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Preparation of stearic acid/modified expanded vermiculite composite phase change material with simultaneously enhanced thermal conductivity and latent heat

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ABSTRACT

A novel stearic acid/modified expanded vermiculite composite phase change material (PCM) was prepared in this study. Titanium dioxide-loaded expanded vermiculite was treated with nitric acid (aEVT) and then used as stearic acid (SA) supporting matrix. The thermal conductivity and latent heats of the SA/aEVT composite PCM were enhanced simultaneously compared with those of SA/expanded vermiculite (EV) and SA/expanded vermiculite with acid treatment (aEV) composite PCMs. The thermal conductivity of SA/aEVT was 0.58 W/mK, which was 11.4% and 20.3% higher than those of SA/EV and SA/aEV, respectively. The latent heats of SA/aEVT were 146.8 J/g at the melting temperature of 65.9 °C and 141.7 J/g at the freezing temperature of 63.4 °C, which were also higher than those of SA/EV and SA/aEV. The results of the thermal cycling test and Fourier transform infrared spectroscopy (FT-IR) indicated that the SA/aEVT composite PCM was thermally stable and chemically inert. Thus, the prepared SA/aEVT is a promising composite PCM for latent heat storage systems.

1. Introduction

In recent years, the energetic and environmental situation reveals the urgent need for improving energy utilization efficiency and protecting environment. Phase change materials (PCMs) for latent heat thermal energy storage have attracted interests due to high energy storage density and latent heat property, small temperature variation from storage to retrieval, and repeatable utilization property [1,2]. PCMs have been demonstrated as an acceptable energy storage in various applications, such as building energy conservation, air-conditioning systems, solar heating systems and insulation clothing [3–6].

Fatty acids, the member of organic PCMs, have great potential for widespread thermal energy storage applications and are environmentally friendly due to their reducibility from vegetable and animal oils [7–9]. However, the leakage in the melted state and poor thermal conductivity (around 0.2 W/mK) are characterized as two key disadvantages, which have restricted their wide applications [10]. Therefore, fatty acids applications are now frequently in the form of form-stable composites that employ a variety of porous materials as supporting matrices, such as expanded perlite [11–13], halloysite [14,15] and expanded vermiculite [8,16,17]. Moreover, the materials with excellent thermal conduction property, including expanded graphite [18,19], carbon nanotubes [20,21] and silica fume [22], have been introduced to enhance the thermal conductivity of the form-stable composite PCM. Unfortunately, the increase of thermal conductivity of the form-stable composite PCM is commonly observed with the decrease of latent heat. Wang et al. [23] used β-Aluminum nitride to improve the thermal conductivity of polyethylene glycol/SiO_2 form-stable composite PCM. However, the latent heat of the composite PCM decreased. Guan et al. [24] implanted network carbon in vermiculite layers to enhance the thermal conductivity of paraffin/expanded vermiculite form-stable composite. Similarly, the latent heat of the composite PCM reduced. This phenomenon was also reported in the other related works [12,13,25]. Therefore, it is necessary to come up with a method to simultaneously improve the thermal conductivity and the latent heats of the composite PCM.

Vermiculite, a magnesium aluminum silicate with 2:1 crystalline structures, has been extensively studied as catalysts, sorbents of heavy metals, thermal and acoustic insulation materials. Several efforts have been directed towards the modification of vermiculite in order to improve the specific surface area, microporosity and surface acidity of vermiculite. As for the application of catalysts, these approaches include acid-activation [26], intercalation with metal oxide pillars (e.g. Al_2O_3, TiO_2) [27,28], immobilizing metal oxide nanoparticles onto the silica nanolayers of exfoliated vermiculite [29]. For the application of thermal and acoustic

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insulation materials, the main approach is expanding vermiculite by a sudden heating at high temperature to form highly porous structure [30]. In recent years, a new application using vermiculite as a PCM supporting matrix has been explored [16,17,24]. Among all the vermiculite-based PCMs, expanded vermiculite is commonly adopted as supporting material to enhance the loading amount of PCMs. The modified vermiculite as used in vermiculite-based catalysts has not been reported in literature relating to composite PCMs.

In this work, expanded vermiculite was modified via a combined approach and then used as stearic acid supporting matrix to prepare a novel composite PCM. The combined approach involved loading titanium dioxide on the surface of expanded vermiculite, and subsequent treating with acid solution. This novel composite PCM exhibited simultaneously enhanced thermal conductivity and latent heat.

2. Experimental

2.1. Materials

Stearic acid (SA, AR), nitric acid (HNO_3, AR), tetrabutyl titanate ($C_{16}H_{36}O_4Ti$, CP), ethanol (CH_3CH_2OH, AR), acetic acid ($C_2H_4O_2$, AR), hydrochloric acid (HCl, AR) were purchased from Sinopharm Chemical Reagent Company. The expanded vermiculite was purchased from Jinli mining industry co., Ltd.

2.2. Preparation of the supporting matrices

The expanded vermiculite (EV), expanded vermiculite with acid treatment (aEV) and expanded vermiculite/titanium dioxide composite with acid treatment (aEVT) were used as the supporting matrices.

The aEV was prepared as follows: the EV was dispersed in HNO_3 solution (4 mol/L) with a ratio of EV mass to volume of HNO_3 solution of 100 g/L and stirred at 90 °C for 2 h. Then, the product was filtrated, dried and ground.

The aEVT was prepared by acid treatment of TiO_2/EV. The composite TiO_2/EV with TiO_2 content of 5 wt% was prepared by a similar method in the literature [27]. The required mass of EV was dispersed in ethanol solution of tetrabutyl titanate and acetic acid. The volume ratio was tetrabutyl titanate:acetic acid:ethanol=3:1:9. The mixture was hydrolyzed by slowly adding 0.2 mol/L HCl solution and the pH was adjusted to 3. The hydrolyzed composite was dried at 80 °C for 5 h and calcined in air at 400 °C for 2 h. The obtained TiO_2/EV was treated with HNO_3 solution in the same process as aEV.

2.3. Preparation of the composite PCMs

The composite PCMs were prepared by vacuum impregnation. The supporting matrix and solid SA were placed in a conical flask with stirrer. The vacuum pump was connected to the conical flask to evacuate air. Then the conical flask was heated under the vacuum condition in order to melt solid SA. SA was easily absorbed under the vacuum condition. After vacuum impregnation, the composite PCM was thermally filtered to remove excess SA.

2.4. Characterization

The phase compositions of the supporting matrices were studied by X-ray diffraction (XRD, Ultima III). The microstructures of the supporting matrix and composite PCM were observed by scanning electron microscopy (SEM, SUPRA 55). The chemical compatibility between SA and the supporting matrix was examined by Fourier transform infrared spectroscopy (FT-IR, Nicolet-5700). The thermal conductivity of the samples were measured by thermal conductivity analyzer (DRL-II). Thermal properties of the samples were measured via differential scanning calorimetry (DSC, Q20) with temperature accuracy within ±0.1 °C and enthalpy accuracy within ±1.0%.

A thermal cycling test was performed to determine the thermal reliability of composite PCM. SA/aEVT with a mass of 5 g was dispersed on a filter paper and then placed into a thermostatic chamber. The sample was heated above the melting temperature and then cooled to room temperature. Thus a thermal cycle, including a melting and freezing process, was completed. The thermal cycles were consecutively repeated 200 times and the filter paper was substituted per 20 cycles. After the sample stood at room temperature in air for 50 days, cycling process were performed again, consecutively repeating 400 times. Thus the total cycling number was 600. A DSC analysis of SA/aEVT after 200 and 600 cycles was performed.

3. Results and discussion

3.1. Characterization of the supporting matrix

The XRD patterns of the supporting matrices are shown in Fig. 1. From the XRD pattern of the EV, the expanded vermiculite consists of phlogopite with minor vermiculite and hydrobiotite. The d_{001}-value of vermiculite is 1.5 nm. According to the XRD patterns of aEV and aEVT, the intensities of diffraction peaks weaken evidently and the diffraction peak of vermiculite disappears, suggesting that EV was delaminated and corroded by acid treatment [26]. The diffraction peak of anatase is observed at $2\theta=25.4°$ in the XRD pattern of the aEVT. The average size (D) of the TiO_2 crystallites is estimated using the Scherrer equation:

$$D=\frac{K\lambda}{\beta\cos\theta}$$

where λ is the wavelength of X-ray radiation ($\lambda=0.15406$ nm), K is the Scherrer constant (K=0.89), and β is the full-width-at-half-maximum of the (101) plane (in radians). The calculated average size of TiO_2 crystallites is 17.7 nm, which is much larger than the d_{001}-value (1.0 nm) of phlogopite. Therefore, the TiO_2 nanoparticles are most likely loaded on the surface rather than the interlamination of expanded vermiculite.

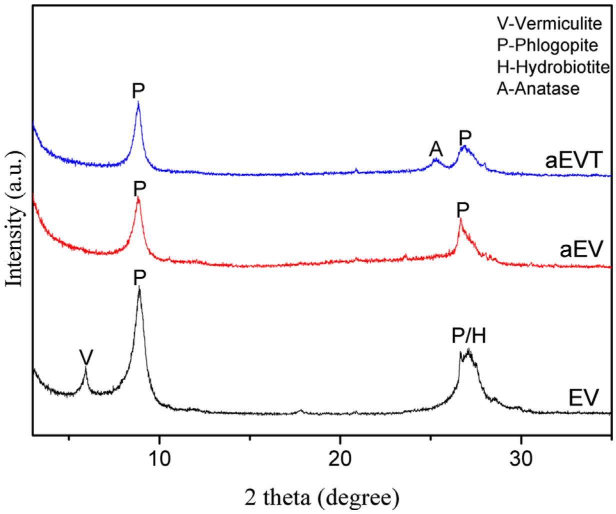

Fig. 1. XRD patterns of EV, aEV, aEVT.