Solar Energy Materials and Solar Cells 174 (2018) 283–291

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

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

Polyethylene glycol-enwrapped silicon carbide nanowires network/expanded vermiculite composite phase change materials: Form-stabilization, thermal energy storage behavior and thermal conductivity enhancement

Yong Deng[a], Jinhong Li[a,*], Hongen Nian[b]

[a] Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing 100083, PR China

[b] Key Laboratory of Comprehensive and Highly Efficient Utilization of Salt Lake Resources, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, 810008, PR China

ARTICLE INFO

Keywords:
Expanded vermiculite
Silicon carbide nanowire filler
Theoretical calculation method
Thermal conductivity enhancement
Thermal energy storage behavior

ABSTRACT

Polyethylene glycol (PEG)-enwrapped silicon carbide nanowires (SiC NWs) network/expanded vermiculite (EVM) form-stable composite phase change materials (PSE fs-CPCMs) were prepared to overcome the disadvantage of form instability during phase transition and improve the slow heat transfer rate of PEG. The flowability was effectively solved by synergy between the pore structures of EVM and surfaces of SiC NWs. PSE3.29 exhibited the maximum adsorption ratio of PEG as high as 73.12 wt%. The heat transfer of PSE fs-CPCMs could be significantly enhanced by the SiC NWs filler, and the thermal conductivity of PSE3.29 reached 0.53 W/m K, which was 8.8 times higher than PEG. Theoretical calculation methods were applied to evaluate the thermal conductivity enhancement ability of SiC NWs. Maxwell-Eucken model (MEM) predicted obviously higher thermal conductivity enhancement than the experimental results due to stronger dependent on lower volume fraction of disperse phase. The prediction results obtained with effective medium percolation theory (EMPT) were in reasonable agreement with experimental values. Thermal energy storage behavior of PSE fs-CPCMs were strongly affected by the confinement effect of nanoscale pore structures of EVM and surface interactions of EVM and SiC NWs. FT-IR, TGA and phase change cycles test results confirmed that the PSE fs-CPCMs exhibited excellent chemical compatibility, thermal stability and reliability.

1. Introduction

Recently, thermal energy storage plays a crucial role in solar energy conservation and utilization due to the rapidly growing consumption of non-renewable energy resource and environmental concerns. Latent heat storage based on phase change materials (PCMs) can provide the high energy storage density and nearly isothermal behaviors during phase transition. In recent years, PCMs have been applied in the fields of solar energy conservation, waste heat recovery, air-conditioning systems, etc. [1]. However, PCMs have obvious drawbacks, such as the flowability during the solid-liquid phase transition and low thermal conductivity. The flowability of liquid PCMs may lead to poor mechanical and safety of thermal energy storage systems. Cellat et al. [2] discovered that the compressive strength of concrete mixtures with 1 wt % PCM was reduced by 12%. Moreover, the compression strength would further reduce when PCM contents were increased to 2 wt%. The thermal conductivity of PCMs dictates the rate that heat reaches the solid-liquid interface [3]. Therefore, low thermal conductivity leads to slow thermal energy charging/discharging rates during the melting/solidification process. Unfortunately, most organic PCMs suffer from inherently low thermal conductivity (~ 0.2 W/m K), which severely limits its application in solar energy conversion [4,5].

Recently, clay mineral-based form-stable composite PCMs (fs-CPCMs) were developed to control the leakage of PCMs during the phase change process [6]. The clay minerals with unique porous structure and considerable specific surface area can encapsulate abundant PCMs under the action of capillary force and surface tension, which can maintain the structural strength and successfully overcome the flowability defect of PCMs. In addition, the excellent chemical compatibility, desirable thermal stability, and light weight are also

* Corresponding author.
E-mail address: jinhong@cugb.edu.cn (J. Li).

http://dx.doi.org/10.1016/j.solmat.2017.09.013
Received 18 June 2017; Received in revised form 25 August 2017; Accepted 10 September 2017

beneficial to thermal energy storage applications in solar energy conversion. Numerous clay mineral-based fs-CPCMs including expanded vermiculite (EVM) [7,8], expanded perlite [9], kaolin [10], diatomite [11] and sepiolite [12] had been reported. However, the clay mineral-based fs-CPCMs have a lower thermal conductivity than expanded graphite-based, graphene oxide nanosheets-based, and metal foam-based fs-CPCMs [6,13].

Considerable efforts have been devoted to developing composite PCMs with enhanced thermal conductivity by dispersing thermally conductive fillers [4,5,9,11,14–16]. The dispersion of these large-sized particle-like fillers may not be stable after long-term application. Adding nano-scale fillers may be an effective approach to solve the above problems due to the small size and surface effects. The thermophysical properties including thermal conductivity, phase change temperature and latent heat of fs-CPCMs are significantly affected by the size, shape, concentration and surface of nano-scale dispersion fillers [15]. Several research groups confirmed that the one-dimensional nanoparticles could particularly improve the heat transfer process of fluids [17,18]. Hence, the one-dimensional nano-scale dispersion fillers are beneficial and suitable to improve the thermal conductivity of fs-CPCMs. For example, carbon nanotubes and nanofibers dispersed into PCMs showed excellent heat transfer behaviors due to their unique physical properties [15,19]. The thermal conductivity enhancement in solid and liquid states of n-Dodecanoic acid PCM containing 1 vol% carbon nanotubes respectively reached 171% and 20% [19]. Silicon carbide nanowires (SiC NWs) with high thermal conductivity (120 W/m K) might be used as one-dimensional nano-scale fillers for effective thermal conductivity enhancement of clay mineral-based fs-CPCMs. SiC NWs with the large specific surface area are also expected to adsorb a large amount of PCMs to increase the encapsulation capacity of clay mineral-based fs-CPCMs. The effects of SiC NWs on thermal conductivity enhancement and thermal energy storage behaviors of mineral-based fs-CPCMs were seldom reported.

Theoretical calculation methods are the effective way to predict the thermal conductivity of clay mineral-based fs-CPCMs and evaluate the enhancement ability of nano-scale dispersion fillers. Unfortunately, few theoretical calculation methods have been developed so far. The pertinence of approximation to the real microstructure of clay mineral-based fs-CPCMs determines the validity and accuracy of a chosen method. Therefore, we attempted to predict the thermal conductivity of clay mineral-based fs-CPCMs combined with the theoretical calculation methods of heterogeneous and porous materials, such as Maxwell-Eucken model (MEM), Effective medium percolation theory (EMPT), and Series and Parallel [20,21].

In this study, polyethylene glycol (PEG) was selected as the phase change material because it had suitable phase change temperature, high phase change enthalpy, desirable chemical stability, and showed no phase separation. EVM with high porosity and unique microstructure served as a form stabilizer. SiC NWs with high thermal conductivity acted as thermal conductivity enhancement fillers. A series of PEG-enwrapped SiC NWs network/EVM (PSE) fs-CPCMs were prepared to overcome flowability during phase transition and improve the slow heat transfer rate of PEG. The thermal energy storage behavior of PSE fs-CPCMs were analyzed in detail. Some effective theoretical calculation methods were developed to evaluate the thermal conductivity enhancement ability of SiC NWs. Based on previous researches [22–25], the prepared PSE fs-CPCMs might be used as potential candidates for thermal energy storage applications in solar energy conversion.

2. Experimental

2.1. Materials

PEG (Mw = 6000) was purchased from Xilong Chemical Reagent Beijing Co., Ltd. China. EVM was obtained from Lingshou County, Hebei Province, China. SiC NWs (Prepared by the chemical vapor deposition method; Length: 50–100 μm; Diameter: 100–600 nm; Thermal conductivity: 120 W/m K) were supplied by Changsha Sinet Advanced Materials Co., Ltd. China.

Table 1
Components of the prepared PSE fs-CPCMs.

PSE fs-CPCMs	EVM weight fractions (wt%)	PEG weight fractions (wt%)	SiC NWs weight fractions (wt%)
PSE0	31.41	68.59	0.00
PSE1.05	29.24	69.71	1.05
PSE2.13	26.74	71.13	2.13
PSE3.29	23.59	73.12	3.29

2.2. Preparation of PSE fs-CPCMs

The PSE fs-CPCMs were prepared by our previously reported method [26]. The temperature of stirring, impregnation and drying oven was maintained at 80 °C. Four kinds of PSE fs-CPCMs (Table 1) were obtained. The maximum adsorption ratio of PEG with good form stability respectively reached 68.59 wt%, 69.71 wt%, 71.13 wt%, and 73.12 wt% and the corresponding ratios of SiC NWs were 0, 1.05 wt%, 2.13 wt% and 3.29 wt%, respectively. Obviously, the encapsulation capacity of PEG increased with the increase in the weight fraction of SiC NWs.

2.3. Characterization

The morphology of EVM, SiC NWs and PSE fs-CPCMs was observed with scanning electronic microscope (SEM, HITACHI S-4800) at an accelerating voltage of 15 kV. The contact angle test was conducted with measuring instrument (KRUSS DSA25). Firstly, the PEG powders were heated to 80 °C to obtain liquid PEG. Secondly, the EVM and SiC NWs powders were respectively pressed into a circular sheet via a hydraulic machine. Then, the melted PEG (about 3 μL) was dripped on the surface of EVM and SiC NWs. Finally, the contact angle was obtained by taking pictures after 5 s. The crystallization of samples was analyzed by X-ray diffraction (XRD, Rigaku DMAX 2400). XRD patterns were collected at a scanning rate of 8°/min in the 2θ range of 8–80° using Copper Kα radiation (λ = 0.1541 nm, 40 kV and 100 mA). Chemical compatibility of PSE fs-CPCMs was investigated by Fourier transform infrared spectroscopy (FT-IR, SHIMADZU FTIR8400). The testing wavenumber range was 3700–400 cm^{-1}. The pore size distribution of EVM determined by Brunauer-Emmett-Teller (BET) was calculated according to Barrett-Joyner-Halenda (BJH) method. The phase change temperature and enthalpy of PSE fs-CPCMs were determined with differential scanning calorimeter (DSC, TA Q100). The heated and cooled temperature ranges were between 0 °C and 80 °C and test rate was 5 °C/min. Each sample of PSE fs-CPCMs was repeated four times to take the mean value as DSC result. Thermal stability of PSE fs-CPCMs was measured by using thermo-gravimetric analysis (TGA, TA Q5000). All samples were heated from 30 °C to 650 °C at a rate of 10 °C/min. The thermal diffusivity of PSE fs-CPCMs was measured by using laser thermal conductivity tester (NETZSCH LFA-427) at room temperature. Then the thermal conductivity λ was calculated by Eq. (1).

$$\lambda = \alpha \cdot C_p \cdot \rho, \tag{1}$$

where α is the thermal diffusivity; C_p represents the specific heat capacity; ρ is the density. The melting and solidifying temperature curves of PSE fs-CPCMs during heating and cooling processes were measured by constant temperature water bath method (melting: 65 °C, solidifying: 15 °C, multi-channels temperature recorder: TOPRIE TP720, Thermocouple: T).