Preparation and properties of polyethylene glycol/unsaturated polyester resin/graphene nanoplates composites as form-stable phase change materials

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\textbf{ABSTRACT}

In this study, a series of poly(ethylene glycol) (PEG)/unsaturated polyester resin (UPR)/graphene nanoplates (GNPs) form-stable PCMs (FS-PCMs) were prepared via a simple melt blending method. In this composite, PEG was used as the phase change material for thermal storage, UPR was introduced as a supporting material to prevent the leakage of melted PEG during the phase change transition and the GNPs were selected as conductive fillers to enhance the thermal conductivity of the polymer-based FS-PCMs. The test results demonstrate that the FS-PCMs exhibit an outstanding form-stable performance because of the cross-linked spatial network of UPR. According to the FT-IR and XRD results, no new chemical bonds form among PEG, UPR and the GNPs. The results obtained from TGA and DSC show that the composites possess an excellent thermal stability and a high energy storage density. Moreover, it is also found that the incorporation of GNPs remarkably enhances the thermal conductivity of the prepared FS-PCMs.

1. Introduction

The rapid consumption of fossil fuels and the increasing imbalance between energy supply and demand are compelling researchers to utilize energy more effectively and develop renewable energy \cite{1}. In recent years, among various forms of advanced latent heat thermal energy storage (LHTES) materials, phase change materials (PCMs) have become the most prevalent and effective technique for thermal energy storage because of their high latent heat storage density, isothermal nature and stable chemical structure, which have been utilized in the fields of thermal management of solar energy, manufacturing thermo-regulated fibers, construction of energy-saving buildings, spacecraft thermal control and water heat recovery \cite{2,3}.

Organic PCMs (OPCMs) are the most common materials for thermal energy management systems due to their desirable properties, including a low degree of supercooling, cost-effectiveness, excellent thermal stability, corrosion resistance, etc. \cite{7}. Among numerous OPCMs, poly (ethylene glycol) (PEG) has proven to be a promising choice because of its high phase change enthalpy, biodegradability, low vapor pressure, non-toxicity and adjustable phase change temperature via simply its tuning molecular weight \cite{6,8,9}. Nevertheless, prior to the practical application of PEG as an OPCM, it is imperative to address two intrinsic drawbacks of PEG: liquid leakage at the solid-liquid phase transition state and low thermal conductivity, which greatly limit its extensive application in LHTES \cite{6,10,12}.

The most common and potential approach to preventing the leakage of OPCMs is their incorporation into supporting materials to prepare form-stable PCMs (FS-PCMs), which can maintain the solid state and avert leakage of OPCMs during the phase transition process \cite{13,14,15,16}. Typically, the supporting materials can be classified into two types: polymers and porous inorganic frameworks. The former refer to poly-pyrrole \cite{17}, polyurethane \cite{18}, comb-like polymers \cite{19}, urea-formaldehyde (UF) resin \cite{20}, polymethyl methacrylate (PMMA) \cite{21}, crosslinked copolymers \cite{22}, and high-density polyethylene (HDPE) \cite{15}. The latter include diatomite \cite{23,24}, graphene aerogels (GAs) \cite{2,25}, expanded perlite \cite{1}, graphene oxide (GO) \cite{26}, porous TiO\textsubscript{2} foams \cite{27} and silica \cite{6,8,28}. Unsaturated polyester resin (UPR) is a linear polymer with ester bonds and unsaturated double bonds and can form a cross-linked spatial network structure after curing. It possesses moderate characteristics including good chemical corrosion resistance, desirable mechanical properties, easy handling and synthesizing, strong intermolecular forces and a competitive price \cite{29,30,31}. In this regard, UPR can be used as a supporting material that is able to firmly confine the PEG molecular chains into its cross-linked spatial network structure.
to provide strength and avoid leakage of the melted PEG. Moreover, the interactions between the terminal hydroxyl groups of PEG and the oxygen atoms of the carbonyl groups or terminal hydroxyl groups of UPR can strengthen the interface with PEG.

Thermal conductivity, which is related to the speed that PCMs absorb and release thermal energy, is a crucial parameter in improving the energy efficiency of PCMs [32]. However, the main defect of FS-PCMs based on polymer matrices is a low thermal conductivity, which restricts their application in thermal storage to a great extent. Consequently, numerous effective methods have been implemented to enhance the thermal conductivity of FS-PCMs [33,34]. A prevalent approach against this shortcoming is to incorporate filler with a high thermal conductivity, including carbon nanotubes (CNTs) [35], graphite nanoplates [36], graphene nanoplates (GNPs) [9,37], silver nanowires [38], copper particles [39] and GO [2,40]. GNPs are thin flat particles that consist of a few layers of graphene sheets and have aroused wide attention because of their outstanding thermal, electronic, mechanical, and optical characteristics, as well as their high aspect ratio [41–43]. Thus, unlike other thermal conductive fillers, the excellent comprehensive properties of GNPs indicate their promise as conductive fillers to dramatically improve the extraordinary reinforcing and functional properties of composite materials, in addition to just improving the thermal conductivity. In this regard, an increasing number of works have investigated the influence of GNPs on the thermal conductivity of polymer-based FS-PCMs. Silakhorl et al. [17] prepared FS-PCMs by adding GNPs to PA/polypyrrole through a polymerization technique and discovered that the thermal conductivity of the FS-PCMs doped with 1.6 wt% GNPs reached up to 0.43 W/(m K), which was 38.7% higher than that of pure PA. Tang et al. [15] utilized a melt blending method to obtain the PA/HDPE/GNPs FS-PCMs and found that the thermal conductivity of the prepared FS-PCMs increased to 0.8219 W/(m K) with 4 wt% GNPs. As shown in the above results, it can be concluded that the graphene materials can efficiently transfer phonons, and this transport in the polymer composites may be faster because of the weak interfacial thermal resistance between graphene and the polymer compared with that of other thermal conductive fillers [41,44,45]; as a result, the graphene-polymer composites exhibit an enhanced thermal conductivity at low filler loading ratios of graphene materials.

Generally, there are various methods to prepare FS-PCMs, such as vacuum impregnation [46], suspension polymerization [17], graft copolymerization [19], the sol-gel method [28], the melt blending method [15], and fusion adsorption [47]. Among these popular methods, the melt blending method, especially for the graphene-based polymer composites, has always been recognized as a practical and promising approach due to its facile and fast fabrication process, mild preparation conditions, low energy consumption and relatively high level of control over the synthesis behavior [41]. Because of these desirable advantages, the melt blending method has been extensively adopted to prepare the FS-PCMs, and the results demonstrate that these FS-PCMs have been successfully synthesized and exhibit good properties.

However, to the best of our knowledge, improvements in the form-stabilization and thermal conductivity of OCPMs using UPR and GNPs have not been reported, especially with an understanding of the effect of different mass fractions of GNPs on the thermal energy storage. Herein, we prepared a series of PEG/UPR/GNPs FS-PCMs by a simple melt blending method that present moderate latent heats and excellent thermal conductivities. In contrast to the previously reported FS-PCMs, the feature of this study is that the prepared composite FS-PCMs firstly utilize UPR, which possesses a cross-linked spatial network structure as a supporting material, and select GNPs as thermal conductive nano-fillers. Therefore, the major objective of this paper is to investigate the influence of GNPs on the various properties of PEG/UPR FS-PCMs, such as chemical structure, microstructure, thermal properties, thermal conductivity and thermal stability. According to the results, the prepared PEG/UPR/GNPs composite FS-PCMs exhibit favorable properties and can be widely utilized in fields related to LHTES.

2. Experimental

2.1. Materials

PEG with an average molecular weight of 4000, as the latent heat storage material, was purchased from Chengdu Kelong Chemical Reagent Factory (China). GNP nanoplates (thickness: < 2 nm, width: < 2 μm, specific surface area: 750 m²/g, purity: > 99%) were purchased from XG Science (USA). Unsaturated polyester resin (UPR), as the supporting material, was a mixture of linear unsaturated polyester and styrene crosslinked monomers of a suitable mass ratio, obtained from Eternal Synthetic Resins Co., Ltd. (Changshu). Benzoyl peroxide (BPO) and N,N-dimethylaniline (DMA) acting as the resin curing initiator and accelerator, respectively, were bought from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (China). All reagents were used without further purification.

2.2. Preparation of the PEG/UPR/GNPs composite form-stable PCMs

In preparation of the PEG/UPR/GNPs composite form-stable PCMs, a novel melt blending method was conducted. Firstly, the GNPs were dispersed in ethyl alcohol via ultrasonication for 0.5 h at 60 °C to obtain a homogeneous suspension. Then, a certain amount of melted PEG was added to the suspension, followed by vigorous stirring at the same temperature for half an hour. Next, the prepared UPR and DMA accelerator were placed into the PEG/GNPs/ethyl alcohol mixture and vigorously stirred for 30 min to prepare a stable solution. To initiate the free radical copolymerization, the BPO curing agent was gradually added to the solution under continuous stirring for 15 min; then, the gelatinization of UPR sols occurred, and the UPR gradually cured. During the process of curing, the PEG was firmly absorbed and confined within the cross-linked spatial network structure of the cured UPR resin. Thus, the PEG/UPR/GNPs FS-PCMs were obtained after vacuum drying. In this study, the mass fraction of PEG in the form-stable PCMs was set as 80 wt%. The amounts of PEG, UPR and GNPs in each sample are summarized in Table 1, and the prepared FS-PCMs are named as S1–S4 according to the different loadings of GNPs. The preparation process of the PEG/UPR/GNPs FS-PCMs is illustrated in Fig. 1.

2.3. Characterization

The chemical structure identification of the form-stable composite PCMs was determined using a Bruker TENSOR II model in a wave-number range of 4000–400 cm⁻¹. The crystallization behavior of the form-stable composite PCMs was characterized by X-ray diffraction (XRD, XPert Powder model, PANalytical B.V, Netherlands) using Cu Kα radiation (λ = 0.154 nm) at a scanning rate of 2°/min. The morphology and microstructure of the samples were obtained using field emission scanning electron microscopy (FESEM) (CARL ZEISS-Sigma, Germany). The phase change properties of the form-stable PCMs were investigated using differential scanning differential scanning calorimetry (DSC) (DSC214, NETZSCH, Germany) at a heating and cooling rate of 10 °C/ min under a constant stream of nitrogen. The thermal conductivity was

Table 1: The compositions of the PEG/UPR/GNPs composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PEG (g)</th>
<th>PEG/UPR</th>
<th>S1 (g)</th>
<th>S2 (g)</th>
<th>S3 (g)</th>
<th>S4 (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG (g)</td>
<td>–</td>
<td>20.0</td>
<td>20.0</td>
<td>20.0</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td>UPR (g)</td>
<td>–</td>
<td>5.0</td>
<td>4.75</td>
<td>4.5</td>
<td>4.25</td>
<td>4.0</td>
</tr>
<tr>
<td>GNPs (g)</td>
<td>–</td>
<td>0</td>
<td>0.25</td>
<td>0.5</td>
<td>0.75</td>
<td>1.0</td>
</tr>
<tr>
<td>Loading of GNPs (wt%)</td>
<td>–</td>
<td>0</td>
<td>0.5</td>
<td>1.0</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>Loading of PEG (wt%)</td>
<td>100</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
</tbody>
</table>