

Thermal properties of C₁₇H₃₆/MCM-41 composite phase change materials



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ABSTRACT

Phase change materials (PCMs) lie at the heart for energy storage technology. In this paper, we proposed a porous media based composite PCM, consisting of Heptadecane (C₁₇H₃₆) as the core and mesoporous silica (MCM-41) as the shell. Basing on the nanostructures we built and verified, the thermal properties of composite were predicted by molecular dynamics (MD) method, including the melting point, latent heat, specific heat capacity and thermal conductivity. Furthermore, the effects of the filling ratio of C₁₇H₃₆, the pore size or porosity of MCM-41 and the temperature were analyzed. It turns out that the composite C₁₇H₃₆/MCM-41 obtains at least 2-fold increase over bulk C₁₇H₃₆ in the thermal conductivity, due to the introduction of supporting material MCM-41. Owing to the size effect of C₁₇H₃₆ filling in nanopores, both the melting point and latent heat of composite are always lower than bulk values of C₁₇H₃₆, while the specific heat capacity of composite is between values of bulk C₁₇H₃₆ and silica film. The specific heat capacity and thermal conductivity increases with rising temperature. The properties of composite are controllable by tailoring the pore size of supporting material or/and filling ratio of core in the pore. The melting point, latent heat and specific heat capacity would rise with the increase of pore size or/and filling ratio. With respect to the thermal conductivity of composite, it drops when the pore size enlarges or the porosity increases while keeping constant filling ratio; while it first rises almost linearly with the increase of core filling ratio, and then keeps stable after the filling ratio reaches 70%. In addition, increasing filling ratio is more effective than enlarging pore size in improving the latent heat, specific heat capacity and thermal conductivity. On the contrary, the melting point is more sensitive to the change in pore size rather than filling ratio, and it is linearly dependent on the inverse pore size. This work is expected to be helpful in providing some fundamental data for the design of porous media based PCM.

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1. Introduction

Phase change materials (PCMs) lie at the heart for energy storage technology, which is one of the most effective ways to alleviate the problems of intermittence and instability of solar energy, and to cope with the energy and environment crisis [1]. PCMs are mainly classified as inorganic and organic groups. Inorganic PCMs have the disadvantages of undercooling, corrosion, and phase separation, which possibly could be overcome by using organic PCMs. However, low thermal conductivity, unsafety, and leakage are serious barriers for wide adoption of pure organic PCMs. Accordingly, the advent of form-stable PCMs has being an indispensable

demands in energy storage field. The form-stable PCMs are divided into two major categories according to phase transition mechanisms [2], the solid–solid PCMs and solid–liquid PCMs. There is more concern among solid–liquid PCMs due to their ability to provide high energy storage density and have the characteristics to store thermal energy at relatively constant temperature [3].

Up to now, three types of form-stable solid–liquid PCMs have been developed including encapsulated, polymer based and porous media based PCMs. Giro-Paloma et al. [4] synthesized new microcapsules by emulsion co-polymerization technique. Paraffin and palmitic acid are encapsulated successfully with a Polystyrene-coethylacrylate (PScEA) shell, and the encapsulated PCMs are considered to have good potential for energy storage. Alkan and Sari [5] prepared a series of fatty acid/polymethyl methacrylate blends. The fatty acids are trapped into polymethyl methacrylate (PMMA) as much as 80 wt.% and the blends keep their

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shapes even when they are heated over the melting point of fatty acid. The availability of the attractive interaction between the fatty acid and the PMMA resulted in good compatibility of the components of the blends. Zhong et al. [6] synthesized three kinds of porous heterogeneous composite PCMs from expanded graphite (EG) and binary molten salts (LiNO₃-KCl, LiNO₃-NaNO₃ and LiNO₃-NaCl) through solution impregnation method. The thermal conductivity of binary molten salts is enhanced by 4.9–6.9 times after impregnation with EG. The phase change properties of composite PCMs show great thermal stability, which is maintained after 100 cycles. Yang et al. [7] prepared PEG/SiO₂ shape-stabilized PCMs with various mass fractions and molecular weights of polyethylene glycol (PEG). It is shown that the silica framework can strongly confine the crystallization of PEG. The crystallinity and thermodynamic performances of the composite PCMs first decline then improve with the increase of the PEG molecular weights, owing to different confinement behaviors of the silica framework. Zhang et al. [8] prepared a series of shape-stabilized PCMs by physical mixing method, which are composed of polyethylene glycol hexadecyl ether (Brij58) or polyethylene glycol octadecyl ether (Brij76) and porous silica (MCM-41). The latent heat increases with the weight of Brij component. The new peak at 18.8° in X-ray Diffraction (XRD) pattern demonstrated that the pore size and the surface adsorption ability of MCM-41 affect the crystallization behavior of Brij molecule. All these reported investigations have shown that the form-stable solid-liquid PCMs have excellent phase change properties. However, the deficiency in thermal conductivity and stability is still a critical issue.

A few research addressing PCMs has been performed on the atomic and molecular scale with molecular simulation method, e.g. molecular dynamics (MD). Most studies focus on the pure bulk PCMs, such as LiF [9], Cu [10], polymethylene [11], and *n*-hexadecane [12]. Some studies have been conducted on single metal nanoparticles, e.g. Fe, Ni, Au and Cu nanoparticles [13,14], mainly focusing on the size effect of the melting and solidification points. However, due to the complex structure of form-stable PCMs, only the group of Rao et al. reported the properties of composite PCMs by MD simulations [15]. They found that the predicted melting point of alkane based PCM slurry is very close to the published experimental values. They also compared the properties of the nano-encapsulated PCM with free and constrained shell. The results show that the nano-encapsulated PCM with a soft shell will enhance the heat transfer and show a positive meaning for thermal energy storage [16]. Molecular simulation provides a method to explore the phenomena of transport and phase transition in PCMs at the molecular level, but it is still far from understanding.

In short, more efforts should be made to gain insight into the thermal properties of composite PCMs, especially the correlations between the nanostructures and thermal properties, as well as the mechanisms of heat transfer with phase change at the meso/nano scale. In this paper, a composite PCM, consisting of Heptadecane (C₁₇H₃₆) as the core and mesoporous silica (MCM-41) as the shell was proposed. The composite nanostructure was built and its thermal properties were predicted by molecular dynamics (MD) simulation. The melting point, specific heat capacity, latent heat and thermal conductivity were obtained, along with the influences of the core filling ratio, pore size or porosity and temperature were considered. This study is expected to shed lights on the composite PCMs and energy storage engineering by utilizing organics and porous silica.

2. Nano-structure models

MCM-41 is a kind of silica-based mesoporous materials, which consists of a hexagonal array of long and unconnected cylindrical

pores with diameters that can be tailored within the range 2–10 nm. The scanning electron microscope image of MCM-41 is shown in Fig. 1 [17]. According to MCM-41 microstructural characteristics, its preliminary simulation model was constructed by deleting atoms in a silica film model. Then, by adding hydrogen atoms, revising the structure, and annealing, we finally obtained a neutral and reasonable nano-structure of MCM-41 as shown in Fig. 2. Besides, the hydrogen mass was added to the carbon mass, a common treatment for hydrogen atoms in MD [18].

To prove the reliability of MCM-41 nano-structural model, we performed both the small-angle and wide-angle XRD simulations on it. The wavelength of X-ray is 1.5406 Å, and the copper target was chosen. The simulated pattern of small-angle XRD shows good agreement with experimental results [19], as illustrated in Fig. 3. Moreover, the pore diameter can be calculated from the wide-angle (5–45°) XRD pattern. According to Bragg Law, $2d\sin\theta = n\lambda$, with positive integer $n = 1$, scattering angle $\theta = 5^\circ$, and where d is the interplanar distance, λ is the wavelength of incident wave, the pore diameter d of MCM-41 was obtained as 8.84 Å, in the same order as the shell wall thickness (7 Å). All these results indicate that the MCM-41 model we built is amorphous, in accordance with the practice.

Paraffin, widely used as a kind of PCMs, composed of various alkanes. Heptadecane (C₁₇H₃₆) is one of the most important components of paraffin. To obtain the crystal structure of heptadecane, we built a simulation box containing 10 C₁₇H₃₆ molecules, which has a lattice constant of 15.86 Å. The initial density of the box was set as 1 g/cm³. Then the geometry optimization and annealing were carried out to get the stable structure, as illustrated in Fig. 4.

The assembled nano-structure of C₁₇H₃₆ filled in the pores of MCM-41 is displayed in Fig. 5(a). It is difficult to use the real atomic structure for the simulation conditioned by the computing capacity, and the atoms on inner surface of MCM-41 channels have the greatest influence on the movement of C₁₇H₃₆ molecules. Consequently, we referred to the simplified model's idea proposed by Ohkubo et al. [20] and simplified the composite structure as shown in Fig. 5(b).

The Materials Studio (MS) package was used for nanostructure construction. The annealing temperatures are chosen for C₁₇H₃₆ from 240 K up to 340 K in steps of 10 K, for MCM-41 from 300 K to 500 K in steps of 20 K.

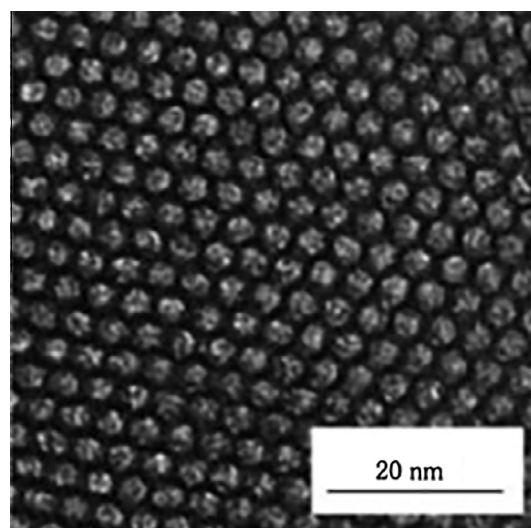


Fig. 1. Scanning electron micrograph of MCM-41 (dark region represents shell wall and bright region represents channels).

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