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Synthesis and properties of microencapsulated paraffin composites with SiO_2 shell as thermal energy storage materials

Guiyin Fang[a,*], Zhi Chen[a], Hui Li[b]

[a] School of Physics, Nanjing University, Hankou Road 22, Nanjing 210093, Jiangsu, China
[b] Department of Material Science and Engineering, Nanjing University, Nanjing 210093, China

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ABSTRACT

Microencapsulated paraffin composites with SiO_2 shell as thermal energy storage materials were prepared using sol–gel methods. In the microencapsulated composites, paraffin was used as the core material that is a phase change material (PCM), and SiO_2 acted as the shell material that is fire resistant. Fourier transformation infrared spectroscope (FT-IR), X-ray diffractometer (XRD) and scanning electronic microscope (SEM) were used to determine chemical structure, crystalloid phase and microstructure of microencapsulated paraffin composites with SiO_2 shell, respectively. The thermal properties were investigated by a differential scanning calorimeter (DSC). The thermal stability was determined by a thermogravimetric analyzer (TGA). The SEM results showed that the paraffin was well encapsulated in the shell of SiO_2. The DSC results indicated that the microencapsulated paraffin composites solidify at 58.27 °C with a latent heat of 107.05 kJ/kg and melt at 58.37 °C with a latent heat of 165.68 kJ/kg when the encapsulation ratio of the paraffin is 87.5%. The TGA results showed that the SiO_2 shells can improve the thermal stability of the microencapsulated paraffin composites due to the synergistic effect between the paraffin and SiO_2.

1. Introduction

Phase change materials (PCMs) have received attention in solar heating system [1,2], building energy conservation [3,4] and air-conditioning systems [5,6]. PCMs are developed for various applications due to their different phase change intervals: materials that melt below 15 °C are used for keeping coolness in air-conditioning applications, while materials that melt above 90 °C are used to drop the temperature if there is a sudden increase in heat to avoid ignition. All other materials that melt between these two temperatures can be applied in solar heating and building energy conservation systems. Many inorganic and organic PCMs (salt hydrates, paraffins, fatty acids/esters, etc.) and PCM mixtures have been studied for latent heat storage application [7,8]. Among the PCMs investigated, paraffins have been widely used due to their high latent heat storage capacity and appropriate thermal properties, such as little or no supercooling, low vapor pressure, good thermal and chemical stability, and self-nucleating behavior [9]. However, they have low thermal conductivity, and need encapsulation in order to prevent leakage of the melted PCM during the phase change process [10]. Now, these problems can be solved by using microencapsulated PCMs. Microencapsulated PCMs (MEPCMs) can greatly increase the heat transfer efficient, enlarge the heat transfer area, reduce PCM reactivity towards the outside environment and control the changes in the volume as phase change occurs [11,12]. Various methods have been developed for the encapsulation of PCMs, such as complex coacervation [13], interfacial polycondensation [14] and *in situ* polymerization [15].

A typical microencapsulation process is the one which uses formaldehyde resins for the protection of PCMs, like melamine–formaldehyde resins [16–18] and urea–formaldehyde resins [19–21]. However, melamine–formaldehyde and urea–formaldehyde resins shell materials usually release poisonous formaldehyde in the application, which can cause environmental and health problems. In addition, due to the chemical constitution of organic PCMs (paraffins, fatty acids/esters, etc.) and organic polymer shell materials, the microencapsulated PCMs are easily flammable, and their application is therefore severely restricted [22].

In this paper, the synthesis and properties of microencapsulated paraffin composites with SiO_2 shell are reported. In the microencapsulated composites, paraffin was used as the latent heat storage material, and SiO_2 served as the inorganic shell material. The paraffin is a favorable organic PCM for thermal energy storage, melting at 59.26 °C with a latent heat of 189.24 kJ/kg and solidifying at 54.75 °C with a latent heat of 193.73 kJ/kg (experimental data of the paraffin in Table 2). SiO_2 is an inorganic amorphous material that is fire resistant [23,24].

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[*] Corresponding author. Tel.: +86 25 51788228; fax: +86 25 83593707.
E-mail address: gyfang@nju.edu.cn (G. Fang).

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Table 1
The compositions of the paraffin and SDS in the oil/water emulsion.

Samples	Compositions
MEPCM1	10 g paraffin + 100 ml distilled water + 0.2 g SDS
MEPCM2	15 g paraffin + 150 ml distilled water + 0.3 g SDS
MEPCM3	20 g paraffin + 200 ml distilled water + 0.4 g SDS

It is known from the above literatures that the encapsulation method of PCMs by sol–gel process is little reported. In addition, because organic PCMs (paraffin, etc.) with organic polymer shell materials have flammability, they are not widely applied in thermal energy storage system. In this research, the SiO_2 shells can improve the thermal stability and flammability of the microencapsulated paraffin composites due to the synergistic effect between the paraffin and SiO_2. Therefore, the latent heat of microencapsulated paraffin composites with SiO_2 shell can be utilized for thermal energy storage in solar heating and building energy conservation systems.

2. Experimental

2.1. Materials

Tetraethyl silicate (Reagent grade, Sinopharm Chemical Reagent Company) was used as the precursor. Anhydrous ethanol (Reagent grade, Nanjing Chemical Reagent Company) and distilled water acted as solvent. Hydrochloric acid (Reagent grade, Nanjing Chemical Reagent Company) was used as the activator. Paraffin (Reagent grade, Nanjing Huakang Chemical Reagent Company) was used as latent heat storage PCM. The paraffin is saturated alkanes (C_nH_{2n+2}) with melting point of 56–60 °C, melting latent heat of 189.24 kJ/kg, specific heat of 1.93 kJ/kg °C and density of 916 kg/m^3. Sodium dodecyl sulfate (SDS) (Reagent grade, Shanghai Chemical Reagent Company) was used as oil–water emulsifier.

2.2. Preparation of paraffin O/W emulsion

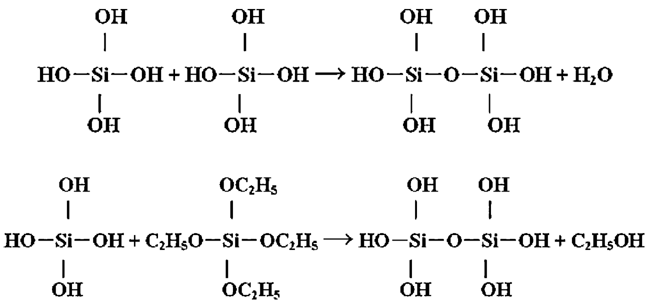
In one beaker, SDS was dissolved in distilled water. Then, paraffin was added into this solution and continuously stirred at a rate of 1000 rpm for 2 h with a magnetic stirrer while the temperature of the solution was controlled at 70 °C using a constant temperature bath. In order to form a stable oil/water emulsion and obtain a better performance of microencapsulated paraffin composites, different amounts of paraffin and SDS were chosen during preparation process. The compositions of the paraffin and SDS in the oil/water emulsion are listed in Table 1. Finally, the paraffin was uniformly dispersed in an aqueous solution containing SDS emulsifier to form a stable O/W microemulsion.

2.3. Preparation of microencapsulated paraffin composites with SiO_2 shell

20 g tetraethyl silicate, 20 g anhydrous ethanol and 40 g distilled water were added to another beaker. The pH of the mixture was adjusted to 2–3 by adding a little hydrochloric acid, the mixture was stirred at a rate of 500 rpm for 30 min with a magnetic stirrer while the temperature of the mixture was controlled at 60 °C using a constant temperature bath. After the hydrolysis reaction of the tetraethyl silicate had taken place, the sol solution as encapsulation precursor was obtained. The hydrolysis reaction mechanism of the tetraethyl silicate is shown in Scheme 1.

$$\mathrm{Si(OC_2H_5)_4 + H_2O \longrightarrow Si(OH)_4 + C_2H_5OH}$$

Scheme 1. The hydrolysis reaction mechanism of the tetraethyl silicate.



$$\mathrm{HO{-}\overset{OH}{\underset{OH}{Si}}{-}OH + HO{-}\overset{OH}{\underset{OH}{Si}}{-}OH \longrightarrow HO{-}\overset{OH}{\underset{OH}{Si}}{-}O{-}\overset{OH}{\underset{OH}{Si}}{-}OH + H_2O}$$

$$\mathrm{HO{-}\overset{OH}{\underset{OH}{Si}}{-}OH + C_2H_5O{-}\overset{OC_2H_5}{\underset{OC_2H_5}{Si}}{-}OC_2H_5 \longrightarrow HO{-}\overset{OH}{\underset{OH}{Si}}{-}O{-}\overset{OH}{\underset{OH}{Si}}{-}OH + C_2H_5OH}$$

Scheme 2. The condensation reaction mechanism of the tetraethyl silicate.

The sol solution was added dropwise into the prepared paraffin O/W emulsion with stirring at a rate of 500 rpm for 4 h using a magnetic stirrer whilst the temperature of the sol solution was controlled at 70 °C using a constant temperature bath. The condensation reaction mechanism of the tetraethyl silicate onto the surface of paraffin droplet is shown in Scheme 2. In Scheme 2, the sol mixture was formed by condensation reactions of the silicic acid and silicic acid or the silicic acid and tetraethyl silicate. After the polymerization process of the sol mixture was completed, the SiO_2 shell was formed on the surface of paraffin droplet. The shell formation process of the SiO_2 is shown in Scheme 3. Finally, white powders were collected by filter paper at normal pressure and washed with distilled water. The microencapsulated composites were dried in a vacuum oven at 50 °C for 20 h. Three kinds of microencapsulated paraffin composites with SiO_2 shell were obtained after drying at 50 °C for 10 h, denoted MEPCM1, MEPCM2 and MEPCM3.

When the mass of distilled water in the solution increases, the hydrolysis process of the tetraethyl silicate can be promoted. However, the concentration of silicic acid may reduce, and the hydrolysis reaction of the silicic acid takes place again. This will prolong condensation reaction process of the tetraethyl silicate.

The hydrolysis reaction of the tetraethyl silicate is very slow at room temperature. In order to accelerate the hydrolysis process of the tetraethyl silicate, the temperature of the mixture was controlled at 60 °C using a constant temperature bath. When the pH of the mixture is 2–3, the sol solution is very steady. Therefore, the hydrochloric acid is added in the mixture to adjust the pH value of the solution.

2.4. Characterization of microencapsulated paraffin composites with SiO_2 shell

The morphology and microstructure of microencapsulated paraffin composites with SiO_2 shell were observed using a scanning electronic microscope (SEM, S-3400N II, Hitachi Inc., Japan). The structural analysis of the microencapsulated paraffin composites with SiO_2 shell was carried out using a FT-IR spectrophotometer. The FT-IR spectra were recorded on a Nicolet Nexus 870 from 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1} using KBr pellets. The crystalloid phase of the microencapsulated paraffin was investigated by XRD (D/MAX-Ultima III, Rigaku Corporation, Japan). The XRD patterns were obtained with continuous scanning mode at the rate of 5° (2θ)/min and operating conditions of 40 kV and 40 mA. The thermal properties of the microencapsulated paraffin composites with SiO_2 shell were measured using a differential scanning calorimeter (Pyris 1 DSC, Perkin-Elmer) at 5 °C/min under a constant stream of argon at a flow rate of 20 ml/min. The accuracy of

$$\mathrm{n\,(Si{-}O{-}Si) \longrightarrow ({-}Si{-}O{-}Si{-})_n}$$

Scheme 3. The shell formation process of the SiO_2.