



Preparation and thermal properties of palmitic acid/polyaniline/exfoliated graphite nanoplatelets form-stable phase change materials



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HIGHLIGHTS

- xGnP is applied to improve the thermal conductivity of PANI based form-stable PCMs.
- The thermal conductivity of the composite PCM is enhanced for 237.5% to 1.08 W/(m K).
- The lowest thermal energy storage capacity of the composite PCM attains 157.7 J/g.

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ABSTRACT

Exfoliated graphite nanoplatelets (xGnP) were applied to enhance the thermal conductivity of polyaniline (PANI) based form-stable phase change materials (PCMs). The xGnP was first dispersed in palmitic acid (PA) uniformly under the assistance of ultra-sonication. The xGnP/PA mixture was then applied to prepare PA/PANI/xGnP form-stable PCMs, in which PANI was obtained by means of surface polymerization of aniline and acted as supporting material. The content of PA in the prepared form-stable PCMs was fixed as 75 wt%. The structure, thermal energy storage properties and thermal conductivity of the PA/PANI/xGnP form-stable PCMs were investigated. The results showed that the thermal conductivity of the prepared form-stable PCMs could be greatly improved by xGnP while the thermal energy storage capacity was maintained. The thermal conductivity and thermal energy storage capacity of the PA/PANI/xGnP form-stable PCM doped with 7.87 wt% of xGnP could attain 1.08 W/(m K) and 157.7 J/g, respectively. The thermal conductivity was 237.5% higher than that of PA/PANI form-stable PCM. The prepared PA/PANI/xGnP form-stable PCM is expected to exhibit better performance in solar thermal energy applications.

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1. Introduction

The utilization of renewable energy has been the central issue of the world in the last decades due to the environment concerns and the depletion and high price of fossil fuel. Solar energy is the most important renewable energy as it is inexhaustible, abundant and clean. Solar energy can be utilized by means of solar-thermal, solar-electrical and solar-chemical conversion [1], among which the solar-thermal and solar-electrical conversion have been in real utilization [2] while the solar-chemical conversion is now being drastically researched in laboratory all over the world [3]. Solar-thermal applications possess the advantages of high photo-thermal conversion efficiency [1] and can be done on a small scale without expensive equipment. However, the fluctuation of solar radiation,

which is resulted from the seasonal and climatic variation, makes thermal energy storage system indispensable in solar thermal energy applications.

Phase change materials (PCMs) are latent heat energy storage materials that possess the advantages of high storage density in small temperature intervals [4–5] and can be applied to store thermal energy collected from solar radiation [6]. Most of the naturally existed materials that can be applied as PCMs are solid–liquid PCMs. Solid–liquid PCMs store or release thermal energy by changing their phases between solid and liquid states. As far as the practical application is concerned, it is worthwhile to transform solid–liquid PCMs into form-stable PCMs. Here the form-stable PCMs are composite materials that contain solid–liquid PCM (thermal energy storage material) and supporting material (maintains the solid shape of the form-stable PCM) [7]. During the last decade, a lot of materials have been utilized to prepare form-stable PCMs. Recently, Kenisarin and Kenisarina [8] have summarized the state of investigations and developments of

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form-stable PCMs. The solid–liquid PCMs in form-stable PCMs are mainly organic compounds, such as paraffin [9], fatty acids [10], fatty alcohol [11,12], polyethylene glycol [13] and their mixtures [14], and in some circumstances inorganic hydrated salt [15] could be applied. The supporting materials are mainly polymers [16] and porous inorganic materials [17].

The thermal conductivity of PCMs is a key factor that affects their applications. Since higher thermal conductivity results in higher thermal energy storing (releasing) speed and hence higher solar thermal energy utilization efficiency, PCMs with high thermal conductivity are appreciated when they are applied to store thermal energy that comes from solar radiation during sun shining period. Unfortunately, the main disadvantage of polymer-based form-stable PCMs is their low thermal conductivity. Hence, thermal conductivity enhancement is required to improve their performances in solar thermal applications [18]. Numerous methods have been proposed to improve the thermal conductivity of solid–liquid PCMs [18–22]. However, improving the thermal conductivity of polymer-based form-stable PCMs remains a rarely concerned field. Recently, Li et al. [23] reported that expanded graphite can be applied to enhance thermal conductivity of a form-stable PCM. However, the worm-like expanded graphite exhibits relatively large particle size and possesses strong ability to absorb organic materials in its pores. As a result, it is difficult to disperse the worm-like expanded graphite into form-stable PCMs uniformly. This difficulty is more obvious for those form-stable PCMs that the polymerization of monomer to form supporting materials is the key step to prepare them. Exfoliated graphite nanoplatelets (xGnP) are particles that consist of several layers of graphene sheets and possess very high aspect ratio and high thermal conductivity [24]. Since the size of xGnP is much smaller than that of worm-like expanded graphite, it is more conducive to incorporate it with matrix materials to improve the electrical, thermal and mechanical properties of composites materials [25]. Furthermore, it is reported that the thermal conductivity of some PCMs can be greatly improved by xGnP [26,27]. In this paper, xGnP was obtained by means of microwave assisted expansion of expandable graphite and followed by ultra-sonication of the obtained expanded graphite. xGnP was then incorporated with a series of form-stable PCMs in which palmitic acid (PA) and polyaniline (PANI) were applied as solid–liquid PCM and supporting material, respectively. The structure, phase change properties and thermal conductivity of the form-stable PCMs doped with xGnP (PA/PANI/xGnP form-stable PCMs) were investigated.

2. Experimental

2.1. Materials

Expandable graphite with average particle size of 500 μm and expansion ratio of 200 mL/g was supplied by Qingdao Graphite Co., Ltd., China. Aniline was distilled under reduced pressure prior to use. All other reagents were of analytical grade and were used as received without further purification. Deionized water was used throughout the experimental process.

2.2. preparation of xGnP/ethanol suspension

The expandable graphite was dried at 60 °C for 12 h prior to expand. The dried expandable graphite was then radiated for 60 s in a domestic microwave oven (WP750, GALANZ) to obtain expanded graphite (expansion ratio: \sim 200 mL/g). xGnP/ethanol suspension was obtained by ultra-sonicating a mixture of 15 mL ethanol containing a certain amount of expanded graphite for 2 h. Normally, the suspension was directly used to prepare PA/PANI/xGnP form-

stable PCMs. However, in order to investigate the structure and morphology of the prepared xGnP, portion of the suspension was filtered and the xGnP was collected and dried at 60 °C for 48 h.

2.3. Preparation of PA/PANI/xGnP form-stable PCMs

The loading of PA in the prepared form-stable PCMs was set as 75 wt%. A series of PA/PANI/xGnP form-stable PCMs were prepared as follows. 2 g PA was added to the xGnP/ethanol suspension mentioned above. The mixture was further ultra-sonicated at 70 °C for 30 min, followed by the evaporation of ethanol under reduced pressure. To the residue, 100 mL water containing 0.5 g cetyltrimethyl ammonium bromide (CTAB) was added. The mixture was vigorously stirred at 70 °C for 1 h to obtain stable emulsion. To the emulsion, a certain amount of aniline was added and the mixture was stirred for another 30 min. Then the emulsion was cooled to room temperature by cold water bath while the stirring was continued. 10 mL water containing ammonium persulfate (APS) was dropped into the mixture under vigorously stirring to initiate the polymerization. The dropping process was completed within 20 min and the molar ratio of aniline and APS was fixed as 1:1.05. The mixture was stirred for another 12 h, and then was filtrated and washed with water till the filtrate was clear. The filter cake was dried under vacuum at 60 °C for 48 h to obtain the PA/PANI/xGnP form-stable PCMs. The doses of PA, aniline and xGnP in each sample were listed in Table 1 and the PA/PANI/xGnP form-stable PCMs are designated as S1–4. PA/PANI form-stable PCM (designated as PA/PANI) in which the loading of PA was set as 75 wt% was also prepared in the same way except no xGnP was added and the PA was directly mixed with CTAB solution to form a stable emulsion.

2.4. Characterization

FT-IR spectra were recorded on a FT-IR spectrometer (AVATAR-360) using KBr pellet (4000–400 cm^{-1}). The surface morphology investigation was carried out on a scanning electron microscope (SEM, JEOL JSM-6380). Before the SEM investigation, the samples were sputtered with gold. Powder X-ray diffraction (XRD) experiments were performed on a Rigaku D/max-gb X-ray diffractometer with a monochromatic detector. Copper Ka radiation was used, with a power setting of 30 kV and 30 mA, and a scanning rate of 5°/min.

Differential scanning calorimeter (DSC, TA, Q2000) was used to investigate the thermal energy storage properties of the prepared form-stable PCMs from 20 to 90 °C with the heating rate of 10 °C/min in nitrogen atmosphere. The thermal stability of the samples was characterized by means of thermogravimetry (TG) on a thermogravimetric analyzer (NETZSCH STA 409 PG/PC) from room temperature to 800 °C with the heating rate of 10 °C/min and N_2 as carrier gas. The thermal conductivity of the samples at room temperature was measured by means of steady-state heat flow method using a thermal conductivity tester (DRX-II-RW, Xiangtan Huafeng Instrument Manufacturing Co., Ltd., Hunan, China). Before measurement, the samples were grinded and pressed under 10 MPa to obtain discs ($\Phi = 30$ mm). The hot plate of the tester was set as 35 °C and the cold plate was cooled by water of 15 °C. A disc was mounted between the two plates. The thermal conductivity of the disc was measured when the temperature of the two plates reached stable for more than 1 h.

3. Results and discussion

3.1. Preparation and characterization of xGnP

Microwave assisted expansion of expandable graphite possesses the merits of quick heating process and high energy

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