Graphite foam as interpenetrating matrices for phase change paraffin wax: A candidate composite for low temperature thermal energy storage

Mani Karthik[a,b,*], Abdessamad Faik[a], Bruno D'Aguanno[a,c]

[a] CIC Energigune, Parque Tecnológico, C/Albert Einstein 48, Miñano, Álava 01510, Spain
[b] Centre for Nanomaterials, International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI), Balapur, Hyderabad 500005, India
[c] Koinè Multimedia, Via Alfredo Catalani, 33, 56125 Pisa, PI, Italy

ARTICLE INFO

ABSTRACT

Paraffin wax-graphite foam (P-wax/G-foam) composite was fabricated by using low cost small scale process aiming to produce a stable phase change material with enhanced thermal transport. Its thermophysical properties such as thermal diffusivity, specific heat and thermal conductivity were examined as a function of temperature. The thermal conductivity of the P-wax/G-foam composite in both solid (2.6 W/m K) and liquid (1.8 W/m K) phases is by a factor of $\approx$ 11 (980%) higher than that of pristine paraffin wax in solid (0.24 W/m K) and by a factor of $\approx$ 16 (1530%) in liquid (0.11 W/m K) phases, respectively. This is due to both the G-foam morphology and graphitic content, allowing a rapid heat transfer to the P-wax. The thermal conductivity behaviour of the composite is also discussed in term of a theoretical model in which the G-foam is described by a 3D interpenetrating matrix for the P-wax. The model shows the self-consistency of all the measured data. The obtained results demonstrated that the stable P-wax/G-foam composite is a promising material for various thermal energy storage applications such as building and vehicle heating and cooling, solar thermal harvesting, and thermal management of electrochemical energy storage and electronic devices.

1. Introduction

Thermal energy storage (TES) with phase change materials (PCMs) can potentially provide higher volumetric TES capacity when compared to sensible energy storage systems [1,2]. Besides, PCMs are well known to be excellent TES materials owing to their advantages such as high fusion latent heat per unit of mass, availability in large quantities, low cost and quasi-constant melting-solidification temperatures. As a result, PCMs represent efficient and cost-effective heat storage media. Thus, they are widely applied in many fields such as solar energy utilization, industrial waste heat recovery, indoor thermal management, active and passive cooling of electronic devices [1–4].

Organic PCMs such as paraffin, fatty acids, polyethylene glycol etc. have good potential applications in TES and have been extensively investigated by many researchers [5,6]. However, the main drawback of the usually proposed organic PCMs is their poor thermal conductivity ($\sim$ 0.1–0.3 W/m K), which prolongs the melting (charging) and solidification (discharging) times of a heat storage unit based on these materials. This shortcoming limits their deployment in large scale technological applications of latent heat TES [3,4]. In order to improve the heat transfer, several techniques have been already proposed for the

heat transfer enhancement of PCMs, which include finned tubes with different configurations [7–10], insertion of a metal matrix into the PCM [11–14], high conductivity particles dispersion within the PCM [15–17], and micro and macro-encapsulation of the PCM [18–20]. Although these techniques mainly achieved to enhance the thermal transport within the PCM, more investigation is needed regarding the chemical corrosion between the PCM and the metal matrix, the minimization of filler materials inside the PCM, the thermal and mechanical stability of TES composites, as well as regarding their cost-effectiveness.

Porous materials with a high thermal conductivity are considered as alternative and promising candidates for the heat transfer enhancement of PCMs because they enhance the heat transfer and, at the same time, they can be properly designed to prevent the leakage of liquid PCMs, owing to the capillary and surface tension forces of the porous structure [17]. In this regard, porous graphite materials, and in particular graphite foam (G-foam) are recognized as potential candidates for thermal conductivity enhancement of PCMs [21–28], due to their low density, large specific surface area, high bulk thermal conductivity, well-aligned crystalline structure, good thermal stability [26,29–34], and good chemical compatibility with PCMs [21].

However, the G-foams existing in the literature have been mostly

---

fabricated by foaming of coal, coal tar pitch and petroleum pitch, followed by very expensive and time consuming high temperature calcination and graphitization processes. For example, the first pitch based macro-porous G-foams were developed by Klett et al. from Oak Ridge National Laboratory (ORNL) [32–34], through a process based on a high graphitization temperature of 2800–3000 °C [32–34], and on the use of a very high pressure/temperature reactor. In order to overcome these drawbacks, and to produce G-foam with moderate thermal conductivity (~ 2–10 W/m K) at below 1000 °C, an alternative simple and economic method was recently reported by our group [35]. More specifically, we reported on the fabrication of highly interconnected-three dimensional G-foam with moderate thermal conductivity by using polymeric precursors as carbon source and polyurethane (PU) foam as a sacrificial template [35].

To further explore the potential application of the G-foams as thermal conductivity enhancement matrices, and to take advantages from the facile and low-cost fabrication method for the production of the G-foam matrix, the present study aims to investigate the thermo-physical, chemical and mechanical behaviour of a composite material made by interpenetrating a phase-change paraffin wax (P-wax) within a G-foam matrix, with a special attention to its heat capacity (C_p) and thermal conductivity (k) properties. This study also aims to analyse the performances of the P-wax/G-foam composite when used as a low temperature thermal energy storage material.

The P-wax was selected as a PCM probe since it possesses desirable properties such as (i) high latent heat of fusion, (ii) low vapour pressure, (iii) very low chemical reactivity, (iv) no phase segregation, (v) stability over thermal cycling, (vi) non-toxicity and (vii) availability at low cost, which all make the P-wax an excellent candidate for TES applications and, in particular, for storing solar-thermal energy and for thermal comfort control when incorporated into building materials [36–38]. The innovative preparation process of the G-foam is described in the first part of the experimental section. The first part is followed by the description of the process to produce the P-wax/G-foam composite, and by the description of the experimental equipments and procedures used to characterize the P-wax, the G-foam and the P-wax/G-foam composite from the morphological, chemical-physical point of view. The section is closed by the illustration of the experimental setup used to measure the performances of the P-wax/G-foam composite when used as a thermal storage material. The results on the bulk properties of the used samples are presented in the result section. Values are reported for the bulk density, total porosity, specific pore surface and volume, compressive strength, thermal conductivity, specific and latent heat and, finally, for the impregnation ratio of the P-wax inside the G-foam. The values of the thermal diffusivity (α), the specific heat (C_p), and thermal conductivity (k),of the P-wax/G-foam composite as a function of temperature are presented and discussedat length. The considered range of T goes from room temperature to well above the melting T of the P-wax. The thermal conductivity results are discussed by considering a theoretical model which describes the P-wax/G-foam composite as a regular 3D lattice of intersecting pores of equal diameters filled by the P-wax. The model gives accurate results, and it can be used as a tool to extract k values in all cases in which the laser flash techniques gives inaccurate results, as in the case of foam-like materials. The result section is closed by the analysis of the P-wax/G-foam composite results when the composite is used under melting-solidification cycles. The remarkable enhancement in the thermal conductivity of the P-wax/G-foam composite, together with its thermal cycling stability, make this composite material a promising material for extensive TES utilizations at low temperature. To give hints in this direction, the results are also contrasted and compared with bulk wax and bulk water. The main paper outcomes are reviewed in the conclusion section.

2. Experimental

2.1. Preparation of the G-foam

The preparation of G-foam was recently reported by our group [35] and the same procedure is followed and reported here.

In a typical synthesis, the resorcinol (24.75 g) is dissolved in a mixture of water (40 ml) and ethanol (40 ml), and the mixture is stirred for 15 min. Then, 37 wt% hydrochloric acid (2.64 g) are added to the above mixture and stirred for 1 h. 37 wt% formaldehyde solution (18.72 g) is added by drops under magnetic stirring. The reaction mixture is further vigorously stirred for another 1 h, and then a homogeneous solution is obtained. The synthetic graphite (40 wt%) and nickel nitrate (40 wt%) with respect to resorcinol formaldehyde (resin) is added to the above mixture and stirred for 2 h. Then, the commercial polyurethane foam (PU-foam, 4 g) is washed with ethanol and dried in a hot air oven at 80 °C. Then, the dried PU-foam is impregnated within the above polymeric reaction mixture, afterwards allowed for ethanol evaporation at room temperature and dried in a hot air oven at 80 °C for 12 h and cured at 150 °C for 24 h. Finally, the polymeric composite foam is carbonised at 1000 °C for 1 h under N_2 gas flow in a tubular furnace with a heating rate of 1 °C/min in order to obtain highly interconnected three dimensional (3D) G-foam.

In this approach, the amorphous carbon can also be converted into graphitic carbon during the carbonaceous process with the presence of metallic Ni particles, which can act as a graphitisation catalyst. During the carbonisation process, the nickel nitrate is decomposed and converted into the corresponding metallic oxides and then the carbon can reduce the metal oxides into elemental metal (i.e. Ni). Then, well dispersed metal particles within the carbon matrix can act as catalysts for the conversion of amorphous carbon into well-defined graphitic carbon [35,39]. Finally, the metal particles in the graphite foam can be easily removed by HCl acid washing. Fig. 1a illustrates a schematic representation of the preparation of G-foam.

2.2. Preparation of P-wax/G-foam composite by impregnation method

The P-wax/G-foam composite was prepared by impregnation method without applying any vacuum process. Fig. 1b represents the preparation of the P-wax/G-foam composite. In a typical preparation, the P-wax (Solid straight-chain hydrocarbons with mp. 65 °C, purchased from Sigma-Aldrich Ltd.) was taken in the glass beaker and melted completely at 75 °C. Then, the G-foam is added into the glass beaker containing the liquid P-wax. After infiltration, the foam piece is removed from the beaker and allowed to cool down. The excess P-wax in the outer surface of the G-foam is removed by carefully scraping with a blade or knife. The digital pictures showing the general aspects of the G-foam before and after impregnation are illustrated in Fig. 1b.

The percentage of infiltration of the P-wax into the G-foam is then determined by using the following equation:

$$I_w = \frac{V_w^{inf}}{V_f} \times 100 = \frac{M_c - M_f}{V_f \rho_w} \times 100 \tag{1}$$

where M_c is the mass of the P-wax/G-foam composite, M_f the mass of the G-foam, V_f is the volume of the G-foam, V_w^{inf} the volume of the infiltrated P-wax, and ρ_w the density of the P-wax.

2.3. Small experimental device for melting-solidification performance test

The melting-solidification performance of the P-wax and the P-wax/G-foam composite were studied by using a small device setup as schematically shown in Fig. 2. In a typical test, 4 g of P-wax was taken in a polypropylene tube and two thermocouples were embedded into the sample. The top of the tube was closed by using glass wool. Two different water baths were used for the melting and solidification