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Study on a PEG/epoxy shape-stabilized phase change material: Preparation, thermal properties and thermal storage performance

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ABSTRACT

In this work, PEG based SSPCMs were successfully prepared using 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) modified epoxy resins as reliable supporting materials in the absence of solvent. The encapsulated PEG acted as phase change functional domains and DOPO was used to enhance the thermal stability of polymeric SSPCMs. The chemical composition and microstructure of prepared SSPCMs were characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). X-ray diffraction (XRD), differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) were conducted to investigate the crystalline properties, phase change properties and thermal stability of SSPCMs. Heat storage and release performance test was conducted to certify the reversible heat storage and release performance of SSPCMs. Thermal cycling test was also performed to illustrate the thermal reliability of SSPCMs. From DSC results, the prepared SSPCMs melted at 67.7 °C and crystallized at 27.9 °C and the corresponding latent heat are 112.0 J/g and 108.0 J/g, respectively. TG results showed that SSPCMs have good thermal stability with the onset decomposition temperature far beyond their working temperature.

1. Introduction

Phase change materials (PCMs) for a wide range of practical application from waste heat utilization to thermal protection of electronics have been deeply studied in last decade because of the energy crisis and continuous deteriorative environment. Energy in the form of latent heat can be stored in the PCMs with an economically feasible way [1–6]. PCMs function by absorbing energy at higher temperature through the melting of crystal and releasing energy at lower temperature during the crystallization process. Many organic compounds including paraffin, polyethylene glycol (PEG), fatty alcohol, fatty acid and their eutectic are common PCMs [2,7–11]. Among them, PEG shows many superior properties such as high latent heat value, good biocompatibility, non-corrosiveness and reasonable price [8,12,13]. However, the lower viscosity of molten PEG can easily lead to leakage problem during phase change process [14,15]. Therefore, some strategies were developed to prevent the leakage of molten PEG [4,9,10,12,15–17]. Shape-stabilized PCMs (SSPCMs) prepared by blending PEG with encapsulation materials provide a rational alternative route for latent heat storage. Their shape is stabilized during phase change process and PEG is encapsulated in the encapsulation materials [16,18]. Hence, the selection of encapsulation materials is a key issue to prepare SSPCMs with favorable properties.

There are two types of encapsulation materials for SSPCMs [11,19–21]. Generally, inorganic porous materials such as vermiculite, perlite, diatomite, and active carbon are attractive encapsulation materials due to their abundant supply and excellent thermal stability [7,12,15,22–25]. Notably, the encapsulation capacity of those materials comes from the capillary and surface tension forces of porous structures. The limited amount of porous structures usually leads to a low encapsulation ratio. Taking diatomite for example, even though it has been dealt with high temperature calcination, acid treatment and alkali leaching before encapsulation, the maximum load of PEG is 63 wt% [12]. Moreover, the loose particle morphology of those inorganic porous materials often require concrete, cement and adhesives to achieve appropriate mechanical strength during its real application, which severely improves the production cost [26–30]. Another type of encapsulation materials is polymers. Compared with inorganic porous encapsulation materials, polymers have relatively higher mechanical strength and good toughness [17,19,23,31–35]. In addition, the outstanding processability of polymers makes SSPCMs economically feasible and imparts SSPCMs with the ability to be processed into desired shapes. Therefore, PEG based SSPCMs using polymeric

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encapsulation materials can be flexible applied in those areas where complex three-dimensional structures and lightweight matrixes are required (e.g. the cooling of electronic chip). However, the poor thermal stability of polymers compared to inorganic porous materials is detrimental for the long term utilization of SSPCMs, especially under higher temperature condition. Little reports are available in literatures with regard to this subject. Therefore, thermal storage properties and thermal stability were studied in this work simultaneously.

In this work, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) with stable phosphaphenanthrene structure was adopted to enhance the thermal stability of epoxy resin. DOPO modified epoxy resin (DMEP) was cured by poly(propylene oxide)-diamine and used as reliable supporting materials, while the encapsulated PEG acted as phase change functional domains. To the best of our knowledge, crosslinked DMEP was the first time to be applied in the preparation of polymeric SSPCMs. In addition, the whole preparation processes were conducted in the absence of solvent, which was friendly to environment. The chemical composition, crystalline properties, microstructure, phase change properties, thermal stabilities and reliabilities were systematic investigated by Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscope (SEM), differential scanning calorimetry (DSC) and thermogravimetric analysis (TG), respectively. Moreover, heat storage and release performance of the prepared SSPCMs were discussed. The results of DSC and FTIR after thermal cycling test were used to illustrate the thermal reliability of synthesized SSPCMs.

2. Materials and methods

2.1. Materials

Novolac-type epoxy (F-48, epoxy equivalent: 190 g mol^{-1}) was purchased from Hunan Jiashengde Materials Technology Co., Ltd. (China). Poly(propylene oxide)diamine (Jeffamine T403, amine equivalent: 67 g mol^{-1}) was obtained from Huntsman Co. Ltd. (China). 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was obtained from Shengshida Technique Trade Co., Ltd. (Huizhou, China). Polyethylene glycol (PEG, molecular weight: 20,000 g mol^{-1}) from Chengdu Kelong Chemical Reagent Co., Ltd. (China) was dried under vacuum at 110 °C for 2 h before use.

2.2. Synthesis of DOPO modified epoxy resin (DMEP)

In a typical synthesis process, 50 g F-48 and 15 g DOPO were added into a 250 ml three-neck round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet and a thermometer. Heating mantle was used to keep the mixture at 160 °C for 4 h under nitrogen atmosphere with continuous stirring. After slowly cooling down to room temperature, DMEP was obtained and collected into a regent bottle. The detailed synthetic route is shown in Scheme 1.

2.3. Preparation of SSPCMs

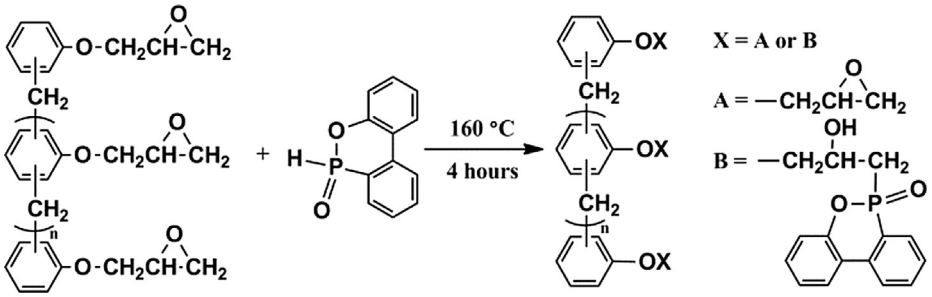
SSPCMs were prepared by thermal curing of DMEP with T-403 serving as curing agent in the presence of PEG. The weight ratio of DMEP to T-403 was fixed as 65/15 and the detailed formulas are recorded in Table 1. In a typical preparation process, DMEP and PEG were mixed in the three-necked 500 ml round-bottom flask at 80 °C for 0.5 h according to the respective stoichiometric ratios. After thoroughly homogenized, a predetermined amount of T-403 was added into the above mixture and kept stirring at 80 °C for 0.5 h. Next, the mixture was poured into a polytetrafluoroethylene mold and performed the thermal curing process. The thermal curing was conducted at 100 °C for 3 h in a vacuum oven. The amine-cured products (also the prepared SSPCMs) were recorded as $DMEP_{PEG-40}$, $DMEP_{PEG-50}$, $DMEP_{PEG-60}$ and $DMEP_{PEG-70}$ according to the weight percentage of PEG. The blank sample (the weight percentage of PEG is 0) was also prepared and named as $DMEP_{PEG-0}$. The corresponding preparation procedure of SSPCMs is shown in Scheme 2.

2.4. Characterization

The shape-stable properties of the synthesized SSPCMs were studied by using a vacuum oven and a digital camera. To confirm the suitable capsulation ratio, the synthesized SSPCMs were prepared at different PEG content (40, 50, 60, 70 and 75 wt%). The pristine PEG and all prepared SSPCMs were placed at vacuum oven to perform the leakage test by heating to 80 °C for 30 min, and then heating to 100 °C for another 30 min. Their appearances at different conditions were recorded by digital camera. FTIR test was conducted on a Nicolet 560 FTIR spectrometer at a step-rate of 4 cm^{-1} from 400 to 4000 cm^{-1}. XRD test was carried out by high-resolution X-ray diffractometer (Rigaku Co., Ltd, Japan) with a scanning rate of 2°/min in a scan range of 2θ from 5° to 50° at room temperature. DSC characterization was performed on a differential scanning calorimeter (DSC 8500 PerkinElmer, USA) with a heating rate of 10 °C/min under nitrogen atmosphere to study the phase change properties. All samples were weighted around 8 mg for

Table 1
Identification and composition of SSPCMs.

Samples	DMEP (g)	T-403 (g)	PEG	PEG content (%)	DOPO content (%)
$DMEP_{PEG-0}$	65	15	0	0	18.75
$DMEP_{PEG-40}$	65	15	53.33	40	11.25
$DMEP_{PEG-50}$	65	15	80.00	50	9.38
$DMEP_{PEG-60}$	65	15	120.00	60	7.50
$DMEP_{PEG-70}$	65	15	186.67	70	5.62



Scheme 1. Synthetic route of DMEP.