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Thermal properties of nano-sized polyethylene glycol confined in silica gels for latent heat storage

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ABSTRACT

Polyethylene glycols (PEG, average molecular weight 2000, and 10,000) are embedded in silica gels (SG) with pore diameters of d = 10–200 nm. The PEG/SG composites were analyzed using differential scanning calorimetry (DSC), scanning electron microscope (SEM) and powder X-ray diffractions (XRD). Inside the nanopores, melting temperatures of the PEG and the depression of the melting points, have linear relation with the reverse pore size. The latent heat is reduced with the decreasing pore size. The composites remained no leakage of PEG above the melting point in pore fillingness of 80%. In a short-term thermal cycling, the composites display stable melting points and heat storage capacities. The diffractions of PEG in the pores show the same patterns with the bulk, revealing a same structure basis with good heat storage performance. The nano-sized PEG act as a series of new phase change materials obtained by adjusting the size.

1. Introduction

With the development of the society, more and more efficient energy storage devices and systems are needed to meet the demand of energy, and to improve the energy efficiency [1]. Phase change materials are also called as latent thermal energy storage materials, which is friendly to the environment [2]. It has been considered as an effective approach for its high energy density, heat recovery with small temperature drop, constant heat source temperature and repeatable utilization [3,4]. Recently, PCMs have been tried to use in many fields such as solar energy utilization, temperature-control greenhouses and textiles, energy-saving building, smart housing, waste heat recovery and heat exchanger [5–8]. Commonly, they are classifies into three types from their phase change nature: the solid-solid, the solid-liquid, and the liquid-gas PCMs. In the last decades, the former two kinds have achieved particular attention in research and practical applications due to their suitable thermal properties. The s-l PCMs are attractive and practical because of their high latent heat density, constant phase change temperature, small volume change, and no or small phase segregation [9]. However, their high fluidity causes the leakage of the melted phase during the phase change process, which reduces their energy storage efficiency, limits the applicability and increases the cost [10]. To solve this problem, the shape-stabilized PCMs have become one of the focuses in the area of latent heat energy storage [11,12]. Recently, the nano shape stabilized PCMs by sol-gel polymerization, polymer network, and grated onto graphene or porous materials are also reported [13–16]. Form these methods, the products normally show specific phase transition temperature, latent heat and other thermal properties. In an alternative way, encapsulation of PCMs in nanoporous is put forward for tuning the phase transition temperature of those with good heat storage performance to expand their regulation temperature range [17,18]. This provides a general method but not necessarily the final product forms. Any method that can change the size of PCMs may have similar effect by this nanoencapsulation technique.

Polyethylene glycol (PEG) is considered as a promising phase change material for thermal energy storage due to its suitable melting point, high latent heat of fusion, congruent melting behavior, slight supercooling and chemical stability [19–21]. Moreover, PEG is a series of polymers with different molecular weights with the melting temperature ranging from 3.2 °C to 68.7 °C, being up to versatile applications. However, PEG is a classical solid-liquid phase change substance, which is less convenient in practical use due to its leakage [22]. Shape-stabilization of PEG by encapsulation in nanoporous materials is worth trying so as to gain advantages as avoiding the leakage of the melted phase during its phase change, and fluidity [11,12,23]. In this method, the control of the phase transition can be estimated from the Gibbs-–Thomson equation by Eq. (1), which describes depression of the melting points of tiny spherical particles. In the derivation of the equation, the heat of fusion can be assumed to decrease with the decreasing sizes as in Eq. (2) [24,25].

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$$T_m(r) = T_m(\infty) + \frac{2T_m(\infty)\sigma_{sl}}{\Delta H_f(\infty)\rho_s r} \quad (1)$$

$$\Delta H_f(r) = \Delta H_f(\infty) + \frac{2\sigma_{sl}}{\rho_s r} \quad (2)$$

where $T_m(\infty)$, $\Delta H_f(\infty)$ and ρ_s are the bulk melting point, heat of fusion and the solid phase density, respectively. $T_m(r)$ and $\Delta H_f(r)$ are the melting point and heat of fusion of crystals with radius r, respectively. σ_{sl} is the solid-liquid interface energy. For the confined system, the radius r and the pore diameter (d) of cylindrical nanopores in a relation of $r = d/2$ [24,26].

In this work, we prepared PEG/SG shape-stabilized PCMs by a blending and impregnation process. Among them, PEG was used as the phase change material, silica gel as supporting material which has disordered three-dimensional interconnected pores. SEM, DSC and XRD techniques were used to characterize morphology of the particles, crystalline property, phase transition behavior, and stability during thermal cycling of the PEG/SG composites. In the nanopores, PEG shows size-dependent transition temperature, latent heat and supercooling. Heat storage capacity of the pore PEG keeps stable in a short term freeze-thaw cycling as the bulk counterpart. Our study can provide new type form-stable polymers for heat storage application with good performance.

2. Experimental

2.1. Materials

PEG with an average molecular weight of 2000 and 10000, SG (d = 10–200 nm), methanol, high purity adamantane, high purity water, high purity indium standard material were used in this experiments. The high purity adamantane was obtained by recrystallizing three times of a commercial product (purity 99%). The source and purity of the compounds are shown in Table 1. The specifications of SG provided by the manufacturer are listed in Table 2.

2.2. Preparation of PEG/SG composites

Shape-stabilized PEG/SG composites were prepared through a physical blending and impregnation process, similar as in the previous work [17,18]. Before use, the silica gel was put into a piece of glass tube and outgassed for ≥3 h in vacuum. Then, a suitable amount of PEG was weighted into the glass tube with the SG powder (> 20 mg) inside. Methanol was added into it in a volume that the solids were just immersed in. After gently shaking, the mixture was heated slowly in a water bath at 55 °C about 9 h until to a constant weight. During the time, the methanol solvent evaporated and a white powder was left on the bottom of the glass tube. The difference in the weight of the SG powder before and after loaded with PEG is nearly the PEG added in the beginning, with a difference within ± 0.6% of the expected value. It indicates the influence of the possibly residual solvent methanol can be negligible. The pore fullness (φ) value can be determined by using relation $\varphi = m_{PEG}/(D_{PEG} m_{SG} V_p)$, where m_{PEG} is the difference in mass of the SG before and after filled with PEG, D_{PEG} the density of the bulk PEG, m_{SG} the mass of SG, V_p the specific pore volume of SG as listed in Table 1. In the composites, the actual φ values of the compounds are about 80%.

Table 1
The source and purity of the compounds.

Chemical name	Source	Purity
PEG	Sinopharm Chemical Reagent Co., Ltd	Analytically pure
Silica gel	Tosoh Finechem Co., Ltd	≥99.5%
Adamantane	Aladdin Chemical Reagent Co., Ltd	99%†
Indium	TA Instruments Co., Ltd	99.99998%
Water	doubly distilled water	Impurity ≤5 ppb‡
Methanol	Kai Tong Chemical Regent Co., Tianjin	Analytically pure

†After recrystallization of three times, admantane contains no impurity peak in gas chromatography detection.
‡The impurity is provided by the manufacturer.

Table 2
Specifications of silica gels as provided by the manufacturer.

Product name	Mean pore diameter (nm)	Specific pore volume ($cm^3 g^{-1}$)	Specific surface area ($m^2 g^{-1}$)
SG100	10	0.9	–
SG150	15	1.15	–
SG300	30	0.9	120
SG1000	100	0.9	25
SG2000	200	0.8	25

2.3. Characterization of the composites

The thermal properties of the pure PEG and its composites were measured using a DSC Q10 (TA Instruments) under a high purity nitrogen atmosphere at a flow rate of 20 ml min^{-1}. The DSC signals of the samples were recorded at a scanning rate of 5 °C min^{-1} in heating process and 2 °C min^{-1} in cooling process at a nitrogen atmosphere in thermal cycling test. All the samples were taken about 3–5 mg, sealed in an aluminum pan. The temperature scale and enthalpy change of the phase transition were calibrated using high purity adamantane ($T_{trs} = -64.43$ °C, $\Delta_{trs}H = 24.05$ J g^{-1}), high purity water ($T_{fus} = 0.01$ °C, $\Delta_{fus}H = 335$ J g^{-1}), high purity indium standard ($T_{fus} = 156.598$ °C, $\Delta_{fus}H = 28.57$ J g^{-1}). From the DSC curves, the melting point and freezing point were obtained by extrapolating a tangent line at the point of maximum slope of the peak to the baseline. Also, the latent heat can be calculated through the integral area of the DSC curves. The temperature on cooling is calibrated according to the ASTM standard E2069. At a rate of 5 °C min^{-1} for both the heating and cooling, the correction of the temperature (ΔT) is 0.18 °C ($n = 4$, $s = 0.02$ °C) using the liquid crystal 4-Cyano-4′-octyloxybiphenyl (8OCB, purity ≥ 99.5%) as the reference material. The true temperature on cooling is the observed value plus ΔT.

The powder X-ray diffraction of the composites was studied to characterize the physical state of the material. The diffraction patterns of the samples were collected at room temperature on a Panalytical Xpert Pro diffractometer using Cu Kα radiation (1.54 Å) source and operating at a power of 40 mA/40 kV in the angle range of $5° \leq 2\theta \leq 45°$ and a step of $2\theta = 0.02°$.

The scanning electron micrographs of the SG powders are obtained using a scanning electron microscope, the field-emission high resolution scanning electron microscopy (SEM, Hitachi s-4800 and FEI F250), to observe the surface morphologies of the porous silica gel coated with gold film.

3. Results and discussion

3.1. SEM and XRD characterization

Fig. 1 shows the surface morphologies of the PEG10k/SG composites, as the representative, by scanning electron microscopy. The PEG10k are loaded in the silica gels with pore diameters of 15, 30, and 100 nm, respectively. The SEM image (a) of the PEG in SG (100 nm) displays clearly the silica gel backbones and the pores spread within them. These are the disordered arrangements of the three-dimensional interconnected pores. Under the SEM image (b) of the PEG in SG (30 nm), one can see backbones of the silica gels and small pores of the matrix without regular packing. The image of the PEG in SG (15 nm) (c) also shows disordered pore network as the larger ones but a bit hard to be discerned because of the resolution of SEM equipment. With the