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Solvent-free preparation and performance of novel xylitol based solid-solid phase change materials for thermal energy storage

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ABSTRACT

Novel polymeric solid-solid phase change materials (SSPCMs) were prepared through solvent-free bulk polymerization by employing polyethylene glycol (PEG) as phase change functional segments, diphenylmethane diisocyanate (MDI) as coupling agent and xylitol as curing agent. Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), polarizing optical microscopy (POM), differential scanning calorimetry (DSC), accelerated thermal cycling testing and thermogravimetric analysis (TG) were conducted to study the chemical structure, crystalline properties, phase change properties, thermal reliability and stability of SSPCMs, respectively. The crosslinked structure gave the obtained SSPCMs solid-solid phase change process. XRD and POM results showed that SSPCMs have the same crystalline structure, lower degree of crystallinity and smaller crystal size with pure PEG. DSC results indicated that SSPCMs are capable of reversible storing and releasing latent heat in the temperature of −10 to 60 °C through phase transitions. Thermal cycling tests demonstrated that SSPCMs have good thermal reliability and chemical stability. TG results testified the thermal stability of SSPCM. The obtained SSPCMs exhibited great potential application in the field of thermal energy storage.

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1. Introduction

The effective utilization of energy and the exploitation of renewable energy sources have become a central issue since the fossil energy crisis and the concern over environment [1,2]. Thermal energy storage (TES) is one of the most prospective methods for increasing the efficiency utilization of energy [3,4]. Latent heat storage is more preferable than other TES systems due to it's relatively high density of energy accumulation over very narrow temperature range [5]. Phase change materials (PCMs) are a series of functional materials with storing and releasing latent heat during phase change process. And PCMs can be employed to adjust and control the environment temperature around them [6,7]. Therefore, PCMs have captured increasing attentions from both academia and industry [8,9], and have been employed in many fields of latent heat TES such as: thermal control in buildings [10]; solar energy storage [11]; electricity [12]; photology [13]; batteries [14] and so forth [15].

In recent years, salt hydrates [16], paraffins [17], fatty acids [18], esters [19], polyethylene glycol (PEG) [20] and some other materials [21] have been extensively studied as PCMs. However, all those PCMs are solid-liquid phase change process, which will restrict their application due to the leakage [22]. So those solid-liquid PCMs are always modified into solid-solid PCM (SSPCMs) to prevent the leakage (such as blended with porous structure material, encapsulated and polymerized to macromolecular) [23,24]. Among those PCMs, PEG has been developed as SSPCMs due to the virtues of diversity kinds, low cost, high enthalpy and good biocompatibility for PEG [25,26]. Fu [27] prepared the phase change materials with PEG as the working phase change substance and Span 80 and Tween 80 as crosslinking agents through bulk polymerization. Peng [28] prepared β-cyclodextrin/diphenylmethane diisocyanate/polyethylene glycol (β-CD/MDI/PEG) crosslinking copolymers for thermal energy storage. In the PCMs, PEG acted as the phase change functional chain and β-cyclodextrin (β-CD) acted as the molecular framework. Nihal Sarier et al. [29] synthesized PEG grafted poly(acrylo nitrile) (PAN) copolymers as a novel solid-solid phase change materials via two step free radical polymerization reaction. And the obtained copolymers can be used as promising TES materials. Kinga Pielichowska reported the synthesis of polyurethane-based PCMs modified with graphene for thermal energy storage, and the PCMs were obtained in situ using a one-step bulk polymerization method [30]. Herein, it is very important and valuable to design and synthesize new PEG based PCMs with novel curing agent.

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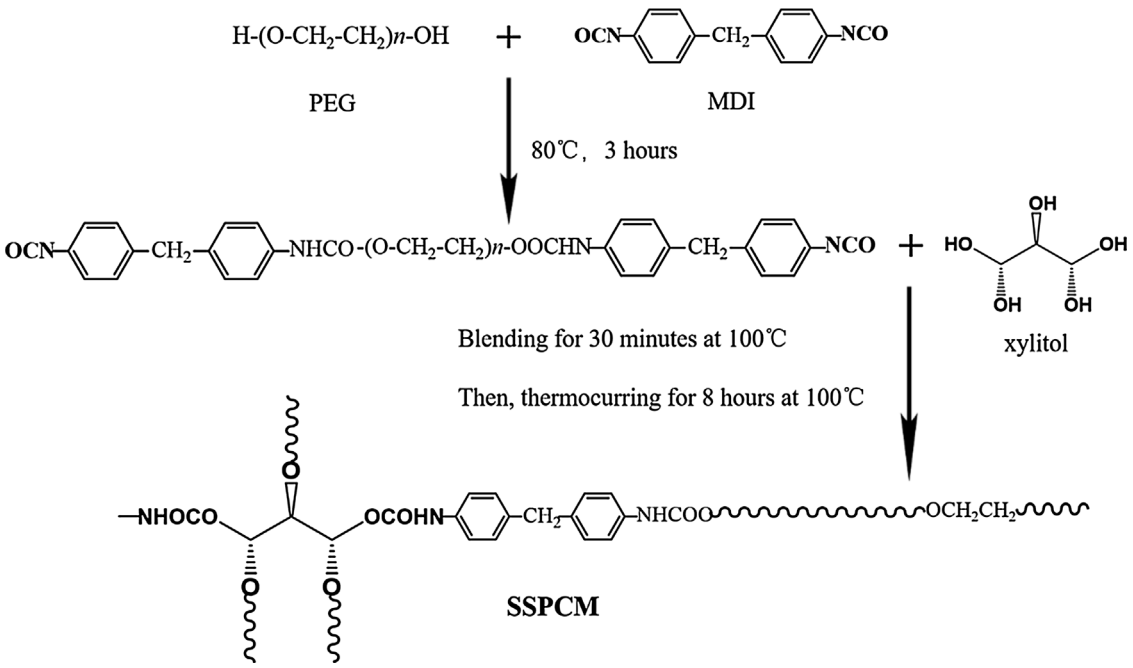

Fig. 1. The synthetic route of SSPCMs.

It is well known that xylitol is biocompatible, biodegradable and nontoxic [31] and is always employed as the medicine and sugar [32]. Therefore, xylitol can be employed as crosslinking reagent to prepare the SSPCMs used for building. In this study, two novel polymeric solid-solid PCMs were prepared through bulk polymerization with PEG acting as phase change functional segments, MDI as coupling agent and xylitol as molecular framework. The chemical structure, crystallization properties, phase change process, phase change behavior and thermal reliability and stability of PCMs were studied by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), polarizing microscope (POM), differential scanning calorimetry (DSC), and thermogravimetric analysis (TG), respectively.

2. Experimental

2.1. Materials

Polyethylene glyol (Mw = 4000 g/mol: PEG4000; Mw = 6000 g/mol: PEG6000) and xylitol were obtained from Kelong Chemical Reagent (Chengdu, China); 4, 4'-diphenylmethane diisocyanate (MDI) was purchased from Yantai Wanhua polyurethane Co., Ltd. (Shandong, China). All chemical reagents were used as received.

2.2. Preparation of SSPCMs

0.025 mol PEG was loaded into a three-neck flask, after the melting of PEG at 80 °C 0.05 mol MDI was added into the flask and then the prepolymer was obtained after 3 h fully blending at 80 °C. Subsequently, 0.01 mol melted xylitol was introduced into the prepolymer at 100 °C, after another 30 min blending the mixture was transferred into an oven. The solid-solid phase change materials (SSPCMs) were obtained after 8 h thermal curing at 100 °C. PCM-4 and PCM-6 represented PEG4000 and PEG6000 based SSPCMs, respectively. In addition, the detailed synthetic route is shown in Fig. 1.

2.3. Characterization

2.3.1. FTIR

The FTIR measurements were performed on Nicolet 560 (Nicolette Co., USA) to study the chemical structure of xylitol, PEG4000, PEG6000, PCM-4 and PCM-6. The scanning was in the range of 4000–400 cm^{-1} with a resolution setting of 4 cm^{-1}. Testing samples of xylitol and PEGs were prepared by the KBr pressed disc technique, and prepared PCMs were measured by attenuated total reflection model.

2.3.2. XRD

XRD was employed to investigate the crystalline behaviors of virgin PEGs and prepared SSPCMs, and the measurement was conducted on Phillips X'Pert Pro MPD diffractometer in Bragg-Brentano geometry at 35 kV and 30 mA. Cu Ka radiation of 1.54056 A° was obtained with a curved graphite monochromator. The diffraction peak data were collected in a range of 2θ = 5–50° by a scanning rate of 0.04°/min at room temperature.

2.3.3. POM

The crystalline morphology of virgin PEGs and prepared SSPCMs was detected by XPR-500D microscope (China) equipped with a video camera. The testing sample was located between a microscope glass and a cover slip.

2.3.4. DSC

Phase change properties of virgin PEGs and prepared SSPCMs were determined by the DSC using the DSC 204 (NETZSCH, Germany). About 8 mg sample were heated from ambient temperature to 100 °C to erase prior heat history of the samples. Then, the sample was cooled to 0 °C to collect DSC cooling data. The second heating scan produced the DSC heating profile. Both heating and cooling temperature scans were carried out at the rate of 10 °C/min under a dry nitrogen atmosphere.

2.3.5. Accelerated thermal cycling testing

To investigate the thermal reliability of the prepared SSPCMs, the accelerated thermal cycling testing was conducted in a high-

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