Solar Energy Materials & Solar Cells 114 (2013) 136–140

Contents lists available at SciVerse ScienceDirect

Solar Energy Materials & Solar Cells

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

Myristic acid/polyaniline composites as form stable phase change materials for thermal energy storage

Ju-Lan Zeng [a,*], Fu-Rong Zhu [a], Sai-Bo Yu [b], Zhong-Liang Xiao [a], Wen-Pei Yan [a], Shuang-Hao Zheng [a], Ling Zhang [a], Li-Xian Sun [a], Zhong Cao [a]

[a] Hunan Provincial Key Laboratory of Materials Protection for Electric Power and Transportation, School of Chemistry and Biological Engineering, Changsha University of Science and Technology, Changsha 410114, People's Republic of China
[b] China Tobacco Hunan Industrial Corporation, Changsha 410007, People's Republic of China

ARTICLE INFO

Article history:
Received 30 October 2012
Received in revised form
26 February 2013
Accepted 7 March 2013
Available online 9 April 2013

Keywords:
Form-stable phase change materials
Thermal energy storage
Myristic acid
Polyaniline

ABSTRACT

Form-stable phase change materials (PCMs) possess the advantages of direct use without additional encapsulation, making their practical applications more feasible comparing to solid–liquid PCMs. In this paper, a new kind of myristic acid (MA)/polyaniline (PANI) form-stable PCMs were readily prepared by means of surface polymerization method. MA and PANI were applied as thermal energy storage material and supporting material, respectively. Morphology and structure characterization revealed that in the form-stable PCMs, MA particles were wrapped by PANI particles, which in turn were polymerized from aniline. Thermal stability and thermal energy storage properties of the prepared form-stable PCMs were investigated by means of thermogravimetry (TG) and differential scanning calorimetry (DSC). The results indicated that the form-stable PCMs exhibited good thermal stability when their phase change temperature was concerned. The highest loading of MA in the form-stable PCM with good form stability could attain 82 wt%, corresponding to the phase change enthalpy of 150.63 J/g.

1. Introduction

Solar thermal energy application has attracted great interest due to the energy crisis, high oil prices, environmental concerns, as well as its low cost [1]. However, the fluctuation of solar radiation makes thermal energy storage system indispensable in the solar thermal energy application. Phase change materials (PCMs) are a kind of latent heat energy storage materials and can be applied to store thermal energy which is collected from solar radiation [2,3]. Solar thermal energy application systems embedded with PCMs show certain advantages over conventional systems where sensible heat storage materials are applied. The main advantage is the high storage density in small temperature intervals. Over the past few decades, extensive efforts have been made to develop PCMs and to apply PCMs for solar thermal energy application systems [2–6] where heat is stored during the period of sun shining and used when heat is needed.

Since PCMs play a key role in solar thermal energy applications, the developing of new PCMs with high performance is very important. PCMs that store or release thermal energy by changing their phase between solid and liquid states are called solid–liquid PCMs. Solid–liquid PCMs have certain shortages to hinder their application, such as the need of encapsulation and high volume change. Consequently, form-stable PCMs, which possess the advantages of high latent heat, shape-stable and direct use without additional encapsulation, etc. are attractive candidates as thermal energy storage materials [7]. Besides, the thermal conductivity of organic solid–liquid PCMs are normally low, so that thermal conductive fillers [8–10] are needed to enhance their thermal conductivity. However, based on the view point of chemical thermodynamics, the fillers will precipitate from the solid–liquid PCMs during their long term melting–crystallizing cycles, and hence the thermal conductive enhancement will be lost. If the fillers are fixed in form-stable PCMs, the precipitation of the fillers will be prevented by the supporting materials and thus the thermal conductivity will be maintained.

Kenisarin and Kenisarina [7] have summarized the state of the art in the developing of form-stable PCMs for thermal energy storage. Normally, a form-stable PCM is composed of a solid–liquid PCM and a supporting material. The solid–liquid PCM acts as thermal energy storage material while the supporting material maintains the solid shape of the form-stable PCM when the temperature is higher than the melting point of the solid–liquid PCM. The solid–liquid PCMs in form-stable PCMs are mainly organic compounds, such as paraffin [11], fatty acids [12], fatty alcohol [13,14], polyethylene glycol [15] and their mixtures [16]. The supporting materials include polymers and inorganic compounds. The solid–liquid PCMs are encapsulated in the

* Corresponding author. Tel./fax: +86 731 85258733.
E-mail address: julan_zeng@yahoo.com.cn (J.-L. Zeng).

0927-0248/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.solmat.2013.03.006

voids of the polymers by means of melt blending [17], electrospinning [18] or in situ polymerization [19], or are grafted to the chains of polymers [20–22], to obtain form-stable PCMs. Inorganic supporting materials are mainly porous materials such as vermiculite [23], halloysite nanotube [24], carbon materials [25,26] and expanded perlite [27], etc. The solid–liquid PCM are impregnated into the pores of the inorganic supporting materials to obtain form-stable PCMs.

Polyaniline (PANI) is a kind of conductive polymer without solid–liquid transition until it is pyrolysed. PANI possesses the merits of good environment stability, lower cost and easy production and can be prepared in a variety of morphology such as nano/micro-tubes [28,29] and porous structure [30]. Furthermore, PANI has been applied in smart windows for dynamic daylight and solar energy control in buildings [31]. As a result, it is worthwhile to investigate the possibility of applying PANI as supporting material to prepare form-stable PCMs. Fatty acids possess the merits of high phase change enthalpy and tunable phase change temperature. An additional advantage is that fatty acids are derived from the vegetable and animal oil that provides an assurance of continuous supply. In this work, myristic acid (MA) is selected as solid–liquid PCM and PANI is selected as supporting material. A new kind of MA/PANI form-stable PCMs are prepared and their properties are investigated. The results show that the as-prepared PCMs exhibit good form-stable property and the highest phase change enthalpy could attain 150.63 J/g, indicating that they can be applied in low temperature solar thermal energy applications.

2. Experimental

2.1. Materials

All reagents were of analytical grade and were obtained commercially. Aniline was distilled under reduced pressure prior to use. All other reagents were used as received without further purification. Deionized water was used throughout the experimental process.

2.2. Preparation of form-stable PCMs

A series of from-stable PCMs were prepared as follows. In general, 0.5 g of sodium dodecylsulfonate (SDS) and certain amount of MA were mixed with 100 mL water. The mixture was vigorously stirred for 1 h at 60 °C to form a stable emulsion. To this emulsion, certain amount of aniline was added and the mixture was stirred for another 0.5 h. The mixture was cooled to 0–5 °C by ice-water bath and then was maintained at this temperature while the stirring was continued. 10 mL of water containing ammonium persulfate (APS) was dropped into the mixture under vigorous stirring to initiate the polymerization. The molar ratio of aniline and APS was fixed to be 1:1. The mixture was stirred for another 12 h at 0–5 °C and then was warmed to room temperature naturally. Afterwards, the mixture was filtrated and washed with water till the filtrate became clear. The form-stable PCMs were collected and dried under vacuum at 50 °C for 48 h. Pure PANI was synthesized in the same way except that no MA was added. The doses of MA and aniline in each sample are listed in Table 1 and the form-stable PCMs are designated as S1, S2, S3, S4, S5 and S6.

2.3. Characterization

The surface morphology of the form-stable PCMs was investigated using a scanning electron microscope (SEM, JEOL JSM-6700F). Before the SEM investigation, the samples were sputtered with platinum. IR spectra were recorded on a FT-IR spectrometer (Avatar-360, Nicolet) using KBr pellet (400–4000 cm^{-1}). Powder X-ray diffraction (XRD) experiments were carried out on a Rigaku D/max2200 X-ray diffractometer with a monochromatic detector. Copper Kα radiation was used, with a power setting of 30 kV and 30 mA, and a scan rate of 5 deg/min. The thermal stability of the form-stable PCMs, MA and PANI was studied by means of thermogravimetry (TG) on a thermogravimetry analyzer (NETZ SCH STA 409 PG/PC) from room temperature to 800 °C with the heating rate of 10 °C/min and N_2 as carrier gas. The analyzer was calibrated using $CaC_2O_4 \cdot H_2O$ (99.9%) prior to the analyses. The thermal energy storage properties of MA and the form-stable PCMs were characterized by differential scanning calorimetry (DSC) (TA Instruments Q2000) from 10 to 100 °C with the heating rate of 10 °C/min in nitrogen atmosphere. Prior to the DSC expe riments, the instrument was calibrated using indium (99.999%) as standard material.

3. Results and discussion

3.1. Preparation and form-stable characteristics of the form-stable PCMs

PANI has been applied as supporting material to prepare form-stable PCM using tetradecanol as solid–liquid PCM [13]. However, the reaction mixture is very difficult to filter. In the present work, the solid in the reaction solution would precipitate quickly after the stirring was stopped and could be filtered easily, indicating that PANI is more suitable to prepare form-stable PCMs with fatty acids. In order to check whether the prepared samples are form-stable or not, the filter cakes of the samples were erected on filter papers in petri dishes. The dishes were then heated at 65 °C for 24 h in an oven and the shape of the filter cakes was observed. The result showed that the filter cake of S1 was slightly deformed and all other filter cakes have maintained their shape. After the filter cakes were cooled to room temperature, the filter papers were examined carefully. Only the filter paper under S1 absorbed appreciable white solid (MA). As a result, the prepared samples except S1 can be viewed as form-stable PCMs.

3.2. Morphology characterization of the form-stable PCMs

The SEM images of the form-stable PCMs with different MA loading are shown in Fig. 1. The figure shows that a layer of small PANI particles was deposited on the surface of MA particles. There are some pores, which comes from the aggregation of small PANI particles, existed in the PANI layer. When the loading of MA in raw materials is 50%, the PANI particles are connected with each other to form a compact shell that wraps the MA particles (Fig. 1a). The shell can prevent the melted MA from flowing when the temperature exceeds the melting point of MA and thus results in form-stable PCM. As the MA loading is increased to 70%, some MA particles which are not fully wrapped by PANI particles can be found (Fig. 1b). However, since PANI is lipophilic, the surface of the PANI particles and the pores in the PANI layer possess the ability to absorb the melted MA when the temperature exceeds the melting point of MA. Besides, the PANI particles construct a network that could prevent the composite PCM from collapsing even when MA melted. Hence, the composite PCM still exhibits the property of form-stability. Actually, in our experiments, the composite PCM was not collapsed even when the MA loading is 90%.

3.3. IR analysis

The IR spectra of PANI, MA and selected form-stable PCMs are shown in Fig. 2. The spectrum of PANI shows the typical characteristics of doped PANI. The bands at 1565 cm^{-1} and 1485 cm^{-1} are related to the C–C stretching vibration of quinonoid and benzenoid rings, respectively. The peak at 1294 cm^{-1} is ascribed to the C–N stretching vibration of the secondary aromatic amine. The vibration