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Preparation and characterization of capric-myristic-stearic acid eutectic mixture/modified expanded vermiculite composite as a form-stable phase change material

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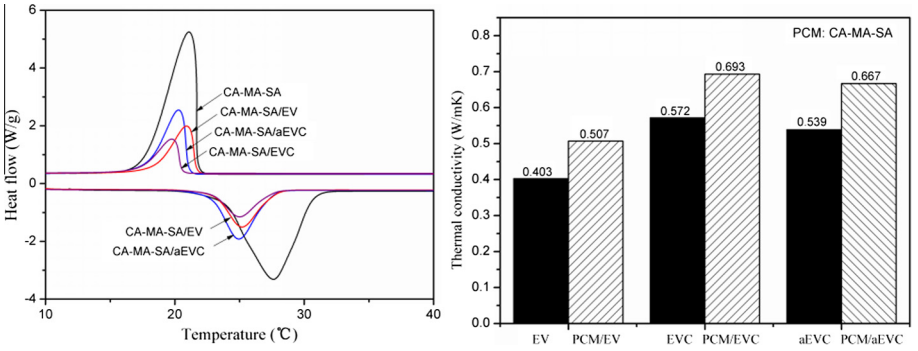
HIGHLIGHTS

- The expanded vermiculite/carbon (EVC) was obtained by in-situ carbonizing CTAB.
- The acid treated EVC (aEVC) was an optimum CA-MA-SA supporting matrix.
- The melting latent heat of the CA-MA-SA/aEVC was 86.4 J/g at 22.92 °C.
- The thermal conductivity of CA-MA-SA/aEVC was 0.667 W/mK.
- The CA-MA-SA/aEVC composite PCM has good thermal and chemical stabilities.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel capric-myristic-stearic acid (CA-MA-SA)/modified expanded vermiculite composite phase change material (PCM) with simultaneously enhanced thermal conductivity and latent heat was prepared in this study. The expanded vermiculite/carbon composite (EVC), obtained by in-situ carbonizing cetyl trimethyl ammonium bromide in the layer of expanded vermiculite, was treated with nitric acid (aEVC) to be used as the CA-MA-SA supporting matrix. The results showed that the thermal conductivity of CA-MA-SA/aEVC was greatly enhanced by introducing carbon and the CA-MA-SA adsorption capacity was improved by the acid-treatment of EVC. The thermal conductivity of CA-MA-SA/aEVC was 0.667 W/mK, which was 31.6% higher than that of CA-MA-SA/expanded vermiculite (EV). The latent heats of the CA-MA-SA/aEVC were 86.4 J/g at the melting temperature of 22.92 °C and 80.43 J/g at the freezing temperature of 21.03 °C, which were also greatly higher than those of CA-MA-SA/EV. The results of the thermo-gravimetric analysis (TGA), thermal cycling test and Fourier transform infrared spectroscopy (FT-IR) indicated that the CA-MA-SA/aEVC composite PCM was thermally stable and chemically inert. Thus, the prepared CA-MA-SA/aEVC composite PCM is a promising material for the building energy efficiency applications.

1. Introduction

Buildings not only consume enormous amount of energy, but also cause huge amount of greenhouse gas around the world. Therefore, energy efficient buildings are recently one of the most important issues since both economic and environmental factors

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nowadays are of great importance in the world [1,2]. Phase change materials (PCMs) for latent heat thermal energy storage (LHTES) have been extensively investigated in building energy conservation applications due to high energy storage density and latent heat property, small temperature variation form storage to retrieval, and repeatable utilization property [3–6].

Fatty acids are organic PCM with typical solid-to-liquid phase change characteristics. They have been recommended as LHTES due to their high latent heat capacity, good chemical and thermal stability, little or no supercooling during phase transition, environment friendly [7,8]. In practice, fatty acids are impregnated into porous building materials to prepare form-stable composites. Considering the strong capillary force generated on a pore with small diameter [9], a variety of natural porous materials with smaller pores such as expanded perlite [10,11], attapulgite [12] and halloysite [13], are frequently used to avoid the leakage of fatty acids during melting process. Additionally, the low thermal conductivity of fatty acids poses a challenge for their applications. In order to solve this problem, the additives with high thermal conductivity, including expanded graphite [14,15], carbon nanotubes [16,17] and silica fume [18], have been introduced to enhance the thermal conductivity of form-stable composites.

Vermiculite is a layered silicate mineral with 2:1 crystalline structure. Layers consist of octahedrally coordinated cations (typically Mg, Fe and Ti) sandwiched between tetrahedrally coordinated cations (typically Si and Al). The isomorphous substitution of Si^{4+} by Al^{3+} leads to a net negative surface charge that is compensated by interlayer exchangeable hydrated cations (Ca^{2+}, Mg^{2+}, Cu^{2+} and Na^{+}). These charge balancing inorganic cations can be mutually exchanged or exchanged by organic cations [19]. The vermiculite volume can be expanded by several times when heated at high temperature for a short duration due to the sudden release of interlayer water. This disrupts the structure and forms a highly porous material named expanded vermiculite. Expanded vermiculite has good physical properties, such as fire resistance, the porous structure, non-toxicity and low density, and is usually used as a lightweight aggregate for plaster, concrete compounds and the component of wallboard filler [20]. In recent years, a new application using expanded vermiculite as a PCM supporting matrix has been explored. Chung et al. [21] used expanded vermiculite as the n-octadecane supporting matrix. Although the prepared composite PCM was thermally stable and chemically inert, the thermal conductivity of composite PCM was low (0.1569 W/mK). Karaipekli and Sari [22] reported that the thermal conductivities of fatty acids/expanded vermiculite composite PCMs were increased in the range of 104–150% by addition of 10 wt% expanded graphite. Guan et al. [23] implanted network carbon in vermiculite layers by in-situ carbonizing sucrose to enhance the thermal conductivity of paraffin/expanded vermiculite composite. Though the thermal conductivity of the composite PCM improved greatly, the latent heats decreased. The similar results were also reported in the other related works [11,24,25]. Therefore, it is necessary to come up with a method to simultaneously improve the thermal conductivity and latent heat of the composite PCM.

In this study, a novel method was proposed to achieve the purpose. The expanded vermiculite/carbon composite was prepared by implanting carbon in layers of expanded vermiculite via in-situ carbonizing cetyl trimethyl ammonium bromide (CTAB). As a cationic surfactant, CTAB is easy to be intercalated into interlayer space of expanded vermiculite. The obtained expanded vermiculite/carbon composite was treated with nitric acid (aEVC) to improve the specific surface area and microporosity of expanded vermiculite, and then used as capric-myristic-stearic eutectic mixture (CA-MA-SA) supporting matrix. The thermal conductivity and latent heats of the CA-MA-SA/aEVC were both higher than those of CA-MA-SA/EV.

2. Experimental

2.1. Materials

Capric acid (CA, $C_{10}H_{20}O_2$, AR), myristic acid (MA, $C_{14}H_{28}O_2$, AR), stearic acid (SA, $C_{18}H_{36}O_2$, AR), nitric acid (HNO_3, AR) and cetyl trimethyl ammonium bromide (CTAB, $C_{19}H_{42}BrN$, AR) were purchased from Sinopharm Chemical Reagent Company. The expanded vermiculite was purchased from Jinli mining industry co., Ltd.

2.2. Determination of eutectic composition

The eutectic mass ratio of fatty acid mixture can be approximately calculated via the Schrader equation [26].

$$T_m = \left[\frac{1}{T_A} - \frac{R \ln X_A}{\Delta H_A}\right]^{-1} \quad (1)$$

where T_m is the phase change temperature of the eutectic mixture, T_A and ΔH_A are the phase change temperature and latent heat of component A, X_A is the mole fraction of component A in the mixture, and R is the gas constant.

The thermal properties of CA, MA and SA measured by differential scanning calorimetry (DSC) are given in Table 1. Through Eq. (1), the theoretical mass ratios of CA-MA, MA-SA, CA-SA eutectic mixtures were firstly calculated, and then the ternary eutectic mass ratio was calculated to be 71.8:23.2:5.0 by regarding the eutectic mixture of CA-MA as a pseudo-single component [27]. Considering the Schrader equation is an approximate calculation formula, the mass ratios of the eutectic mixtures need to be verified by experiments [26]. The mass ratios and melting temperatures of eutectic mixtures measured by DSC are shown in Table 2. The ternary phase diagram of CA-MA-SA can be expressed in the form of equilateral triangle as shown in Fig. 1. The experimental eutectic points of CA-MA, MA-SA and CA-SA are labeled as A, B, and C, respectively. Point E, the theoretical eutectic point of CA-MA-SA is located into the small triangle formed by KA, DB and HC. A series of CA-MA-SA mixtures with different mass ratios (CA:MA:SA = 71.8:23.2:5.0; 71.8:22.5:5.7; 71.8:23.9:4.3; 71.1:23.2:5.7; 72.5:23.2:4.3; 72.5:22.5:5.0; 71.1:23.9:5.0) were prepared and then measured by DSC. Among them, the CA-MA-SA with the mass ratio of 72.5:22.5:5.0 has the lowest melting temperature. In order to further verify 72.5:22.5:5.0 as the eutectic composition, the mixture was tested by DSC performed at a slow heating rate of 1 °C/min. The DSC curve is shown in Fig. 2. As seen from Fig. 2, only one solid–liquid phase change peak was observed, which evidenced ternary eutectic forming [28]. The determined eutectic composition in this work has little difference with the reported value of CA:MA:SA = 72.65:21.17:6.18 by Ke et al. [26].

2.3. Preparation of CA-MA-SA eutectic mixture

The CA-MA-SA eutectic mixture was prepared by heating-ultrasonic method. 7.25 g CA, 2.25 g MA and 0.5 g SA were mixed uniformly in a sealed beaker followed by melting and blending at 70 °C for 40 min. Then the mixtures were cooled to the room temperature and conserved under sealed condition.

Table 1
Thermal properties of CA, MA and SA.

Fatty acids	Melting temperatures (°C)	Latent heats of melting (J/g)	Molar mass (g/mol)
CA	30.51	155.5	172.27
MA	52.32	184.5	228.37
SA	67.20	199.1	284.48