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Study on preparation and thermal energy storage properties of binary paraffin blends/opal shape-stabilized phase change materials

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ABSTRACT

The binary paraffin blends/opal composites as shape-stabilized phase changed materials were prepared by adsorbing binary paraffin blends into the natural porous opal. In this study, binary forms of three commercial paraffins (n-octadecane, paraffin wax and liquid paraffin) with different melting temperatures were compound together by the fusion method, and the optimum mixed proportions were determined through differential scanning calorimetry (DSC) analysis. Raw opal was thermally treated in order to improve the adsorption capacity of opal before using as the supporting material. The microstructure and chemical structure of the binary paraffin blends/opal composites were characterized by scanning electronic microscope (SEM) and Fourier transformation infrared (FT-IR) spectroscope. From the FT-IR analysis, there was no chemical interaction between binary paraffin blends and opal. The SEM results showed that the pore size of calcined opal among particles was improved after calcination, and the paraffin blends were well adsorbed and dispersed into the porous structure of the opal because of the capillary effect and physical surface tension forces. There was no leakage of the liquid paraffin from the composites even in the melting state. The thermal properties and thermal stability were investigated by DSC and a thermal cycling test, respectively. The DSC results showed that the phase-transition temperature and the latent heat of the PN2/calcined opal composite PCM were 24.91 °C and 59.04 ± 0.84 J/g, respectively, which was suitable to be used as the indoor thermal energy storage building material. The thermal cycling test results indicated that the prepared sample was thermally reliable and chemically stable.

1. Introduction

The requirement for the indoor comfort-ability of living environment is becoming higher and higher along with the improvement of the living standards. As a result, the energy consumption for air conditioning, heating and illumination in commercial buildings and housing apartments increased significantly [1,2]. The excessive energy consumption caused a series of crises, such as shortage of fossil fuels, environmental pollution and continuous growth of carbon dioxide emission [3]. Thermal energy storage (TES) including latent heat storage and sensible heat storage has turned out to be a perspective and low cost technique for increasing the energy conservation efficiency and enhancement of the comfort level in buildings [4]. In the past few years, phase change materials (PCMs) have attracted more and more attention in the field of energy conservation [5,6].

PCMs can be classified into organic and inorganic materials according to their component. Organic PCMs have received considerable attention due to their high latent heat density, appropriate phase-transition temperature and stable physical and chemical properties [7]. Paraffin is a typical organic PCMs which consists of saturated hydrocarbons (straight-chain n-alkanes (CH_3–$(CH_2)_n$–CH_3)). As compared with the other PCMs, paraffin has a relatively high thermal density and good thermal properties. Moreover, paraffin is chemically inert and stable, reliable, non-corrosive, odorless, inexpensive and nontoxic [8–10]. The melting point and latent heat have a relationship with the chain length in paraffin. Single type of paraffin is limited in applications for its fixed phase change temperature. As a result, paraffin waxes with different melting points can be blended together according to certain proportions in order to obtain suitable phase-transition temperature [11,12].

The pure organic PCMs have some drawbacks in application practices, such as low conductivities and liquid leakage during the

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phase change process [13]. In order to solve these problems, the shape-stabilized PCMs have been developed recently which are prepared by integrating organic PCMs into some appropriate supporting materials. Porous inorganic minerals have been recommended as desirable supporting materials because of their high adsorption capacity, low weight, low cost, non-toxicity and inertness [14]. There have been many researches on the preparation and investigation of the form-stable PCMs based on the porous minerals, such as porous carbon [15–17], graphite [17–23], halloysite [24], diatomite [25–27], perlite [26], bentonite [28–31], attapulagite [32] and gypsum [33–35]. The available research results indicate that the form-stable composite PCMs based on porous minerals have a good application prospect in the thermal storage field. The opal is a sort of amorphous siliceous mineral with special porous structure and adsorption capacity. It is widely used in industry as a catalyst carrier, filler adsorbent, filter agent and wastewater purifier. Moreover, opal can be a type of low weight building materials as a desirable carrier of PCMs for energy storage in buildings.

In this study, binary paraffin blends/opal composite PCMs were prepared using the fusion adsorption method. The raw opal was firstly calcined at different calcination conditions in order to improve the adsorption capacity. Then, the adsorption capacity of the raw and calcined opal was studied. Three paraffins with different melting points and latent heat were chosen as the PCMs. Before integration of paraffin into the porous opal, different paraffins were compounded together in order to adjust phase-transition temperature. Finally, the paraffin blends were adsorbed into the pores of opal, and the microstructure, chemical and thermal property of the obtained composite materials were characterized by SEM, FTIR and DSC. Moreover, the thermal reliability of paraffin/opal composite PCMs was evaluated by a couple of thermal cycling tests.

2. Experimental

2.1. Materials

The opal sample used as the supporting material was kindly supplied by Jinzhou Shenhong Company (Liaoning, China). The main chemical constituents of the opal are given in Table 1, which was determined by an X-ray fluorescence spectrometer instrument (Spectra X-lab 2000). N-octadecane and the other two kinds of commercial paraffin used as thermal storage materials were all chemically pure without any further purification. N-octadecane was supplied by Sinopharm Chemical Reagent Co., Ltd. (Guangdong, China). Liquid paraffin and paraffin waxes were purchased from Xilong Chemical Co., Ltd. (Guangdong, China) and Huayong Paraffin Co., Ltd. (Shanghai, China), respectively.

2.2. Preparation of the n-octadecane/paraffin/opal composites

The opal was thermally treated in order to improve the adsorption capacity of the raw opal. Then, the calcined opal samples with different specific surface areas and pore properties were obtained. The liquid paraffin/paraffin wax, liquid paraffin/n-octadecane blends and n-octadecane/paraffin wax blends with different mass ratios were mixed evenly in a 50 ml beaker in order to obtain the proper phase changed materials. The compositions of the three paraffin blends are listed in Table 2. The obtained blends was heated at 65 °C until they melted completely and stirred at 200 rpm for 30 min by a constant temperature magnetic stirring apparatus. Then thermal properties of paraffin blends were investigated by a differential scanning calorimeter (DSC).

Table 1
Chemical compositions of the untreated opal.

Constituent	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	Other
Ratio (%)	88.46	6.18	1.29	0.25	0.37	0.34	0.73	0.16	3.88

After confirming the optimum ratio of paraffin blends, the form-stable composite PCMs were prepared by using a simple and practicable fusion adsorption method as described previously [36,37]. The form-stable composites were prepared by directly mixing evenly the three obtained paraffin blends in melted state at 65 °C with different mass proportions of opal in a 100 ml beaker. The phase changed composite materials were adsorbed by the porous structure of opal during the impregnation process. The maximum absorption ratio of phase changed composite materials in the composite PCMs was determined by leakage tests which have been described previously [37–39]. The more the paraffin blend loaded on opal, the darker the exterior color of prepared composite PCM. The leaking test was carried out by increasing the paraffin blends by 1 wt% from 20 wt%. When the loading amount was too much, there were agglomerations or an excess of paraffin blends adhering to the beaker wall, which means leakage of paraffin occurs during the melting process. Afterwards, the samples were put in a water bath at a constant temperature of 80 °C and stirred using a magnetic stirring apparatus at 300 rpm for 20 min. At last, the prepared samples were dried at room temperature.

2.3. Characterization of the n-octadecane/paraffin/opal composites

Specific surface area analyses based upon N_2 adsorption/desorption were carried out with a Micromeritics Tristar 3000 automated gas adsorption. The samples were pre-heated at 105 °C under the flow of N_2 on a Micrometrics Flowprep 060 degasser before the measurement. The morphology was observed by a scanning electron microscopy (SEM, S-3500N, FEI Company). Fourier-transform infrared spectroscopy (FT-IR) was undertaken by a Thermofisher Nicolet 6700 spectrometer. The samples were prepared at potassium bromide (KBr) pellets. The infrared spectra of prepared samples between 400 and 4000 cm^{-1} were recorded. The latent heat and the melting temperature were measured by a differential scanning calorimeter (DSC, series Q2000, TA®). Approximately 2–4 mg of sample was heated in a nitrogen atmosphere at a rate of 10.0 °C/min from 0 °C to 100 °C. The DSC analyses in this paper were performed according to previous literatures [40–42]. Every presented DSC data in this paper was calculated according to the results of at least four individual analyses.

3. Results and discussion

3.1. Determination of the optimum proportion of binary paraffin blends

The admirable phase-transition temperature of PCMs for heating and cooling indoor application in buildings should be close to

Table 2
Sample identification and composition.

Sample ID	Composition (wt%)
PP1	Paraffin wax (85)+liquid paraffin (15)
PP2	Paraffin wax (70)+liquid paraffin (30)
PP3	Paraffin wax (45)+liquid paraffin (55)
PP4	Paraffin wax (25)+liquid paraffin (75)
PN1	Liquid paraffin (10)+n-octadecane (90)
PN2	Liquid paraffin (15)+n-octadecane (85)
PN3	Liquid paraffin (20)+n-octadecane (80)
PN4	Liquid paraffin (25)+n-octadecane (75)
NP1	N-octadecane (10)+paraffin wax (90)
NP2	N-octadecane (20)+paraffin wax (80)
NP3	N-octadecane (30)+paraffin wax (70)
NP4	N-octadecane (40)+paraffin wax (60)