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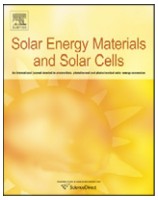

Preparation of capric acid/halloysite nanotube composite as form-stable phase change material for thermal energy storage

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ABSTRACT

A novel form-stable composite as phase change material (PCM) for thermal energy storage was prepared by absorbing capric acid (CA) into halloysite nanotube (HNT). The composite PCM was characterized by TEM, FT-IR and DSC analysis techniques. The composite can contain capric acid as high as 60 wt% and maintain its original shape perfectly without any CA leakage after subjected to 50 melt-freeze cycles. The melting temperature and latent heat of composite (CA/HNT: 60/40 wt%) were determined as 29.34 °C and 75.52 J/g by DSC. Graphite (G) was added into the composite to improve thermal storage performance and the thermal storage and release rates were increased by 1.8 times and 1.7 times compared with the composite without graphite, respectively. Due to its high adsorption capacity of CA, high heat storage capacity, good thermal stability, low cost and simple preparation method, the composite can be considered as cost-effective latent heat storage material for practical applications such as solar energy storage, building energy conservation and agricultural greenhouse in the near future.

1. Introduction

Latent heat thermal energy storage (LHTES) using PCM has attracted interest in solar storage and utilization due to its ability to provide a high storage density at nearly isothermal conditions [1,2]. So far, many PCMs such as salt hydrates, paraffins, fatty acids and their mixtures have been widely investigated for LHTES [3–6]. Among them, capric acid is taken as a promising PCM because of its proper melting temperature range, high latent heat capacity, good chemical and thermal stability, little or no supercooling during the phase transition, nontoxicity and noncorrosivity against metal containers [7]. However, it is clear that the melted capric acid has to be kept in a closed tank or container to prevent leaching during the phase transition [8,9]. Therefore, special latent storage device or elements such as a heat exchanger or lots of containers to encapsulate the PCM are needed, which increase the cost. Moreover, the low thermal conductivity of CA leads to low heat transfer rate during the heat discharging process, which also limits its utility areas. This problem can be solved by dispersing graphite due to its excellent thermal conductivities in the range of 10–70 W/mK [10,11].

Recently, a new type PCM called form-stable composite PCM based on high density polyethylene was developed for their attractive advantages such as direct use without an outer container and easy preparation with desirable dimensions [12–14]. However, its application was hampered by high cost of encapsulation. There were very few literatures that aimed to use clays as absorbents to prepare form-stable composite PCMs for thermal energy storage [15–17]. Compared with high density polyethylene, clays are readily obtainable and much cheaper. Moreover, several advantages like high adsorption capacity, high heat storage capacity, good thermal stability and direct usability without extra encapsulation render the composite potential heat storage material for practical application.

HNT is a two-layered aluminosilicate clay mineral, which is available in abundance in China as well as other locations around the world. It is chemically similar to kaolin, differing mainly in the morphology of crystals [18]. HNTs possess hollow nanotubular structure and large specific surface area. Their novel physical and chemical properties have provided opportunity as low-cost adsorbents and have been reported in literatures [19–22]. However, there is not any literature that aims to use halloysite as adsorbent to prepare form-stable composite PCM.

In this study, a new form-stable PCM was prepared by absorbing CA into the pores of halloysite nanotubes by the capillary and surface tension forces. In order to improve the thermal conductivity of the form-stable composite, we also introduced high thermal conductivity of graphite into the composite. The results indicated that the composite had a high adsorption capacity of CA, high heat storage capacity and good thermal stability.

2. Experimental

2.1. Materials

Capric acid was used as a latent heat storage material. It was supplied by Chemical Reagent Co., Ltd. (Tianjin, China). Halloysite

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clay from Henan Province (China) was milled and sieved followed by oven dried at 373 K for 24 h. Graphite was supplied from the Grenada Development Carbon Materials Co., Ltd. (Nanjing, China).

2.2. *Preparation of the form-stable composite PCM*

The HNT and CA were mixed in ethanol solution. The mixture was irradiated ultrasonically for 90 min, and then stirred and refluxed under 60 °C for 2 h in a water bath. After the recovery of ethanol by simple distillation, the mixture was dried at 70 °C. In order to find the maximum adsorption capacity of CA, the CA/HNT composite were prepared using different weight ratios of 50:50, 55:45, 60:40 and 65:35, respectively. In order to increase thermal conductivity of the form-stable composite PCM, graphite (5 wt%) was added in the mixture at the beginning. The following preparation was consistent with the same method mentioned above. Thermal conductivities of the form-stable CA/HNT and CA/HNT/G composite PCMs were measured by a thermal property analyzer (TC 3010, Xiatech Electronic Technology Co., Ltd.).

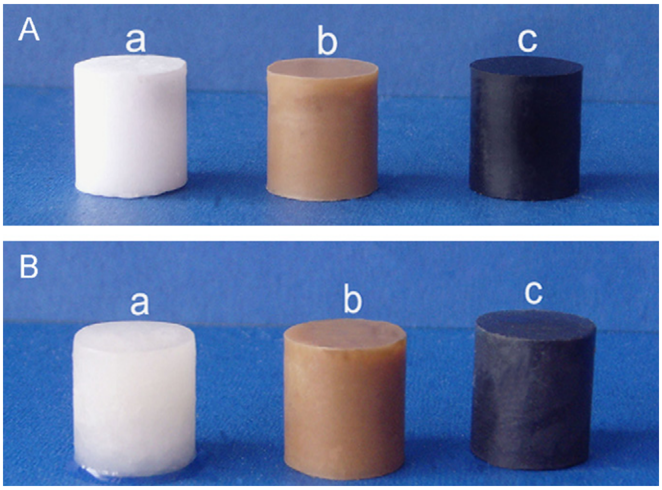

Fig. 1. Images of the pure CA (a), CA/HNT (b) and CA/HNT/G (c) samples at room temperature (A) and after heated at 40 °C (B).

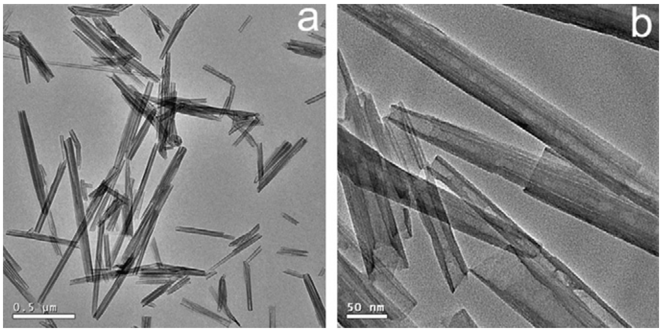

Fig. 2. The TEM images: (a) HNT and (b) form-stable CA/HNT composite PCM.

2.3. *Characterizations of HNTs and the CA/HNTs composite PCM*

The Brunauer–Emmet–Teller (BET) surface area and pore-size distribution of the HNT and the composite were measured by a specific surface area analyzer (Quantachrome NOVA4200e). The microstructures of the HNT and the composite PCM were observed using a transmission electron microscope (TEM, FEITEC-NAIG2). The form-stable composite PCM was characterized using the FT-IR spectroscopy (NEXUS FT-IR). The phase change temperature and latent heat of the composite PCM were measured using a differential scanning calorimeter (STA449C, NETZSCH) at a heating rate of 2 °C/min in a purified nitrogen atmosphere. In order to verify the form-stable performance of the prepared composite PCMs, thin slices (12 mm diameter, 11 mm thickness) were prepared by compressing the CA, CA/HNT (60/40 wt%) and CA/HNT/G (60/35/5 wt%) composite powder in a tablet machine, respectively.

2.4. *Test of thermal storage and release rates*

Thermal performance test was conducted using the constant temperature water bath method [16,23]. Two glass test tubes with the same shell thickness and diameter were used: one containing the form-stable CA/HNT composite as reference and the other containing the CA/HNT composite with 5 wt% graphite (CA/HNT/G). Two thermocouples were placed in the centers of the test tubes, respectively. The test tubes were put into a water bath at a constant temperature of 10 °C. After the temperature reached balance, the two tubes were rapidly placed into another water bath at a constant temperature of 40 °C, where the composite PCM performed process of heat storage. After the heat storage was finished, the composite were immediately subjected to solidification process at a constant temperature of 10 °C, where the composite PCM performed process of heat extraction. The temperature variations of the composite were automatically recorded by a PC via data logger (Agilent 34970A) with a temperature measuring accuracy of ±1.5 °C at time intervals of ten seconds.

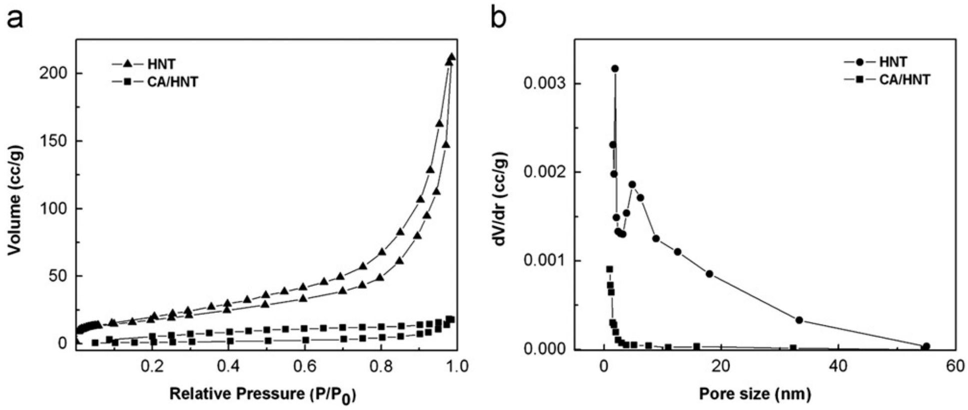

Fig. 3. Isothermal adsorption–desorption curves (a) and pore distribution curves (b) of HNT and CA/HNT composite PCM.