Graphene–nickel/*n*-carboxylic acids composites as form-stable phase change materials for thermal energy storage

Weidong Liang, Guodong Zhang, Hanxue Sun, Pinsong Chen, Zhaoqi Zhu, An Li*

College of Petrochemical Technology, Lanzhou University of Technology, Lanzhou, PR China

ABSTRACT

Superoleophilic graphene–nickel foam (PDMS–G–NF), which was prepared by coating graphene nanosheets onto nickel foam followed by surface modification with polydimethylsiloxane (PDMS), was used as porous supporting material to prepare form-stable phase change materials (PCMs) composites. Owing to the strong hydrophobic and superhydrophilic wettability of PDMS–G–NF, PCMs can be absorbed spontaneously into PDMS–G–NF and can stay stable without leakage even over their melting points. The incorporation of PCMs into PDMS–G–NF does not change the crystal structure but lowers the crystallinity size of PCMs in the composites, which is confirmed by X-ray powder diffraction (XRD) analysis. The latent heat of PDMS–G–NF/PCM composites was measured in the range of 42.3–123.41 kJ kg^{-1}. Taking advantages of the simple process and good stability the PDMS–G–NF should be ideal candidates as an alternative to traditional PCMs, which may have great potentials for renewable energy saving applications.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The increasingly serious energy crisis and continuous increase in greenhouse gas emissions drive people to more effectively utilize various sources of energy. However, most of renewable resources are intermittent providers of energy due to environmental constraints, e.g. solar energy. Therefore, efficient energy storage devices and systems are of critical importance to improve the energy efficiency and reduce the gap between energy demand and energy generation. Phase change materials (PCMs) can store and release latent heat when its phase change occurs [1–3]. Taking advantages of high heat storage density, thermal heat storage and release at small temperature change and easy control, PCMs possess great potentials for various applications such as solar energy saving, industrial waste heat recovery, building energy saving, electronic temperature control equipment, etc.

Generally speaking, phase change materials are mainly composed of organic and inorganic materials. Compared with inorganic PCMs, organic PCMs have the characteristic of low corrosion; they melt and freeze repeatedly without phase segregation that leads to consequent degradation of their latent heat of fusion [4,5]. The organic phase change materials includes paraffin waxes (or *n*-alkanes), polyethylene glycols (PEGs), and fatty acids. Fatty acids have been widely studied due to their high latent heat storage capacity and appropriate thermal properties [6–8]. However they have low thermal conductivity, and need encapsulation in order to prevent leakage of the melted PCM during the phase change process. This problem is expected to be solved by storing the PCMs into supporting materials to form form-stable PCM composites. In recent years a plenty of form-stable PCM composites have been reported in previous literatures by incorporating PCM immerses into porous materials, including gypsum [9], diatomite [10], graphene aerogel [11], SiO$_2$ [12], conjugated microporous polymers [13] and ceramic composites [14] by means of natural immersion approach. Therefore, preparing porous materials with a better thermal conductivity as form-stable PCM composites should be a significant topic.

Graphene has recently been reported to possess unique electrical, optical and thermal transport properties [15–20]. The desired thermal conductivity [18] and electrical conductivity make graphene significant in providing enhanced thermal and specific surface area properties in thermal management systems [21]. Moreover porous graphene acts as superwetting coatings on a grid, due to its hydrophobic property, good mechanical flexibility and van der Waals interactions between the graphene nanosheets and with other substrates [22]. In this study, we coated graphene nanosheets onto nickel foam followed by surface modification to prepare superoleophilic graphene–nickel foam as porous supporting material. By a simple impregnation method, various *n*-carboxylic acids can be easily absorbed into the supporting material to form-stable composites. The prepared composites show not

---

only good thermal stability but also high latent heat, which make them promising candidates as heat storage materials for real application.

2. Experimental

2.1. Sample preparation

2.1.1. Preparation of superoleophilic graphene–nickel foam (G–NF)

We prepared graphene with chemical reduction of graphene oxide in DMF as reported [23,24]. The resulting graphene/DMF suspension, which was centrifuged to remove the bigger particles and diluted with DMF, was used in the following experiments. The commercial nickel foam substrate which was washed with acetone and dried before using was dipped into the graphene/DMF suspension and dried at 100 °C. This process was repeated to coat the graphene nanosheets on the substrate. Subsequently, some amount of graphene–nickel foam and a piece of polydimethylsiloxane (PDMS) film were placed in a sealed glass container and heated at 234 °C for 1 h. The resulting product was named as PDMS–G–NF.

2.1.2. Preparation of PCMs

The PDMS–G–NF sample which was placed on a glass container was immersed into the molten PCM (such as PA). Due to the superoleophilicity of PDMS–G–NF and capillarity, the molten PCM was absorbed naturally into PDMS–G–NF. Then, the PDMS–G–NF/PCM composite was dried to constant weight (90 °C, 0.07 MPa). The results of PDMS–G–NF as form-stable phase change materials composites with different *n*-carboxylic acids are shown in Table 1.

2.2. Analytical instrumentation

Scanning electron microscopy (SEM) images were obtained with a field emission gun scanning electron microscope (JSM-6701F, JEOL, Ltd.) after coating samples with Au film. Water contact angle measurements for samples were performed on a contact angle meter (DSA100, Kruss). X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB250xi spectrometer (Thermon Scientific). XRD measurements were performed on a Rigaku with a Cu tube source and scans were taken at 2θ from 2° to 50°. The thermal properties of microcapsule was measured by differential scanning calorimetry (DSC, 851e, METTLER-TOLEDO) at a heating or cooling rate of 5 °C/min in the range of 10–100 °C under a argon atmosphere. The thermal conductivities of the samples were investigated by using a thermal conductivity testing instrument (LFA 447 Nanoflash, NETZSCH).

3. Results and discussion

SEM was performed to evaluate the morphology of materials. As seen in Fig. 1a, the treated nickel foam exhibited nano- or micro-size along with rough surface composed of stacked layers of graphene sheets (Fig. 1a inset). The higher-magnification image reveals more clearly the graphene nanosheets with wrinkled surface topology and folding edges on the skeleton of nickel foam (Fig. 1b), whose intrinsic hydrophobicity is favorable to the absorption of PCM [25–29]. To further improve its hydrophobic property, modification with a low-surface-energy material such as PDMS is necessary. The water contact angles (CA) of G–NF were measured to be 144.9° after modification with PDMS. Such strong surface hydrophobicity makes water droplets sperial on the surface of PDMS–G–NF (Fig. 1e). The diesel oil CA for the PDMS–G–NF samples was found to be nearly 0°, implying a strong affinity to oils. Based on the strong surface superoleophilicity of the PDMS–G–NF sample, the *n*-carboxylic acids such as PA, MA and SA can be easily incorporated into the PDMS–G–NF samples to form-stable PCM composites. As shown in Fig. 1c and d the pores of PDMS–G–NF are homogeneously filled by PA, which illustrates that *n*-carboxylic acids have been impregnated into PDMS–G–NF due to the effect of superoleophilicity and the surface absorption of graphene. As shown in Fig. 1f the melt PA (dyed with Red oil O) distributed on the surface of a hot water bath (85 °C) is quickly and spontaneously absorbed into the PDMS–G–NF, owing to both the capillary action of its surface pores and its superoleophilicity [30,31].

In addition to superoleophilicity, these prepared graphene-coated nickel foam samples also show excellent thermal stability. As shown in Fig. 2, the thermal decomposition temperature for both G–NF and PDMS–G–NF samples is higher than 500 °C with weight loss 1.7% and 0.4%, respectively. The thermal stability of PDMS–G–NF was better than that of the G–NF, due to the PDMS film as a protective layer which prevented the decomposition of graphene. Moreover the PDMS–G–NF sample is totally insoluble in any organic solvent, indicating excellent chemical stability [32,33]. These unique physicochemical properties as well as their super-oleophilicity make the PDMS–G–NF samples promising candidates as porous medium for preparation of PDMS–G–NF/PCMs composites, which are used for practical energy storage.

To further investigate the effect of surface chemical compositions on the surface wettability of PDMS-treated G–NF, XPS was performed. As seen in Fig. 3, the pure nickel foam peaks at 854.6 eV and 531.6 eV are attributed to Ni2p, and O1s, respectively. In contrast, the peaks of the G–NF at 856.7 eV, 532.5 eV and 285.06 eV are attributed to Ni2p, O1s, and C1s, respectively. Furthermore, the content was calculated to be 3.53 at% of nickel. It illustrates that the surface of nickel foam is almost covered by graphene film. For PDMS-treated

Table 1
The thermal properties of the *n*-carboxylic acids and composite PCMs.

Samples names	PCM percentage (%)	Melting			Freezing		
		Onset temperature (°C)	Peak temperature (°C)	Latent heat (kJ kg^{-1})	Onset temperature (°C)	Peak temperature (°C)	Latent heat (kJ kg^{-1})
Pure parafin	100.0	50.6	58.2	130.54	54.6	52.1	135.7
PDMS–G–NF/parafin	31.17	51.3	58.5	41.52	57.2	50.9	42.3
Pure MA	100.0	52.0	55.8	207.69	50.6	51.8	207.0
PDMS–G–NF/MA	49.90	54.2	59.8	102.54	53.1	47.7	103.3
Pure PA	100.0	62.4	65.2	188.00	60.8	59.1	209.1
NF/PA	17.30	62.4	65.5	34.87	60.3	58.6	36.18
G–NF/PA	43.68	62.7	68.4	86.24	60.2	55.8	91.34
PDMS–G–NF/PA	59.02	62.4	68.4	126.34	60.0	54.9	123.41
PDMS–G–NF/PA 200 cycles	54.60	62.8	69.3	113.81	60.2	54.7	114.18
Pure SA	100.0	54.1	56.7	173.07	53.2	52.0	197.8
PDMS–G–NF/SA	53.29	51.4	59.6	89.49	53.1	50.5	105.4