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Linear polyurethane ionomers as solid–solid phase change materials for thermal energy storage



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ABSTRACT

Linear polyurethane (PU) ionomers were synthesized as solid–solid phase changing materials (PCMs) for thermal energy storage. Poly(ethylene glycol)s (PEGs) with 6000 and 10,000 g/mol number average molecular weight were used as latent heat storage materials, and 4,4-diphenylmethane diisocyanate (MDI), N-methyldiethanolamine (MDEA) and 1,3-Propanesulfonate (PS) were used as supporting materials. The phase change enthalpies of PU ionomers were 142.5 J/g and 152.3 J/g respectively, which were much close to the highest reported value of the branched PUPCM or the cross-linking PUPCM. The results of Fourier transform infrared spectroscopy (FT-IR) and atomic force microscopy (AFM) suggested a high degree of phase separation existed in PU ionomers. And the thermal resistance of PU ionomers was improved by the introduction of ionic groups.

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1. Introduction

Scientists all over the world have recently been in search of new and renewable energy sources due to the continuous increase in the levels of greenhouse gas emissions and the climb in fuel prices. One of the options is to develop energy storage devices, which is as important as to develop new sources of energy. It leads to saving of premium fuels and makes the system more cost effective by reducing the wastage of energy and capital cost. Latent heat storage based on phase change materials (PCMs) is a particularly attractive technique, since it provides a high heat storage density and has the capacity to store heat as latent heat of fusion at a constant temperature corresponding to the phase transition temperature of the PCMs. Compared with other PCMs, solid–solid PCMs show obvious advantages: no liquid or gas generation, small volume change and no seal needed. One of the prospective solid–solid PCMs is poly(ethylene glycol) based polyurethane (PEG-PU). Poly(ethylene glycol) (PEG) as a phase change ingredient (soft segment) is covalently bonded to diisocyanate acting as a skeleton (hard segment) to keep the material in solid state after the melting of PEG. Much research [1–5] has been focused on synthesizing PEG-PU solid–solid PCMs to improve thermal properties including phase change enthalpy and thermal resistance by altering their dimensional shapes from linear to long-chain branch,

hyperbranch or cross-linking. Meng [1] prepared linear polyurethane (PU) solid–solid PCM using 1,4-butane diol as chain extender, and its phase change enthalpy was about 100 J/g. Xi [6] reported long-chain branched PU solid–solid PCM using synthetic tetrahydroxy compound as chain extender and its phase change enthalpy was 137.4 J/g with more than 80 wt% PEG 6000. Cao [7] and Liao [8] prepared hyperbranched PUs using hyperbranched polyester (Boltorn[®]H20) as chain extender. The phase transition enthalpies of the both were 138.2 J/g and 125.0 J/g with 90 wt% PEG 6000 respectively. Li [9] reported cross-linking PUPCM using pentaerythritol as chain extender and its phase change enthalpy was 152.97 J/g with about 95 wt% PEG 10,000. However, linear PUPCMs with low energy storage density are thermoplastic and can be processed directly, and branched PUPCMs or cross-linking PUPCMs with high phase transition enthalpy cannot be processed directly according to the above reports, which means the high thermal energy storage capability conflicts with the good processibility.

To increase the phase transition enthalpy of PEG-PU, the key lies in improving the crystallinity of PEG as soft segment in PU. However, hard segments dispersing in soft domains act as impurity, which interfere with PEG's crystal growth [10,11]. In addition, the interaction between hard segment and soft segment such as hydrogen bond constrains the free movement of PEG, which hinders PEG from agglomerating and crystallizing. An investigation [12] on PU ionomers suggested that introducing ions into PU improved the degree of phase separation and hard segment domain cohesion, which both nearly completely removed hard segments from soft phase [12,13]. It was in favor of the purity and

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continuity of soft domains without the disruption of hard segments. Also, ionization decreased the interaction between hard segment and soft segment [14]. Moreover, it was reported [15] that incorporation of ionic groups into hard segments led to a relative high degree of soft segment crystallization. Based on these opinions, it was suspected that ionization would contribute to the free movement of PEG molecular and crystal formation. In this paper, linear PU ionomer PCMs were synthesized by using PEGs as latent heat storage materials with 4,4-diphenylmethane diisocyanate (MDI), N-methyldiethanolamine (MDEA) and 1,3-Propanesulfonate (PS) as supporting materials. Linear PU ionomers are thermoplastic and can be processed directly. And it was found that PU ionomers have rather high heat storage. To the best of our knowledge, linear PU ionomers for heat storage have not been reported to date. The properties of PU ionomers were investigated with differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR), atomic force microscopy (AFM), thermogravimetric analysis (TGA), wide angle X-ray diffraction (WAXD), and polarization optical microscopy (POM) respectively.

2. Experimental

2.1. Materials

PEG ($M_n=6000$ and $10,000$ g/mol), 1, 4-butane diol (BDO) and N,N-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent, China). MDI was supplied by HuaFon Industrial Group (Zhejiang, China). DMF was dried by 4 Å molecular sieves before use. MDEA and PS were purchased from Aladdin Reagent Co. (Shanghai, China).

2.2. Samples preparation

PEG was placed into a 500 mL round-bottom, four-necked separable flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and condenser. Water was evaporated at reduced pressure at $110\text{ }^\circ\text{C}$ in an oil bath for 2 h. MDI in distilled DMF was added when PEG cooled to $70\text{ }^\circ\text{C}$ under a nitrogen atmosphere. The reaction mixture was stirred for 3 h and NCO-terminated prepolymer was obtained. Later, MDEA and some DMF were fed into the reactor, and the mixture was stirred for an additional 2 h. To make PU with linear macromolecule, the mole ratio $([\text{NCO}]_{\text{MDI}}/([\text{OH}]_{\text{MDEA}} + [\text{OH}]_{\text{PEG}}))$ was 1:1 strictly. Then, PU solution was obtained. Solution of PS in some tetrahydrofuran was added in the obtained PU solution. Finally, PU ionomers were prepared by refluxing this mixture for further 2 h at $60\text{ }^\circ\text{C}$. The synthesis route and the recipes of PU ionomers are shown in Scheme 1 and Table 1, respectively. PU ionomer solution was placed onto release paper and kept at room temperature for two weeks, then dried in a vacuum oven at $60\text{ }^\circ\text{C}$ for characterization.

2.3. Characterization

The phase change temperature and the enthalpy of the samples were measured with a differential scanning calorimeter (DSC, Q-1000, TA Instrument, USA) in a nitrogen atmosphere. The flow rate of N_2 was maintained at $50\text{ mL}\cdot\text{min}^{-1}$. All samples (5–10 mg) sealed in aluminum pans were heated and cooled at a rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. The sample were heated from -40 to $120\text{ }^\circ\text{C}$ and kept at $120\text{ }^\circ\text{C}$ for 3 min to erase the thermal history and subsequently cooled to $-40\text{ }^\circ\text{C}$. Then, the sample was reheated to $120\text{ }^\circ\text{C}$ at the same heating rate. The crystallinity (X_c) of the samples were calculated according to the Eq. (1) [1,7,16].

$$X_c(\%) = \Delta H_{\text{ionomer}} / \Delta H_{\text{PEG}}^0 \times 100\% \quad (1)$$

where $\Delta H_{\text{PEG}}^0 = 196.8\text{ J/g}$ is for the 100% crystalline PEG [17–19] and $\Delta H_{\text{ionomer}}$ —the enthalpy of fusion of the second heating run of PU ionomers under the investigation determined by DSC.

FT-IR spectra of PU ionomers and PUs without ionization were taken in an EQUINOX-55 (Bruker). Each sample was scanned 64 times at a resolution of 4 cm^{-1} .

AFM (Nanoscope III a, Veeco Instruments Inc., Santa Barbara, CA.) in tapping mode was employed to study the as-cast films of PU ionomers. The scans were taken at ambient conditions. Phase data were recorded with a standard silicon tapping tip on a beam cantilever. The length of the silicon probes is $125\text{ }\mu\text{m}$. The spring constant of the cantilever is between 10 and 130 N/m , and the resonance frequency is $204\text{--}497\text{ kHz}$.

The thermal analysis was performed by a thermogravimetric analysis SDT Q600 system (TA Instrument, USA) in a nitrogen atmosphere. About 10 mg dried sample was set into an alumina crucible and weighed. The samples were scanned over the temperature range from room temperature to $800\text{ }^\circ\text{C}$ at a heating rate of $5\text{ }^\circ\text{C}/\text{min}$.

The crystalline was studied using wide angle X-ray diffraction (WAXD) (Bruker, D8 advance, Cu Ka radiation using a curved graphite receiving monochromate), with a step of 0.02° at a speed of $4^\circ/\text{min}$ from 10° to 80° at room temperature. The crystallinity (X_c) was calculated using the method described by Young and Lovell [20]. The area of the X-ray diffraction curve due to scattering from the crystalline phase (A_c) and from the amorphous phase (A_a) could be separated, the crystallinity of the samples could be calculated by the following equation

$$X_c(\%) = A_c / (A_a + A_c) \times 100\% \quad (2)$$

A polarizing optical microscope (POM, made in Guangzhou Liss optical instrument Co., Ltd, China) equipped with a hot stage and a controller was used to observe the morphologies of pure PEGs and PU ionomers at above and below their phase change temperature.

3. Results and discussion

The DSC measurement on pristine PEG 6000 and PEG 10000 (Fig. 1) showed that the melting peaks were located at $62.0\text{ }^\circ\text{C}$ and $63.5\text{ }^\circ\text{C}$ in the heating cycle, suggesting that phase transition took place. And the phase transition enthalpies of pristine PEG 6000 and PEG 10000 were 178.6 J/g and 187.2 J/g (Table 2), respectively. Similarly, the DSC curves of PU ionomer-6 and PU ionomer-10 displayed melting peak at $57.1\text{ }^\circ\text{C}$ and $60.8\text{ }^\circ\text{C}$. The phase transition enthalpies of PU ionomer-6 and PU ionomer-10 reached 142.5 J/g and 152.3 J/g , respectively. The cooling DSC curves (Fig. 1) and data (Table 2) showed that similar quantities of heat of pristine PEGs and PU ionomers were released. Both pristine PEGs and PU ionomers underwent phase transition with high transition enthalpy. And the phase change enthalpy increased with the crystallinity (enhanced structure organization) from Table 1. In general, the DSC curves of PU ionomers were similar to those of pristine PEGs because the structure of PU ionomers contained PEG units. However, the phase change temperatures and the enthalpies of PU ionomers were lower than those of pristine PEGs. The PEG's free movement was restricted after the active hydroxyl end groups of PEG reacted with diisocyanate [1,9]. Consequently, the arrangement and the orientation of PEG molecules were partially suppressed by the steric effect and thus the smaller crystalline regions were obtained, which caused the transition point and the enthalpy to fall to a certain degree [21].

Compared with other PUPCMs used PEG 6000 as soft segment [6–8], the phase transition enthalpy of PU ionomer-6 was 142.5 J/g , slightly higher than the highest phase transition enthalpy, 138.2 J/g

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