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Synthesis and thermal properties of novel solid-solid phase change materials with comb-polyurethane block copolymer structure for thermal energy storage

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ABSTRACT

A series of novel comb-polyurethane phase change materials (CP-PCMs) with poly(ethylene glycol) (PEG) as side chain were synthesized through the reaction between diethanolamine-modified methoxypolyethylene glycol (DMPEG) with diisocyanate and 1,4-butanediol (BDO). The structure and phase change property of CP-PCM were characterized by gel permeation chromatography (GPC), ^{1}H nuclear magnetic resonance (^{1}H NMR), Fourier transform infrared (FTIR) spectroscopy, and polarization optical microscopy (POM). The ^{1}H NMR and FTIR spectra confirmed the success synthesis of CP-PCM. The POM images showed that CP-PCM possessed a completely crystalline structure and smaller spherulites compared with the pristine methoxypolyethylene glycol (MPEG). The influence of phase change property of CP-PCMs was also investigated using differential scanning calorimetry (DSC). The results showed that the CP-PCM synthesized using isophorone diisocyanate (IPDI) or 1,6-hexamethylene diisocyanate (HDI) as diisocyanate and MPEG with molecular weight of 5000 as soft segment possessed optimal phase change property. In addition, the phase change enthalpy and temperature of CP-PCMs decreased as the weight percentage of MPEG decreased.

1. Introduction

Efficient utilization of energy resources is necessary given the serious shortage of mineral resources and increasing deterioration of ecological environments. One prospective technique to improve the energy efficiency is the application of phase change materials (PCMs), which store and release large amount of heat energy during the phase change process [1–4]. PCMs have been widely used for energy storage in various fields such as, waste heat recovery, smart air-conditioning buildings, telecommunications and microprocessor equipment, agricultural greenhouse, and solar energy storage [5–7].

Poly(ethylene glycol) based polyurethane (PEG-PU), where PEG (as a phase change ingredient) is covalently bonded to polyisocyanate (as a skeleton) to keep the material in solid state during its phase change process, is considered as a potential PCM for energy storage and temperature control because of its relatively high phase change enthalpy, good chemical and thermal stability, nontoxicity and convenient melting temperature range [8–12]. Research about the relationship between structure and thermal energy storage capability of PEG-PU has been studied extensively [13–16]. Su et al. [17] synthesized a linear polyurethane PCM (with phase change enthalpy of about 100 J/g) by using PEG as soft segment, and 4,4-diphenylmethane diisocyanate (MDI) and BDO as hard segment via bulk polymerization. Chen et al. [18] prepared three novel polyurethane PCMs with different crosslinking structures, in which inositol, dipentaerythritol and sorbitol were individually employed as molecular skeleton and PEG was used as phase change functional chain. The study found that spatial hindrance of the skeleton influenced the movement of PEG in PCMs. Peng et al. [19] prepared a hyperbranched polyurethane solid–solid PCM by using PEG, β-cyclodextrin and MDI via a two-step condensation reaction. The phase change enthalpy observed was more than 100 J/g. Overall, convenient phase change temperature and high phase change enthalpy are of prime importance in PEG-PU fabrication. However, the covalent bonds between polyisocyanate and PEG restrict the movement and crystallization of PEG, thereby decreasing the phase change enthalpy of PEG-PU [20–23].

In our previous research, a novel comb-polyurethane solid–solid PCM (CP-PCM) of high thermal energy storage capability was synthesized through the reaction between diethanolamine-modified methoxypolyethylene glycol (DMPEG) with IPDI and BDO [24].

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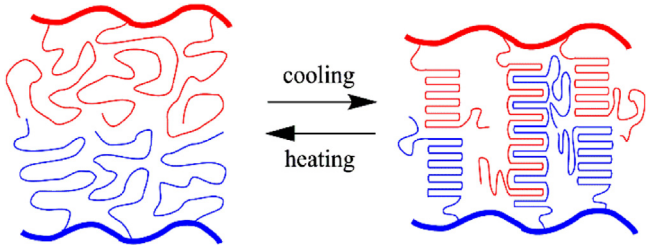


Scheme 1. Schematic illustration showing the crystallizing and decrystallizing of comb-polyurethane PCM.

While both ends of PEG were linked with IPDI in the common linear PEG-PU, only one end of DMPEG was linked with IPDI in CP-PCM. Therefore, the arrangement and orientation of PEG in CP-PCM were more active, which made CP-PCM an efficient PCM with high phase change enthalpy (Scheme 1).

In this study, a series of DMPEG with different molecular weight was synthesized, and then the novel comb-polyurethane phase change materials based on DMPEG, BDO, and diisocyanate were prepared via a two-step condensation reaction (Scheme 2). The structure and composition of synthesized CP-PCM were researched by gel permeation chromatography (GPC), Fourier transform infrared (FTIR) spectroscopy, ^{1}H nuclear magnetic resonance (^{1}H NMR), and polarization optical microscopy (POM). In addition, the effects of the molecular weight of MPEG, the weight percentage of MPEG in CP-PCMs, and the types of diisocyanate on energy storage of CP-PCMs were investigated by differential scanning calorimetry (DSC) respectively.

2. Experimental

2.1. Materials and instruments

MPEG with the average molecular weights of 1000, 2000, 4000, 5000, 10,000 and 20,000 were purchased from Aladdin Reagent Co. Inc., America. Acryloyl chloride was purchased from Shanghai Chemical Reagent Co. Inc., China. 2,4-tolylene diisocyanate (TDI), 1,6-hexamethylene diisocyanate (HDI), MDI and IPDI were purchased from Sigma–Aldrich Reagent Co. Inc., America. Triethylamine, diethanolamine, BDO, and other common reagents were purchased from Chengdu Kelong Co. Ltd., China. Table 1 summarizes relevant information on the provenance and purity of the starting materials.

Table 1
Provenance and mass fraction purity of the starting materials.

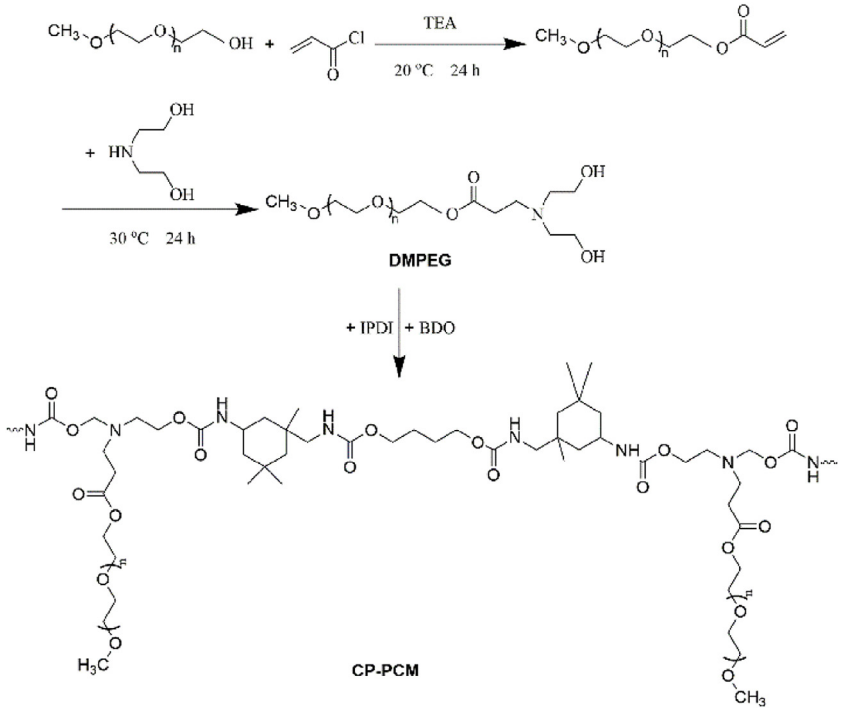
Chemical	Source	Purity	Purification method
MPEG[a]	Aladdin	0.99	none
IPDI	Sigma Aldrich	0.99	none
TDI	Sigma Aldrich	0.99	none
HDI	Sigma Aldrich	0.99	none
MDI	Sigma Aldrich	0.99	none
acryloyl chloride	Aladdin	0.98	none
diethanolamine	Chengdu Kelong Co. Ltd., China	0.99	none
1,4-butanediol	Chengdu Kelong Co. Ltd., China	0.99	none

[a] MPEG with molecular weights of 1000, 2000, 4000, 5000, 10,000 and 20,000.

2.2. Synthesis of diethanolamine modified MPEG

MPEG (M_n = 5000, 10.00 g, 2 mmol), triethylamine (0.20 g, 2 mmol), and dichloromethane (DCM, 150 mL) were added to a round bottomed flask. Acryloyl chloride (0.18 g, 2 mmol) dissolved in DCM (30 mL) was added dropwise at 0 °C. The reaction mixture was stirred at 25 °C for 24 h. Then, the solid salt was filtered and the filtrate was concentrated under reduced pressure. The crude product was purified by recrystallization in ethanol at −20 °C three times. At last, methoxypolyethylene glycol ether acrylate (MPEGAC) was obtained by drying the precipitate under vacuum.

Then, DMPEG was synthesized by a Michael addition between MPEGAC and diethanolamine. MPEGAC (10.18 g, 2 mmol), diethanolamine (0.84 g, 2 mmol), and ethanol (150 mL) were added to a flask at 25 °C. After stirring 24 h, the reaction solution was crystallized at −20 °C and a crude product was obtained



Scheme 2. Synthetic route of CP-PCM.