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Synthesis, characterization, and thermal energy storage properties of a novel thermoplastic polyurethane phase change material

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ABSTRACT

This study focuses on the design and synthesis, thermal energy storage properties and thermal stability of a novel thermoplastic polyurethane solid–solid phase change material (PUSSPCM) for thermal energy storage. The PUSSPCM was synthesized via the two-step condensation reaction of 4,4′-diphenylmethane diisocyanate, polyethylene glycol and a novel tetrahydroxy compound (terephthalic acid bis-(2-hydroxy-1-hydroxymethyl-ethyl) ester) and characterized by Fourier transform infrared spectroscopy and ^{1}H nuclear magnetic resonance techniques. Thermal energy storage properties and thermal stability of as-synthesized PUSSPCM were also measured. DSC results indicate that the phase change temperatures and latent heats of the as-synthesized PUSSPCM are in the ranges of 22.4–48.4 °C and 143.9–153.5 J/g, respectively. TGA results confirm that the initial degradation temperature of the PUSSPCM is at 323 °C, which proves that PUSSPCM has good thermal stability. More significantly, the as-synthesized PUSSPCM can be directly melted and processed, and has a wide processing temperature range. Based on these results, it can be concluded that the synthesized PUSSPCM, as a novel phase change material (PCM), has significant energy storage potential due to its suitable phase change temperatures, higher latent heats, good thermal stability and processing performances.

1. Introduction

The energy storage and reuse have attracted considerable attention as energy crisis has become more and more serious [1]. An effective way of energy storage is the use of polymer-based solid–solid phase change materials due to advantageous properties including high storage density, no liquid or gas generation, small volume change, no need for additional encapsulation, non-corrosiveness and non-toxicity [2]. However, the excellent polymeric solid–solid phase change materials have rarely been designed and synthesized.

In recently years, some attempts had been made to synthesize the outstanding polymer-based phase change materials. Ke et al. [3] prepared complex polymeric solid–solid PCMs through the blend of porous polyurethane and polyethylene glycol. Cao et al. [4] synthesized a hyperbranched polyurethane phase change material via a two-step reaction process of PEG with hyperbranched polyester polyalcohol (Boltorn®H20) and MDI. Sarı et al. [5] prepared polystyrene-graft-PEG6000 copolymer through graft polymerization. The previous research results indicate that the excellent polymer-based phase change material should include high latent heat, suitable phase change temperature, chemical stability and non-corrosiveness, being of abundant supply and at a low cost [6]. All of the above, high latent heat and a suitable phase change temperature are of prime importance. However, such phase change material had rarely been reported.

The properties of materials depend on their structure. Some multifunctional compounds have been linked to the molecular structure of PCMs for synthesizing the polymer-based PCMs with higher latent heat and suitable phase change temperature. Li et al. [7] prepared a solid–solid phase change heat storage material via the two-step condensation reaction of PEG_{10000} with tetrafunctional pentaerythritol and MDI. The as-synthesized PCM has high latent heat. However, the phase change temperature of as-synthesized PCM was not obviously improved as the cross-linked structure was present in molecular structure of the PCM. It was also because of the existence of cross-linked structure that the material cannot be melted and processed, and its wide practical application was restricted. Xi et al. [8] prepared a series of thermoplastic PCMs through the step-growth polymerization of PEG with THCD and MDI. Although the synthesized PCMs own high latent heats and can be melted and processed, their phase change temperatures are still too high to meet the requirements of practicable application in textile products, telecommunications,

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microprocessor equipment and constructions. In our recent research work, we designed and synthesized a novel thermoplastic polyurethane solid–solid phase change material (PUSSPCM) via a two-step condensation reaction. The results show that the as-synthesized phase change materials not only have excellent phase change properties and suitable phase change temperature but also can be dissolved, melted and direct processed, produced in large-scale.

2. Experimental

The synthesis was carried out through a two-step polymerization process under an inert atmosphere of nitrogen in a three-neck round-bottomed flask fitted with an overhead stirrer. First, 0.002 mol 4,4′-diphenylmethane diisocyanate (MDI) was dissolved in 20 ml freshly distilled N,N-dimethylformamide (DMF) and yielded a clear solution. And then, 0.001 mol dried polyethylene glycol (PEG, $\overline{M}_n=6000$) was added into the above solution under a flow of nitrogen at 0 °C. After that, the mixture was slowly heated to 80 °C. Completion of the reaction was monitored by the disappearance of strong absorption peaks of –OH in PEG molecule using FT-IR spectroscopy. And then, predetermined amount of terephthalic acid bis-(2-hydroxy-1-hydroxymethyl-ethyl) ester (TABE) and 20 ml freshly distilled DMF was mixed and added into the three-neck round-bottomed flask by dropping; the reaction mixture was stirred at 80 °C for 6 h. Second, NCO-terminated modified polyethylene glycol monomethylether (MMPEG) was added, and the reaction was continued at 80 °C for 6 h. At last, the reaction mixture was cast in a special glass pan and set in a vacuum oven at 80 °C for 48 h for further reaction and removal of DMF. The sample was kept in vacuum at 25 °C for two weeks prior to testing. During the reaction process, the content of phase change units is kept at 80 wt% and the total amount of –NCO groups is kept to be equal to that of –OH groups.

The composition and structure, crystalline morphology, phase change properties, and thermal resistant property of the samples were characterized by a Fourier transform infrared spectrometer (FT-IR), ^{1}H nuclear magnetic resonance spectrometer (^{1}H NMR), wide-angle X-ray diffraction (WAXRD), polarizing optical microscopy (POM), differential scanning calorimeter (DSC), and thermogravimetry analysis system (TGA).

3. Results and discussion

Composition and structure of PUSSPCM: FT-IR spectrum of the as-synthesized sample was tested for understanding the composition and structure of PUSSPCM (Fig. 1a). For a comparison, FT-IR spectra of TABE, MDI, and PEG are also shown in Fig. 1a. As clearly seen, the hydroxyl group of TABE at 3352 cm^{-1} and the isocyanate group of MDI at 2280 cm^{-1} tend to polymerize. The strong peaks emerging at 2879 and 1100 cm^{-1} belong to the stretching vibration peaks of –CH$_2$– and –C–O– for PEG (soft segments), respectively. In the multi-benzene ring structure (rigid segment), the characteristic peaks of –N–H, –C=O and benzene ring are located at 3344 cm^{-1}, 1720 cm^{-1}, 1707 cm^{-1}, 1597 cm^{-1}, 1539 cm^{-1}, 1512 cm^{-1} and 1466 cm^{-1}. These results confirm that PUSSPCM has been successfully synthesized. In ^{1}H NMR spectrum of PUSSPCM (Fig. 1b), the proton peaks correspond to the structure of PUSSPCM. The results of ^{1}H NMR spectrum of PUSSPCM are in good agreement with those of FT-IR spectra.

Physical properties of PUSSPCM: The physical properties of the as-synthesized PUSSPCM are illustrated in Table 1. The results indicate that the as-synthesized sample is dissolvable in tetrahydrofuran (THF), DMF, and dimethyl sulfoxide (DMSO). There is not any residual gel in the dissolved process of as-synthesized PUSSPCM. The melting point and the initial degradation temperature of PUSSPCM are at 182 °C and 323 °C (TGA curve), respectively. These facts demonstrate that the PUSSPCM is a thermoplastic polymer, and can be melted and processed.

Thermal energy storage properties of PUSSPCM: The WAXRD is an important technology method to research crystalline properties of phase change material. Compared with WAXRD patterns of PEG6000 and PUSSPCM (Fig. 2a), both PEG6000 and PUSSPCM have two main diffraction peaks at about 19.1° and 23.3°. The typical POM images also exhibit that both PEG6000 and PUSSPCM own the spherulite morphology with an obvious cross-extinction pattern under polar light at room temperature (Fig. 2b). These results indicate that PEG units in the as-synthesized PUSSPCM have the same crystal structure as the pure PEG [9].

Furthermore, the POM images further prove that both PEG6000 and PUSSPCM undergo a phase transition, but their phase

Table 1
Physical properties of PUSSPCM.

Dissolving properties (g/100 ml)			Melting and processing properties	
THF	DMF	DMSO	Melting point (°C)	The initial degradation temperature (°C)
21.83	32.51	32.62	182	323

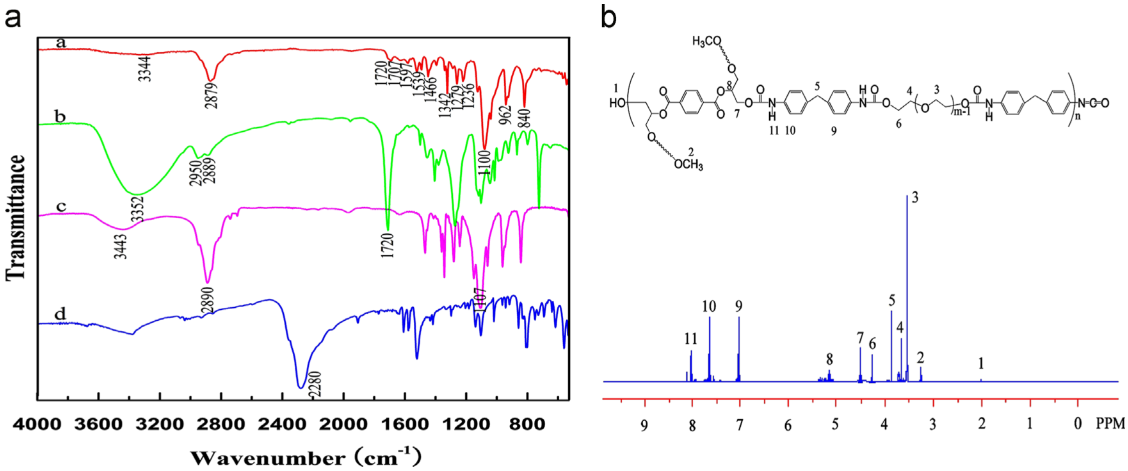

Fig. 1. FT-IR and ^{1}H NMR spectra of PUSSPCM: (a) FT-IR spectra and (b) ^{1}H NMR spectrum.