



Thermal performance and shape-stabilization of comb-like polymeric phase change materials enhanced by octadecylamine-functionalized graphene oxide

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ABSTRACT

A series of comb-like polymeric phase change materials, composed of poly(ethylene-graft-maleic anhydride)-g-octadecanol (EMC18) and octadecylamine-functionalized graphene oxide (GO-C18) and graphene oxide (GO), denoted as EMC18@GO-C18 and EMC18@GO, respectively, have been prepared through a solution mixing method. The structure, thermal performance, energy storage and release capability, cycle stability are deeply characterized. Shape-stability for EMC18@GO-C18 and EMC18@GO shows a bigger improvement than that of bulk EMC18 because of the framework role of 2D GO nanosheets. At 160 °C, no liquid leakage appears in EMC18@GO-C18, exhibiting a superior shape stabilization temperature to EMC18@GO, which is contributed by its enhanced interfacial compatibility from the introduced octadecyl side chains. Thermal performance shows a highly dependence upon the content of GO or GO-C18 nanofillers, and the thermal cycling stability reaches 500 times. Four thermal cycles are well repeated for the fabric coated by EMC18@GO-C18-2%, and no energy efficiency loses. The maximum temperature difference and thermal buffering time is −15 °C and 375 s at 70 °C working temperature. Good structure stabilization and thermal performance of EMC18 doped by GO-C18 offers a chance to approach the high-efficient thermal energy storage materials.

1. Introduction

Thermal energy storage (TES) materials have attracted an extensive interest in recent years [1–3]. As a green, clean and high efficient TES, phase change materials (PCMs) have been widely developed and designed with the low- and high-molecular weight *n*-paraffin, polyethylene glycol and *n*-fatty acid, etc. [4,5]. These PCMs are highly applied in various fields such as energy-saving buildings [6–8], waste heat recycling [9], thermo-regulated fibers and fabrics [10–12]. However, the problems of the liquid leakage and the worse structure stability limit their further explorations. So, a good structure stabilization followed by a high TES capability is an important issue for PCMs, especially for retaining a balanced energy storage ability and thermal cycling performance.

Recently, many works are focused on preparation of the hybrid composites PCMs with organic and inorganic materials as the supporting matrix/the shape stabilizer. At most, the inorganic porous materials such as diatomite [13,14], silicon nanopowders [15,16], and carbon-based nanofillers (such as graphene [17–19], expanded graphite [20–24], carbon nanotube [25–27], and carbon nanospheres [28] are

widely selected in light of their physical adsorption ability and large surface area. In our previous studies, taking active carbon [29] and porous silicon powder (MCM-41) [30] as the supporting framework, poly(ethylene glycol) alkyl ether/MCM-41 shape-stabilized PCMs are prepared through the physical adsorption technique. However, the existence of confined crystallization, originated from the surface adsorption of nanopores, limits the balance between the energy efficiency and the thermal performance. Recently, 2D-nanosheet framework materials, graphene oxide (GO), have been widely explored as a supporting matrix to prepare the composite PCMs [31–33]. Mehrali et al. reported an enhanced thermal conductivity of palmitic acid doped by graphene nanoplatelets with 300, 500 and 750 m²/g specific surface areas [17]. Qi et al. reported the enhanced form-stability of PEG by doping 4 wt% GO, and no liquid leakage appeared when the temperature increased to 150 °C, demonstrating a good shape stabilized property [34]. Our studies also prove that the incorporated GO nanosheets can effectively improve the shape stability of poly(styrene-co-maleic anhydride)-g-octadecanol (SMAC18) comb-like polymeric phase change material at a 2 wt% loading [35]. However, their interfacial compatibility is worse in light of the weak physical adsorption action. The deposition and

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separation phenomenon occurs during the multiple thermal cycles. Recently, Amir et al. reported thermal conductivity property of alkyl-functionalized GO and analyzed the structure of GO under the varied alkyl chains length [36]. Harshal et al. discussed the lubrication property of lube oil modified by alkylated graphene, and the doped alkylated graphene (0.02 mg/mL) offers a good compatibility with oil, showing a decreased friction and wear performance [37].

By regulating the molecular chain structure, we designed a series of comb-like polymeric phase change materials (CLPPCMs) such as N-alkylated polypyrrole [38], poly(styrene-co-maleic anhydride)-g-alkyl alcohol [39], poly(ethylene-graft-maleic anhydride)-g-alkyl alcohol [40], poly(vinyl alcohol)-g-isocyanate-fatty alcohol [41] and S-octadecylated PVC [42]. Owing to the protection of polymeric backbone, the thermal storage units of alkyl side groups exhibit little volume expansion and no liquid leakage during the phase change process [43,44]. The form-stabilized temperature also gets much enhanced compared with the typical PCMs. To the best of our knowledge, however, little studies report a synergistic application of alkylated GO as interfacial modifier and shape stabilizer for CLPPCMs. Through the molecular chain interaction between the alkyl chains, an obvious enhanced shape stability and cycling performance is well approached in this paper.

Herein, in this paper, series of comb-like polymeric phase change materials, composed of poly(ethylene-graft-maleic anhydride)-g-octadecanol (EMC18) and octadecylamine-functionalized graphene oxide (GO-C18) and GO, denoted as EMC18@GO-C18 and EMC18@GO, respectively, have been prepared through a solution mixing method. The comparison of GO and GO-C18 nanosheets on the structure, shape stability, thermal behavior and phase change energy of EMC18 are characterized in depth. And, the shape-stabilized mechanism and the thermal energy storing/releasing behavior are also discussed from the aspect of the molecular interaction and the physical adsorption role.

2. Experimental

2.1. Materials

Poly(ethylene-graft-maleic anhydride)-g-octadecyl (EMC18) ($M_w = 13,829$, $M_w/M_n = 3.5$) comb-like polymer was fabricated in our lab [40]. Natural graphite powers (325 mesh) were supplied by Qingdao Laixi Graphite Co. Ltd. Octadecylamine (ODA), toluene, and ethanol were provided by Tianjin Guangfu Fine Chemical Research Institute and used as received.

2.2. Preparation of GO and GO-C18 nanosheets

Firstly, GO was prepared through the natural graphite powers via the modified Hummers method. Then, octadecylamine (ODA) functionalized GO (GO-C18) was obtained by a facile solution method. The dispersed ODA in ethanol solution was slowly dropped into GO solution (1 mg/ml) under a strong ultrasonication for 0.5 h. After that, GO/ODA ethanol solution was stirred at 60 °C for 12 h under N_2 , showing a color change to the black. Subsequently, the obtained raw GO-C18 products were washed with hot ethanol for several times to remove the residual ODA, and then the vacuum-filtrated GO-C18 was freezing-dried.

2.3. EMC18@GO and EMC18@GO-C18 composite PCMs

The preparation of EMC18@GO and EMC18@GO-C18 composite PCMs was described as follows. GO-C18 nanosheets were firstly dispersed in ethanol via ultrasonication for 0.5 h to obtain a homogeneous suspension. EMC18 was dissolved in toluene at 75 °C under a magnetic stirring. Then, the GO-C18 suspension was slowly dropped into EMC18-toluene solution under stirring. After the evaporated solvent at 130 °C, EMC18@GO-C18 composites were vacuum dried at 30 °C until a constant mass. The mass fraction of GO-C18 in EMC18@GO-C18 composites varied from 0.5 to 2 wt% (0.5, 1 and 2 wt%). Similarly,

EMC18@GO-x% composite also were fabricated through the same procedure for a comparison.

2.4. Characterization

The FTIR spectra of ODA, GO and GO-C18 were performed on Nicolet iS5 (Thermo-Fisher Co. Ltd., USA) at 4 cm^{-1} resolution in a transmission mode. The morphology of GO, GO-C18, EMC18@GO and EMC18@GO-C18 was characterized by field-emission scanning electron microscopy (SEM, S4800, Hitachi, Japan) and transmission electron microscopy (TEM, H-7600, Hitachi, Japan) with 10 kV and 100 kV accelerating voltage, respectively. X-ray patterns of GO and GO-C18 were obtained by X-ray powder diffraction (XRD, Bruker D8 DISCOVER) with Cu K α radiation ($\lambda = 1.54\text{ \AA}$) at 40 kV and 150 mA. The thermal property of EMC18, EMC18@GO and EMC18@GO-C18 were characterized by DSC (NETZSCH 200 F3, Germany) in the range of -20 to $120\text{ }^\circ\text{C}$ at a scanning rate of $10\text{ }^\circ\text{C}/\text{min}$, and the second run was recorded. Thermal stability was detected by thermogravimetric analysis (NETZSCH STA 409 PC/PG TG-DTA, Germany) from room temperature to $800\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under nitrogen.

2.5. Shape stabilization performance

The shape stability of EMC18, EMC18@GO and EMC18@GO-C18 was characterized by a direct visual observation [35]. Each specimen with 12 mm diameter and 1 mm thickness was molded under 5 MPa pressure. The sample morphology change is recorded with temperature changing from room temperature to $160\text{ }^\circ\text{C}$. Digital pictures were shot and compared at a predetermined temperature to give a clear morphology variation.

2.6. Thermal reliability behavior

Thermal reliability analysis was carried out in a Linkam THMS600 heating/freezing stage with temperature ranging between 0 and $80\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C}/\text{min}$. After 500 heating/cooling cycles of EMC18@GO-2% and EMC18@GO-C18-2%, DSC and FTIR were employed to compare the phase change performance and structure stability.

2.7. Thermal storage and release capability

The test apparatus for the energy storage and release capability has been described in our previous studies [35,40]. The experiment was carried out at two oil bathes with a predetermined temperature at 30 and $75\text{ }^\circ\text{C}$, respectively. For EMC18, EMC18@GO-2% and EMC18@GO-C18-2%, the temperature-time curve during the heating and cooling process was obtained by a thermocouple (ECNTER-305, ECNTER technology, Taiwan). The temperature was recorded every 5 s.

The coated non-woven fabrics ($16 \times 10\text{ cm}$) with EMC18, EMC18@GO and EMC18@GO-C18 PCMs were prepared. Taking a $100\text{ }^\circ\text{C}$ oven as a heating source, and a $2.4 \times 2.4 \times 0.5\text{ cm}$ folded fabric is used to compare and analyze the thermal storing behavior. At the same time, a blank fabric is used as a control. The temperature was recorded every 5 s.

3. Results and discussion

3.1. Characterization of GO and GO-C18 nanosheets

The morphology of GO and GO-C18 nanosheets is characterized through TEM (Fig. 1a and b). GO shows a large flake, while GO-C18 gives a wrinkled and aggregated stacking sheet. This is attributed to the inter-sheet interactions of the carbon nanosheets and the molecular interaction of C18 alkyl chains [45]. New bands at 1637 cm^{-1} , 1546 cm^{-1} and 1209 cm^{-1} shown in Fig. 1c are assigned to C=O, -NH bond of amide, respectively, demonstrating the successful incorporation

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