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Carbon nanotube/paraffin/montmorillonite composite phase change material for thermal energy storage

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ABSTRACT

A composite phase change material (PCM) comprised of organic montmorillonite (OMMT)/paraffin/grafted multi-walled nanotube (MWNT) is synthesized via ultrasonic dispersion and liquid intercalation. The microstructure of the composite PCM has been characterized to determine the phase distribution, and thermal properties (latent heat and thermal conductivity) have been measured by differential scanning calorimetry (DSC) and a thermal constant analyzer. The results show that paraffin molecules are intercalated in the montmorillonite layers and the grafted MWNTs are dispersed in the montmorillonite layers. The latent heat is 47.1 J/g, and the thermal conductivity of the OMMT/paraffin/grafted MWNT composites is 34% higher than that of the OMMT/paraffin composites and 65% higher than that of paraffin.

1. Introduction

Phase change material (PCM) can absorb and/or releasing a significant amount of latent heat due to a phase transition when the phase transition temperature is within a specified temperature range. PCM has achieved wide application in the field of energy storage and thermal insulation, such as building energy (Zhang et al., 2004; Li et al., 2013, 2010), air-conditioning (Harold et al., 1975), solar thermal storage (Cabeza et al., 2007; Schossig et al., 2005; Wu and Fang, 2011; Nithyanandam and Pitchumani, 2014), temperature regulating textiles (Nihal and Emel, 2007; Sánchez et al., 2010) and electronic thermal control (Simone et al., 2008; Huang et al., 2011). Different phase change materials have different phase change temperatures and phase transition enthalpies. Paraffin is perhaps the most common phase change material because of a characteristic of high storage density, minimal tendency to supercool , low vapor pressure of the liquid phase, chemical stability, non-toxicity, and relatively low cost (Wang et al., 2009; Kuznik et al., 2011; Nihal et al., 2011).

Various technologies, including microencapsulation (Su et al., 2007; Cho et al., 2002; Onder et al., 2008; Qiu et al., 2013), adsorption (Zhang et al., 2004), adsorption (Zhang et al., 2004) and intercalation (Fang et al., 2010; Li et al., 2012) are used to synthesize composite PCMs. Composite PCMs synthesized by different techniques have distinct characteristics in thermal, mechanical, and physical properties. Currently, composite PCMs with high thermal performance and durability have become the subject of study (Li et al., 2011; Karaipekli and Sari, 2010; Zhang et al., 2014; Cai et al., 2015).

Montmorillonite (MMT) is a natural layered material and the main ingredient is silicate. The chemical formula of MMT is $A1_2O_3 \cdot 4SiO_2 \cdot 3H_2O$, and MMT is 2:1 type layered silicate – i.e., each unit cell of MMT contains two layers of silicon oxygen tetrahedra and one layer of aluminum (magnesium) oxygen octahedra. The tetrahedra and octahedra are connected through the shared oxygen atoms. The thickness of each layer is 1 nm and the closely packed arrangement forms a highly ordered crystal structure. MMT exhibits poor compatibility with organic molecules because the surface of MMT and the interspace between the layers are hydrophilic. Thus, MMT requires organic modification to form composites with organic components.

The ultrasonic dispersion method has higher intercalating efficiency than other traditional intercalating composite methods, such as the solvent evaporation method and the mechanical intercalated method. It is easy-controlled and environment friendly. The energy consumption can be reduced remarkably (Sato et al., 2008).

In order to improve the shape-stability and thermal properties of PCM, we synthesized OMMT/paraffin/grafted MWNT composite

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PCM by ultrasonic dispersion and liquid intercalation. Cetyl trimethyl ammonium bromide was used in organic modification of montmorillonite. The novelty in the paper is the preparation method of the composite PCM and the formation of the intercalation micro-structure with MMT and MWNT, which lead to the improvement of the thermal properties of PCM.

XRD and SEM were used to characterize the composition and structure of composite PCM. DSC and thermal constant analyzer were used to characterize the thermal properties of the composite PCM.

2. Materials and experimental method

2.1. Materials

Na-montmorillonite (Na-MMT, Zhejiang Fenghong New Material Co.) with purity >88% and CEC: 85 meq/100 g was selected for the experiments. The organic montmorillonite (OMMT) was home-made with Cetyl trimethyl ammonium bromide (Kao et al., 2012). Paraffin with a phase transition temperature of 26 °C (Shijiazhuang Caldecott Phase Change Materials Co., Ltd) and cetyl trimethyl ammonium bromide (CATB, Chengdu Kelong Chemical Reagent Factory, AR) were acquired from commercial sources. Multi-walled carbon nanotubes (MWNT, Shenzhen) were acquired and grafted carbon nanotubes (grafted MWNT) were prepared. A schematic diagram of the grafted MWNT is showed in Fig. 1.

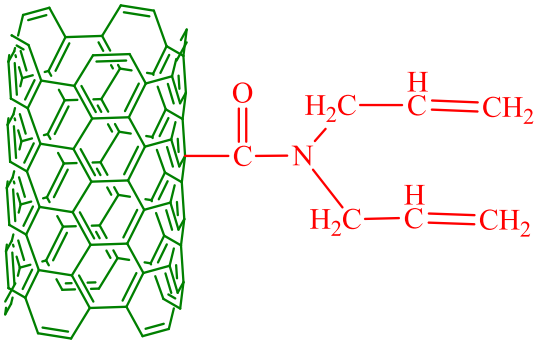

Fig. 1. The schematic diagram of the grafted MWNT.

2.2. Synthesis of OMMT/paraffin composite PCM

Composite PCMs with OMMT/paraffin and OMMT/paraffin/-grafted MWNT were prepared by the procedures described below.

2.2.1. Synthesis of OMMT/paraffin composite PCM

(1) 10 g OMMT was added to ethanol in a three-necked flask, and the solution was stirred at 1500 rpm and 40 °C until uniform to obtain a suspension of OMMT.
(2) 6 g PCM were dissolved in ethanol, and the solution was added to the suspension of OMMT. The mixture was stirred for 10 min.
(3) The mixture was stirred at 75 °C. Ethanol was recycled by condensation in vacuum until completely evaporated.
(4) The product was dried in vacuum at 60 °C for 24 h. The product was ground to obtain the OMMT/paraffin composite PCM.

2.2.2. Synthesis of OMMT/paraffin/grafted MWNT composite PCM

(1) 10 g OMMT was added to ethanol in a three-necked flask. The solution was stirred at 1500 rpm and 60 °C until uniform to produce a suspension of OMMT.
(2) 6 g PCM and 0.16 g grafted MWNT were dissolved in ethanol. The solution was added to the suspension of OMMT and stirred for 10 min. The mixture was placed in an ultrasonic water bath at 60 °C for 30 min. After that, the mixture was placed in a water bath at 75 °C and stirred. Ethanol was recycled by condensation in vacuum until evaporated.
(3) The product was dried in vacuum at 60 °C for 24 h, then ground to obtain the OMMT/paraffin/grafted MWNT composite PCM.

2.3. Characterization and testing

The surface morphology of PCM composites was examined by SEM imaging at 20 kV (Sirion 200, FEI Company, Netherlands). Structural analysis was performed by X-ray diffraction (XRD, Smart Lab 3, RIGAKU, Japan) using a Cu target. Interlayer spacings of the clays were measured before and after intercalation and modification. The enthalpy of the composite phase change was measured by calorimetry (DSC, DSC 200 F3 Maia, NETZSCH, Germany). The enthalpy of composite PCM was characterized by DSC (200 F3 Maia, NETZSCH Co., Germany). The scanning temperature range is from −20 °C to 60 °C. The scanning rate was 5 degree per minute. Finally, thermal conductivity, thermal diffusivity and heat capacity of composite samples were measured using a Hot Disk Thermal Constant Analyser (TPS2500, Hot Disk AB Company, Sweden). The methodology of measurement adopted with the hot disk is the Transient Plane Source Method. The specimen was a cylinder with height of 20 mm and diameter of 30 mm. Two same specimens were piled tightly and a probe with a radius of 3.189 mm was inserted between them. The schematic diagram of the thermal conductivity test is shown in Fig. 2. The heat storage and release properties of composite PCMs were examined by multi-channel temperature recorder (TOPRIE-TP700, Bost, Shenzhen).

3. Results and discussion

3.1. XRD analysis

The X-ray diffraction patterns of Na-MMT, OMMT, OMMT/-paraffin and OMMT/paraffin/grafted MWNT PCMs are shown in Fig. 3. The characteristic peak of the (001) crystal plane of Na-MMT appears at $2\theta = 5.86°$. The layer spacing is calculated according to the Bragg equation (Eq. (1))

$$2d \sin\theta = n\lambda \quad (1)$$

where d is the layer spacing, θ is the glancing angle, λ is the X-ray wavelengths, and n is the diffraction series. When λ is 0.15418 nm and n is 1, $d = 1.508$ nm.

After organic modification with CTAB, the characteristic peak of the (001) crystal plane of MMT shifted to $2\theta = 4.20°$ corresponding to $d = 2.104$ nm. No new diffraction peaks appeared (Fig. 3(b)), indicating that inserting CTAB molecules into MMT layers increased the layer spacing of montmorillonite. The organic modification alters the polarity of interface and the microenvironment of the interlayers. Consequently, the polarity of the interlayers is reduced and the lipophilicity of the interlayers is increased, providing a favorable condition for organic PCM molecules to insert into the MMT interlayers. Fig. 3(c) shows that the (001) peak shifts to $2\theta = 3.06°$, corresponding to $d = 2.88$ nm for OMMT/paraffin, when PCM inserts into the interlayers of OMMNT.

Fig. 3 also shows that the interlayer spacing of OMMT/paraffin/-grafted MWNT composite PCM is 2.91 nm, which is slightly greater than that of OMMT/paraffin, indicating that the grafted MWNT does not insert into the interlayer completely.