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Novel form stable phase change materials based on the composites of polyethylene glycol/polymeric solid-solid phase change material

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ABSTRACT

This study deals with the preparation and characterization of the composites of polyethylene glycol (PEG)/the synthesized polymeric solid-solid phase change material (SSPCM) as novel form stable phase change material (FSPCM) for thermal energy storage. The synthesized SSPCM can play two roles in the FSPCM: the supporting material and the phase change working substance. The influence of PEG content on crystalline properties and phase change behaviors of the FSPCMs was investigated. The polarizing optical microscopy (POM) images of FSPCMs show that all FSPCMs have the spherocrystal morphology, and the spherocrystal size of SSPCM increases with the increasing of PEG percent. The results from differential scanning calorimetry (DSC) indicate that the prepared FSPCMs with different PEG contents have high thermal storage density, and the enthalpy efficiency of them is much higher than that of the traditional FSPCMs due to the synergistic phase change effect of PEG and SSPCM. The Fourier transform infrared spectroscopy (FTIR) spectrum and DSC curve of the FSPCMs after thermal cycling are almost the same as those of the original samples, which indicates that the FSPCMs have excellent thermal reliability and reusability. The work not only supplied a kind of novel FSPCMs with high performances, but also proposed a new way to solve the problem of enthalpy decline of traditional FSPCMs and synthesized polymeric SSPCMs compared with solid-liquid PCMs.

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1. Introduction

Latent heat storage systems using phase change materials (PCMs) have been applied in various areas such as solar energy systems, space based power plants, central air-conditioning systems and energy efficient buildings due to the high energy storage density and quasi isothermal behavior of PCMs during the heat storage and release processes [1–8]. There are two common types of PCMs according to the phase change state: solid-liquid PCMs (SLPCMs) and solid-solid PCMs (SSPCMs). In the last decades, the ordinary SLPCMs (e.g., inorganic hydrous salts, paraffin waxes, long chain fatty acids, polyethylene glycol, etc.) have been studied and applied extensively in thermal energy storage for their advantages of large latent heats, numerous species and inexpensiveness [3,4]. However, special encapsulated container are needed for SLPCMs because of the generation of liquid phase in the phase change process of SLPCMs, which inevitably makes extra thermal resistance and higher running costs. To solve this problem, form stable (or shape-stabilized) PCMs (FSPCMs) have become a research hotspot in the area of latent heat energy storage in the past decade [9–23].

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Generally speaking, FSPCMs are mainly composed of two parts: phase change working substances (namely the common SLPCMs) and the supporting materials (usually inorganic materials with porous/lamellar structure [9–13] or polymers with high melting point [14–23]). The biggest merit of FSPCMs for thermal energy storage is that their solid form can be kept well when the ambient temperature is higher than the phase change temperature of the used SLPCMs. A lot of methods to prepare FSPCMs with various shapes and dimensions have been used and reported, such as vacuum impregnation [9], sol-gel [10], melt blending [11,12], solution/melt intercalation [13], solution casting [14–16], micro-encapsulation [17,18], twin-screw extrusion molding [19], in situ polymerization [20], electrospinning [21–23], etcetera. From previous studies, although the addition of supporting material was beneficial to the shape stabilization of melting phase change ingredients in the FSPCMs, it inevitably degraded the thermal storage density of the FSPCMs. Consequently, on the condition that the PCMs could be encapsulated in the matrix network without any leakage, the mass fraction of PCMs in composite should be maximized as much as possible. However, the augment of PCM content in FSPCMs is hugely limited. Therefore, minimizing the negative impact of the supporting materials on the phase change latent heat of FSPCMs may be another feasible way to obtaining FSPCMs with high enthalpies.

In this work, we have provided a new idea to prepare FSPCMs with high phase change enthalpies. A polymeric SSPCM with ideal phase change behaviors was synthesized and then it was selected as the supporting material of the novel FSPCMs for the first time. Glucose was selected as the skeleton and polyethylene glycol (PEG) was used as the phase change functional chain in the polymeric SSPCM, and PEG also acts as phase change working substance in the prepared FSPCMs. Solid-liquid phase transition of PEG and solid-solid phase transition of SSPCM would occur simultaneously in a certain temperature range in the FSPCMs (we name the phenomena as synergistic phase change), thus the phase change enthalpies of prepared FSPCMs would be raised greatly compared with the synthesized SSPCM and the traditional FSPCMs due to the synergistic effect. In order to differentiate the novel FSPCMs in this work and the traditional FSPCMs in the previous researches, the novel FSPCMs with synergistic phase change property are named synergistic PCMs (abbreviated as SPCMs). The phase transition behaviors, crystalline properties, thermal reliability and stability of the prepared SPCMs were investigated using differential scanning calorimetry (DSC), X-ray diffraction (XRD)/polarizing optical microscopy (POM) and thermogravimetry analysis (TG), respectively.

2. Experimental part

2.1. Materials

PEG (analytical grade, $M_n=8,000$, from Amresco Co., USA) and glucose (from Tianjin Yongda Chemical Regents Co. Ltd., China) were degassed and dried in a round flask under high vacuum at 100 °C for 3–4 h. 4,4'-diphenylmethane diisocyanate (MDI, from Aladdin Chemistry Co. Ltd., China) was heated to 60 °C and kept for 2 h under vacuum and then filtered by a heated filter. *N,N*-dimethylformamide (DMF) was dried using 5 Å molecular sieve for 48 h, and then distilled before use.

2.2. Preparation of SPCMs

There are four steps for the preparation of SPCMs, and the corresponding synthetic route is shown in Fig. 1. Firstly, the calculated amount of PEG and MDI (molar ratio of PEG to MDI=1:2) were dissolved in DMF with stirring in a thermostatic oil-bath at 70 °C for 6 h, and the prepolymer of PEG/MDI was obtained in this process. Secondly, the DMF solution of glucose (molar ratio of glucose to MDI=1:5) was slowly dropped into the above mixture, and then stirring at 70 °C for 24 h. thirdly, extra PEG with different content (0, 50, 60, 70, 75, and 80%, w/w) were added in the reaction mixture and then it was poured into a beaker. Thermal curing was conducted at 80 °C for 24 h in the drying oven. Lastly, the products were kept in vacuum at 40 °C for two weeks to eliminate any volatile matter before testing. The final material without extra PEG (0 wt% extra PEG) is the crosslinked PEG/MDI/glucose copolymer, and it is labeled as SSPCM.

To verify the form stable characteristic of the prepared composite materials, the leakage test were performed as follows: pristine PEG (as the reference) and the blends with the same weight were heated to 70 °C (above the melting temperature of PEG) simultaneously and kept the temperature constant until pristine PEG melt completely. Then, the samples were cooled to room temperature. The heating-cooling process was cycled for 10 times. The blends that do not permit leakage of melted PEG from the blends were recognized as form-stable PCMs. The result showed that the maximum content of PEG in the PEG/SSPCM blend without melted PEG leakage is 70 wt%. The composite PCMs with extra PEG contents of 50 wt%, 60 wt% and 70 wt% are labeled as SPCM-1, SPCM-2 and SPCM-3, respectively.

2.3. Characterization

2.3.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of samples were obtained using Infrared Spectrophotometer (NICOLET-760, Nicolet Co., USA) in the wavenumber range of 400–4000 cm^{-1} . Before the measurement, every sample was mixed with KBr powders and then pressed into a small pellet.

2.3.2. X-ray diffraction (XRD)

XRD patterns of the samples were recorded at room temperature on an automatic powder diffractometer (D8 Advance, Bruker-AXS, Germany) with Ni-filtered Cu K α radiation at 40 kV and 30 mA. The scans were obtained in the range of $5^\circ < 2\theta < 50^\circ$ by using a 0.02° step programmed with a collection time of 0.1 s per step.

2.3.3. Polarizing optical microscopy (POM)

An observation of POM images was performed on a polarizing microscope (XPN-300E, Shanghai Changfang Optical Instrument Co., Ltd, China) equipped with a video camera. The sample was placed between a microscope glass and a cover slip and heated with a hot stage.

2.3.4. Differential scanning calorimetry (DSC)

The phase transition properties of samples were measured by DSC curves using a Simultaneous Thermal Analysis Apparatus (STA 449 F3 Jupiter[®], Netzsch, Germany). The instrument was calibrated using the onset temperatures of melting of indium and zinc standards, as well as the melting enthalpy of indium. The DSC analyses were carried out at 2 °C/min heating/cooling rate under a constant stream of nitrogen at a flow rate of 30 ml/min. To eliminate the heat history of the sample, the samples (5–10 mg) sealed in an aluminum pans were firstly heated from 25 °C to 100 °C and then cooled from 100 °C to 25 °C. For the second scan, the samples were heated and cooled under the same conditions. All DSC curves of the samples were recorded from the second scan, and the onset temperatures of melting and crystallization, as well as melting and crystallization enthalpies, were also determined from the second scan. All DSC measurements were repeated three times for each sample in order to minimize the uncertainty. The phase change temperatures and enthalpies were reported as average values with standard deviations.

2.3.5. Thermogravimetry analysis (TG)

The thermal stability of the samples was characterized by TG curves also using a Simultaneous Thermal Analysis Apparatus (STA 449 F3 Jupiter[®], Netzsch, Germany). About 10 mg of sample was placed into an aluminium oxide crucible and the profiles were recorded from room temperature to 600 °C under a nitrogen atmosphere at a heating rate of 10 °C/min.

2.4. Accelerated thermal cycling test

In order to confirm the reusability, thermal reliability and stability of the prepared SPCMs, the accelerated thermal cycling test was conducted. The test was performed by a hot stage (STC200, Instec, USA) as the following step. The aluminium pan loaded appropriate amount of sample was put on a hot stage with a typical thermal cycling program consisted of 100, 250 and 500 consecutive heating and cooling processes (in the temperature interval of 25 °C–100 °C), and the time was set about 20 min for each complete heating-cooling process. Afterwards, thermal properties and chemical stability of SPCMs after thermal cycling were investigated by DSC and FTIR analysis.

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