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Preparation and thermal properties of form-stable phase change materials composed of palmitic acid/polypyrrole/graphene nanoplatelets

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ABSTRACT

In this study, the thermal conductivity of form-stable phase change materials (PCMs) is improved by the addition of graphene nanoplatelets (GNPs). In the first step, the dispersed GNPs were mixed with palmitic acid (PA) particles using an ultra-sonication method. Then, the prepared material was added to form-stable phase change materials (PA/PPy) obtained by a polymerisation technique. The amount of PA particles remained constant in the prepared form-stable phase change materials. FT-IR and SEM analyses were used to investigate the structure and surface morphology of form-stable PCMs, respectively. The thermal properties, stability and conductivity of the materials were also characterised using DSC, TGA and thermal conductivity analysis, respectively. The results indicated that GNPs had a significant effect on improving the thermal conductivity of form-stable PCMs (PA/PPy). By doping 1.6% of GNPs, the thermal conductivity and thermal capacity of PA/PPy/GNPs form-stable PCMs could reach up to 0.43 W/m K and 151 J/g, respectively. In other words, thermal conductivity increased by 34.3% in comparison with PA/PPy form-stable PCMs. The prepared PA/PPy/GNPs form-stable PCMs are anticipated to show improved performance for solar thermal energy storage applications.

1. Introduction

Renewable energy plays an important role in the world due to environmental concerns and the considerable price of fossil fuel. Solar energy, which is inexhaustible, abundant and clean, is the most promising form of renewable energy. There are different forms of energy, such as solar–thermal, electrical and chemical; of these, the conversion of solar energy to thermal and electrical energy has been applied successfully, but solar–chemical conversion is still in the research stage [1,2]. The significant thermal conversion efficiency, low price and small scale of equipment are the main advantages of solar thermal applications [3]. A significant drawback of solar energy is the diurnal fluctuation of solar radiation, which makes the use of thermal energy storage indispensable.

In this regard, latent thermal energy storage in the field of phase change materials (PCMs) has significant merits, such as a high storage density at small temperature intervals and low storage media costs [4,5]. Materials that are used as solid–liquid PCMs therefore have a capacity for thermal energy storage. A form-stable PCM is defined as a composite structure with solid–liquid PCMs and supporting materials [6]. A significant part of the available literature has addressed form-stable PCMs. Kenisarin and Kenisarina published a paper in which they reviewed the latest developments of form-stable PCMs [7]. In general, latent heat thermal storage materials such as paraffin [8–10], fatty acids [11] and their mixtures [12,13], are mostly used as solid–liquid PCMs in a stable form. When the temperature exceeds the melting temperature of the solid–liquid PCM, the polymers and inorganic materials act as supporting material [14–21].

One of the main factors in thermal energy storage is high thermal conductivity of PCMs, which improves the speed of thermal storage/release and the efficiency of the solar thermal device. However,

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Table 1
Properties of graphene nanoplatelets (GNPs).

Specific surface area (m^2/g)	300
Width (μm)	Less than 2
Thickness (nm)	Less than 2
Thermal conductivity (W/m K)	Parallel to surface: 3000 Perpendicular to surface: 6
Density (g/cm^3)	2.2
Carbon content	>99%

one major drawback of PCMs combined with polymer structures is their low thermal conductivity [22]. Therefore, it is worthwhile to improve the thermal conductivity of form-stable PCMs to consequently improve performance. Studies have been published on the role of copper [23], nickel foam [24], carbon nanotubes (CNTs) [25], carbon nanofibers (CNFs) [26], carbon foam [27] graphene oxide [28], and graphene platelets (xGnP) [29,30] in improving the thermal conductivity of phase change materials. Furthermore, previous research has indicated that copper nanowire [31], Ag nanowire [32] and expanded graphite [33] have a positive impact on the thermal conductivity of form-stable phase change materials. However, the significant particle size of worm-like expanded graphite and its ability to absorb organic material make the dispersion of expanded graphite in form-stable PCMs a challenging issue [22]. This problem is more obvious when considering a polymer structure as a supporting material. Graphene nanoplatelets (GNPs) are particles that consist of several layers of graphene sheets and possess a high aspect ratio and high thermal conductivity [29]. Because the size of GNPs is much smaller than that of worm-like expanded graphite, GNPs are more conductive and can thus be incorporated with matrix materials to improve the electrical, thermal and mechanical properties of composite materials [34].

The major objective of this study was to investigate the effect of GNPs on PA-PPy form-stable PCMs, which were prepared for a previous study [35]. Different percentages of GNPs were integrated in form-stable-PCMs containing PA and PPy as the solid–liquid PCM and supporting material, respectively. Form-stable PCMs doped with GNPs (PA/PPy/GNPs form-stable PCMs) were studied in terms of structure, thermal properties and thermal conductivity. The palmitic acid/polypyrrole/graphene nanoplatelets as form-stable PCM prepared in this study is suitable for heating and cooling applications in building such as water heating and floor heating.

2. Experimental

2.1. Materials

Palmitic acid (PA) was used as a latent heat storage material with a melting point of 61–62 °C. Pyrrole (Py) (C_4H_5N), ammonium persulphate (APS) ($(NH_4)_2S_2O_8$) and sodium dodecylsulphonate (SDS) operated as supporting material, oxidant and surfactant, respectively. GNPs with a specific surface area of 300 m^2/g were purchased from XG Sciences (USA). Table 1 shows the properties of these graphene nanoplatelets. All commercial chemicals were used as received without further purification. Water purification was performed using distillation followed by deionisation with the aid of ion-exchange resins.

2.2. Preparation of PA/PPy/GNPs form-stable phase change materials

Material preparation begins with the dispersion of GNPs in 20 ml of ethanol by ultrasonication for half an hour at 70 °C. Then, a constant amount of PA (2.4 g) is added to the GNPs/ethanol followed by ultrasonication for half an hour under the same conditions to achieve a homogenous mixture. Next, 0.5 g of sodium dodecylsulfonate (SDS) was added to 100 ml of water and heated under stirring until reaching a temperature of 70 °C. Then, the PA/GNPs/ethanol mixture was added to this solution and stirred for 1 h at 70 °C to prepare a stable emulsion. Pyrrole monomer was added to the solution and stirred for half an hour under the same conditions. Then, the temperature of the solution was reduced to 5 °C with the help of an ice bath. To initiate polymerisation, 20 ml of water containing ammonium persulphate (APS) was added dropwise to the solution over the course of 15 min. The molar ratio of pyrrole and APS was kept constant at 1:1. The mixture was stirred for 12 h, then washed and filtered with water until the filter became clear. The products were dried at 70 °C in a vacuum oven to obtain PA/PPy/GNPs form-stable phase change materials. Table 2 indicates the amount of PA, PPy and GNPs in each sample, designated as S1, S2, S3 and S4.

2.3. Characterisation of form-stable PCMs

The thermal properties and chemical structure of form-stable PCMs were investigated using a differential scanning calorimeter (DSC) (model: METTLER TOLEDO 820C) and Fourier transform infrared spectrophotometer (FTIR) (model: Bruker tensor 27), respectively. Moreover, thermogravimetric analysis (TGA) (model: METTLER TOLEDO SDTA 851) was used to measure the thermal stability and weight loss of the form-stable PCMs. The resulting degradation rate was measured as a function of temperature. The microstructure of the samples was investigated by scanning electron microscopy (SEM) (model: SU8000 HITACHI). X-ray diffractometry (XRD) (model: EMPYREAN, PANALYTICAL) was employed for the analysis of the crystalloid phase of the form-stable PCMs. A Hot Disk Thermal Constants Analyzer (TPS 2500S, Hot Disk AB, Sweden), based on design principles ideal for screening homogeneous and isotropic products, was used to measure the thermal conductivity of the form-stable phase change materials. In addition, the compact hydraulic press powder pelletiser with the pressure of 2 ton was used for compacting the samples into pellets in a steel mould with a diameter of 12 mm.

3. Results and discussion

3.1. Form stability of prepared form-stable PCMs

In our previous study, form-stable PA/PPy was prepared successfully [35]. It was found that the highest percentage of PA in the form-stable PCMs was approximately 79.9%. Because the purpose of this study is to explore the effect of GNPs on the thermal conductivity of form-stable PCMs, the PCM content was kept constant at 79.9% while the content of PPy and GNPs was changed. For uniform dispersion of GNPs and PA, ethanol was used as the solvent. The form-stable PA/PPy/GNPs were prepared based on the method described in our previous work [35]. For investigating the form-stability of the samples, the samples were stored in an oven at 80 °C (Fig. 1a and b). It is interesting to note that the shape of the prepared form-stable PCM disks remained unchanged (Fig. 1d). However, the PA disc was completely melted and deformed in the testing process (Fig. 1c). These findings further support the favourable stability of the form-stable PCMs (PA/PPy/GNPs).

3.2. FT-IR analysis

Fig. 2 depicts the FTIR spectra of PA, PPy, GNPs and form-stable PCMs. The spectrum of PA at 1698.1 cm^{-1} corresponds to the C=O stretching vibration. Moreover, the peaks at 2914.2 cm^{-1} and 2848.6 cm^{-1} illustrate the symmetric stretching vibration of PA. The in-plane bending vibration on the —OH group of palmitic acid, the out-of-plane bending vibration of the —OH functional group and