Preparation and Property of Paraffin/CaCO₃ Composite as Form-Stable Phase Change Material for Thermal Energy Storage†

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In this work, a paraffin/CaCO₃ composite phase change material with a paraffin capacity of 50 wt % was prepared using a microemulsion method. The paraffin was used as the phase change material for thermal energy storage and CaCO₃ served as the supporting material for improving the thermal stability of the composite. The as-obtained composite was characterized by X-ray diffractometer, Fourier transformation infrared spectroscopy, scanning electronic microscopy and differential scanning calorimeter. The composite can maintain its original shape perfectly without any paraffin leakage after subjected to 30 melt-freeze cycles, in which the paraffin was well dispersed in the porous network of CaCO₃, observed by SEM.

Key Words: Composite, Phase change materials, Synthesis, Thermal property.

INTRODUCTION

Due to the shortage in energy and the demand for functional materials in thermal energy management, phase change materials (PCMs) is becoming more and more important for storing thermal energy and adjusting temperature through storing and releasing large amounts of latent heat during phase change process[1]. Paraffins have been widely used due to their high latent heat storage capacity and appropriate physico-chemical properties[2]. However, the direct utilization of organic phase change materials for latent heat storage have some difficulties because of their inflammability and the need of special sealed package to prevent their leakage during the solid-liquid phase transitions. These problems can be solved by designing form-stable composite phase change materials which can remain in solid shapes even when the working materials change from solid to liquid[3]. Combining the advantages of organic phase change materials for the thermal energy storage and good stability of inorganic materials, a novel kind of composite phase change materials were developed using organic phase change materials as working materials and inorganic materials as supporting materials[4].

This paper presents recent study on the preparation and thermal property of paraffin/CaCO₃ composite as form-stable phase change material for thermal energy storage. The as-obtained composite phase change material was characterized by XRD, FTIR, SEM and DSC analysis techniques.

EXPERIMENTAL

Anhydrous calcium chloride and sodium carbonate (Reagent grade, Sinopharm Chemical Reagent Company) were used as the precursors. Distilled water was used as solvent. Sodium dodecyl sulfate (SDS) (Reagent grade, Shanghai Chemical Reagent Company) was used as oil-water emulsifier. Paraffin (Reagent grade, Shanghai Southeast Chemical Engineering Company) was used as latent heat storage phase change material. The paraffin is saturated alkanes (C_nH_{2n+2}) with melting point of 56-58 ºC, melting latent heat of 144 kJ/kg.

In a beaker, 0.2 g sodium dodecyl sulfate was dissolved in 50 mL of distilled water. Then, paraffin was added into this solution and continuously stirred for 1 h on a magnetic stirrer while the temperature of the solution was controlled at 70 ºC using a constant temperature water bath. The paraffin (4 g) was dispersed in the aqueous solution to form O/W micro-emulsion. Then, anhydrous calcium chloride (4.4392 g, 40 mmol) and sodium carbonate (4.2396 g, 40 mmol) was succe-ssively dissolved in the microemulsion under continuous stirring at 70 ºC. The mixture was stirred for 2 h with a magnetic stirrer while the temperature of the mixture was controlled at 70 ºC. Finally, white powders were collected and washed with distilled water. The paraffin/CaCO₃ composite with a paraffin capacity of 50 wt % was obtained after dried in a vacuum oven at 50 ºC for 24 h.

The crystalloid phase of the samples was investigated by X-ray diffractometer (XRD, Philips X' Pert PRO SUPER, Holand). The FT-IR spectra of the samples were recorded on a Nicolet 380 from 4000-400 cm^{-1} using KBr pellets which were prepared by pressing pellets containing 100 mg KBr and 1 mg of sample. The morphology and microstructure of paraffin/CaCO$_3$ composites were observed using a field emission scanning electron microscopy (FESEM, JEOL JSM-6700F, Japan). The phase change temperature and latent heat of the paraffin/CaCO$_3$ composite phase change materials were measured using a differential scanning calorimeter (NETZSCH DSC 200 F3) at 5 ℃/min in air, in which the sample was sealed in an aluminum pan.

RESULTS AND DISCUSSION

The XRD patterns of CaCO$_3$, paraffin and paraffin/CaCO$_3$ composite are shown in Fig. 1. The XRD pattern in Fig. 1a is consistent with that of Rhomb-centered CaCO$_3$ of hexagonal system (JCPDS 86-2343). The XRD peaks shown in Fig. 1c are due to the crystallization of paraffin. Compared with the XRD patterns of CaCO$_3$ (Fig. 1a) and paraffin (Fig. 1c), the XRD pattern shown in Fig. 1b of the paraffin/CaCO$_3$ composite presents the two sets of XRD peaks in conformity with those of CaCO$_3$ and paraffin.
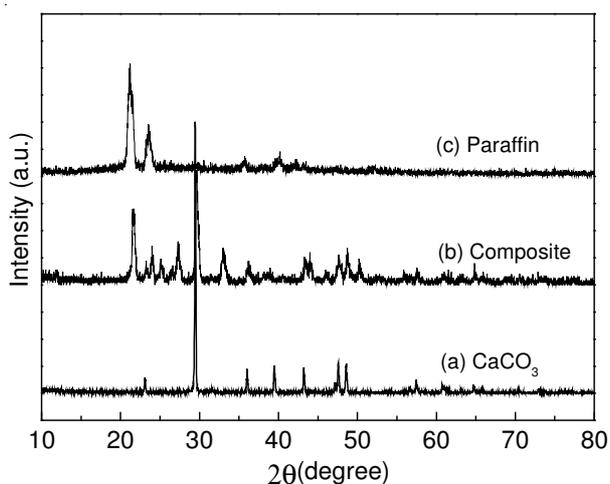
Fig. 1.   XRD patterns of (a) CaCO$_3$, (b) paraffin/CaCO$_3$ composite and (c) paraffin

Fig. 2 shows the FT-IR spectra of CaCO$_3$, paraffin and paraffin/CaCO$_3$ composite. The FT-IR spectrum of CaCO$_3$ shown in Fig. 2a is quite characteristic with a very intense broad band centering at 1420 cm^{-1} and several sharp bands at 1795, 873 and 710 cm^{-1}, which is consistent with that reported in the literature[5]. The broad band at 3600-3000 cm^{-1} represents the stretching and bending vibrations of -OH functional group of the adsorbed water in the sample. Fig. 2b shows the spectrum of the paraffin. The peak at 2917 cm^{-1} signifies the symmetrical stretching vibration of its -CH$_3$ group, the peak at 2843 cm^{-1} represents the symmetrical stretching vibration of the -CH$_2$ group. The peaks at around 1465 cm^{-1} belong to the deformation vibration of -CH$_2$ and -CH$_3$ and the peak at 719 cm^{-1} represents the rocking vibration of -CH$_2$[6]. As shown in Fig. 2c, the absorption peaks of CaCO$_3$ at 1795, 873 and
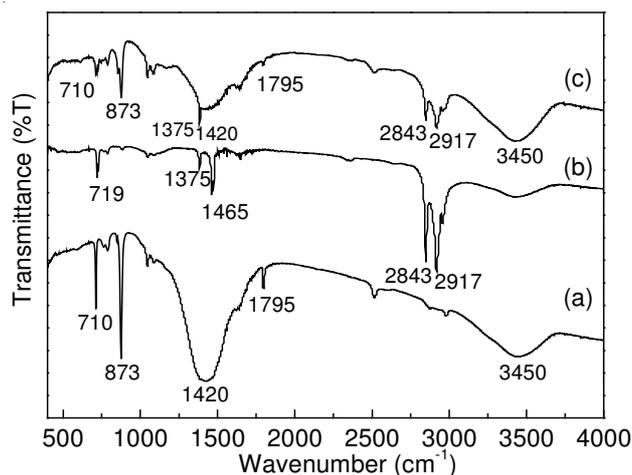
Fig. 2.   FT-IR spectra of (a) CaCO$_3$, (b) paraffin, (c) paraffin/CaCO$_3$ composite

710 cm^{-1} also appear in the spectrum of paraffin/CaCO$_3$ composite. The absorption peaks of the paraffin at 2917, 2843, 1375 and 719 cm^{-1} are not changed in the spectrum of paraffin/CaCO$_3$ composite, indicating that there is no chemical reaction between the paraffin and CaCO$_3$.

The morphology and microstructures of CaCO$_3$ and paraffin/CaCO$_3$ composite were observed by FESEM. The FESEM images are shown in Fig. 3. As shown in Fig. 3a, the CaCO$_3$ powder has a rough surface with porous structure and the sizes of the CaCO$_3$ particles lie in the range of 100-500 nm. In the paraffin/CaCO$_3$ composite (Fig. 3b), the pore space of CaCO$_3$ matrix was filled by paraffin. The CaCO$_3$ matrix should provide the mechanical supporting for the whole composite and prevented the seepage of the melted paraffin due to the effect of capillary and surface tension forces between the paraffin and the porous network of the CaCO$_3$. The result indicates that the better supporting and encapsulation effect would be obtained when the filled capacity of paraffin in the paraffin/CaCO$_3$ composite is as high as 50 wt %.

The thermal properties of paraffin and paraffin/CaCO$_3$ composite have been characterized by DSC measurements. Fig. 4a shows the melting-solidifying DSC curves of the first phase change cycle. The phase change characteristic of the composite is close to that of the paraffin. There are two endothermic peaks in the melting DSC curve and two exothermic peaks in the solidifying DSC curves. The small peak represents solid-solid transition process and the big peak denotes solid-liquid melting process or liquid-solid solidifying process[2]. Before the melting, the solid-solid transition is induced by phase transformation from an ordered phase to a more disordered rotator phase. In Fig. 4a, solid-liquid melting peak and liquid-solid solidifying peak were used to calculate the melting and solidifying latent heat value, respectively. The melting and solidifying temperatures are measured to be 56.0 and 50.5 ℃ for the paraffin, 56.0 and 45.1 ℃ for the composite. The melting and solidifying latent heats are measured to be 143.5 and 144 kJ/kg for the paraffin, 55.3 and 51.7 kJ/kg for the composite. Fig. 4b shows the DSC curves during 30 phase-change cycles of the paraffin/CaCO$_3$ composite. The DSC curves in 30 phase-change cycles fully coincide and the phase change temperature and latent heat are identical in each
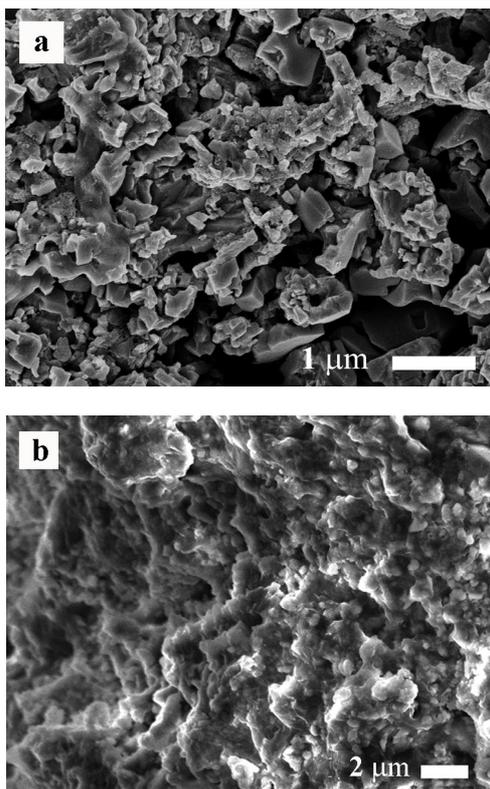
Fig. 3.   FESEM images of (a) CaCO₃ powder and (b) paraffin/CaCO₃ composite
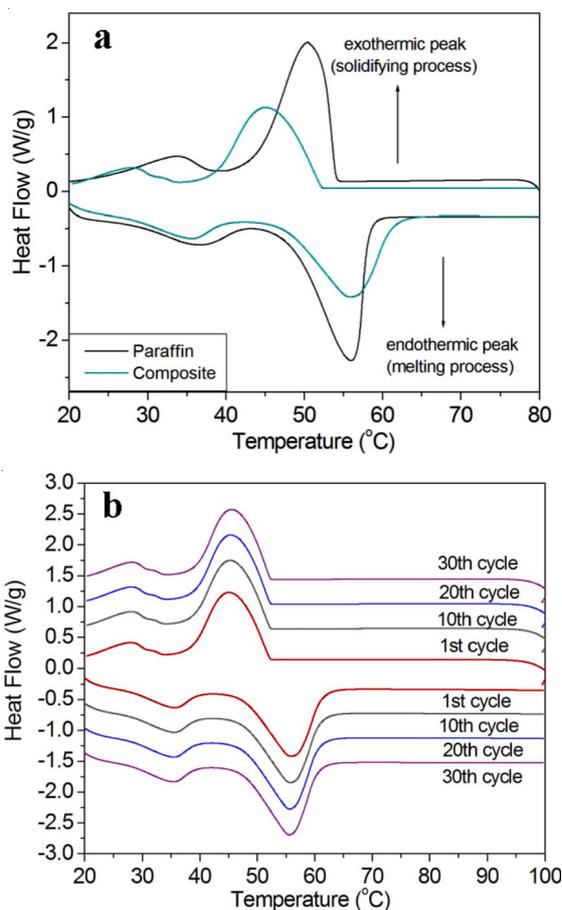
Fig. 4.   (a) Melting-solidifying DSC curves for the first phase change cycle of paraffin and paraffin/CaCO₃ composite, (b) DSC curve during 30 phase-change cycles of paraffin/CaCO₃ composite

melting-solidifying cycle, indicating that the sample has a good cycle performance in storage/release of thermal energy. This is due to that the paraffin in the composite is confined to the pore space of $CaCO_3$ matrix which prevented the flow of the melted paraffin.

Conclusion

The synthesis, microstructures and thermal property of the form-stable paraffin/$CaCO_3$ composite phase change material are reported. In the composite, paraffin was used as the latent heat storage material and $CaCO_3$ served as the inorganic supporting material for improving the thermal stability. The paraffin is well confined to the porous network of $CaCO_3$ and the leakage of melted paraffin from the composite can be prevented when it was heated above the melting temperature of the paraffin. The results indicate that the composite has a high adsorption capacity of paraffin, high heat storage capacity and good thermal stability. Besides, several advantages like low cost, simple preparation and direct usability without extra encapsulation render the composite potential heat storage material for practical application.

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