



Fabrication and characterization of diethylene glycol hexadecyl ether-grafted graphene oxide as a form-stable phase change material

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ABSTRACT

A novel form-stable phase change material (FSPCM), namely, diethylene glycol hexadecyl ether-grafted graphene oxide (E_2C_{16} -g-GO), was fabricated by an esterification reaction. As E_2C_{16} was modified with GO for the first time, the optimal E_2C_{16} and GO reactant ratio and reaction time were determined to be 6:1 and 6 h, respectively. The successful synthesis and chemical structure of E_2C_{16} -g-GO were confirmed by various spectroscopy and microscopy techniques. The thermal properties and stability of E_2C_{16} -g-GO were characterized by DSC and TGA. The melting and crystallization points of E_2C_{16} -g-GO are 43.3 °C and 29.4 °C, respectively. The latent heats of melting and crystallization are 70 and 72 J/g, respectively. The degradation temperature of E_2C_{16} -g-GO is approximately 20 °C higher than that of E_2C_{16} , indicating that it has good thermal stability. Furthermore, E_2C_{16} -g-GO exhibits good shape-stability and excellent thermal reliability and structural stability, indicating that it is a promising FSPCM for energy storage applications.

1. Introduction

Thermal energy is one of the main sources of energy in nature, which could be an important global energy concern due to the waste of this energy [1]. Numerous strategies have been presented for the development of efficient devices or functional materials to improve the utilization of thermal energy. Among the different forms of thermal storage, including sensible, latent and chemical energy storage, latent heat storage based on organic phase change materials (PCMs) has been the most studied and widely applied approach [2,3]. Organic PCMs with excellent energy storage-releasing capability have attracted extensive attention and have been applied in solar power plants [4], thermal management of buildings [5], thermal protection of electronic devices [6], and thermal-regulated textiles [7], etc. Diethylene glycol hexadecyl ether [$HO(CH_2CH_2O)_2C_{16}H_{33}$, E_2C_{16}] is not only a widely used non-ionic surfactant, but it is also a superior phase change material due to its high heat storage density, isothermal operating characteristics, and extreme thermal stability [8–10], which have been many studies in our lab. Tang et al. [11] investigated the crystal structure and phase change properties of polyoxyethylene hexadecyl ether (E_nC_{16}) with various numbers of repeat units (n). The results show that the number of repeat units significantly affects the phase change properties of E_nC_{16} . The crystal structure of E_nC_{16} for $n \geq 10$ is monoclinic, and E_nC_{16} is a class of promising PCMs. Han et al. [12]

synthesized a series of cellulose-g- E_2C_{16} solid–solid PCMs. These copolymers exhibit superior solid–solid phase change behavior, and superior thermal stability to that of E_2C_{16} . Nevertheless, the direct utilization of E_2C_{16} was limited by its liquid leakage during the phase transition process [13].

In recent years, the modification of PCMs by application of nanostructured materials such as carbon nanotubes (CNTs) [14], graphene [15] and nanoparticles [16] has attracted tremendous interest. Among these materials, graphene oxide (GO), a layered two-dimensional carbon material, has become the focus of many investigations due to its extraordinary characteristics such as excellent mechanical properties, exceptional thermal properties and low cost [17]. In previous studies, GO was added to PCMs by physical blending to fabricate shape-stabilized PCMs [18]. In this case, only physical interactions that are weak and unstable are present between GO and the PCMs. As is well known, some different oxygen-containing functional groups are present on the basal planes and edges of GO nanosheets including hydroxyls, carboxyls and epoxides [19,20], which provide numerous active sites to graft PCMs onto the surface of GO by different multifunctional coupling agents or chemical reactions [21,22] such as esterification, amidation, ring-opening reactions. A recent study completed by our group found synergistic phase change behavior in poly(hexadecyl acrylate)-g-GO fabricated by in situ free radical polymerization [23].

To date, there has been no information available about the

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fabrication and properties of E_2C_{16} modified with GO nanosheets. In this study, E_2C_{16} was covalently grafted onto GO nanosheets via an esterification reaction instead of physical blending. The optimum reactant ratio and time were determined to fabricate a satisfactory product. The chemical structure, phase change properties and thermal reliability and stability of the fabricated E_2C_{16} -g-GO were investigated in detail.

2. Experimental

2.1. Materials

Diethylene glycol hexadecyl ether (E_2C_{16} , 99%) was obtained from Sigma-Aldrich Co. Ltd. Natural graphite (NG) powders (325 mesh) were purchased from Qingdao Laixi Graphite Co. Ltd. 4-Dimethylaminopyridine (DMAP) was analytical grade and was provided by Shanghai Aladdin Bio-Chem Technology Co. Ltd. and used as received. *N,N'*-dimethylformamide (DMF, AR) was purchased from Tianjin Guangfu Fine Chemical Research Institute, and residual water was removed with a 5 Å molecular sieve prior to use. *N,N'*-dicyclohexylcarbodiimide (DCC), sulfuric acid (H_2SO_4 , 98%), potassium permanganate ($KMnO_4$, 99.3%), potassium peroxodisulfate ($K_2S_2O_8$, AR), phosphorus pentoxide (P_2O_5 , AR), hydrogen peroxide (H_2O_2 , 30%) and hydrochloric acid (HCl, 37%) were also provided by Tianjin Guangfu Fine Chemical Research Institute and used as received.

2.2. Fabrication of E_2C_{16} -g-GO

GO powders were fabricated from NG powders using a modified Hummers' method with a pre-oxidation step, as reported in our previous work [24,25]. E_2C_{16} -g-GO was fabricated successfully by an esterification reaction with E_2C_{16} as a thermal storage material and GO as the supporting substance [26,29]. The terminal hydroxyl groups of E_2C_{16} was covalently grafted onto the carboxyl groups on the edge of GO rather than absorbed or partially absorbed by the GO nanosheets. The schematic depiction of the E_2C_{16} -g-GO synthesis is shown in Fig. 1, and the detailed procedure of E_2C_{16} -g-GO (S-2) is described as follows: first, 100 mg of GO powder was dispersed in 50 mL of anhydrous DMF and sonicated for 1 h to form a homogeneous suspension. Then, 600 mg of E_2C_{16} monomer was added to the GO suspension. Under mechanical agitation and a nitrogen atmosphere, 0.39 mmol of DCC and 0.08 mmol of DMAP were successively added and were used as an activating agent and a catalyst to facilitate the esterification reaction. The final mixture was kept at 60 °C for 6 h. After the reaction ended, the obtained suspension was poured into an HCl solution to remove the unreacted DMAP, and then centrifuged and washed with deionized water (at least five times) until the upper liquid was colorless. The fabricated product was collected by centrifugation and freeze drying until a constant mass was obtained.

Several E_2C_{16} -g-GO copolymers were synthesized by changing the mass ratio of E_2C_{16} to GO, as listed in Table 1. Then, Several E_2C_{16} -g-GO copolymers were synthesized by changing the reaction times, as summarized in Table 2.

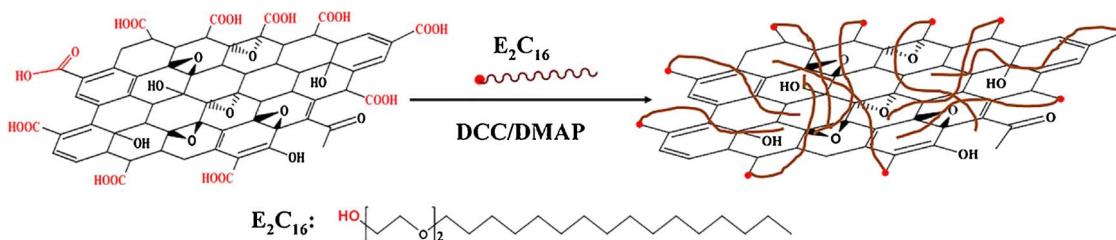


Fig. 1. Schematic depiction of E_2C_{16} -g-GO synthesis via an esterification reaction.

Table 1

E_2C_{16} -g-GO synthesized with various mass ratios of E_2C_{16} and GO.

Sample No.	E_2C_{16} :GO (mass%)	DCC/DMAP (mol%)	t (h)	T (°C)
S1	2:1	5:1	12	60
S2	3:1	5:1	12	60
S3	4:1	5:1	12	60
S4	5:1	5:1	12	60
S5	6:1	5:1	12	60
S6	7:1	5:1	12	60

Table 2

E_2C_{16} -g-GO synthesized with various reaction times.

Sample No.	t (h)	E_2C_{16} :GO (mass%)	DCC/DMAP (mol%)	T (°C)
S-1	3	6:1	5:1	60
S-2	6	6:1	5:1	60
S-3	9	6:1	5:1	60
S-4	12	6:1	5:1	60
S-5	15	6:1	5:1	60

2.3. Characterization

Fourier transform infrared spectra (FT-IR) were recorded using a KBr disk in the wavenumber range of 4000–500 cm^{-1} using an FT-IR spectrometer (Bruker Tensor37, Germany) at a resolution of 4 cm^{-1} . The morphology was examined by transmission electron microscopy (TEM, Hitachi H-7650, Japan). X-ray photoelectron spectroscopy (XPS) was performed with a Genesis 60 spectrometer (Edax, U.S.A.) equipped with an Al $K\alpha$ radiation source ($h\nu = 1486.4$ eV). Raman patterns were obtained using a Raman spectrometer (Horiba XploRA PLUS, Japan) equipped with a 532 nm wavelength laser. Crystallization behaviors were characterized via an X-ray diffractometer (Bruker D8 DISCOVER, Germany) at room temperature, and the 2θ scan range was 5–40°. The phase change properties were characterized using a differential scanning calorimeter (DSC, NETZSCH 200 F3, Germany) in the range of –30–120 °C. The NETZSCH 200 F3 differential scanning calorimeter was equipped with calibration samples (such as *n*- $C_{10}H_{16}$, In, Sn, Bi, Zn and CsCl) and corrected biannually. The test program was as follows: Specimen of 5–10 mg was encapsulated in an aluminum pan under a nitrogen atmosphere (0.2 MPa) and first heated from –30 °C to 120 °C at the rate of 10 °C/min and kept at 120 °C for 2 min. Subsequently, the specimen was cooled to –30 °C at the rate of –10 °C/min and kept at –30 °C for 2 min. Finally, the specimen was heated again to 120 °C at the same rate of 10 °C/min. DSC thermograms of the first cooling scan and second heating scan were recorded [11,27]. Thermogravimetric analysis (TGA) was performed using a thermogravimetric analyzer (NETZSCH STA409PC, Germany) at temperatures ranging from 25 °C to 800 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. Shape-stabilized tests were performed by visual observation [27]. The samples were pressed into a disc with a diameter of 12 mm and thickness of 1 mm, and then placed into an oven for 10 min under the pre-determined temperature in the range from room temperature to 70 °C with intervals of 10 °C. Then, the disc size and morphology changes were recorded. Multiple thermal cycling test was conducted in a high-

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