enthalpy was only resulted

from the additives. The mixture was stirred with a magnetic stirrer for 3 h. Finally the composite material was natural cooled in room temperature.

2.3. Characterizations

The morphologies of EG, exfoliated graphite sheet, graphene and composite material were investigated by means of a scanning electron microscope (SEM, FEI Quanta TM 250). Before the examinations, all samples were coated with a thin layer of gold. Fourier transform infrared spectroscope (FTIR) were applied to determine the chemical structure of composites. Thermal conductivity of composites at 20 °C was measured by means of steady-state heat flow method using the thermal conductivity tester (DRX III, Xiangtan Instrument Manufacturing Co., Ltd, China), where the error was ±3%. The latent heat of paraffin, paraffin/graphene composites and paraffin/exfoliated graphite sheet composites were obtained by differential scanning calorimeter (DSC, Q100, Ninjing dazan institute of electrical and mechanical, China), which worked in a nitrogen atmosphere with a linear heating rate of 5 °C min^{-1}, the nitrogen flow rate was 60 ml min^{-1}. The thermal stability of paraffin, paraffin/graphene composites and paraffin/exfoliated graphite sheet composites were obtained by thermogravimetric (TG) analysis, in a nitrogen atmosphere with a linear heating rate of 10 °C min^{-1}. Furthermore, the nitrogen flow rate was 80ml min^{-1} and the test temperature range was 30 °C–600 °C.

3. Results and discussions

3.1. The morphology structures of additives

In this section, the morphology structures of the graphene and exfoliated graphite sheet have been analyzed, as presented in Fig. 1. It could be observed from Fig. 1(a) that the raw expanded graphite was similar to worm-like structure. Moreover, a large amount of extremely thin flake in worm-like expanded graphite could be clearly observed at higher magnification imaging. Fig. 1(b) showed the morphology structure of exfoliated graphite sheet, which was analogous to a scrap of paper. The morphology structure of graphene was shown in Fig. 1(c). Comparing with present exfoliated graphite sheet, the larger layer-structure and tortuosity were obtained for graphene.

3.2. The dispersion stability of composites

In order to achieve better stable dispersion of graphene and exfoliated graphite sheet in paraffin, the composite surfactant was added to the composites. Fig. 2 showed the liquid dispersion stability of paraffin/graphene composites at 75 °C hot water bath which ensured that composites was kept in liquidus phase. Three tubes were filled with different mass fraction of paraffin/graphene composites. Moreover, the ratio of paraffin: Surfactant A: Surfactant B was kept as 100:3:3. Obviously, no stratification appeared until 305 min at high temperature. This indicated that adding surfactant was able to increase the stability of composites. Moreover, more than 50 times cyclic heating and cooling tests have been conducted to ensure the dispersion stability and thermal properties.

3.3. The morphology structures of composites

Fig. 3 presented the SEM photographs of the composites. Fig. 3(a) and (b) were the morphology structures of paraffin/graphene composites. Fig. 3(c) and (d) were the morphology structures of paraffin/exfoliated graphite sheet composites. It was easily obtained that graphene and exfoliated graphite sheet were uniformly distributed in the paraffin from Fig. 3(a) and (c). The