Solar Energy Materials and Solar Cells 178 (2018) 273–279

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

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

Preparation and thermal properties of fatty acid/diatomite form-stable composite phase change material for thermal energy storage

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ARTICLE INFO

Keywords:
CA-LA eutectic
Diatomite
EG
PCM
Thermal conductivity

ABSTRACT

Phase change materials can be incorporated with building materials to make kinds of composite material, which can be applied in building systems due to their excellent thermal energy storage properties. In this study, a novel form-stable composite PCM CA-LA/Diatomite was prepared using vacuum impregnation method by combining a eutectic mixture of capric-lauric acid (CA-LA) as phase change material (PCM) and diatomite as supporting material. The composite products were characterized by using XRD, FT-IR and SEM analyzing methods. The thermal properties of the composite were measured by Differential Scanning Calorimetry (DSC). The results showed that the composite material melted at 23.61 °C with a latent heat of 87.33 J/g and solidified at 22.50 °C with the latent heat of 86.93 J/g. TGA investigation revealed that the composite had excellent thermal durability above their working temperature ranges. The thermal cycling test showed the composite has a good thermal reliability after 200 thermal cycles. What's more, the expanded graphite was added into the composite in order to increase the heat transfer performance. The results showed that the thermal conductivity of the composite increased gradually by 39.7%, 61.6%, 77.6% and 114.2% for the EG fractions of 3%, 5%, 7%, and 10%, respectively. As a result, the CA-LA/Diatomite/EG composite material of has a potential to be applied in modern buildings and solar energy systems due to its excellent thermal properties, good chemical and thermal reliability and high thermal conductivity.

1. Introduction

In recent years, energy storage and new energy development have attracted great focus due to the low energy utilization efficiency and the shortage of fossil energy [1,2]. Thermal energy storage received great attention and can be recognized as one of the most important energy storage forms. Among the thermal energy storage systems, latent heat thermal energy storage with a phase change material (PCM) have been aroused concern due to its properties of storing and releasing thermal energy during melting and solidification. The PCM with high storage density and small temperature change from storage to retrieval has been researched in many fields [3,4].

Researches focused on combining the PCMs into building materials to improve thermal comfort of light-weight buildings have been carried out for several decades [5,6]. The main processes in previous studies was direct immersion [7] or macro-capsules [8] to integrate the PCM into buildings materials. However, these methods will make the system expensive. The low thermal conductivity will limit the heat transfer rate of the whole system. Building materials impregnated with PCMs is a new technic which could overcome most of these issues and develop more effective energy storage products for building applications.

In recent years, kinds of PCMs such as paraffin [9,10], polyhydric alcohols [11,12], inorganic salt [13] and fatty acids [14] have been studied for impregnating them into building materials. Among the researched PCMs, fatty acids was regarded as the material with extensive application prospect because of it's good compatibility, lower cost, non-toxic, non-flammable and good thermal properties [15–17]. Previous studies [18,19] show that the fatty acids of capric acid (CA) and lauric acid (LA) show excellent properties for thermal energy storage, however, their phase change temperatures are very high, which limits their

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https://doi.org/10.1016/j.solmat.2018.01.032
Received 24 July 2017; Received in revised form 17 January 2018; Accepted 22 January 2018

application in buildings. Fortunately, their phase change temperature can be lowered by co-melting CA and LA to form the eutectic (CA-LA) according to the law of eutectic effect.

Diatomite is a natural porous material with excellent properties such as high absorptivity, multi-shape, high porosity, light-weight, high purity, rigidity, and inertness. The chemical composition and the physical structure of diatomite make it suitable for many scientific and industrial purposes. Thus, diatomite is a feasible candidates as an economical and light-weight building material for incorporating CA-LA as the PCM for thermal energy storage in buildings. What's more, in order to enhance the heat transfer rate of the composite PCM of diatomite and fatty acid, some materials with high thermal conductivity such as metal particles [20], carbon fibers [21], and expanded graphic [22] can be added to improve the heat transfer rate. The expanded graphite (EG) has been considered as the excellent thermal conductivity additive due to its advantageous properties: being inert to chemical reaction, uniformly dispersing into PCMs, being compatible with the PCMs having lower density than that of other high thermal conductivity materials such as metals and carbon fibers.

This study aimed to prepare a form-stable phase change material with a suitable phase change temperature, high phase change latent heat and good thermal conductivity, which can be used in the thermal energy storage systems for modern buildings. In this work, the CA-LA eutectic was prepared firstly. Then the CA-LA eutectic was absorbed into the diatomite to prepare the form-stable phase change materials (fs-PCMs) by vacuum impregnation method. The crystalloid phase, chemical structure and morphology of the fs-PCMs were determined by the X-ray diffractometer (XRD), Fourier transformation infrared spectroscope (FT-IR) and scanning electronic microscope (SEM). The thermal properties and thermal stability were measured by Differential Scanning Calorimetry (DSC) and thermogravimetric analysis (TGA). Besides, the EG was added to the fs-PCMs to enhance the thermal conductivity. The thermal conductivity of CA-LA/diatomite/EG was also investigated.

2. Experimental

2.1. Materials

Capric acid (CA, $C_{10}H_{20}O_2$, 97.5% pure,) and lauric acid (LA, $C_{12}H_{24}O_2$, 97.5% pure) purchased from Tianjin Guangfu Fine Chemical Research Institute, China, were selected as PCMs. The diatomite was supplied by Beijing Bioanalysis Technology Company, China. Table 1 shows the chemical compositions of diatomite. Expanded graphite (EG, average particle size: < 50 µm; density: 320 kg/m^3, thermal conductivity: 5.2 W m^{-1} K^{-1}) was purchased from Sinopharm Chemical Reagent Co., Ltd. It was used to increase the thermal conductivity of the composite PCM. The surface area of the EG was measured as 40 m^2/g by gas adsorption technique (BET).

2.2. Preparation of fs-PCMs

According to the previous researches [23,24], the theoretic ratio, phase change temperature and enthalpy of the CA-LA eutectic were firstly calculated via Eqs. (1) and (2).

$$T = \left(\frac{1}{T_A} - \frac{R\ln X_A}{H_A}\right)^{-1} \quad (1)$$

Table 1
Chemical constituents (wt%) of Diatomite.

Material	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	MgO	else
Diatomite	97.91	1.04	0.65	0.21	0.12	0.05	0.02

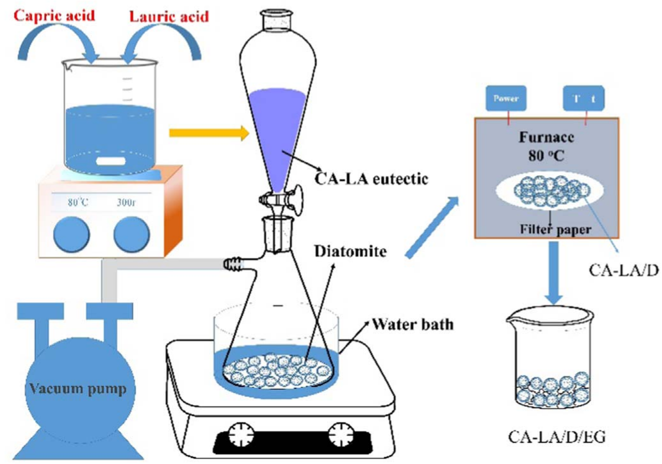

Fig. 1. The experimental process for preparation of fs-PCMs.

$$H = T \times \sum_i^n \frac{X_i H_i}{T_i} \quad (2)$$

where T and H is the phase change temperature and enthalpy of fatty acid eutectics; T_A, X_A and H_A are the phase change temperature, mass fraction and latent heat of the A acid; and R is the gas constant. X_i, H_i, and T_i are mole fraction, enthalpy and phase change temperature of pure PCM. Fig. 1 shows the experimental procedures to prepare CA-LA/diatomite samples. Firstly, the CA-LA eutectic were prepared using melting-blending method with the calculated mole ratio of CA: LA = 67.6:32.4 and the theoretical melting point and enthalpy of the eutectic were calculated as 26.2 °C and 138.5 J/g. The diatomite was put into a conical flask which was placed into the water bath at 80 °C and vacuumed to 0.01 MPa to evacuate air from the porous of diatomite. The evacuation process continued for 30 min. Then, the melted CA-LA eutectic was added into the conical flask through a separatory funnel with mass ratio of CA-LA: diatomite = 9:1. And the CA-LA was vacuumed impregnated into the porous of diatomite for 1 h. After that, the vacuum process was ended and air was allowed to enter the flask again to force the melted CA-LA to penetrate into the pore space of the diatomite. Lastly, the CA-LA/diatomite samples was put into the filter paper repeatedly to clear away the surface CA-LA eutectics. The finally samples were achieved utile no melted CA-LA leak traces been found in the filter paper and the quality change of the composite was under 1% after thermal filtering treatment. What's more, different fraction expanded graphite (EG) was added into the fs-PCMs to increase the thermal conductivity. The EG was mixed with diatomite and impregnated with the CA-LA eutectics.

2.3. Characterization of fs-PCMs

The chemical stability of the fs-PCMs were tested by Fourier transformation infrared spectroscope (FT-IR, Spectrum 100, Perkin-Elmer) and X-ray diffraction (XRD, XD-3, Cu Kα1 radiation, λ = 1.5406 Å, Purkinje General Instrument Co., Ltd.). The morphology and microstructure of the fs-PCMs were characterized by the scanning electron microscope (SEM, JSM-IT3000, Japan Electron Optics Laboratory Co., Ltd.). The different scanning calorimeter (DSC, 2014 polyma, NETZSCH) was used to analysis the thermal properties of fs-PCMs at 5 °C/min under a constant stream of nitrogen. The accuracy of temperature measurements was ± 0.2 °C and the enthalpy accuracy was ± 3%. The thermal stability of the fs-PCMs was determined by the thermal gravity analysis (TGA, STA 8000, Perkine-Elmer) from room temperature to 600 °C. The thermal conductivity of fs-PCMs was tested using the laser thermal conductivity method which needed tree parameters and calculated by the Eq. (3).