Study on preparation of montmorillonite-based composite phase change materials and their applications in thermal storage building materials

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Abstract

Three composite phase change materials (PCMs) were prepared by blending butyl stearate, dodecanol and RT20 with an organically modified montmorillonite (MMT), respectively. After the three composite PCMs were characterized by DSC, it was indicated that the RT20/MMT composite PCM was a good candidate for building applications due to its large latent heat, suitable phase change temperature and good performance stability. Compared with RT20, the RT20/MMT composite PCM exhibited higher heat transfer efficiency and had good compatibility with gypsum due to the combination with MMT. The composite gypsum boards containing RT20/MMT composite PCM had the function of reducing building energy consumption by reducing the indoor temperature variation, and the function was enhanced with the increase in the mass ratio of the RT20/MMT composite PCM.
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1. Introduction

A phase change material (PCM) can absorb or release a large quantity of latent heat when it changes phase from solid state to liquid state or vice versa, which has very important applications for thermal energy storage [1–4]. Incorporating suitable phase change materials into the walls, ceiling and floor of buildings can render it feasible to capture solar energy directly and store significant amounts of thermal energy in the building envelope without the large structural mass associated with sensible heat storage, which helps to decrease the frequency of internal air temperature swings and maintain the temperature closer to the desired temperature for a longer period of time [5,6].

Since the 1970s, several researchers have tried to use phase change materials in buildings to enhance the thermal comfort of lightweight constructions [7–9]. The selection of PCMs was almost directed towards the use of organic materials in an effort to avoid some of the problems inherent in inorganic materials, such as the need for a special container due to their corrosiveness, tendency of super cooling, segregation etc. Two general means were proposed for incorporation of organic PCMs within construction elements: simple immersion of conventional wallboards in molten PCMs or encapsulation of PCMs in high density polyethylene pellets mixed with a gypsum wallboard material [10,11]. Although the former method was simple and low cost, the impregnated wallboard was inflammable owing to leakage of the liquid PCM to the surface of the wallboard, especially after the PCM experienced several heating–cooling cycles. The latter method suffered from the cost for encapsulation of PCMs and protection against

destruction of the capsules, although the capsule shell could prevent liquid leakage and interaction between the PCMs and the matrix materials. In recent years, formaldehyde free micro-encapsulation of PCMs allows PCMs to be readily integrated into conventional construction materials, and there is no need to protect the micro-capsules against destruction due to their small diameters [12,13]. However, micro-encapsulating PCMs suffered from complicated polymerization processes, and micro-capsule shells made of polymers with low thermal conductivity deteriorated the heat transfer rate of the PCM. Therefore, it is necessary to develop a novel route for incorporating PCMs into building materials, which is simple and low cost and can improve the thermal conductivities of organic PCMs and the compatibilities of organic PCMs with building materials.

In this paper, a novel route for incorporating organic PCMs into building materials was developed. Firstly, three composite PCMs were prepared by blending three organic PCMs with an organically modified montmorillonite. After the three composite PCMs were characterized by differential scanning calorimetry (DSC), the most suited composite PCM for building applications was selected; then, novel composite gypsum boards were fabricated using the selected composite PCM and gypsum powders; and finally, investigations on the thermal storage performances of the composite gypsum wallboards were performed.

2. Experimental Section

2.1. Preparation and characterization of Montmorillonite-based composite PCMs

2.1.1. Organic modification of Montmorillonite

Na^+-montmorillonite (Na-MMT) with an exchange capacity of 85 mequiv/100 g was obtained from Nanhai Non-Metallic Mines Corp., China. Hexadecyltrimethyl ammonium bromide (CTAB) was used as received. Organic modification of the Na-MMT was performed as follows [14]: Firstly, 10 g of CTAB were dissolved in 200 ml of hot water (75 °C) to obtained a solution of CTAB, and 20 g of Na-MMT were dispersed into 800 ml of hot water (75 °C) with continuous stirring. Then, the CTAB solution was poured into the hot dispersion of the Na-MMT under vigorous stirring. Concentrated hydrochloric acid was used to adjust the pH of the dispersion to ca. 6. After the dispersion was stirred at 75 °C for 90 min, the product was filtered, washed three times with hot water and dried to obtain an organically modified montmorillonite (Org-MMT).

2.1.2. Preparation of Montmorillonite-based composite PCMs

Butyl stearate (BS), dodecanol and RT20 were used as the organic PCMs. RT20 was purchased from Rubitgherm GmbH Corp., which was liquid saturated hydrocarbons. The BS/MMT composite PCM, the dodecanol/MMT com-

posite PCM and the RT20/MMT composite PCM were prepared as follows: A definite quantity of the organic PCM was mixed with 10.0 g of Org-MMT in a mortar under grinding; after blended thoroughly, the mixture was placed into an oven with the temperature of 50 °C for 30 min; after cooling, the mixture was ground again to obtain the MMT based composite PCM.

2.1.3. Characterization

X-ray diffraction (XRD) patterns of the Na-MMT and the Org-MMT were obtained using an X-ray diffractometer (D/max-IIIA, Japan). DSC measurements of the organic PCMs and the MMT based composite PCMs were performed on a differential scanning calorimeter (DSC2910, Ta Instrument Inc., USA) under a N_2 atmosphere, and the scanning rate was 5 °C min^{-1}. The heat storage and release rates of the MMT based composite PCM were measured in comparison with the organic PCM using the method described by Xiao et al. [15].

2.2. Fabrication of composite gypsum boards and testing of their thermal storage performances

2.2.1. Fabrication

Two pieces of composite gypsum boards with 20% and 50% mass ratio of the MMT based composite PCM were fabricated as follows: Firstly, a definite quantity of the MMT based composite PCM, gypsum powders and water were mixed to prepare a well proportioned slurry. Then, the prepared slurry was placed in a stainless steel mold (size: 70 mm × 70 mm × 70 mm); after being vibrated for a few minutes, the mold was placed at room temperature for 24 h. Finally, the mold was taken down, and the composite gypsum board was dried in a vacuum drier at 50 °C before use. Several pieces of ordinary gypsum boards were fabricated by the same process using the slurry in the absence of the MMT based composite PCM.

2.2.2. Testing of thermal storage performances

A sketch of the experimental apparatus for testing the thermal storage performances of the composite gyp-
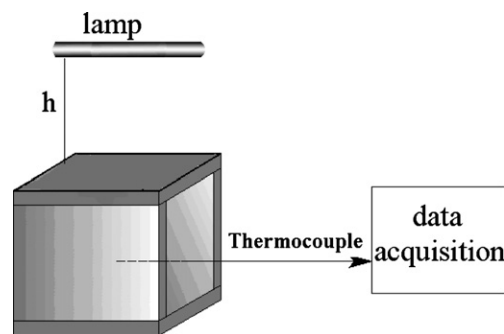

Fig. 1. A sketch of the experimental apparatus for testing the thermal storage performances of the composite gypsum boards.

sum boards is shown in Fig. 1. A small test room (70 mm × 70 mm × 70 mm) was set up using 6 pieces of gypsum boards, which, except the top board, were ordinary gypsum boards. An ordinary gypsum board and the two composite gypsum boards with 20% and 50% of the MMT based composite PCM were used as the top board, respectively. A halogen tungsten lamp (500 W) as the light source for simulating the sun was placed over the top boards of the test rooms at different distances One thermocouple linked to a data acquisition/switch unit (Agilent 34970A) was placed in the center of the test room for recording the indoor temperature of the test room. When the lamp was switched on, the indoor temperature variation of the test room began to be monitored. After an hour, the lamp was switched off. Monitoring the temperature variation continued until the test room cooled.

3. Results and discussion

3.1. Characterization of the Na-MMT and Org-MMT

Montmorillonite is composed of silicate layers of ca. 1 nm thickness and 200–300 nm lateral dimensions and is widely used as a filler for building materials. The internal and external metal cations in montmorillonite can be exchanged by other inorganic or organic ions, for example quaternary alkyl ammonium ions. Fig. 2 shows the XRD patterns of the Na-MMT and Org-MMT. It can be seen that the Na-MMT showed a diffraction peak at 6° of 2θ, which was assigned to the interlayer platelet spacing (001 diffraction peak) with a spacing of 1.4572 nm. For the Org-MMT, a displacement of the peak to a lower angle ($2\theta = 4.5°$) was observed. In this case, the interlayer distance had increased to 1.9028 nm, suggesting that Na cations were exchanged by the hexadecyltrimethyl ammonium cations. The intercalation of the hexadecyltrimethyl ammonium cations with long alkyl made the interlayer platelet spacing in the montmorillonite enlarged to 3.36 nm. The organophilic modification by CTAB made the montmorillonite compatible with organic compounds [16].
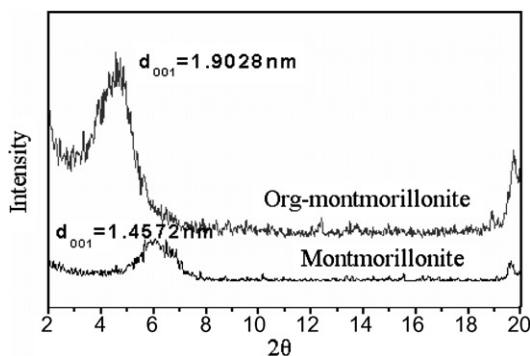

Fig. 2. The XRD patterns of the Na-montmorillonite and the organically modified montmorillonite.

3.2. Characterization of the montmorillonite-based composite PCMs

3.2.1. Selection of organic PCM

In building applications, only PCMs that have a phase transition close to human comfort temperature (20 °C) can be used. The phase change temperatures of butyl stearate (BS), dodecanol and RT 20 are close to 20 °C. The BS/MMT composite PCM, the dodecanol/MMT composite PCM and the RT20/MMT composite PCM were prepared by blending butyl stearate (BS), dodecanol and RT20 with the prepared Org-MMT, respectively. The mass ratio of the organic PCM in its corresponding composite PCM was 40%. The DSC curves of the three organic PCMs and their corresponding composite PCMs are shown in Fig. 3. It can be seen from Fig. 3a that, several phase change peaks were observed for butyl stearate, where the phase change temperature for the main peak at 27.71 °C was 24.53 °C, and its latent heat was 104.6 J/g. Compared with butyl stearate, a new phase change peak at 45.98 °C was observed for the BS/MMT composite PCM, and the latent heat of the main peak at 25.30 °C was as small as 41.81 J/g. It can be seen from Fig. 3b that dodecanol exhibited one sharp phase change peak at 24.5 °C, which the phase change temperature was 20.1 °C and the latent heat was 183.8 J/g. Compared with dodecanol, a broad phase change peak was observed for the dodecanol/MMT composite PCM, indicating that the phase change temperature of the dodecanol/MMT composite PCM deviated from the desirable temperature range for building applications. It can be seen from Fig. 3c that, except a small phase change peak at −2.65 °C, one sharp phase change peak at 26.55 °C was observed for RT20, which showed the phase change temperature was 23.24 °C and the latent heat was 134.1 J/g. The RT20/MMT composite PCM exhibited a main sharp phase change peak at 24.2 °C with 53.6 J/g of latent heat. Although a slight shift in the phase change temperature from 23.24 °C for RT20 to 20.8 °C for the RT20/MMT composite PCM was observed, the phase change temperature of the RT20/MMT composite PCM still remains in the suitable temperature range for building applications. Furthermore, the latent heat of the RT20/MMT composite PCM was larger than that of the BS/MMT composite PCM. It was revealed that, among the three kinds of MMT based composite PCMs, the RT20/MMT composite PCM was the best candidate for building applications owing to its large latent heat and suitable phase change temperature. Moreover, it can be seen from Fig. 3c that the latent heat value of the RT20/MMT composite PCM with 40% RT20 was almost equivalent to the calculated value based on the mass ratio of RT20 in the composite.

3.2.2. Performance stability of the RT20/MMT composite PCM

Considering that the latent heat value of the RT20/MMT composite PCM would increase with the mass ratio of RT20, the RT20/MMT composite PCM with 60% RT20
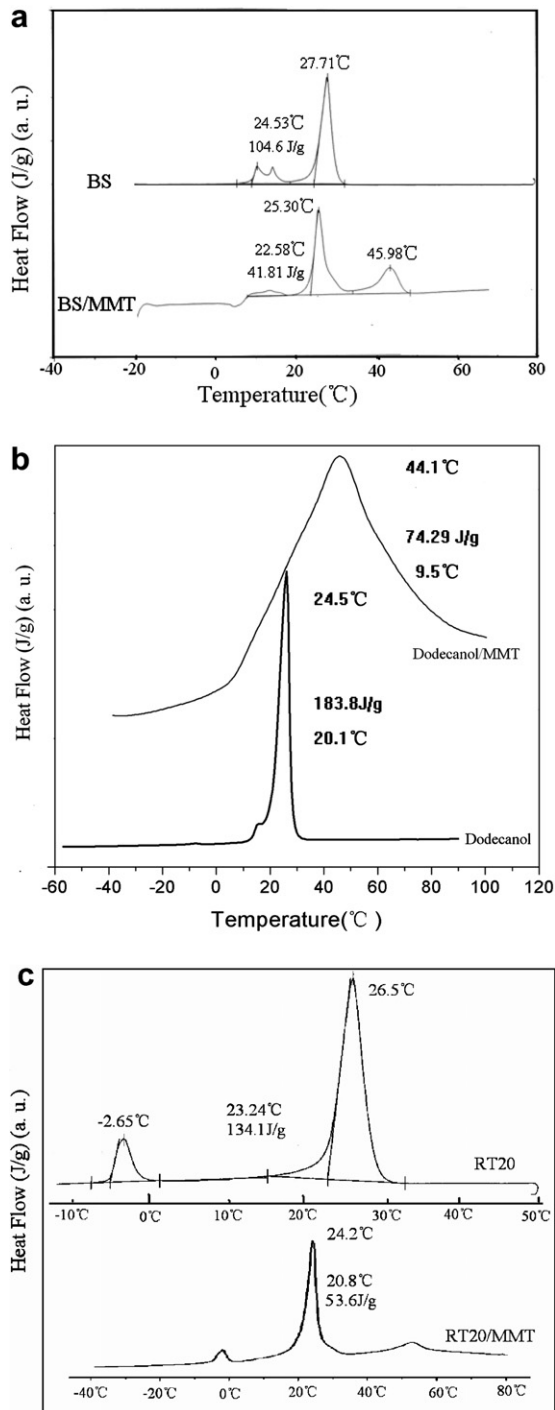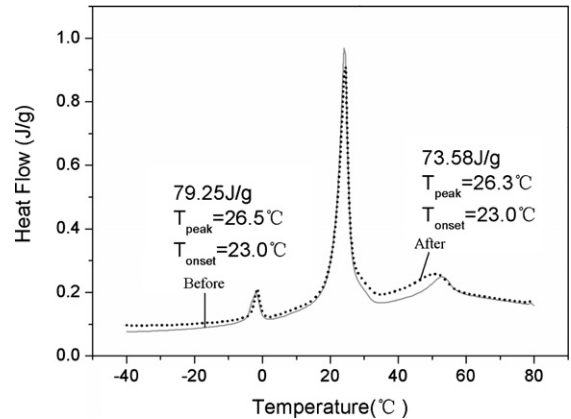
Fig. 4. The DSC curves of the RT20/montmorillonite composite PCM with 60% of RT20 before and after experienced 1500 times heating–cooling cycles test.

and after experiencing 1500 heating–cooling cycles, and only a slight reduction in the latent heat from 79.25 J/g before the test to 73.58 J/g after the test was observed. It was suggested that the RT20/montmorillonite composite PCM with 60% of RT20 exhibited good performance stability. It is known that montmorillonite has a large surface area (ca. 800 m^2/g), and is an excellent absorbent for some organic compounds [17]. In the RT20/MMT composite PCM, RT20 was absorbed by the Org-MMT, which could effectively prevent liquid leakage of RT20 when it changed phase from solid state to liquid state.

3.2.3. Comparison on thermal storage and release rates of RT20 and the RT20/MMT composite PCM

Thermal storage and release rates are important properties of PCMs. It is known that organic compounds suffer from poor heat conductivity, which may deteriorate the heat transfer efficiencies of thermal storage systems [18]. Fig. 5 shows the heating and cooling curves of RT20 and the RT20/MMT composite PCM. It can be seen from Fig. 5a that, during heating, after the phase change from solid state to liquid state was completed, it took 420 s for RT20 to raise its temperature from 20 °C to 29 °C, whereas it took only 220 s for the RT20/MMT composite PCM. From Fig. 5b, it can be seen that, during cooling, after the phase change from liquid state to solid state is completed, it took 720 s for RT20 to drop its temperature from 30 °C to 21 °C, whereas it took only 350 s for the RT20/ montmorillonite composite. These results indicate that the heat storage and release rates of the RT20/MMT composite PCM were obviously higher than those of RT20. Montmorillonite is an inorganic non-metallic mineral with heat conductivity larger than that of organic compounds. It was reasonable that the conductivity of the RT20/MMT composite PCM was larger than that of RT20 due to the combination with montmorillonite. When the RT20/ MMT composite PCM changed phase, since the heat transfer rate in the phase change process was controlled by heat conduction, the RT20/MMT composite PCM exhibited
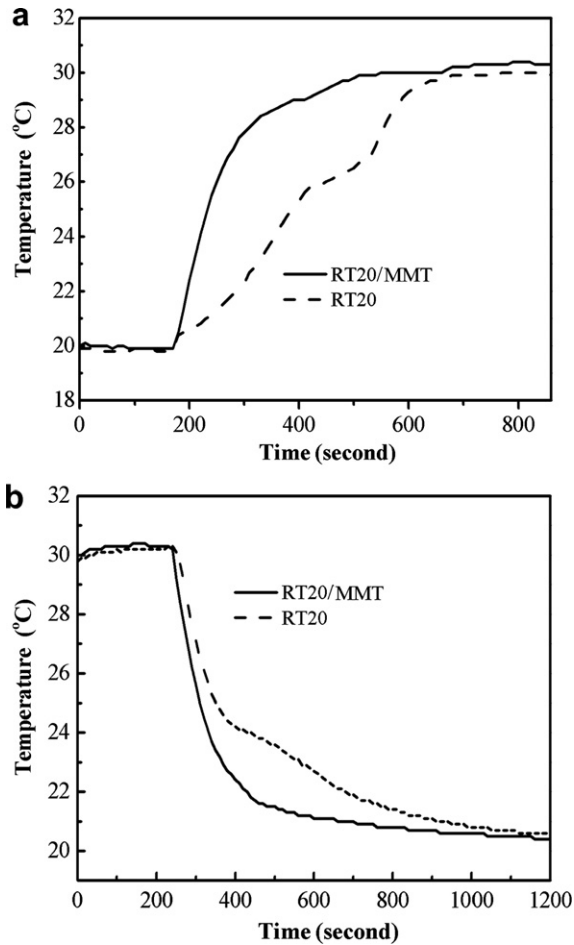

Fig. 3. The DSC curves of the three organic PCMs and their corresponding montmorillonite ased composite PCMs. (a) Butyl stearate; (b) dodecanol; (c) RT20.

was prepared. In order to examine the performance stability of the RT20/MMT composite PCM, the composite PCM was allowed continuously to experience 1500 heating–cooling cycles. The DSC curves of the RT20/MMT composite PCM with 60% RT20 before and after experiencing 1500 heating–cooling cycles are displayed in Fig. 4. It can be seen that the phase change temperature of the composite PCM experienced little change before

Fig. 5. Heating and cooling curves of RT20 and the RT20/montmoril-lonite composite PCM. (a) Heating curve; (b) Cooling curve.
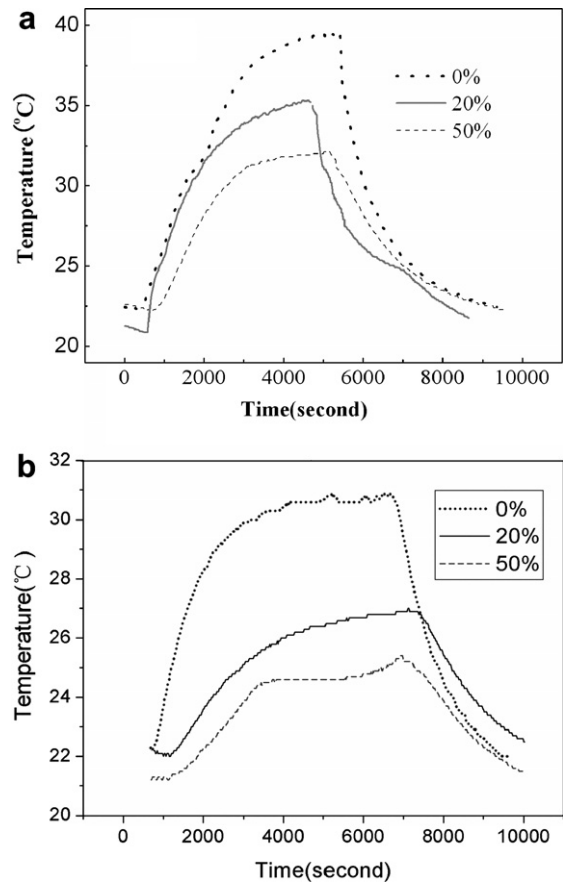

Fig. 6. The indoor temperature variations of the three test rooms with different top boards at different distances between the lamp and the top boards. (a) 30 cm; (b) 45 cm.

higher heat transfer efficiency owing to its large conductivity, as compared with RT20. It was revealed that the combination of organic PCMs with MMT is an effective route to improve the thermal conductivities of organic PCMs.

3.3. Thermal storage performances of novel composite gypsum boards

It was observed that the composite gypsum boards prepared using the RT20/MMT composite PCM and gypsum powders exhibited enough mechanical properties, suggesting that the montmorillonite-based composite PCM had good compatibility with gypsum powders. Fig. 6 shows the indoor temperature variations of the test rooms with different top boards at different distances between the lamp and the top board. It can be seen from Fig. 6a that, when the lamp was fixed at a distance of 30 cm over the top boards of the test rooms, the rising rates of the indoor temperatures in the three curves were almost the same at the initial stage of irradiation; however, after the time exceeded 2500 s, the rising rates of the indoor temperatures in the three curves were distinct: the indoor temperature rapidly increased for the test room with an ordinary gypsum board

as the top board, slowly climbed for the test room with the composite gypsum board containing 20% of the RT20/MMT composite PCM as the top board and showed little change for the test room with the composite gypsum board containing 50% of the composite PCM as the top board. As a consequence, the test rooms with different top boards reached different peak temperatures: 40 °C for the ordinary top board, ca. 35 °C for the top board containing 20% of the RT20/MMT composite PCM and ca. 31 °C for the top board containing 50% of the RT20/MMT composite PCM. It was indicated that the indoor temperature variation of the test room was reduced with the increase in the mass ratio of the RT20/MMT composite PCM in the top board. It can be seen from Fig. 6b that, when the lamp was fixed at a distance of 45 cm over the top boards, the test rooms with different top boards also reached different peak temperatures: 31 °C for the ordinary gypsum board, ca. 27 °C for the top board containing 20% of the RT20/MMT composite PCM and ca. 24 °C for the top board containing 50% of the RT20/MMT composite PCM. It was indicated that, although the indoor temperature of the test room declined with the increase in the distance between the lamp and the top board of the test room, the indoor temperature variation of the test room still was

reduced with the increase in the mass ratio of the RT20/MMT composite PCM in the top board. It was revealed that the novel composite gypsum boards containing the RT20/MMT composite PCM had a function of reducing energy consumption by reducing the indoor temperature variation, and the function is enhanced with the increase in the mass ratio of the RT20/MMT composite PCM.

4. Conclusions

After Na-MMT was organically modified, the interlayer platelet spacing of the MMT was enlarged from 1.4572 nm to1.9028 nm. Compared with the BS/MMT composite PCM and the dodecanol/MMT composite PCM, the RT20/MMT composite PCM was a good candidate for building applications due to its large latent heat, suitable phase change temperature and good performance stability. Compared with RT20, the RT20/MMT composite PCM exhibited higher heat transfer efficiency and had good compatibility with gypsum owing to the combination with montmorillonite. The novel composite gypsum boards containing the RT20/MMT composite PCM had a function of reducing energy consumption by reducing the indoor temperature variation, and the function is enhanced with the increase in the mass ratio of the RT20/MMT composite PCM.

Acknowledgements

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