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Experimental study on a novel form-stable phase change materials based on diatomite for solar energy storage

Zhonghao Rao[a,*], Guangtong Zhang[a], Taotao Xu[a], Kun Hong[b]

[a] School of Electrical and Power Engineering, China University of Mining and Technology, Xuzhou 221116, PR China
[b] Jiangsu Provincial Engineering Laboratory for Advanced Materials of Salt Chemical Industry, Huaiyin Institute of Technology, Huainan 223003, PR China

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ABSTRACT

PCM has been investigated for solar energy storage in recent years. The magnesium nitrate hexahydrate was chosen as PCM due to the suitable melting temperature and high latent heat for solar thermal energy in this paper. In order to prevent the leakage during the phase transition, a novel form-stable composite PCM based on diatomite was prepared by the vacuum impregnation method. The micromorphology, chemical structure, crystalloid phase, thermal properties, supercooling degree, thermal conductivity and thermal reliability were investigated by SEM, XRD, FT-IR, DSC, self-designed device and hot-wire method. FT-IR spectra indicated that there was no chemical reaction during the preparation process. The supercooling tested by the self-designed device was just 0.3 °C which can be neglected. The melting and freezing temperature measured by DSC and step-cooling curve method were 88.89 °C and 83.5 °C, respectively. Furthermore, the latent heat was 69.39 J/g and the adsorptive capacity was 46.78% according the pure PCM used in this study. The thermal reliability test was performed and the results showed that the thermal properties basically unchanged after 2000 thermal cycles.

1. Introduction

Solar thermal energy storage has played an important part in energy conservation and efficient utilization with the increasing consumption of fossil fuels. Latent thermal energy storage (LTES) using phase change materials (PCM) had many advantages in comparison with sensible thermal energy storage due to its higher energy storage density and nearly constant temperature during phase transition [1,2]. The LTES has been considered as one of the most promising ways for solar thermal energy storage which was the incentive factor for this article. Depending on the type of PCM, it can be divided into organic and inorganic materials. Moreover, the inorganic PCM could be salt hydrates, molten salts and some metals. It was not difficult to find that salt hydrates with lower melting temperature below 60 °C such as sodium sulfate decahydrate (SSD) [3,4], calcium chloride hexahydrate (CCH) [5] and sodium acetate trihydrate (SAT) [6,7] were widely investigated. Magnesium nitrate hexahydrate (MNH) melted in temperature interval of 89–95 with the heat of fusion varying from 150.2 J/g to 166.9 J/g [8]. In addition, there was no phase separation in the phase change process and MNH showed good thermal reliability in the repeated melting and solidification tests [9]. Also, Nagano et al. discovered that MNH could be used as the basis for the development of a new heat storage composition and later, they developed a different heat storage materials on the basis of MNH [10]. Therefore, MNH was a promising PCM used in solar heat storage applications [1,11].

However, leakage was existed during the solid-liquid change process for salt hydrates. Therefore, the form-stable PCM [12,13] and encapsulated PCM [14] were proposed. The form-stable PCM composed of phase change substances and supporting materials was studied to prevent the liquid PCM leakage. In previous literature, many form-stable composite PCMs have been reported by incorporating PCMs into porous materials in a variety of ways. Organic PCMs were impregnated into expanded graphite (EG) [15,16], carbon fiber (CF) [17,18], silicon dioxide [19,20] and clay minerals [21,22]. Inorganic form-stable composite PCMs using salt hydrates and molten salts as the phase change substances and EG [23,24], silica matrix [25,26], sepiolite [27], expanded graphite oxide [28], calcium silicate [29], poly(acrylamide-*co*-acrylic acid) copolymer hydrogels [30] as supporting materials were prepared. Diatomite, a type of natural non-metallic mineral materials, was selected as the supporting material resulting from a variety of unique properties including highly porous structure, thermostability, excellent absorption capacity, chemical inertness, low density and relatively low price [31,32]. For example, Qian et al. [33] prepared form-stable composite PCM by blending diatomite with polyethylene glycol (PEG), lithium nitrate ($LiNO_3$) and sodium sulfate (Na_2SO_4), respectively, via a vacuum impregnation method or a facile mixing and

* Corresponding author.
E-mail address: raozhonghao@cumt.edu.cn (Z. Rao).

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sintering method. The results showed the maximum loads of PEG, $LiNO_3$ and Na_2SO_4 could respectively reach 58%, 60% and 65%. In addition, the composite PCM composed of phase change substance and diatomite as supporting materials were prepared in references via different methods which indicated that diatomite was a better supporting material for PCM [21,34–42].

In previous references, there were very few published available papers on the use of diatomite as supporting matrix to shape stable hydrated salts PCM. In this study, a new kind of form-stable composite PCM was prepared by the vacuum impregnation method using MNH as PCM and diatomite as the supporting material. Additionally, the properties of diatomite have been characterized and the leakage tests examining the performance of the composite PCM also have been conducted out. Moreover, the thermophysical properties have been performed in order to achieve for preliminary work for solar thermal energy storage.

2. Experimental procedure

2.1. Material

The materials used in this research were the analytical grade. Diatomite was used as the raw material purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and magnesium nitrate hexadrate was taken from Weng Jiang Reagent Co., Ltd. (Guangdong, China). Prior to the experiments, raw diatomite samples were sieved by 200 mesh sieves. Then samples were dried at 105 °C for 24 h to remove existing water. Meanwhile, magnesium nitrate hexadrate samples were dried at 40 °C for 10 h before being used.

2.2. Preparation of form-stable PCM

In this study, the form-stable composite PCM were prepared by vacuum impregnation method using diatomite as supported material and MNH as PCM. A series of composites with different mass ratio of MNH was prepared. The compositions of the samples were listed in Table 1. MNH and demonized water were mixed in a beaker at 95 °C with stirring. The corresponding diatomite samples were added into the beaker when MNH completely melted while kept stirring. Subsequently, the composites were put on vacuum condition (-0.06 MPa) in the vacuum drying oven at 95 °C until no extra water was existed. Finally, the composites were obtained after being dried at 40 °C until the mass did not change.

2.3. Characterization

The morphology analysis and chemical constituent of the diatomite samples and form-stable composite PCM were performed by scanning electron microscopy (SEM, ZEISS EVO 18, Germany) and X-ray fluorescence spectrometer (XRF, PANalytical B.V., Netherlands) analysis. The particle size distribution was examined by using a particle size analyzer (Mastersizer 2000, Malvern Instrument Ltd., UK). Pore size distribution, pore volume and specific surface area base upon N_2 adsorption-desorption were carried out (Autosorb iQ Station 2, Quantachrome Instruments, USA). The crystalloid phase and chemical structure of samples were characterized by utilizing the Fourier transformation infrared spectroscope (FT-IR, Nicolet iS5, USA) and the technique X-ray diffractometer (XRD, Bruker D8 Advance, Germany). Differential scanning calorimetry (DSC, TA Instrument Inc., USA, accuracy: ±0.01 °C for melting and freezing temperature, ±0.1% for latent heat) was used to perform the thermal properties of samples including melting temperature and latent heat of prepared materials. These experiments were carried out in the temperature range of 50–120 °C with heating and cooling rate of 2 °C/min. The samples were placed into the closed aluminum pans and measured in the atmosphere of dry nitrogen with the flow rate 50 ml/min.

Table 1
Samples identification and composition.

Sample ID	Composition (wt%)
MNHD-1	magnesium nitrate hexahydrate (10) + diatomite (90)
MNHD-2	magnesium nitrate hexahydrate (20) + diatomite (80)
MNHD-3	magnesium nitrate hexahydrate (30) + diatomite (70)
MNHD-4	magnesium nitrate hexahydrate (40) + diatomite (60)
MNHD-5	magnesium nitrate hexahydrate (50) + diatomite (50)
MNHD-6	magnesium nitrate hexahydrate (60) + diatomite (40)
MNHD-7	magnesium nitrate hexahydrate (70) + diatomite (30)
MNH	magnesium nitrate hexahydrate (100) + diatomite (0)

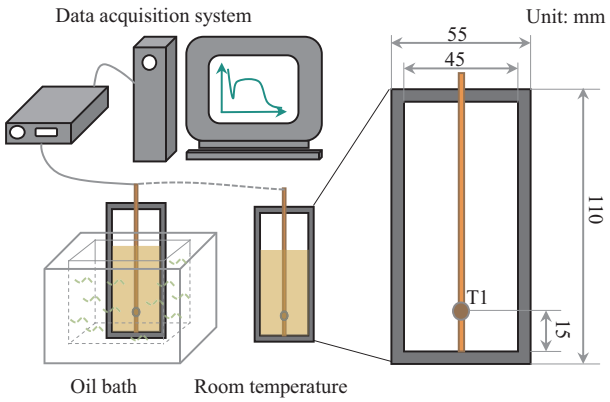

Fig. 1. Self-designed experimental device for supercooling test.

Supercooling of MNH and the form-stable composite PCM were tested using the self-designed experimental apparatus shown in Fig. 1. According to the corrosion test in reference [43] aluminum was chosen as the material of the test container with a cylindrical shape including a round lid. The outer and inner diameter were 55 mm and 45 mm, respectively. K-type thermocouples (T1) and the data acquisition system were used to record the temperature automatically per second. The distance between T1 and the bottom was 15 mm. In the supercooling experiments, the test container with MNH or composite PCM were heated in oil bath firstly until the value of T1 was 120 °C. Then, the test container would be put at the room temperature (about 24 °C) condition. Therefore, the step-cooling curves could be obtained and analyzed.

The thermal conductivity of the composite PCM was measured by a Thermal Conductivity Meter (TC3000E, Xiatech Electronic Technology Co., Ltd., accuracy: ±3%) using the hot-wire method. In order to keep them in thermal equilibrium, a high-temperature heating module was used. Before being measured, 5 g composites powder weighed by a balance (ME55, Mettler Toledo Instrument Co., Ltd., Shanghai, China) was pressed to be a tablet with the diameter of 30 mm at 10 MPa for 3 min. Furthermore, from the viewpoint of long-term using, the thermal reliability tests were performed.

3. Results and discussions

3.1. Micromorphology of MNHD-5

Fig. 2 demonstrated the micromorphology of section microstructures for the pure diatomite used in this study and sample MNHD-5. In Fig. 2(a) and (b), it can become quite clear that diatomite had highly porous network structure in disc-like shapes, as expected, indicating the high porosity and large specific area. However, there were some impurities and fragments showed in Fig. 2(a). In this study, the raw diatomite without further treatment was used only for convenience. As indicated in Fig. 2(c) and (d), MNH was completely