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A comparative study of myristic acid/bentonite and myristic acid/Eudragit L100 form stable phase change materials for thermal energy storage

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ABSTRACT

In this work, the influence of type of supporting materials on the performance of form stable phase change materials (FSPCMs) was investigated. Two kinds of FSPCMs containing myristic acid (MA) were prepared using an inorganic material (bentonite) and a polymer (Eudragit L100) individually as the supporting material. The morphology, composition, crystalline properties, phase transition properties and heat storage/release performances of MA/bentonite FSPCMs (abbreviated as FSPCM-B) and MA/Eudragit L100 FSPCMs (abbreviated as FSPCM-E) were researched comparatively. The results show that the maximum MA content of FSPCM-B and FSPCM-E without melt MA leakage is 50 wt% and 70 wt%, respectively. All the prepared FSPCMs have good thermal reliability and reusability, and phase transition enthalpies of FSPCM-B are obviously lower than those of FSPCM-E with the same MA mass fraction. Due to the high thermal conductivity of bentonite, the heat transfer rate of FSPCM-B is exactly higher than that of FSPCM-E. This study will provide insights into the design and application of FSPCMs with inorganic matrix and polymeric matrix.

1. Introduction

Phase change materials (PCMs), also called latent heat storage materials, are a kind of functional materials for thermal energy storage by storing and releasing amount of latent heats during their phase change processes. According to their phase change states, PCMs are often divided into three categories: solid–liquid PCMs, solid–solid PCMs and liquid–gas PCMs [1,2]. Compared with solid–solid PCMs and liquid–gas PCMs, solid–liquid PCMs have been extensively researched and applied for several decades because of high latent heat density, lower cost and various choices [3]. However, containers are needed to avoid the leakage of liquid phase, which results in extra thermal resistance and running cost. Aiming at the shortcoming of solid–liquid PCMs, form stable PCMs (FSPCMs) composed of supporting materials and phase change working substances (i.e., solid–liquid PCMs) have been developed. The FSPCMs could keep the solid state even as the ambient temperature is higher than the melting temperature of the used solid–liquid PCMs due to the supporting and encapsulated effect of the matrix.

From the reported literatures, inorganic materials with porous/lamellar structure (e.g., expanded graphite [3–8], diatomite [9–11], expanded perlite [12,13], vermiculite [14], cement [15], etc.) or polymers with high melting point (e.g., HDPE [16–18], polyacrylic resin [19–21], melamine formaldehyde copolymer [22], etc.) were usually selected as the supporting materials of FSPCMs. Also, ordinary organic solid–liquid PCMs including polyethylene glycol [1–3,7,11,26], paraffin wax and long chain alkanes [5,6,8,15–18,20,21,27], fatty acids and their eutectics [4,9,10,12–15,19,23–25] were often used as the corresponding working substances of FSPCMs. FSPCMs could be prepared by a variety of methods such as solution casting [19], melt solidification [7,10,16–18], vacuum impregnation [4–6,9,11–14], microencapsulation [20–22], electrospinning [2,23–26], etc. Generally, the phase change properties of FSPCMs were varied and controlled by changing the types and content of solid–liquid PCMs. In fact, the type of supporting materials also has a significant influence on the performances of FSPCMs, which is regrettably neglected in the previous studies. A lot of FSPCMs with various supporting materials were reported in recent years, but as far as we know, few literatures focused on the performances comparison of FSPCMs with inorganic matrix and polymeric matrix.

Bentonite is an absorbent aluminum phyllosilicate, and its main uses are for drilling mud, binder, absorbent and as a groundwater

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barrier. Due to its nano-layer structures, high thermal conductivity and low cost, bentonite also could be used as the supporting material of FSPCMs [27]. Eudragit® L100 (EL100) is a copolymer of methacrylic acid and ethyl acrylate (1:1), and it has wide applications for the pH sensitive characteristic. In the present work, bentonite and EL100 were individually selected as the inorganic matrix and polymeric matrix of the FSPCMs, and two kinds of FSPCMs containing myristic acid (MA) were prepared via vacuum impregnation and solution casting, respectively. The comparative studies of MA/bentonite FSPCMs and MA/EL100 FSPCMs on morphology, composition, crystallization properties, thermal properties and heat storage/release performances have been carried out by scanning electronic microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), differential scanning calorimetry (DSC), and temperature–time curves, respectively.

2. Experimental part

2.1. Materials

Bentonite [$Al_2O_3 \cdot 4(SiO_2) \cdot H_2O$, purchased from Aladdin Chemistry Co. Ltd, China], Eudragit® L100 (EL100, from RÖhm GmbH, Germany, $M_w \sim 135{,}000$), myristic acid (MA, analysis grade, from Tianjin Kemiou Chemical Regents Co. Ltd, China) and ethanol (analysis grade, from Tianjin Kemiou Chemical Regents Co. Ltd, China) were used without further purification.

2.2. Preparation of MA/bentonite FSPCMs

The MA/bentonite FSPCMs (abbreviated as FSPCM-B) were prepared using the vacuum impregnation method [9,11–14]. A suction flask connected to a vacuum pump and a sealed constant-voltage funnel, and the suction flask was placed in a water bath with magnetic stirring. An amount of bentonite sample was placed inside the suction flask, and the ethanol solution of MA was placed in the sealed constant-voltage funnel. After the vacuum process was to be continued for 60 min at the vacuum pressure of 20 kPa to evacuate air from layered bentonite, the valve of the constant-voltage funnel was turned open to allow the MA solution to flow into the flask to cover the bentonite sample. Then, air was allowed to enter the flask again to force the MA solution to intercalate into the layered space of bentonite. The suction flask loaded mixed suspension was put into the water bath at 60 °C under reduced pressure until ethanol was volatilized completely. Finally, the product was dried in a vacuum drying oven at 40 °C for 24 h. Following this procedure, the composite PCMs with different MA mass fractions (10%, 20%, 30%, 40%, 50%, 60%, 70% and 80%, w/w) was prepared. The maximum mass fraction of MA in the composites without melt MA leakage was determined by the following heating–cooling test: the MA/bentonite composites were heated to 65 °C (above the melting temperature of MA) and then cooled to room temperature, and the process was cycled for 10 times. The result showed that the maximum MA weight percentage in FSPCM-B was 50 wt% of the total weight of the composite. FSPCM-B with 10 wt%, 20 wt%, 30 wt%, 40 wt% and 50 wt% MA were labeled as FSPCM-B1, FSPCM-B2, FSPCM-B3, FSPCM-B4 and FSPCM-B5, respectively.

2.3. Preparation of MA/EL100 FSPCMs

The MA/EL100 FSPCMs (abbreviated as FSPCM-E) were prepared using the solution casting method. Firstly, EL100 solution and a series of MA/EL100 mixed solutions with different MA mass fractions (10%, 20%, 30%, 40%, 50%, 60%, 70% and 80%, w/w) were prepared in ethanol. Then, the mixed solutions were poured into the glass panes respectively, and the casting films of EL100 and MA/EL100 composites were obtained by volatilization of ethanol at room temperature. Subsequently, the casting films of the samples were placed in the vacuum dryer at 40 °C for 24 h to remove the residual ethanol. In order to test MA exudation from the composites, the heating–cooling test as mentioned above was also carried out. The maximum MA mass fraction in FSPCM-E was found to be 70 wt% of the total weight of the composite. FSPCM-E with 10 wt%, 20 wt%, 30 wt%, 40 wt%, 50 wt%, 60 wt% and 70 wt% MA were labeled as FSPCM-E1, FSPCM-E2, FSPCM-E3, FSPCM-E4, FSPCM-E5, FSPCM-E6 and FSPCM-E7, respectively.

2.4. Thermal treatment process

In order to further test the form stable characteristic and thermal reliability of the prepared FSPCMs, the thermal treatment process was carried out as follows: pristine MA powders, FSPCM-B5, FSPCM-E5 and FSPCM-E7 were placed in the drying oven at 65 °C (higher than the melting point of MA) for 5 h, and then took out for measurements. And the thermal treated samples were labeled as MA (T), FSPCM-B5 (T), FSPCM-E5 (T) and FSPCM-E7 (T).

2.5. Characterization

The morphology of MA, bentonite, EL100 casting film and the prepared FSPCMs before and after treatment was observed with a scanning electron microscope (FEI-Quanta 200, FEI, Holland) at acceleration voltage of 30 kV under low vacuum. The samples were gold-coated prior to the SEM measurement.

FTIR spectra of the samples were taken in a Infrared Spectrophotometer (NICOLET-760, Nicolet co., USA) in the wavenumber range of 4000–400 cm^{-1}. The samples were mixed with KBr and then pressed into a pellet.

XRD patterns of the samples were recorded in the reflection mode at room temperature on an automatic powder diffractometer (D8 ADVANCE, brukeraxs, Germany) with Ni-filtered Cu Kα radiation at 40 kV and 30 mA. The scans were obtained by using a 0.02° step programmed with a collection time of 0.1 s per step. Measurements were performed in the range $5^\circ < 2\theta < 50^\circ$.

The phase transition properties of pure MA and the FSPCMs before and after thermal treatment were determined by DSC curves using a Simultaneous Thermal Analysis Apparatus (STA 449 F3 Jupiter®, Netzsch, Germany). Indium and zinc were used for calibration. About 10 mg of the dried sample was weighed into an aluminum crucible, and then it was carried out the heating–cooling cycles from 20 °C to 100 °C at a heating/cooling rate of 2 °C/min in a nitrogen atmosphere. Thermal conductivity of samples was measured by a thermal property analyzer (TC 3010, Xiatech Electronic Technology Co., Ltd., China).

2.6. Test of heat storage/release performances

The test of heat storage and release performances was determined by the heating and cooling curves of the samples, which was conducted by a thermocouple (CENTER-309, CENTER Technology, Taiwan) and two oil bathes as the following steps [2,27]. In the experimental set-up, the temperature of the two oil bathes was set at 30 °C and 80 °C. The sample was put into a 10 ml tube and a thermocouple was put in the middle of the sample. The tube was firstly heated in the oil bath with the constant temperature of 80 °C. When the temperature of the sample showed in the thermocouple remained constant, the tube was immediately transferred into another oil bath with the constant temperature of 30 °C. The test was terminated until the temperature of the sample had stopped falling. The multichannel temperature recorder was used to record