Available online at www.sciencedirect.com
SCIENCE DIRECT®
Energy Conversion and Management 47 (2006) 3185–3191
ENERGY CONVERSION & MANAGEMENT
www.elsevier.com/locate/enconman

A novel solid–solid phase change heat storage material with polyurethane block copolymer structure

Jing-Cang Su, Peng-Sheng Liu *

Department of Chemistry, Institute of Polymer Science, Xiangtan University, Xiangtan 411105, Hunan Province, PR China

Received 9 August 2005; accepted 15 February 2006
Available online 29 March 2006

Abstract

A novel polymeric solid–solid phase change heat storage material (PCM) with polyurethane block copolymer structure (PUPCM) composed of high molecule weight polyethylene glycol (PEG) as soft segment, 4,4′-diphenylmethane diissyanate (MDI) and 1,4-butanediol (BDO) as a chain extender were synthesized by a two step process. DSC, POM, SEM and WAXD tests were performed to investigate the phase transition behaviors and crystalline morphology. The results indicated that the PUPCM showed typical solid–solid phase transition properties, e.g. suitable transition temperature, high transition enthalpy and good thermal stability. It is a functional polyurethane with good energy storage effect, and the heat storage mechanism of PUPCM is the transfer between crystalline and amorphous states of the soft segment PEG of PUPCM, and the hard segment, serving as ''physical cross-links'', restricted the molecular chain of the soft segment's free movement at high temperature. Thus, PUPCM can keep its solid state in the transition processing.

Keywords: Polyurethane; Solid–solid phase change material; Polyethylene glycol; Heat storage

1. Introduction

Latent heat storage is one of the most efficient ways of storing thermal energy due to its high storage density and small temperature variation in the storing and releasing heat processes. Phase change materials (PCMs) are the materials using latent heat to store energy. In recent years, as the energy crisis is becoming more and more serious, PCMs are attracting lots of attention. A great number of organic, inorganic, polymeric and eutectic PCMs have been studied [1–6]. Among the various kinds of PCMs, polymeric solid–solid PCMs are fairly recently developed functional PCMs, which have been found to exhibit many desirable characteristics, e.g. no liquid or gas generation, small volume change, no receptacle needed to seal them, being processed into arbitrary shape, even being used as a system material directly [6–10]. Thus, it can simplify techniques and reduce cost greatly.

* Corresponding author. Tel.: +86 732 8292736.
E-mail addresses: su2376053@163.com (J.-C. Su), lpsh@xtu.edu.cn (P.-S. Liu).

0196-8904/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.enconman.2006.02.022

At present, there are two kinds of polymeric solid–solid PCMs. One kind is compound materials obtained by dispersing PCMs into higher melting point polymeric materials acting as supporting materials [11,12]. As long as the temperature is below the melting point of the supporting materials, the compound materials can keep their solid shape even when PCM changes from solid to liquid. They are generally called form stable PCMs or shape stabilized PCMs. The other kind is synthesized by chemical methods [13,14], Chemical grafting or blocking copolymerization are used to make good solid–liquid PCMs as the energy storage working materials component of solid–solid phase change materials. However, there are several defects in most of the polymeric solid–solid PCMs reported in previous work, e.g. the transition temperature is too high, the transition enthalpy is low and the thermal property is unstable. All these defects greatly limit their applications.

In this paper, a novel polymeric solid–solid PCM, segment polyurethane solid–solid phase change material (PUPCM), was synthesized by reacting calculated amounts of high molecule weight polyethylene glycol (PEG), a typical polymeric solid–liquid PCM, as the soft segment with 4,4′-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BDO) as hard segment. The properties of PUPCM were investigated with differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD), scanning electronic microscopy (SEM) and polarization optical microscopy (POM).

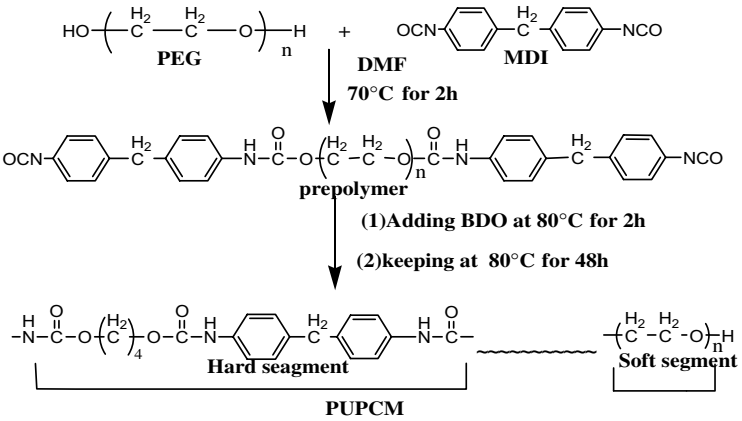
2. Material and methods

2.1. Materials

Polyethylene glycol (PEG, $M_n = 10{,}000$, from Shantou Guanghua Chemical Reagent Co. Inc., China) was degassed and dried in a round flask under high vacuum (20 Pa) at 100–120 °C for 3–4 h. 4,4′-Diphenylmethane diisocyanate (MDI, from Wanhua Chemical Reagent Co. Inc., China) was used as received. Dimethylformamide (DMF, from Shantou Guanghua Chemical Reagent Co. Inc., China) and 1,4-butanediol (BDO, from Shanghai Medical Chemical Reagent Co. Inc. China) were dried by 5 Å molecular sieve for 24 h followed by distillation before use.

2.2. PUPCM synthesis

The synthesis was conducted in a two step polymerization process under an inert atmosphere of nitrogen in flame dried glassware as shown in Scheme 1. First, a predetermined amount of dried PEG and MDI in freshly distilled DMF were mixed with stirring under nitrogen at 60–70 °C for 2 h to make a NCO-terminated prepolymer. In the second step, the stoichiometric amount of the chain extender 1,4-BDO was added by drops, and the reaction was continued at 80 °C for 2 h. The reaction mixture was then cast on a special mold and



Scheme 1. Synthetic route to PUPCM.