Nano Energy (2016) **19**, 78-87

Available online at www.sciencedirect.com

ScienceDirect

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

COMMUNICATION

Surface functionalization engineering driven crystallization behavior of polyethylene glycol confined in mesoporous silica for shape-stabilized phase change materials

Jingjing Wang[a], Mu Yang[a], Yunfeng Lu[b], Zhaokui Jin[a], Li Tan[c], Hongyi Gao[a], Shuang Fan[a], Wenjun Dong[a,*], Ge Wang[a,*]

[a]*Beijing Key Laboratory of Function Materials for Molecule & Structure Construction, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, PR China*
[b]*Department of Materials Science and Engineering, University of California, Los Angeles, CA 90034, USA*
[c]*Institute for Advanced Materials and Technology, University of Science and Technology Beijing, Beijing 100083, PR China*

Received 13 July 2015; received in revised form 30 October 2015; accepted 1 November 2015
Available online 10 November 2015

KEYWORDS
Surface functionalization engineering;
Crystallization behavior;
SBA-15;
Shape-stabilized phase change materials

Abstract

Crystallization behaviors of organic phase change materials (PCMs) confined in porous supports, which are determined by the interactions between PCM molecules and channel surface of the supports, are a prerequisite for the storage and release of latent heat in PCMs. In this work, surface functionalization was engineered to regulate the interactions between a PCM of polyethylene glycol (PEG) and internal/external surfaces of a support of SBA-15 and the crystallization/stabilization behavior of PEG, and yield desirable thermal properties of the PEG confined in SBA-15 channels. To investigate the effect of the internal/external surfaces of SBA-15 on the crystallization/stabilization behavior of PEG, SBA-15 supports were modified with various functional terminals, such as NH_2-SBA-15-NH_2 and NH_2-SBA-15-CH_3. The fusion enthalpy was increased from 0 J/g of PEG/HO-SBA-15-OH composite to 88.2 J/g of PEG/NH_2-SBA-15-CH_3 composite. The amino groups modified on the internal surface of SBA-15 reduced the hydrogen bond interactions between PCM molecules and the channel surface of the supports, and also altered the adsorption conformation of the PEG chains from train structure to loop structure, which is conducive to the stretching and crystallization of the PEG chains. Further, the methyl groups grafted on the external surface of SBA-15 restrained the spillover of PEG molecules from the channels due to the opposite polarities of PEG molecules and methyl groups. Crystallization behavior of the PEG molecules in channels of SBA-15 driven by surface functionalization

---

[*]Corresponding authors.
E-mail addresses: wdong@ustb.edu.cn (W. Dong), gewang@mater.ustb.edu.cn (G. Wang).

http://dx.doi.org/10.1016/j.nanoen.2015.11.001

engineering yields a controllable phase change enthalpy of PEG/SBA-15 composite and provides a general approach for the controlling of the thermal properties of PCMs.

Introduction

With the rapid depletion of natural energy resources including fossil fuels, the development of new energy storage materials to reduce the gap between supply and demand of energy is becoming increasingly urgent [1-3]. Given their high energy density, heat recovery with small temperature variation, repeatable utilization and long-term stability, PCMs, alternatively known as "latent heat-storage materials", have been extensively applied in various advanced applications, such as solar energy harvesting [4,5], temperature-controlled greenhouses [6], re-writeable Blu-Ray disks [7] and smart textiles [8]. According to phase change states, PCMs can be classified into three major categories: solid-liquid, solid-solid and liquid-gas [9]. Solid-liquid PCMs in particular have attracted ample attention owing to their high latent heat density and small volume change. However, the leakage of solid-liquid PCMs from the thermal storage system still hinders their practical applications [10]. Considerable efforts have been devoted to introducing new supporting materials and development of shape-stabilized solid-liquid PCMs to address these technical issues [11,12].

Recently, metal foams [13], polymers networks [14] and microcapsules [15], have been developed as supports to achieve shape-stabilized PCMs. In particular, inorganic porous container for PCMs have sparked enormous interest due to their high specific surface areas, large porous volume, unique sorption properties and excellent thermal stability. For example, Wang et al. [9] developed active carbon and mesoporous carbon supports to stabilize PEG, and the hexagonally ordered pore structures of the mesoporous carbon contributed to the PEG entering into the channels of the support. Kadoono et al. [10] employed silica molecular sieves (SBA-15) with hexagonally ordered pore structures as container to stabilize fatty acid, and the ordered pore structures could improve heat recovery during the phase change. The ideal phase change latent heat of shape-stabilized PCMs reaches their theoretic values [16], and even is higher than the theoretic value due to potential chemical energy [17]. Interestingly, when small molecular PCMs, such as octadecane, octadecanol, stearic acid or sebacic acid, were stabilized in the channels of SBA-15, these small molecular PCM composites showed good thermal performance. However, when PEG was stabilized in mesoporous SBA-15, phase change latent heat of this composite was disappeared. PEG as a favorable organic PCM for thermal energy storage has been widely applied due to good chemical stability, no toxicity and controlled melting point with its different molecular weight [9]. How to activate the latent heat of long chains polymer PCMs, such as PEG, confined in SBA-15 channels still remains a challenge.

The polymer crystallization process involves primary nucleation and secondary crystal growth stages [18]. Based on thermodynamic analysis, PEG crystal growth is a thermodynamically feasible process [19]. The primary nucleation is triggered by thermal fluctuations of polymer chains at an early stage of polymer crystallization [20], followed by continuous growth of the primary nucleus to form a stable crystalline phase [21-23]. Thus, the inhibition of phase change latent heat in the PEG/SBA-15 composite can be ascribed to the lack of fluctuation of PEG chains in SBA-15 channels. Therefore, the adsorption conformation of PEG chains affected by the interactions between PEG molecules and internal surface of SBA-15 should be investigated comprehensively.

The crystallization behavior of the PEG is a prerequisite for the storage and release of the PEG's latent heat [9]. PEG in SBA-15 is complicated and differs from that of bulk PEG, which is mainly attributed to the interactions between the PEG molecules and the channel surface of the supports [9,24]. Usually, the crystallization behavior of polymers can be controlled by engineering the surface properties of the substrate [25,26]. In this paper, the effect of the interactions between PEG molecules and internal surface of silica support on crystallization behavior of the PEG confined in the support channels was investigated for the first time. Different kinds of functional terminal groups, such as -NH_2 and -CH_3, were grafted on the internal/external surface of SBA-15 to regulate the crystallization/stabilization behavior of PEG. Then, SBA-15/PEG shape-stabilized PCMs with a high PEG load, large phase change latent heat and good thermal cycling stability were achieved. The thermal properties of the PCMs can be tailored by controlling the surface properties of the supports, which can pave the way for further investigation of PEG/inorganic framework composites through surface functionalization engineering of the supports.

Experimental

Preparation of PEG/SBA-15 composites

HO-SBA-15-OH (pristine SBA-15), NH_2-SBA-15-NH_2 and NH_2-SBA-15-CH_3 were prepared according to previous works (Supporting information, Fig. S1) [27-29]. NH_2-SBA-15-NH_2 refers to amino groups on the external and internal surfaces, and NH_2-SBA-15-CH_3 refers to amino groups on the internal surface and methyl groups on the external surface. The structural schematic diagram of various SBA-15 are depicted in Fig. 1.

PEG/SBA-15 composites were fabricated by a blending and impregnating method. Firstly, PEG was dissolved in absolute ethanol, and then SBA-15 was added to the PEG solution and the resulting solution was stirred vigorously for 4 h. Finally, the mixture was dried at 80 °C overnight until the ethanol solvent completely evaporated. Other small molecular PCMs, such as