Solar Energy 167 (2018) 158–164

Contents lists available at ScienceDirect

Solar Energy

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

Synthesis and properties of phase change microcapsule with SiO_2-TiO_2 hybrid shell

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ARTICLE INFO

Keywords:
Heat storage
Microencapsule
Paraffin
Phase change

ABSTRACT

In this paper, SiO_2-TiO_2/paraffin phase change microcapsules with different contents of paraffin are prepared via sol-gel method. SiO_2-TiO_2 act as a shell and paraffin is used as a core. Scanning Electron Microscope (SEM), Laser particle size analyzer, Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffractometer (XRD), Differential Scanning Calorimeter (DSC) and Hot Disk are employed to characterize the morphology, chemical structure and thermal properties of SiO_2-TiO_2/paraffin microcapsules. The results show that there is no reaction between SiO_2-TiO_2 and paraffin. The average particle size is 11.38 μm when the encapsulation rate of paraffin is 39.8%. The latent heat and the phase change temperature of the SiO_2-TiO_2/paraffin microcapsule is 93.7 J/g and 29.0 °C, respectively. After 1000 times of heat storage-release cycles, the latent heat of the microcapsule was decreased by 6.58% and the encapsulation ratio was decreased by 2.62%. The thermal conductivity of the microcapsule is 11.63% higher than that of paraffin.

1. Introduction

A phase-change material (PCM) is a substance with a high heat of fusion when melting and solidifying at a certain temperature. Heat is absorbed or released when phase-change happens (Ascione et al., 2014; Gao et al., 2007; Li and Wu, 2011; Oró et al., 2012; Cai et al.,2015; Li et al., 2016). Organic PCM is a favorable PCM with a characteristic of little supercooling and good thermal stability (Jamekhorshid et al., 2014). However, organic PCM has a disadvantage of leakage and shows a large volume change during the phase change process. This disadvantage can be overcome by compounding organic PCM with inorganic materials using sol-gel method (Farid et al., 2004; Feczkó et al., 2016; Giro-Paloma et al., 2015). In the process of gel formation, organic PCM is encapsulated in the gel network. After the evaporation of water, three-dimensional network structure is gradually formed, and paraffin is dispersed uniformly in the three-dimensional network (Latibari et al., 2013). Under the effect of the surface tension and capillary force, the organic PCM is trapped in the network.

Many attempts have been carried out to encapsulate PCM (Qiu et al., 2013; Wang et al., 2016; Yang et al., 2015). Latibari et al. (2013), Hawlader et al. (2003) prepared encapsulated paraffin particles by complex coacervation as well as spray-drying methods. Microcapsules prepared either by coacervation or the spray-drying method have a thermal energy storage/release capacity of about 145–240 J/g. Sarı et al. (2010) prepared microencapsulated n-heptadecane with polymethylmethacrylate(pmma) shell by emulsion polymerization method.

However, the microPCMs with polymeric shells has poor thermal stability, flammability and toxicity. This shortcoming restricts their application in building materials. Therefore, the microPCMs in inorganic shells are developed recently.

Li et al. (2013) prepared a novel microencapsulated phase change composite of paraffin/SiO_2. The latent heat of the composite was 45.5 J/g and the encapsulation ratio of paraffin was 31.7%. The paraffin/SiO_2 composite could maintain its heat storage performance perfectly after 30 times of melting–freezing cycles. Tang et al. (2014a,b) prepared carbon nanotube/PEG/SiO_2 composite. The composite exhibited characteristics of light-thermal conversion, form-stable effect, and high thermal conductivity. Tang et al. (2014a,b) also prepared PEG/SiO_2-Al_2O_3 with enthalpy of 124 J/g. The thermal conductivity of PEG/SiO_2 was improved by 12.8% after being added with 3.3 wt% of Al_2O_3. Fang et al. (2010) prepared microencapsulated paraffin composites with SiO_2 shell as thermal energy storage materials by sol–gel methods. The microencapsulated paraffin composites solidify at 58.27 °C with a latent heat of 107.05 kJ/kg and melt at 58.37 °C with a latent heat of 165.68 kJ/kg when the encapsulation rate of the paraffin is 87.5%.

However, the microPCMs with SiO_2 shells has poor mechanical performance and cracks easily in the application (Cao et al., 2014).

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https://doi.org/10.1016/j.solener.2018.04.016
Received 19 September 2017; Received in revised form 22 March 2018; Accepted 6 April 2018

Titanium dioxide nanoparticles have been paid a special attention because of the characters of the photocatalyst properties and good thermal stability. Titanium dioxide is helpful to improve the thermal stability, mechanical performance of microPCMs and make the microcapsule show photocatalyst properties. Little work reported the phase change microcapsules with SiO_2-TiO_2 shell up to now. In this paper, silicon dioxide and titanium dioxide were used to form a shell on the surface of paraffin via a hydrolysis-condensation reaction. The microcapsules with different contents of paraffin were prepared via the sol-gel method. The structures of the microcapsules were characterized. The thermal properties of the microcapsules with different contents of paraffin were compared.

2. Experimental

2.1. Materials

Anhydrous ethanol (Sinopharm Chemical Reagent Co., Ltd. China) and deionized water were used as solvents. The anhydrous ethanol is analytical reagent (AR) and the percentage content of the anhydrous ethanol is not less than 99.7%. Paraffin (The density is 0.759 g/ml) with the phase change temperature of 28.4 °C was purchased from Rubitherm PCM Co., Ltd., China. Titanium butoxide (TBOT, AR), Tetraethylorthosilicate (TEOS, AR), Sodium dodecyl sulfate (SDS) and Hydrochloric acid (HCl, AR) were purchased from Sinopharm Chemical Reagent Co. Ltd., China. The percentage content of TBOT is not less than 98.5%. The percentage content of HCl is 36–38%. SDS is chemical pure (CP) and the percentage content is not less than 97%.

2.2. Preparation of SiO_2-TiO_2/paraffin microcapsules

The formation process scheme of SiO_2-TiO_2/paraffin microcapsules is shown in Fig. 1.

20 g deionized water was added in the three-necked flask and the pH value was adjusted to 2.45 with hydrochloride acid. After being added with 10 ml of ethanol and 10.4 g of TEOS, the mixture was stirred at 500 r/min and 60 °C for 2 h. Then, the mixture was refluxed and the silica sol was obtained. Paraffin (10 g, 20 g) was added in 100 ml of deionized water with 1% of SDS. The mixture was processed with ultrasonic vibration for 15 min to obtain an emulsion of paraffin. The emulsion was dropped to the silica sol and stirred for 30 min. After the mixture was cooled to 0 °C, it was stirred at 500 r/min with addition of 17 g TBOT and 40 ml ethanol to obtain the gel. After being aged at room temperature for 2 days, the gel was washed twice with alcohol, and then washed twice with the deionized water. After being dried under vacuum, the phase change microcapsules were obtained and named as PCM1 (containing 10 g paraffin) and PCM2 (containing 20 g paraffin), respectively. During the preparation, SiO_2-TiO_2 microcapsules were obtained if paraffin was not added.

2.3. Characterization of SiO_2-TiO_2/paraffin microcapsules

The surface morphology of the microcapsule was examined by a Sirion Field Emission Scanning Electron Microscope (SEM, Sirion 200, FEI Company, Netherlands). The accelerating rate was 20.0 KV. The phase structure was characterized by an X-ray diffractometer (XRD, D/max-2500, Rigaku, Japan). The XRD measurement was performed at a scan speed of 0.15 s/step from 10° to 90° for 2θ. FTIR (NicoletiS10, America) was used to analyze the chemical structure of microcapsules. The wave number was from 400 cm^{-1} to 4000 cm^{-1}. The thermal properties were measured with a DSC instrument (DSC 200 F3 Maia, NETZSCH Group, German) in nitrogen atmosphere from −20 °C to 60 °C at the heating rate of 5 °C/min. The experiments were repeated for three times on each sample. The results acquired from the DSC measurements were reproducible with standard deviation typically less than ± 2.0%

The actual encapsulation rate (M_{F2}) was calculated as Eq. (1).

$$M_{F2} = \frac{\Delta H}{\Delta H_P} \times 100\% \quad (1)$$

where, ΔH is the enthalpy of microcapsules, ΔH_P is the enthalpy of paraffin.

The thermal conductivities of paraffin and the phase change microcapsules were measured by a Hot Disk Thermal Constant Analysers

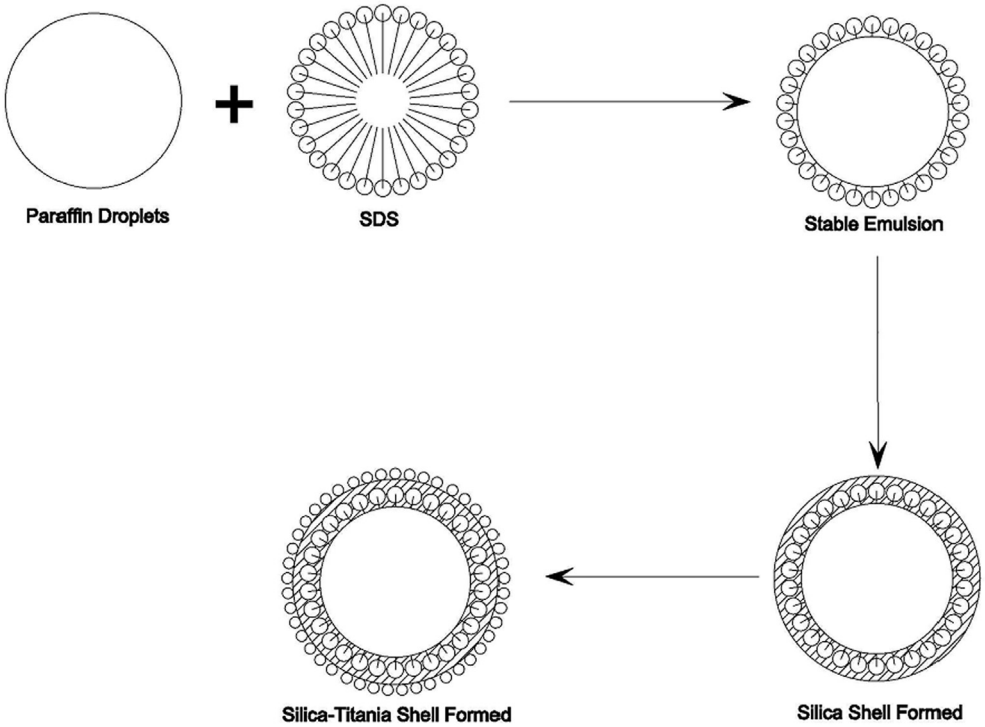

Fig. 1. schematic diagram of preparation of SiO_2-TiO_2/paraffin microcapsules.