Applied Thermal Engineering 117 (2017) 622–628

Contents lists available at ScienceDirect

Applied Thermal Engineering

journal homepage: www.elsevier.com/locate/apthermeng

Research Paper

A facile synthesis of solid-solid phase change material for thermal energy storage

Weibo Kong, Xiaowei Fu, Zhimeng Liu, Changlin Zhou *, Jingxin Lei *

State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, No. 24, First South Section First Ring Road, Wuhou District, Chengdu 610065, China

HIGHLIGHTS

- Solid-solid phase change materials based on PEG and PAPI were prepared.
- The brief and concise method made the industrial applications of PCMs possible.
- The maximum latent heat of prepared PCMs reached 111.7 J/g.
- The prepared PCMs show the potential for thermal energy storage application.
- The prepared PCMs will make an effective utilization of waste energy.

ARTICLE INFO

Article history:
Received 8 July 2016
Revised 12 October 2016
Accepted 12 October 2016
Available online 13 October 2016

Keywords:
Phase change material
Thermal energy storage
Polyurethane
Shape stabilization

ABSTRACT

Thermosetting polyurethane based on Polyethylene glyol and Polyaryl polymethylene isocyanate was prepared through solvent-free bulk polymerization for solid-solid phase change materials. Chemical structure, crystallization behavior, phase change behavior, thermal reliability and thermal stability of Polyethylene glyol based phase change materials were extensively studied by fourier transform infrared spectroscopy, X-ray diffraction, polarizing optical microscopy, differential scanning calorimetry, thermal cycling testing and thermogravimetric analysis, respectively. The polarizing optical microscopy and X-ray diffraction results indicated that the crystal structure of prepared phase change materials was not affected by the crosslink structure. Differential scanning calorimetry measurements showed that prepared phase change materials possess high latent heat and appropriate phase change temperature for the application of thermal energy storage. The maximum latent heat of phase change materials in melting and freezing process reached 111.7 J/g and 110.4 J/g, respectively. Thermal cycling test and thermogravimetric analysis results demonstrated the good thermal reliability and stability of prepared phase change materials. The prepared phase change materials showed the potential for thermal energy storage application and will make an effective utilization of waste energy.

1. Introduction

Phase change materials (PCMs) have received considerable attention and became increasingly important aspect for exploitation of thermal energy storage in last decades [1]. PCMs demonstrate a high enthalpy of fusion and crystallization, which can store and release large amounts of energy as latent heat during the phase transition [2–4]. Hence, the PCMs have been applied in many fields such as construction engineering [5], solar energy storage [6], biomedical engineering [7], automotive and electronic application [8]. According to the phase transition state, PCMs can be classified into four types: solid-gas, gas-liquid [9], solid-liquid [10], and solid-solid [11]. Solid-gas and gas-liquid PCMs have high latent heat, however the large volume changes during the phase transition limit their wide applications [12]. Solid-liquid PCMs must be encapsulated with framework materials to prevent the leakage of solid-liquid PCMs when the temperature is above the phase change temperature (T_{pc}) [13]. Comparing with gas-liquid/solid and solid-liquid PCMs, solid-solid PCMs have advantages of no gas or liquid generation and smaller volume change during the process of energy storing and releasing [14].

Many materials have been studied for the development of PCMs, such as paraffins wax, fatty acid [15], inorganic and organic compounds [16], polyalcohols [17] and some other polymers [18]. Polyethylene glyol (PEG) equipped with many properties such as

* Corresponding authors.
E-mail addresses: chouscu@scu.edu.cn (C. Zhou), jxlei@scu.edu.cn (J. Lei).

http://dx.doi.org/10.1016/j.applthermaleng.2016.10.088
1359-4311/

high phase change latent heat [19], suitable Tpc [20], biocompatibility [21], biodegradability and low cost [22], was often used as the solid-liquid phase change materials. Li and his [23] group prepared the cellulose-graft-PEG solid-solid PCMs by using 4,4-diphenylmethane diisocyanate (MDI) as coupling reagent, while a plenty of dimethylformamide (DMF) were used as solvent to reduce the viscosity of the reactive system. Xi and his group [24] synthesized a form stable thermoplastic polyurethane solid–solid phase change material via employing PEG as soft segments, MDI and tetrahydroxy compound as hard segments. The DMF and THF were used as solvent as well. Li and Ding [25] reported a synthesis method via the two-step condensation reaction of PEG10000 with pentaerythritol (PE) and MDI in DMF solvent. Su and Liu [26] prepared polyurethane block copolymer as solid–solid PCMs by solution polyaddition, and the PCM was composed of PEG as soft segment, MDI and 1,4-butanediol (BDO) as hard segments. For all of the mentioned above, PEG based solid-solid PCMs with high latent heats and appropriate phase change temperatures for application were synthesized. However, a large amount of solvent such as DMF was employed in the reaction process. The solvent result in the increasing cost of PCM and the negative effect on the material performance and environment. Therefore, the preparation of polymeric solid-solid PCMs with solvent-free process will be a potential subject. In addition, according to the discussion above, the two-step method was typically utilized to synthesize the PEG based solid-solid PCMs, and the prepolymerization is essential. It is necessary to explore a brief and simple method to adapt the practical application.

It is well known that Polyaryl polymethylene isocyanate (PAPI) is a polyfunctional isocyanate, and can be used as coupling reagent and crosslink agents in the reaction with polyalcohols. In this paper, PEG6000, PEG8000 and PAPI were employed to prepare the thermosetting solid-solid PCMs through a solvent-free and brief synthesis route. In the prepared solid-solid PCMs, the PEG and PAPI act as phase change ingredient and crosslink agents, respectively. In addition, the two components solid-solid PCMs based on PEG and PAPI are prepared via a brief way for the first time. The chemical structure, crystallization behavior, phase change behavior and thermal reliability and stability of obtained solid–solid PCMs were extensively studied by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), differential scanning calorimetry (DSC) and thermogravimetric analysis (TG), respectively.

2. Experimental

2.1. Material

Polyethylene glyol (Mw = 6000 g/mol: PEG6000; Mw = 8000 g/mol: PEG8000) was purchased from Kelong Chemical Reagent (Chengdu, China); Polyaryl polymethylene isocyanate (PAPI, Mw = 381 g/mol; NCO wt% = 33.07% average functionality is 3) was supplied by Yantai Wanhua polyurethane Co., Ltd. (Shandong, China). All chemical used were analytically pure, and used as received.

2.2. Preparation of solid-solid PCMs

The solid–solid PCMs were produced without any solvents by a concise bulk polyaddition route and the corresponding preparation strategy is shown in Fig. 1. Taking the PEG6000 based PCM as an example, firstly 30 g (0.005 mol) PEG6000 was introduced into a 100 mL beaker at 80 °C, after melting of PEG6000, 1.17 g (0.0034 mol) PAPI was poured into the beaker and fully blending was performed for 20 min. Subsequently thermal curing was conducted at 80 °C for 2 h in a drying oven. After that, the thermosetting solid-solid PCMs with PAPI as curing reagent were received. This facile preparations strategy avoided the employment of solvents such as DMF and THF and simplified the prepolymerization of PEG described in previous research.

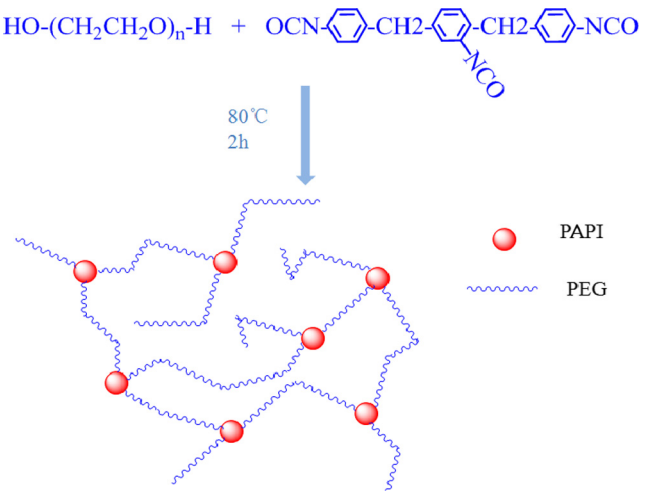

Fig. 1. The scheme of the synthesized route.

The solvent-free thermosetting PCMs based on PEG600 and PEG8000 as phase change functional chains were named as PCM-6 and PCM-8, respectively.

2.3. Characterization

The FTIR was employed to investigate the chemical structure of PEG6000, PEG8000, PCM-6 and PCM-8, the measurements were performed on the an infrared spectrometer (Nicolet 560, Nicolette Co., USA) with a resolution setting of 4 cm^{-1}. The scanning was in a range of 4000–400 cm^{-1}. Testing samples of PEG6000 and PEG8000 were prepared by the KBr pressed disc technique (about 1 mg KBr of sample and 100 mg of KBr). PCM-6 and PCM-8 were measured by ATR (attenuated total reaction).

X-ray diffraction measurement of PEG6000, PEG8000, PCM-6 and PCM-8 were performed on Phillips X'Pert Pro MPD diffractometer in Bragg-Brentano geometry at 35 kV and 30 mA. Cu Ka radiation of 1.54056 Å was obtained with a curved graphite monochromator. The data were collected in a range of $2\theta = 5–50°$ by a scanning rate of 0.04°/min at room temperature.

The crystalline structure of PEG6000, PEG8000, PCM-6 and PCM-8 was studied by XPR-500D microscope (China) equipped with a video camera. The testing sample was located between a microscope glass and a cover slip.

The DSC measurement was utilized to analyze the phase change temperature and latent heats of samples. The measurement was performed on a differential scanning calorimeter (DSC 204 Phoenix, Netzsch, Germany) in a nitrogen atmosphere at a heating or cooling rate of 10 °C/min with weight of the sample being about 8 mg. All samples were heated from ambient temperature to 110 °C and kept for 3 min in order to erase prior processing history of the samples. Then, the sample was cooled from 110 to 0 °C to collect DSC cooling data. A second heating scan from 0 to 110 °C produced the DSC heating profile.

In order to investigate the thermal reliability, reusability and stability of the prepared solid–solid PCMs, the accelerated thermal cycling testing was performed in a high-low temperature chamber. The samples were casted into cube (1 cm × 1 cm × 1 cm) and following transferred into the chamber. The tests were performed with 100 consecutive heating/cooling processes with a heating rate