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Preparation and characterization of melamine/formaldehyde/polyethylene glycol crosslinking copolymers as solid–solid phase change materials

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ABSTRACT

A kind of solid–solid phase change materials (SSPCMs), melamine/formaldehyde/polyethylene glycols (MFPEG) crosslinking copolymers, was synthesized referring to the reaction mechanism and conditions of amine–aldehyde condensation reaction and aldolization. The composition and chemical structure, thermophysical and crystallographic properties of MFPEG crosslinking copolymers were investigated by Fourier transform infrared spectroscopy (FT-IR), ¹H nuclear magnetic resonance spectrometer (¹H NMR), differential scanning calorimetry (DSC), thermogravimetry analysis system (TGA), wide-angle X-ray diffraction (WXR) and polarization optical microscopy (POM). The results indicate that MFPEGs crosslinking copolymers possess excellent phase change properties and an applicable temperature range. The maximal latent heat enthalpies of heating and cooling cycle are 109.4 and 103.9 J/g, respectively. The decomposing temperature range of MFPEGs is about 340–455 °C in nitrogen atmosphere.

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1. Introduction

The depletion of fossil energy and the increasing atmospheric temperature have been a threat to the survival and development of human for a long time. The threat has made the utilization of renewable energy sources an inevitable problem [1]. Solar application and industrial waste heat recovery are promising ways to surmount such problem [2]. So the energy storage technology becomes more and more imperative. Latent heat thermal energy storage technique is an extremely attractive one among the energy storage methods, because it can be employed not only in solar energy storage but also in waste heat recovery [3,4] and electric power conversion of peak load shifting [5,6].

Phase change materials (PCMs) are effective latent heat thermal energy storage media. Practically, PCMs are often divided into solid–solid PCMs (SSPCMs), solid–liquid PCMs, solid–gas PCMs, and liquid–gas PCMs [7]. Because the volume of gas varies with a great range, the solid–gas PCMs and liquid–gas PCMs are rarely applied in practice. Most conventional PCMs store or release energy by solid–liquid phase transitions, yet the liquid state substances are less in harmony with outer environment. In view

of this, more and more attention has been paid to the preparation, characterization and application of SSPCMs. The SSPCMs carry on storing or releasing energy by solid–solid phase transitions. During the process, no liquid or gas generated, accordingly no recipient is needed to seal SSPCMs in [8].

Polyethylene glycols (PEGs) of average molecular weight from 800 to 20,000 g/mol are functional materials for latent heat thermal energy storage due to their excellent features such as suitable melting and crystallizing temperature range, congruent melting and solidifying behavior, relatively high phase change enthalpy of fusion and solidification during its melting/freezing temperature range, eco-friendly and so on [9–11]. Nevertheless, economic and efficient method to get PEG composites with reliable thermal stability, non-leakage and fire-proofing properties is a key to promote their practical application. Fortunately, form-stable PCMs, shape-stabilized PCMs [9,12,13], and potential precursors of SSPCMs can be easily prepared [8,14–18] for the reaction between the functional end groups (–OH), polar parts (–O–) in their molecular chains of PEGs and lots of reagents by generating chemical bonds or hydrogen bonds etc.

In spite of this, there are lots of defects hidden in the PCMs containing PEGs. Leakage is the chief disadvantage of the shape-stabilized PCMs or form-stable PCMs, which are prepared by physical methods such as vacuum impregnation [12] or solution casting [13]. Increasing frequency of heating and cooling will lower

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the practical application life of the PCMs mentioned above. On the other hand, complexity of chemical methods of synthesizing SSPCMs with PEGs is a remarkable obstacle in the practical application for energy storage.

In this study, a kind of SSPCMs with crosslinking structure composed of PEGs at different molecular weight as energy-storage ingredient and melamine as crosslinking functional reactant, are synthesized through two steps and characterized by Fourier transform infrared spectroscopy (FT-IR), ^1H nuclear magnetic resonance spectrometer (^1H NMR), differential scanning calorimetry (DSC), thermogravimetric analysis system (TGA), wide-angle X-ray diffraction (WXR) and polarization optical microscopy (POM). The infusible and insoluble MFPEG crosslinking copolymers with higher phase change enthalpy and suitable transition temperature is a kind of SSPCMs with practical application value.

2. Materials and methods

2.1. Materials

Polyethylene glycol (PEG; M_w : 6000) was obtained from Hai'an Petrochemical Plant, industrial grade. PEG with M_w : 1000, 2000, 4000, 10,000 were supplied by Tianjin Institute Guangfu Fine Chemical Company, AR. Formaldehyde aqueous solution (w%: 36%) and acetic acid were purchased from Beijing Chemical Plant, AR. Reagents all above were used as received.

2.2. Synthesis of MFPEG crosslinking copolymers

The synthesis was conducted through two main steps: Step a, melamine, formaldehyde (w%: 36%), and PEG were added into three necks round bottomed flask with an overhead stirrer at mass ratio 1:m:n ($4 < m < 6$, $1 < n < 20$), with water as reaction medium. The temperature was set at a certain value varying from 30 °C to 70 °C. The pH of the solution was adjusted to 6.0–7.0 by adding acetic acid. Then a precursor mixture was prepared by stirring gently for 2–3 h. All above were fulfilled in a ventilation device. Step b, the mixture of precursor was put into a constant temperature oven at 110 °C, MFPEG crosslinking copolymers was obtained when the water in the precursor mixture had been evaporated exhaustively. The synthesis route is shown in Fig. 1. Both the steps refer to the mechanism of amine–aldehyde condensation reaction and aldolization.

2.3. Characterization

The chemical structures of melamine, PEG6000 and MFPEG6000 copolymer were characterized by a FT-IR spectrometer (Perkin Elmer, Spectrum 100, USA) and a NMR spectrometer (Bruker, mq 20, German). FT-IR measurements were performed on KBr disks and

the wavenumbers range is 4000–650 cm^{-1} and the resolution is 4 cm^{-1} . ^1H NMR spectra were recorded using deuterated dimethyl sulfoxide as solvents (concentration ≈ 10 mg/mL).

The phase change properties of PEG and MFPEG cross-linking polymer were characterized by a differential scanning calorimeter (DSC, TA instruments, DISCOVER, USA) with the range of 10–90 °C at a rate of ± 10 °C/min under a nitrogen atmosphere.

Thermal stabilities of melamine, PEG and MFPEG were investigated by a Thermogravimetric Analyzer (TGA, Netzsch STA409PC, German) with the range of 45–580 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. The temperature at less than 5% mass-loss was recorded as a thermal stability.

The crystallization behaviors of melamine, PEG and MFPEG cross-linking polymer were characterized by a wide-angle X-ray diffraction (WXR, Rigaku, Ultima IV, Japanese), and the scan range was at 5–50°(2 θ).

The crystallization state of PEG and MFPEG copolymer was observed by a polarization optical microscopy (POM, Olympus, BX51-P, Japanese) equipped with a video-camera. The sample was placed between a microscope glass and a cover slip and heated with a Leitz350 hot stage.

3. Results and discussion

MFPEG crosslinking copolymers obtained at the mass ratio 1:m:n ($4 < m < 6$, $1 < n < 20$, melamine:formaldehyde:PEG) show similar structure and properties, and similar differences between samples with different PEGs can be observed. For consistency of discussion, we selected the sample prepared at mass ratio 1:5:5 as an illustration.

3.1. Structural characterization of MFPEG crosslinking copolymers

The synthesized MFPEG crosslinking copolymers were characterized structurally by FT-IR and ^1H NMR spectroscopy methods. Fig. 2 shows the FT-IR analysis results of melamine, PEG6000 and MFPEG6000. As can be seen from the spectrum of melamine, five peaks in the 3000–3500 cm^{-1} range, at 3469, 3417, 3325, 3187, 3123 cm^{-1} confirm the observations of reference [19], which are vested in the stretch vibration of N–H in secondary amines [20]; the absorption peaks at 1651, 1022 cm^{-1} are assigned to the bending vibration and the twisting vibration of N–H respectively; the absorption peaks at 1551, 814 cm^{-1} are attributed to deformation vibration of triazine ring. The FT-IR spectrum in Fig. 2 shows many characteristic peaks of the pristine PEG6000 at 3357, 2871, 1455, 1351, 1249, 1106, and 950 cm^{-1} . It is obvious that the peak at 3357 cm^{-1} is attributed to the stretching vibration of functional group of O–H. The peaks at 2871 and 950 cm^{-1} represent the stretching vibration of functional group of $-\text{CH}_2-$ of PEG. The peak

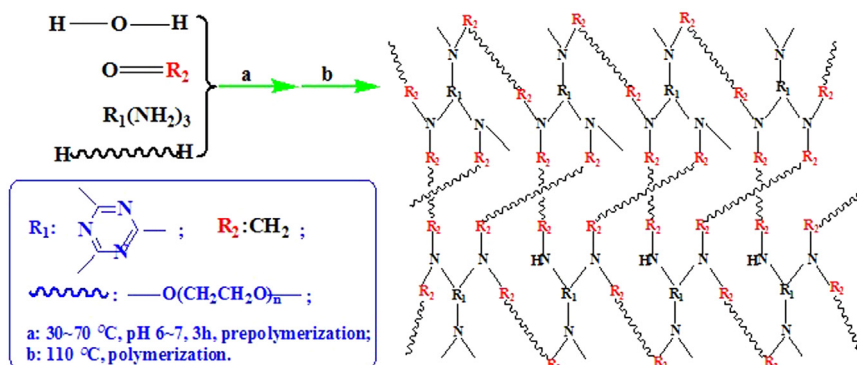


Fig. 1. Synthesis scheme to network structure of MFPEG crosslinking.

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