Synthesis of shape-stabilized paraffin/silicon dioxide composites as phase change material for thermal energy storage

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Abstract The shape-stabilized paraffin/silicon dioxide (SiO$_2$) composite phase change materials (PCM) were prepared by using sol–gel methods. Paraffin was used as the PCM, and silicon dioxide was acted as the supporting material. Fourier transformation infrared spectroscope (FT-IR) and scanning electronic microscope were used to determine the FT-IR spectra and microstructure of shape-stabilized paraffin/silicon dioxide composite PCM, respectively. The thermal properties and thermal stability were investigated by a differential scanning calorimeter and a thermogravimetric analysis, respectively. The SEM analysis showed that the paraffin was well dispersed into the porous network of silicon dioxide. DSC analysis indicated that the mass content of paraffin in silicon dioxide was up to 92.1%, and paraffin/silicon dioxide composites had solidifying temperature of 57.07 °C, solidifying latent heat of 59.66 kJ/kg, melting temperature of 58.10 °C, and melting latent heat of 139.59 kJ/kg.

Introduction

Thermal energy storage (TES) plays an important role in conserving available energy and improving its utilization due to the discrepancy between energy supply and demand can be overcome by implementation of a proper energy storage system. Among the various TES methods (sensible, latent, and thermochemical), the latent TES employing a phase change material (PCM) is the most effective way of the TES due to its advantages of high energy storage density and its isothermal operating characteristics [1–3].

PCMs which can absorb/release high latent heat during the melting/solidifying process, have been receiving attention for different applications such as waste heat recovery [4, 5], solar heating system [6–9], and building energy conservation [10–12] in recent years. Many inorganic and organic PCMs (salt hydrates, fatty acids/esters, paraffins, etc.) and PCM mixtures have been studied for latent heat storage application [13, 14]. Among the investigated PCMs, paraffin has been widely used due to their high latent heat storage capacity and proper thermal properties such as little or no supercooling, low vapor pressure, good thermal and chemical stability, and self-nucleating behavior [15–17]. However, it also has undesirable properties, such as low thermal conductivity and need encapsulation for preventing leakage of melted PCM during phase change process, which results in extra thermal resistance and cost [18]. Now, these problems can be solved using shape-stabilized or form-stable PCM composites which can be prepared by encapsulation of PCM into a polymeric structure such as high-density polyethylene (HDPE) [19–21] and styrene–butadiene–styrene (SBS) copolymer [22, 23]. In addition, the expanded graphite can also act as supporting materials of the form-stable PCM composites [24, 25]. However, due to the chemical constitutions of organic PCMs (paraffins, etc.) and organic-polymer-supporting materials (HDPE, SBS and so on), the form-stable PCMs is easily flammable, which has severely restricted the wide applications [26].

In this article, it is reported that the synthesis of shape-stabilized paraffin/silicon dioxide composites as PCM. In

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Table 1 DSC data of paraffin, PCM1, PCM2, and PCM3

Sample name	Melting			Solidifying			PCM content ratio (%)
	Onset temperature (°C)	Peak temperature (°C)	Latent heat of fusion (kJ/kg)	Onset temperature (°C)	Peak temperature (°C)	Latent heat of fusion (kJ/kg)	
Paraffin	50.97	58.52	151.56	58.37	56.18	−144.62	100.0
PCM1	51.42	56.85	35.05	58.62	57.07	−27.70	23.2
PCM2	51.57	57.80	35.80	59.55	56.85	−32.51	23.6
PCM3	50.20	58.10	139.59	58.00	57.07	−59.66	92.1

this new composite material, paraffin was used as the latent heat storage PCM and silicon dioxide was served as the inorganic supporting material, which provided structural strength and prevented the leakage of the melted paraffin. Paraffin which melts at 50.97 °C with a latent heat storage capacity of 151.56 kJ/kg (experimental data of paraffin in Table 1) is a favorable organic PCM for TES. The silicon dioxide is inorganic multiple porous material, which has no flammability. So the latent heat of this shape-stabilized composite PCM can be utilized during the thermal energy charging and discharging cycles in the waste heat recovery and solar heating systems.

Experiments

Materials

Tetraethyl silicate (Reagent grade, Sinopharm Chemical Reagent Company) was used as the precursor. Paraffin (Reagent grade, Nanjing Huakang Chemical Reagent Company) was acted as latent heat storage PCM. Anhydrous ethanol (Reagent grade, Nanjing Chemical Reagent Company) and distilled water were served as solvent. Hydrochloric acid (Reagent grade, Nanjing Chemical Reagent Company) was used as activator.

Preparation of shape-stabilized paraffin/silicon dioxide composite PCM

20-g tetraethyl silicate, 20-g anhydrous ethanol, and 35-g distilled water were added into a 250-ml flask. The pH of the mixture was adjusted to 2–3 by dropping a little hydrochloric acid, then the mixture was stirred at the rate of 500 rpm for 60 min and the temperature of the mixture was controlled at 60 °C by a constant temperature magnetic stirrer. After reaction of hydrolysis and polycondensation of tetraethyl silicate, the sol mixture was obtained.

During several experiments, 3-, 5-, and 8-g melted paraffin were added into above sol mixture, respectively.

The mixture was stirred at the rate of 1000 rpm for 80 min and the temperature of the mixture was controlled at 70 °C to form composite PCM sol, then the composite PCM sol was dried in an oven at 70 °C for 2 h to obtain the composite PCM gel. In order to prepare shape-stabilized paraffin/silicon dioxide composite PCM, the composite PCM gel was dried again in a vacuum oven at 70 °C for 12 h. Finally, three kinds of shape-stabilized paraffin/silicon dioxide composite PCMs were obtained and named PCM1, PCM2, and PCM3, respectively.

Characterization of shape-stabilized paraffin/silicon dioxide composite PCM

The morphology and microstructure of the shape-stabilized paraffin/silicon dioxide composite PCM were observed through a scanning electronic microscopy (SEM, S-3400N II, Hitachi Inc, Japan). The structural analysis of shape-stabilized paraffin/silicon dioxide composite PCM was conducted using a FT-IR (FTIR Spectra was recorded on a Nicolet Nexus 870 from 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1} at room temperature on a KBr pellet.) spectrophotometer. The thermal properties of the shape-stabilized paraffin/silicon dioxide composite PCM were obtained using a differential scanning calorimeter (Pyris 1 DSC, Perkin–Elmer) at 5 °C/min under a constant stream of argon at flow rate of 20 mL/min, the accuracy of enthalpy was ±5% and the accuracy of temperature was ±0.2 °C. The thermal stability of the shape-stabilized paraffin/silicon dioxide composite PCM was determined by thermogravimetric analysis (Pyris 1 TGA, Perkin–Elmer) under a constant stream of nitrogen at flow rate of 20 mL/min, heated from room temperature to 65 °C in 3 min and kept at 65 °C for 30 min. The working temperatures of this shape-stabilized paraffin/silicon dioxide composite PCM are usually between 50 and 60 °C for TES, which is higher than the melting temperature of paraffin, so in the TGA experiments, the samples are heated from room temperature to 65 °C and kept at 65 °C for 30 min to determine their thermal stability.
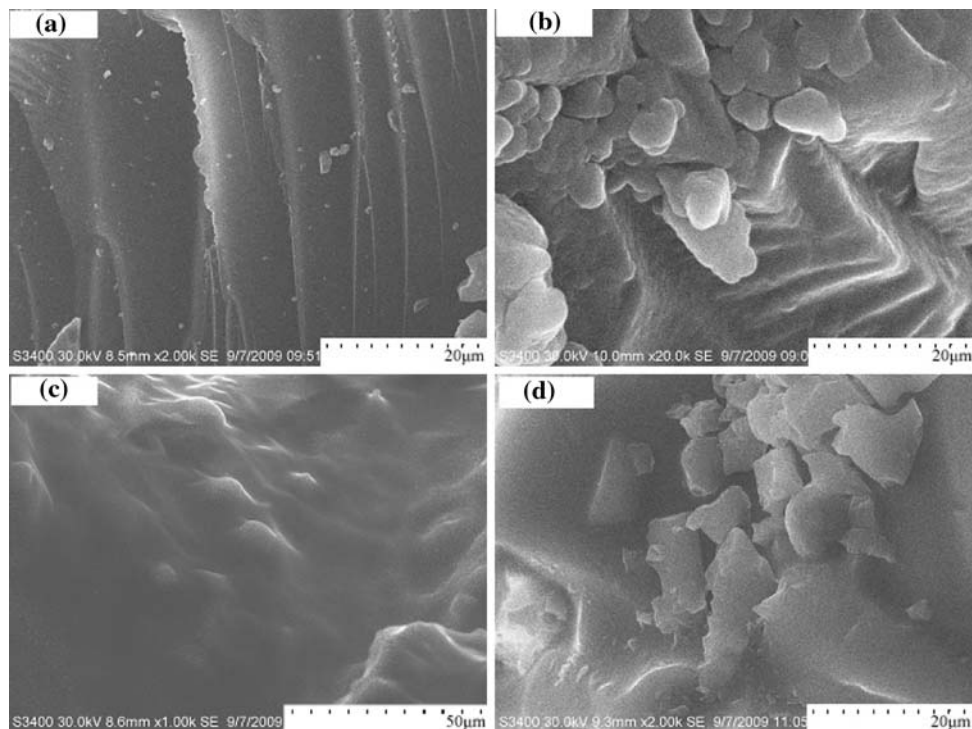
Results and discussion

FT-IR analysis of shape-stabilized paraffin/silicon dioxide composite PCM

The FTIR spectra of the paraffin, SiO_2, and PCM3 are shown in Fig. 1. Figure 1a shows the spectrum of paraffin. The peaks at 2917 and 2849 cm^{-1} signify the stretching vibration of C–H, the peaks at around 1463 cm^{-1} belong to the deformation vibration of –CH_2 and –CH_3, and the peak
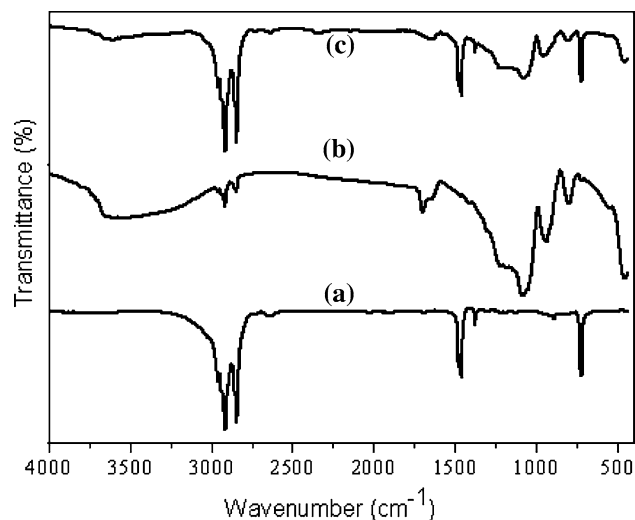
Fig. 1 FT-IR spectra of the (*a*) paraffin, (*b*) SiO_2, and (*c*) PCM3

at 719 cm^{-1} represents the rocking vibration of –CH_2. Figure 1b illustrates the spectrum of SiO_2. The peaks at 1083, 797, and 455 cm^{-1} signify bending vibration of functional group of Si–O. The function group of Si–OH is seen at 967 cm^{-1}. The absorption band at 3200–3600 cm^{-1} and 1650–1700 cm^{-1} represent, respectively, the stretching vibration and bending vibration of functional group of –OH of H_2O, which was adsorbed into the pores of SiO_2. The peaks at 2917 and 2849 cm^{-1} signify the stretching vibration of –CH_3 and –CH_2 group, respectively.

It is observed in Fig. 1c that the absorption peaks of paraffin at 2917, 2849, 1463, and 719 cm^{-1} also appear in the PCM3 spectra, which confirm that the paraffin was dispersed into the network of solid SiO_2. As can be seen in Fig. 1c, there is no shift in the absorption peaks of paraffin/SiO_2 composites when compared with the spectrum of SiO_2. This result indicates that there is no chemical interaction between the functional groups of paraffin and SiO_2. The paraffin was retained easily into the pores of SiO_2 by capillary and surface tension forces [27] and so leakage of the melted paraffin from the composites was prevented.

Microstructure of shape-stabilized paraffin/silicon dioxide composite PCM

Figure 2 shows SEM photographs of the silicon dioxide, PCM1, PCM2, and PCM3. It can be observed in Fig. 2a that silicon dioxide has rough and accidental microstructure. Figure 2b, c, and d present that paraffin were embed

Fig. 2 SEM photographs of the **a** silicon dioxide, **b** PCM1, **c** PCM2, and **d** PCM3

and dispersed into the network of solid silicon dioxide, respectively. In the photographs, the white and black parts represent the paraffin and silicon dioxide in the composite PCMs as can be seen in Fig. 2b–d. The multiple porous structure of silicon dioxide provided a mechanical strength to the whole compound and prevented the seepage of the melted paraffin due to the effect of capillary force and surface tension force of silicon dioxide porous network.

The maximum mass percentage of paraffin dispersed into the composites was determined as 92.1 wt%. There was no leakage of the paraffin from the composites up to this mass ratio even when it melts.

Thermal properties of shape-stabilized paraffin/silicon dioxide composite PCM

The DSC results of paraffin, PCM1, PCM2, and PCM3 are presented in Figs. 3, 4, and Table 1. Comparing the latent heat data of shape-stabilized composites with that of pure paraffin, the PCM mass ratio could be determined by Eq. 1. The η is the mass ration of the PCM in the composites, ΔH_{PCM} represents the latent heat of fusion of shape-stabilized composites, and ΔH_{PA} represents the latent heat of fusion of paraffin measured by the DSC.

$$\eta = \frac{\Delta H_{PCM}}{\Delta H_{PA}} \times 100\% \tag{1}$$

As shown in Table 1, paraffin is used as PCM for TES. PCM1, PCM2, and PCM3 in Table 1 represent, respectively, shape-stabilized composites prepared, which 3-, 5-, and 8-g melted paraffin were added into the sol mixtures in preparation process. When increasing the PCM mass from 3, 5 to 8 g, the mass ration of the PCM in the composites increases from 23.2, 23.6 to 92.1%. For shape-stabilized
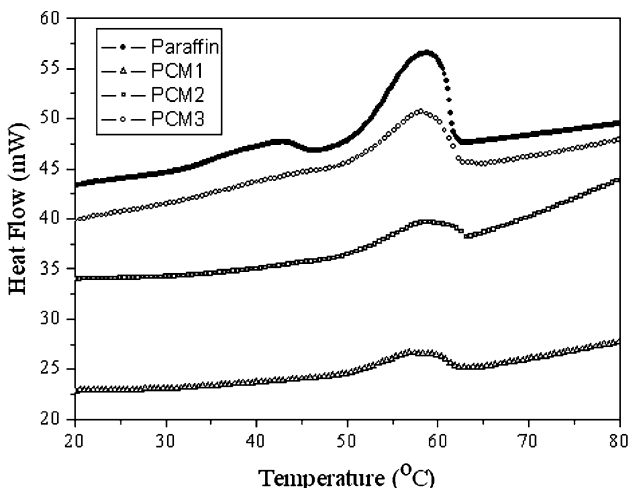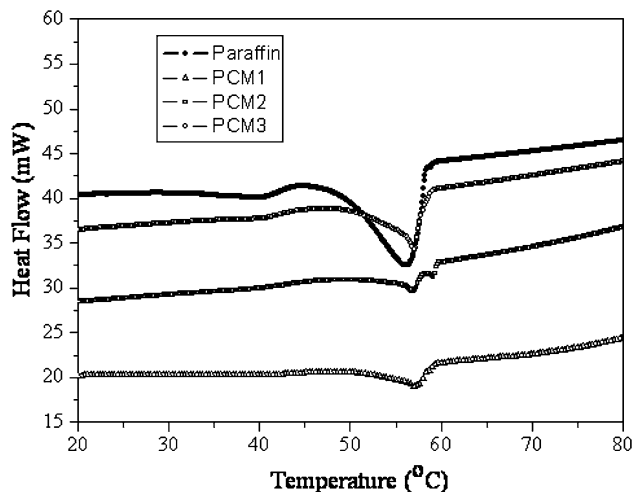

Fig. 4 The solidifying DSC curves of paraffin, PCM1, PCM2, and PCM3

composite PCMs, only the PCMs absorb/release thermal energy during the melting/solidifying process, so high PCM content will result in a high latent heat storage capacity. It is known that the melting latent heat of PCM3 is 139.59 kJ/kg and larger than that of PCM1 and PCM2.

Thermal stability of shape-stabilized paraffin/silicon dioxide composite PCM

The TG curves of PCM1, PCM2, and PCM3 are illustrated in Fig. 5. It is observed that the variations of weight loss rate in PCM1, PCM2, and PCM3 are faster during initial 5 min due to water vapor evaporated, which was adsorbed into the pores of SiO_2, and then the weight loss rates are nearly invariable, which indicates water vapor in the pores of SiO_2 has been eliminated. As can be indicated in Fig. 5,

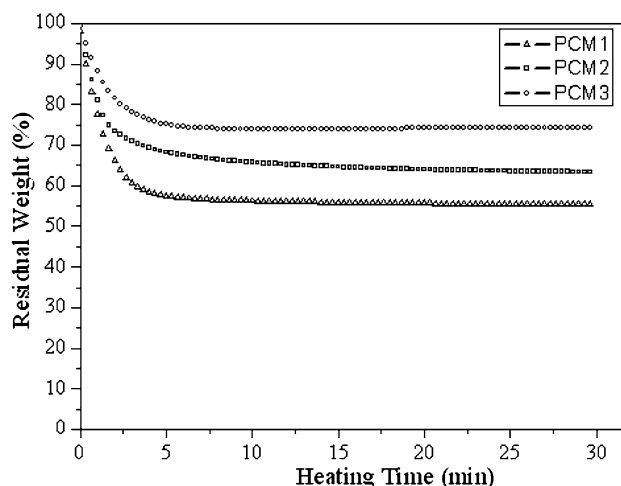Fig. 3 The melting DSC curves of paraffin, PCM1, PCM2, and PCM3

Fig. 5 TG curves of PCM1, PCM2, and PCM3

the weight loss rates of PCM1, PCM2, and PCM3 are 42.72, 35.62, and 25.13%, respectively. The weight loss rates of PCM1 and PCM2 are larger than that of PCM3 owing to the PCM contents in PCM1 and PCM2 are smaller than that of PCM3, so much more water molecules from ambience was adsorbed into the pores of SiO_2.

Conclusion

The preparation and characterization of shape-stabilized paraffin/SiO_2 composites are demonstrated, paraffin is used as the PCM and SiO_2 is used as the supporting material. The mass content of paraffin in SiO_2 is up to 92.1%. The paraffin/SiO_2 composites have the solidifying temperature of 57.07 °C and solidifying latent heat of 59.66 kJ/kg, and the melting temperature of 58.10 °C, and melting latent heat of 139.59 kJ/kg. The paraffin is well dispersed into the porous network of SiO_2 by capillary and surface tension forces and so leakage of the melted paraffin from the composites is prevented. The shape-stabilized paraffin/SiO_2 composites have better thermal stability after water in the pores of SiO_2 is eliminated. This method can also be utilized to disperse many other organic PCMs into SiO_2 for different TES applications.

References

1. Akgun M, Aydın O, Kaygusuz K (2008) Appl Therm Eng 28:405
2. Zalba B, Marin JM, Cabeza LF, Mehling H (2003) Appl Therm Eng 23:251
3. Felix Regin A, Solanki SC, Saini JS (2008) Renew Sustain Energy Rev 12:2438
4. Yagi J, Akiyama T (1995) J Mater Process Technol 48:793
5. Azpiazu MN, Morquillas JM, Vazquez A (2003) Appl Therm Eng 23:733
6. Sharma A, Tyagi VV, Chen CR, Buddhi D (2009) Renew Sustain Energy Rev 13:318
7. Shukla A, Buddhi D, Sawhney RL (2009) Renew Sustain Energy Rev 13:2119
8. Saman W, Bruno F, Halawa E (2005) Sol Energy 78:341
9. Hammou ZA, Lacroix M (2006) Energy Convers Manag 47:273
10. Tyagi VV, Buddhi D (2007) Renew Sustain Energy Rev 11:1146
11. Dincer I (2002) Energy Build 34:377
12. Zhang YP, Zhou GB, Lin KP, Zhang QL, Di HF (2007) Build Environ 42:2197
13. Hasnain SM (1998) Energy Convers Manag 39:1127
14. Kenisarin M, Mahkamov K (2007) Renew Sustain Energy Rev 11:1913
15. Cho K, Choi SH (2000) Int J Heat Mass Transf 43:3183
16. He B, Setterwall F (2002) Energy Convers Manag 43:1709
17. Trp A (2005) Sol Energy 79:648
18. Liu X, Liu H, Wang S, Zhang L, Cheng H (2006) Energy Convers Manag 47:2515
19. Inaba H, Tu P (1997) Heat Mass Transf 32:307
20. Ye H, Ge XS (2000) Sol Energy Mater Sol Cells 64:37
21. Sari A (2004) Energy Convers Manag 45:2033
22. Xiao M, Feng B, Gong KC (2002) Energy Convers Manag 43:103
23. Zhang YP, Lin KP, Yang R, Ding HF, Jiang Y (2006) Energy Build 38:1262
24. Zhang ZG, Fang XM (2006) Energy Convers Manag 47:303
25. Sari A, Karaipekli A (2007) Appl Therm Eng 27:1271
26. Cai YB, Wei QF, Huang FL, Lin SL, Chen F, Gao WD (2009) Renew Energy 34:2117
27. Wang WL, Yang XX, Fang YT, Ding J (2009) Appl Energy 86:170