Energy Conversion and Management 103 (2015) 251–258

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Tunable thermal conduction character of graphite-nanosheets-enhanced composite phase change materials via cooling rate control

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A R T I C L E I N F O

Article history:
Received 9 April 2015
Accepted 21 June 2015
Available online 2 July 2015

Keywords:
Thermal energy storage
Composite PCMs
Thermal conductivity
Enthalpy
Cooling rate

A B S T R A C T

This work is concerned with the influence of cooling rates on the thermal conduction behavior of nano-enhanced PCMs for thermal energy storage. 2-dimensional graphite nanosheets of different sizes have been applied to prepare the eicosane-based composite PCMs. Comprehensive measurements on the thermal storage properties of the prepared composite PCMs were also performed considering the factors including particle size as well as loading level. Results strongly revealed the tunable thermal conduction behavior of the solid-state composite PCMs versus cooling rate. As the cooling rate was ascended from 2.03 to 30.94 °C/min, more than 25% drop of the solid-state thermal conductivity was observed for the samples containing graphite nanosheets. Besides a percolation threshold around 1 wt.%, measured thermal conductivities increased linearly with the particle concentration, achieving the highest value of 1.57 W/m K by GNS-30 at 5 wt.%. Moreover, the graphite nanosheets with a larger size were found to cause higher improvement in thermal conductivity, and also the relatively higher viscosity of PCM suspensions. DSC results indicated the decrease in latent heat capacity of samples is negligible after the incorporation of graphite nanosheets.

1. Introduction

Currently, surging proportion in total power generating capacity of renewable energies, such as solar and wind energies, greatly raises the significance of grid-scale storage to minimize the generation dispatch cost and improves system reliability in an overload or contingency situation [1]. There is an abundant array of energy storage innovations including electricity storage and pumped hydro storage, driven chiefly by the grid-scale utilization of intermittent renewable-energy sources [2]. For instance, thermal energy storage (TES), or thermal storage, is one of the efficient and low-cost approaches available that cater to end-use energy demand through energy redistribution [3]. Compared with the sensible thermal storage, a latent thermal energy storage (LTES) system incorporating phase change materials (PCMs) exhibit a much higher energy storage density, and thus make renewable energy resources more attractive and easier to integrate into power distribution networks [4,5]. However, questions still remain on how fast the charging/discharging process will be, thereby the approaches concerning the applicability of advanced materials are urgently required.

Graphene is ideally suited for implementation in multiple energy storage applications by chemical, electrochemical and thermal means due to its exceptional attributes, such as lightweight, large surface area, and excellent electrical/thermal conductivities [6]. It has been widely reported that a family of graphene-related materials, including monolayer graphene, double and few (<10) layer graphene, exfoliated graphite and graphene nanoplatelets (GNPs), serve as excellent thermal conductivity reinforcers toward the preparation and utilization of PCM-based composites for TES systems [7–19]. According to the investigations noted above, the key to enhancing the thermal conductivity of PCMs by using graphene-related nanomaterials is optimizing the particle morphologies so as to increase the specific surface areas. Xiang and Drzal [20] have reported that the xGNPs with lateral size of about 15 μm is superior to those with 1 μm in improving the thermal conductivity of paraffin-based composites. A similar conclusion regarding the particle size was presented by Debelak and Lafdi [21] who adopted exfoliated graphite nanosheets as fillers to enhance the thermal conductivity of a resin. Yu et al. [22]

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http://dx.doi.org/10.1016/j.enconman.2015.06.062
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compared the performance of epoxy-based composites containing graphite nanoplatelets with controlled aspect ratios ranging from 30 to 200, and found the nanoplatelets with the highest aspect ratio led to the greatest thermal conductivity enhancement. Nevertheless, there is still lack of studies focusing on the quantitatively geometric influences of 2-dimensional carbon nanomaterials on the thermal conductivity of composite PCMs. Additionally, a high cooling rate under rapid and intense heat loads would sharply decrease the crystallinity, thus result in the decrease of latent enthalpy [23]. Similarly, the cooling-rate-dependence crystal structure of PCMs would further affect the heat diffusion across particle-PCM interface, a strong need exists for investigating the effective thermal conductivity under different cooling conditions [24,25].

In this study, ball-milling method is used to exfoliate expanded graphites (EG) into a series of graphite nanosheets, which served as nanofillers in the preparation of composite PCMs. The effects of the solidification process on the solid-state thermal conductivity of composite PCMs are investigated under various cooling rates. Meanwhile, other thermal energy storage properties of the prepared samples including phase change temperature, latent heat of fusion, dynamic viscosity and heat transfer efficiency are also examined.

2. Experimental

2.1. Materials

Graphite nanosheets have been prepared through thermal expansion, ball milling, filtration and sonication as illustrated in Fig. 1. The starting graphite powders provided by Qingdao Graphite Co., Ltd., China were used to yield EG using a microwave oven with an overall power of 800 W. In order to obtain graphite nanosheets with different sizes, the suspensions of *N*-Methyl-2 pyrrolidone (NMP) in the presence of the prepared EG were treated by means of ball milling for 30, 60 and 180 min, respectively. The NMP played a vital role in the ball milling process by reducing the energetic penalty for mechanical exfoliation and avoiding graphite nanosheets from re-agglomeration [26]. After that, the graphite nanosheets were filtrated repeatedly using DI water, followed by drying at 80 °C in a vacuum oven for 48 h. Eicosane (purity > 99 wt.%) with the melting point near 37 °C was supplied by the TCI Co., Ltd., China and used as PCM in present work. The prepared graphite nanosheets were dispersed in the molten eicosane at different contents (1, 2 and 5 wt.%) by stirring and sonication for 10 h. Finally, the liquid mixture was injected into a cylindrical mold with a diameter of 3 cm and a height of 1.5 cm and then cooled down to ambient temperature.

2.2. Material and morphology characterizations

The crystalline structure of the prepared graphite nanosheets was identified using an X-ray diffractometer (XRD, X'Pert PRO) with Cu Ka X-ray radiation ($k = 0.154$ nm). The diffraction value was recorded in the 2θ range of 10–80° with a step size of 0.017°. Scanning electron microscope (SEM, Hitachi SU-70) and transmission electron microscope (TEM, Hitachi HT7700) were used to image the actual morphologies of EG and graphene nanosheets. Following a spin coating procedure, atomic force microscopic (AFM) image of graphite nanosheets was collected by a Vecco Dimension Edge AFM using Si tips (MPP 11100-10) under a tapping mode. The morphology of crystalline PCMs under various cooling rates was determined by microscopic observations (Nikon, Eclipse E600W POL). Fourier transform infrared spectroscopy (FTIR) characterization was carried out at ambient temperature using a FTIR spectrometer (Nicolet, Magna IR 560). Thermogravimetric analysis (TG) was carried out on a TGA analyzer (TA Instruments Co, TGA Q5000) in an air atmosphere. Raman characterization was performed using a LabRAM ARAMIS, Horiba Jobin Yvon with a 532-nm-wavelength laser.

2.3. Thermal storage performance tests

In order to explicitly regulate the cooling rate of samples, two water baths at different constant temperatures were introduced to serve as cold and hot sources. The high-temperature water bath was set at 60 °C and the low-temperature one were set at 10 and −10 °C, respectively. A cylindrical mold containing the sample of nearly 15 mL was first placed into a specially designed aluminum container that had been immersed into the high-temperature water. It is noteworthy that the top of the mold was covered with an insulator to assure good temperature homogeneity inside the sample. After temperature equilibrium was achieved for more than 30 min, the sample-containing mold was quickly transferred to another aluminum container in the low-temperature water. In an extreme case, a quenching process using liquid nitrogen as the cold source was involved to attain a rapid cooling rate. During the whole process as mentioned before, temperature variation of samples was monitored by a RTD (PT100) that had been calibrated to an uncertainty of ±0.2 °C. Thermal conductivity measurement was carried out at room temperature (25 ± 1 °C) by a Hot Disk Thermal Constants Analyzer (Hot Disk AB, TPS 2500S), which is based on a transient plane source (TPS) technique. The heating power and heating time applied in the measurements were 200 mV and 5 s, respectively. The claimed accuracy (±3%) of the TPS instrument was verified with highly purified ethylene glycol. The rheological analysis of the suspensions containing graphite nanosheets was made on a rotary rheometer (Brookfield, DV-3T) with the aid of a water-jacketed adaptor. The accuracy (±1%) and reproducibility (±0.2%) at the full-scale range of the rheometer were validated with a Brookfield standard fluid prior to measurement. The energy storage performance including enthalpy and phase change temperature was determined using a differential scanning calorimeter (Netzch, DSC 200 F3 maia) under protection of nitrogen. A ramping/cooling rate of 5 °C/min between 10 °C and 70 °C were used for all runs. The DSC instrument was calibrated with a standard high-purity indium specimen before test. In order to erase prior thermal history, each sample (8–12 mg) was heated to 70 °C at 10 °C/min and kept for 10 min. The actual heat transfer efficiency of the prepared specimens was evaluated by the heat storage and release test, the detail of which has been reported in our previous work [27]. It is noted that multiple

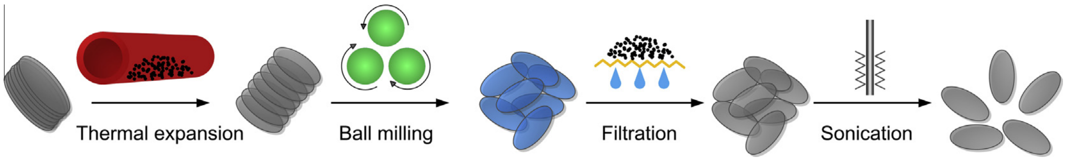

Fig. 1. Schematic diagram of graphite nanosheets preparation.