Hybrid network structure of boron nitride and graphene oxide in shape-stabilized composite phase change materials with enhanced thermal conductivity and light-to-electric energy conversion capability

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ABSTRACT

Graphene oxide (GO) and boron nitride (BN) are introduced into polyethylene glycol (PEG) as supporting materials and thermally conductive fillers to improve shape-stability and thermal conductivity. The obtained PEG/BN/GO composite phase change material (PCM) with 4 wt% GO and 30 wt% BN exhibits a thermal conductivity as high as 3.00 $W\,m^{-1}\,K^{-1}$, 10-fold higher than that of pure PEG. Owing to the hybrid network structure of GO and BN in the matrix, the shape-stability of the composite PCM is greatly enhanced, even when compressed by a constant normal force of 5 N as the temperature rises to 120 °C. Simultaneously, the thermal energy storage density of the composite PCM reaches 107.4 $J\,g^{-1}$, which ensures the potential application to realize an efficient light-to-electric energy conversion and storage. The composite PCM maintains stable thermophysical properties and chemical structure after 100 cycles of melting and freezing. The enhanced comprehensive performance of the composite PCMs contributes to enabling their practical application for effective energy conversion, storage and utilization, especially for the lasting renewable solar energy.

1. Introduction

Phase change materials (PCMs) for latent heat thermal energy storage (LHTES) are considered as one of the most promising energy storage techniques to utilize thermal energy from the surrounding environment, solar irradiation, surplus heat, waste heat from industrial processes, vehicles and electronic products, etc [1–3]. Considering the fact that solar energy is the most abundant and lasting renewable source available, the direct conversion of solar energy to thermal energy by means of PCMs has received a great deal of interest in recent years [4–9]. Therefore, the new and meaningful challenge about how to utilize the stored heat from sunlight emerges and is inevitable. The stored heat from a heat source or solar irradiation has been further used to generate electricity and realize heat-to-electric or light-to-electric energy conversion making full use of PCMs associated with a commercial thermoelectric device [2,10]. However, the poor photo-absorption (pale color) of PCMs makes it difficult to directly utilize solar irradiation to drive the PCMs for energy conversion [1]. Additionally, the inherently low thermal conductivity and easy leaking in the melted state of PCMs reduce the heat transfer rates and limit the

practical applications [11,12].

To solve the above drawbacks inherent in PCMs, composite PCMs have been fabricated by introducing various functional materials. Many types of carbon materials, such as carbon nanotubes (CNT) [13,14], expanded graphite (EG) [15,16], and graphene nanomaterials (GN) [11,17–21], have been employed as thermally conductive fillers to enhance the thermal conductivity of PCMs [22]. Similar to carbon materials, boron nitride (BN) served as thermally conductive fillers to improve thermal conductivity of the composites, including composite PCMs and electrically insulating polymer composites with high thermal conductivity, has received significant attention owing to its excellent thermal conductivity, electrical insulating property, stable chemical property and relatively low cost [23–27]. Furthermore, supporting materials, such as GN [12,28–32], EG [33,34], polymers,[35–37], diatomite [38,39], expanded vermiculite [40,41], etc., have been developed to prepare shape-stabilized PCMs [42]. It is worth noting that compared with other supporting materials, graphene oxide (GO) exhibits great potential in fabricating polyethylene glycol (PEG) based shape-stabilized PCMs owing to the strong intermolecular hydrogen bonding interactions between PEG and GO [29,43]. That is to say,

reaching excellent shape-stabilized effect needs less content of GO, which contributes to ensuring relatively high energy storage density for PCMs because less working substance is replaced by the supporting materials. Additionally, GO can also be used as effective photon captor and molecular heater to promote photoabsorption and solar energy conversion for PEG based composite PCMs [44].

In our previous work, BN and BN coated by polydopamine have been verified to be effective thermally conductive filler in PEG matrix for multifunctional composite PCMs with high thermal conductivity [10]. In the current work, BN and GO sheets are adopted to improve the thermal conductivity and photoabsorption of PEG based PCMs simultaneously. Furthermore, adding a small quantity of GO into the PEG/BN composite PCMs greatly promotes the formation of the hybrid network structure of fillers, which endows the composite PCMs with prominent shape-stability even when compressed by a constant normal force of 5 N as the temperature rises to 120 °C, much higher than the melting point (65 °C) of PEG. In addition, the obtained PEG/BN/GO composite PCM exhibits considerable phase change enthalpy as high as 107.4 J g^{-1} and outstanding thermal reliability after 100 melting and cooling cycles. The valid energy storage density ensures a promising application for the composite PCM to realize a direct solar-to-electric energy conversion and storage.

2. Experimental

2.1. Materials

PEG (Mn = 10, 000) was obtained from Aladdin Reagent (Shanghai, China). Natural graphite flakes (NG) with an average particle size of 200 mesh and a purity of over 99.9% and BN powder (10–15 μm, purity > 99%) were purchased from Shenghua Research Institute (Changsha, China) and Qinhuangdao Eno High-Tech Material Development Co., Ltd., respectively. All the reagents including phosphoric acid (H_3PO_4), potassium permanganate ($KMnO_4$), concentrated sulfuric acid (H_2SO_4), hydrochloric acid (HCl), hydrogen peroxide (H_2O_2) and absolute alcohol were purchased from Haihong Chemical Reagents Company (Chengdu, China) and used as received.

2.2. Preparation of composite PCMs

Firstly, GO was prepared from EG powder obtained by thermal expansion of NG with an improved Hummers' method [45]. In brief, a 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (720:80 mL) was added into a three-necked bottle containing EG power (6.0 g). $KMnO_4$ (36.0 g) was slowly added to the mixture in sequence under continuous stirring, while maintaining a reaction temperature at 35 – 40 °C. Subsequently, the resulting mixture was heated to 50 °C and stirred for 12 h. After that the mixture was poured into plenty of ice-water and dropped with a proper amount of 30% H_2O_2 until no bubbles were produced, resulting in a bright yellow color. The mixture was successively washed with HCl and deionized water to remove the metal ions and the acid, respectively, until the pH was neutral. Finally, the solid GO was obtained by vacuum freeze drying.

The composite PCMs were prepared using a facile solution blending. GO was first dispersed in absolute alcohol with ultrasonication (KQ-400KDB, 40 kHz, 400 W) for 1 h. After that BN was added under ultrasonic bath treatment and stirring. When the mixture was heated to 90 °C, PEG power was added into the solution followed by vigorously stirring for 3 h to adequately evaporate the solvent. The GO loading in each sample was maintained at 4 wt% and BN loading was 0 wt%, 10 wt%, 20 wt% and 30 wt%, and the obtained composites were labeled as 4GO, 4GO10BN, 4GO20BN and 4GO30BN, respectively. For comparison, the composite PCMs without GO were fabricated and labeled as PEG, 10BN, 20BN, 30BN in like manner.

2.3. Characterization

Morphologies of samples were examined under a field-emission scanning electronmicroscope (SEM, JEOL JSM-5900LV, Japan) at an accelerating voltage of 20 kV. Fourier-transform infrared (FTIR) spectrum was recorded on a Nicolet 6700 FTIR spectrometer (Nicolet Instrument Company, USA) with a resolution of 4 cm^{-1} using the KBr pellet method (transmission mode). X-ray diffraction (XRD) pattern was collected by A Rigaku UltimaIV diffractometer (Rigaku, Japan) with Cu Kα radiation (λ = 0.15406 nm) at a generator voltage of 40 kV. The phase change temperatures and enthalpies of the samples were measured using a different scanning calorimeter (DSC, TA Q20, USA) at a scanning rate of 10 °C min^{-1} in a purified nitrogen atmosphere. The thermal conductivity measurements were conducted on a Hot Disk Thermal Constant Analyzer (TPS 2500, Hot Disk AB Company, Sweden) by a transient plane heat source method at room temperature. The cylindrical samples (~2.5 mm thick and ~15 mm in diameter) were prepared by compression molding and subsequently polished by sandpaper to ensure good contact between the sample surfaces and the probe. An infrared thermal imager (Fluke Ti27) was used to directly record the temperature distribution in the heat transfer process of pure PEG and the composite PCMs. Dynamic rheological measurements were conducted by using a stress-controlled rheometer (AR 2000, TA Instruments, USA) equipped with parallel-plate geometry (diameter: 25 mm). The frequency sweep was carried out in a frequency range of 0.01–100 Hz with a strain of 0.1%. The diameter and the thickness of disk-shaped samples were ~25 mm and ~1.5 mm, respectively.

2.4. Shape-stabilization test

The shape-stabilization test was performed by the observation of the samples placed on a hot stage with increasing temperature and the dimension change of samples based on the change of gap values, through taking the corresponding digital photographs and the gap value monitoring of the dynamic rheometer, respectively. During the test of change of gap values in the dynamic rheometer, the change was recorded at a heating rate of 2 °C min^{-1} from 35 °C to 120 °C and a constant normal force set to be 5 N. To maintain the normal force at the set value, the gap value will sensitively and automatically adjust with the increase of temperature. If the sample has a poor shape-stability and is easy to leak above the melting point of PEG, the gap value will decrease with increasing temperature. Conversely, the gap value will basically remain invariable. Here, the dimension change (%), a ratio of actual value to initial value for each sample, was defined to reflect the shape-stability of PEG and composite PCMs.

2.5. Light-to-electric energy conversion and storage

The light-to-electric energy conversion was performed using a CEL-HXUV300 xenon lamp (CEAULIGHT, China) with an AM 1.5 filter, a CEL-NP2000 optical power meter (CEAULIGHT, China) and a commercial Seebeck thermoelectric device at room temperature (~ 26 °C), and a Keithley electrometer (2400, Cleveland, Ohio, USA) was used to record the real-time current (*I*). The sample absorbing and collecting heat from simulated light source and a vacuum cup filled with a heat sink under tap water (~ 24 °C) were used as heat and cold sources, respectively.

3. Results and discussion

3.1. Shape-stabilization property

The shape-stabilization properties of PEG and the composite PCMs were first characterized by means of a leakage test. The samples were placed directly on a heating stage with increasing temperature from 30 to 90 °C and each selected temperature was maintained for ~ 10 min,