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Solvent-free synthesis and properties of novel solid–solid phase change materials with biodegradable castor oil for thermal energy storage

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ABSTRACT

Polyurethane polymers were directly synthesized via bulk polymerization as novel solid–solid phase change materials (SSPCMs) for thermal energy storage. Polyethylene glycols (PEGs) with 4000 and 6000 g/mol number average molecular weight were used as phase change functional chain, castor oil as the skeleton, diphenylmethane diisocyanate (MDI) and hexamethylene diisocyanate (HDI) were individually served as coupling reagent. The molecular structure, crystalline properties, phase change performances, thermal reliability and stability of the synthesized SSPCMs were investigated by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and thermogravimetry analysis (TG), respectively. The XRD patterns and POM images showed that the synthesized SSPCMs have the same crystalline structure and confined crystallization compared with pristine PEG. The DSC results indicated that the synthesized SSPCMs have high latent heats and a suitable phase change temperature range, and the maximum latent heats in melting and freezing process for the SSPCMs are 117.70 J/g and 109.00 J/g, respectively. Thermal cycling test and TG analysis results indicated that synthesized SSPCMs have good thermal reliability and stability. The prepared SSPCMs show large potential application in the area of solar energy storage.

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1. Introduction

In recent years, the energy crisis and continuous deterioration of environment have made the utilization of renewable energy sources and the development of environment-friendly materials become a crucial topic [1,2]. To address these problems, thermal energy storage (TES) technique has gained extensive attention from both academia and industry [3,4]. In general, phase change materials (PCMs) as a class of TES systems are the most attractive mothed owing to high-energy storage density and isothermal nature of PCMs during the heat storage and release process [5,6]. Therefore, the PCMs had been regarded as one of the most wildly used TES materials in the field of solar energy utilization [7], buildings materials [8], waste heat recovery [9], temperature-regulating fibers and electronics [10,11]. In last decades, the pristine PCMs including various inorganic salt hydrates [5], polyethylene glycol (PEG) [12,13], paraffin waxes [14,15], fatty acids [16,17] and their eutectics [18,19] have been studied and applied extensively in the TES areas. Nevertheless, a special packaging technique is necessary to encapsulate the micronized PCMs during the solid–liquid phase change process, which is the challenge in applications of pristine PCMs. Compared with pristine PCMs, the polymeric solid–solid PCMs exhibit many unique properties: needless encapsulation, easiness to use, no leakage when used [20]. Given these remarkable characteristics, polymeric solid–solid PCMs have been studied and developed by grafting, blocking and crosslinking copolymerization [21,22].

Based on the advantages of solid–solid PCMs, some researchs have prepared the excellent polymeric solid–solid PCMs. Cao et al. [23] prepared a series of hyperbranched polyurethane phase change materials (HB-PUPCMs) by solution polymerization, which was composed of PEG as soft segment, 4,4′-diphenylmethane diisocyanate (MDI) and hyperbranched polyester (Bolton H20) as a support skeleton. Xi et al. [24] reported the synthesis of thermoplastic polyurathane solid–solid PCMs with a newly designed tetrahydroxy compound (THCD). In its molecular structure, the PEG was employed as the soft segments, MDI and THCD as hard

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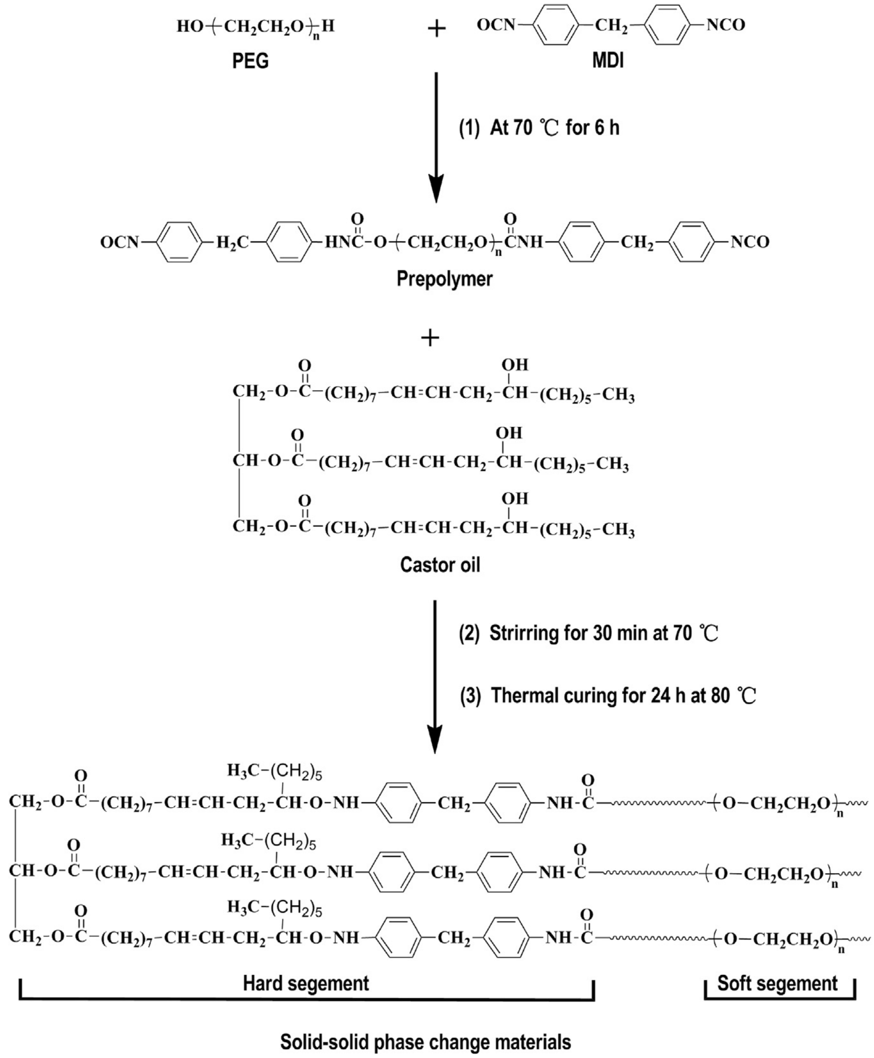

Fig. 1. Synthetic route of solid–solid PCMs.

segments. However, a large amount of dimethylformamide (DMF) was required during the synthetic process. Cheng et al. [6] synthesized three kinds of novel polymeric solid–solid PCMs with different crosslink structure. In the solid–solid PCMs, hexahydroxy compounds (sorbitol, dipentaerythritol and inositol) and MDI were acted as molecular skeleton, PEG was used as the phase change functional chain, and toxic organic solvent (DMF) was introduced as well. Other polymeric solid–solid PCMs, such as cellulose/MDI/PEG [25], poly(vinyl alcohol)/MDI/PEG [26], pentaerythritol/MDI/PEG [27], were successfully synthesized. All of the above, a large number of organic solvent such as DMF was involved in the preparation process. It not only difficult to remove completely, but also undesired for the application of textiles and buildings [28]. Therefore, solvent-free preparation polymeric solid–solid PCMs will be a potential subject. On the other hand, the end of PEG chains are all linked with rigid benzene ring groups of MDI in the molecular structure of solid–solid PCMs discussed above. The steric hindrance of rigid benzene ring group causing the arrangement and orientation of PEG chains near hard segment sites are partially suppressed, and then the heat storage density of solid–solid PCMs decreases in a certain degree [6,18,24,23,29]. Therefore, minimizing the unnecessary influence of the hard segments on the phase change latent heat of solid–solid PCMs may be another feasible method to obtaining solid–solid PCMs with high latent heats.

As we know, castor oil (CO) is one of the most widely available biodegradable, low toxicity and sustainable vegetable oil. Its major ingredient, ricinoleic acid (12-hydroxy-cis-9-octadecenoic acid), is a hydroxyl containing fatty acid ester, and an average number of hydroxyl per molecule is 2.7. So castor oil can be used directly for the preparation of polyurethanes without further modification [30,31]. In this paper, a series of novel polymeric solid–solid PCMs were directly synthesized via bulk polymerization by employing PEGs as phase change functional chain, castor oil as the skeleton, MDI and hexamethylene diisocyanate (HDI) were individually served as coupling reagent. In addition, the castor oil was used as reactants in solid–solid PCMs synthesis for the first time. It is believe that the biodegradable castor oil can potentially make good the biodegradability of synthesized solid–solid PCMs [32]. The synthesized solid–solid PCMs possess high latent heats and the synthetic route did not involve the use of any toxic organic solvent. The influence of the diisocynate type on the crystalline properties and phase transition properties of the synthesized solid–solid PCMs were discussed in more detail. The synthesized solid–solid PCMs were investigated with Fourier transform infarared (FT-IR), X-ray diffraction (XRD), polarization optical microscopy (POM), differential scanning calorimetry (DSC) and thermogravimetric analysis (TG), respectively.

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