Applied Energy 184 (2016) 241–246

Contents lists available at ScienceDirect

Applied Energy

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

Form-stable phase change materials with high phase change enthalpy from the composite of paraffin and cross-linking phase change structure

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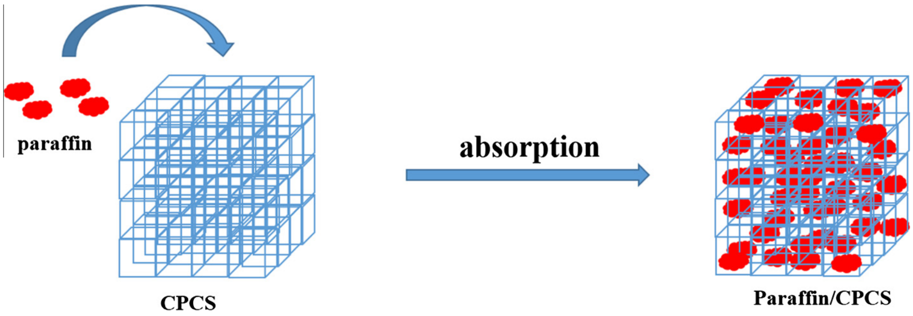
HIGHLIGHTS

- Novel phase-change composite was prepared by crosslinking and blending.
- The phase change latent heat of the composite was more than 210 J/g.
- The phase-change composite exhibits excellent form-stable effect during phase change process.

GRAPHICAL ABSTRACT

3-D net structure of CPCS prevent more paraffin from flowing, so paraffin content without any leakage can reach 74 wt%, with the phase change enthalpy 210.6 J/g.



ARTICLE INFO

Article history:
Received 9 August 2016
Received in revised form 19 September 2016
Accepted 3 October 2016

Keywords:
Phase change composite
Phase change enthalpy
Form stable

ABSTRACT

Large phase-change latent heat and good shape stability are of critical importance in the practical application of phase-change materials for thermal energy storage. This study focuses on a novel strategy to obtain novel phase-change materials with high phase-change enthalpy and form-stable characteristics from the simple composite of paraffin with cross-linking phase-change structure. The structure, thermal properties, crystalline properties, shape-stabilized properties, and thermal stability of the composite materials were determined and analyzed. The phase transition enthalpy of the material can reach 210.6 J/g at a paraffin weight content of 74%. This result was higher than most of the previously reported form-stable PCMs. The shape of the composite was unchanged even after being placed on a 100 °C hot plate. This effect was attributed to the supporting mechanism of cross-linking phase-change structure.

1. Introduction

Thermal energy as an important utilization mode of energy, is closely related to human life and social production. Thermal energy storage (TES) is widely used to solve the strong timeliness problem of the supply and demand of thermal energy [1–3] and to improve the utilization efficiency of thermal energy [4–7]. Among the numerous methods of TES, phase-change materials (PCMs) are a promising option because they can store and release great amounts of latent heat during the process of phase transition, which can be utilized in construction energy conservation, waste heat recovery, solar energy utilization and other fields [8–13]. Numerous classical PCMs, such as fatty acid [14], fatty alcohol [15], paraffin [16,17], and polyethylene glycol [18–24], have been studied and reported. Among these PCMs, paraffin has attracted considerable attention because of its high heat of fusion, an extensive range of phase-transition temperature, good chemical

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http://dx.doi.org/10.1016/j.apenergy.2016.10.021
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resistance, and low cost [15,25]. However, the inherent liquid leakage caused by the typical solid–liquid phase transition of paraffin limits its applications in thermal energy storage. Many effective strategies have been reported to prevent paraffin from leaking. Particularly, the composition of paraffin with a supporting material is an effective approach to improve its shape stability for its successful use [26–29]. However, the phase change enthalpies of the reported composite PCMs are low (mostly less than 150 J/g) because the supporting materials do not exhibit phase-change behavior.

Herein, we reported a new strategy to synthesize form-stable phase change composites with high enthalpy by replacing traditional supporting materials. Contrast to the previously reported composite PCMs, the features of this study is that the new materials we prepared used cross-linking polyurethane PCM matrix as supporting materials, which has PEG chain segment and porous structure providing its inherent phase change characteristic and shape-stabilized property. The phase change enthalpy of the novel materials can reach 210.6 J/g, which is much higher than most of the previously reported PCMs. The materials also have excellent shape-stabilized property and thermal stability performance. These satisfactory performances reveal the potential of the materials for application in building, temperature constant, waste heat recovery and other TES fields.

2. Experimental

2.1. Materials

Polyethylene glycol (PEG, $M_n = 10{,}000$, Sinopharm Chemical Reagent Beijing Co. Ltd) was dried at 80 °C in vacuum drying oven for 24 h prior to use. Analytical-grade toluene (Tianjin Damao Chemical Reagent Factory, China) was dried using a 5 Å molecular sieve before using. 27 wt% tris (4-isocyanatophenyl) methane in ethylacetate (TTI, Zhengzhou Alfachem Co., Ltd., China), technical-grade paraffin (ShangHai Joule wax Co., Ltd, China) and dibutyltin dilaurate (DBTDL, Tianjin Kemiou Chemical Reagent Co. Inc.) were used as received.

2.2. Preparation of composites

Paraffin and the cross-linking phase-change structure (CPCS) composite materials were prepared through in situ doping method (Fig. 1). First, anhydrous PEG10000 (0.5 mmol), TTI (0.75 mmol) and DBTL (three drops, used as catalyst) were placed in 50 mL fresh distilled toluene and mechanically stirred at 55–60 °C (Fig. 1a). The solution got sticky gradually after 30 min condensation reaction. The CPCS was obtained. Then, a certain amount of paraffin was added. The CPCS quickly absorbed the paraffin toluene solution and formed a polymer gel quickly (Fig. 1b). Thus, the target PCM composite was achieved after vacuum drying. The maximum mass fraction of paraffin without any leakage was 74 wt% after a heating test.

2.3. Characterization

The chemical structure of CPCS and paraffin/CPCS composite were characterized by a Fourier-transform infrared (FT-IR) spectrophotometer (FT/IR-6700). Scanning electron microscopy (SEM) images were taken to confirm microstructure of CPCS with a FEI Nova Nano SEM 450 apparatus. X-ray Diffraction studies (XRD, D/Max2400, Japan) were carried out over a 2θ range of 5–80° at room temperature to monitor crystal form of PEG and paraffin. The thermal properties of PCMs were measured at 5 °C/min heating and cooling rate in a N_2 atmosphere using a DSC204 (NETZSCH, Germany).

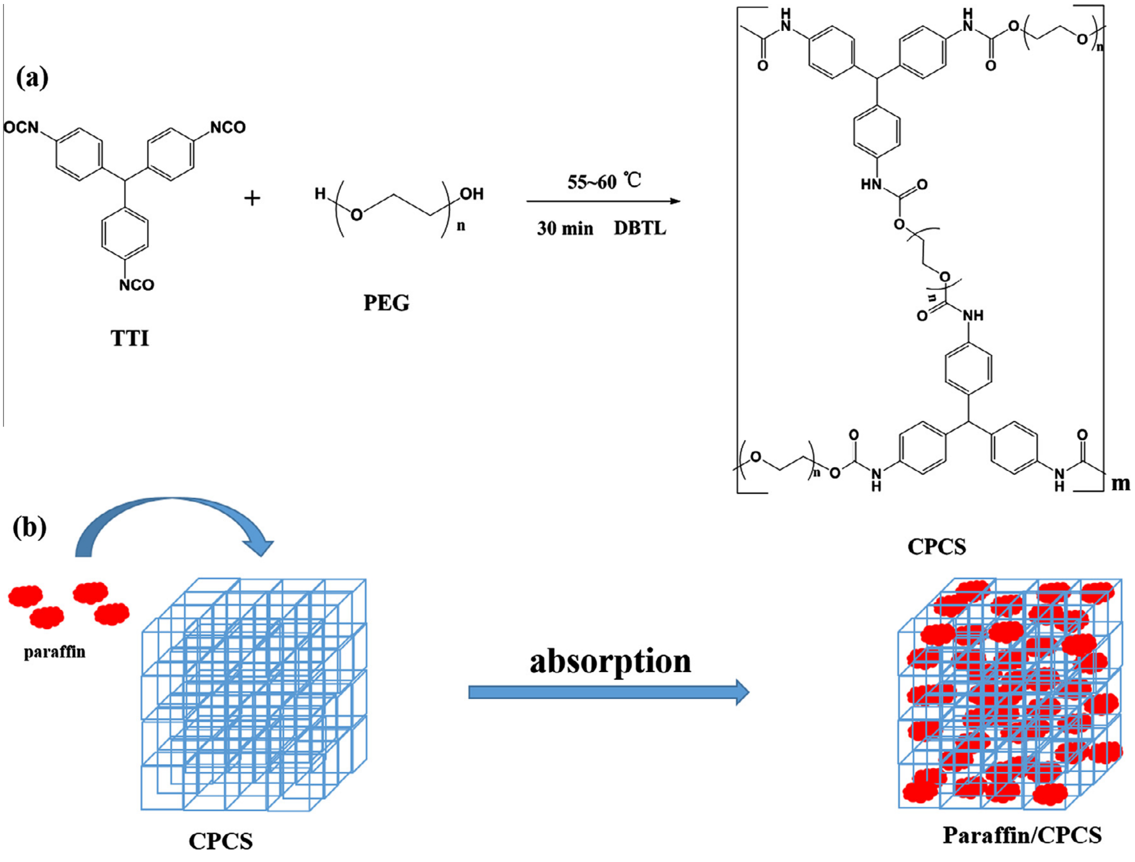

Fig. 1. Synthetic diagram for paraffin/CPCS composite.