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Preparation and characterization of novel nanoencapsulated phase change materials

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ABSTRACT

A kind of novel nanoencapsulated PCM with polystyrene as the shell and *n*-octadecane as the core was synthesized by the ultrasonic-assistant miniemulsion in-situ polymerization, and its morphology, structure and thermal properties were characterized by TEM, FT-IR, XRD, DSC and TG. The nanocapsules were regular spherical and ranged from 100 nm to 123 nm in size. All the characteristic peaks of *n*-octadecane and styrene were observed in the FT-IR spectrum of the nanoencapsulated PCM. The XRD result suggested that *n*-octadecane was encapsulated by the shell of polystyrene. The phase change temperature of the nanoencapsulated PCM was very closer to that of *n*-octadecane, and its latent heat was equivalent to that of the calculated value based on the mass ratio of *n*-octadecane measured by TG.

1. Introduction

Thermal energy storage (TES) is considered as one of the most important advanced energy technologies, and an increasing attention has been paid to utilization of the technique for thermal applications [1,2]. 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. Latent thermal energy storage based on the PCMs is the most important TES technology, which has very wide applications ranging from heating to cooling [3–5]. PCMs are usually classified into two categories: inorganic PCMs and organic PCMs. Although inorganic PCMs possess large latent heat, there are some problems inherent in organic PCMs, such as the need for special container due to their corrosiveness, tendency of super cooling, segregation, etc. Organic PCMs suffer from low conductivity, instability and liquid leakage. Therefore, encapsulation of PCMs is an effective solution for the above problems inherent in inorganic and organic PCMs.

In recent years, several kinds of microencapsulated PCMs prepared by in-situ polymerization, interface polymerization and coacervation, had been utilized in many fields including latent functionally thermal fluids, thermoregulating textiles, thermal storage building materials, etc. [6–14]. However, in some fields especially in latent functionally thermal fluids, microencapsulated PCMs had not well done under repeated cycling, because the large particles of the microencapsulated PCM not only increased the fluid's viscosity, but also were often crushed during pumping. Therefore, it is necessary to develop nanoencapsulated PCMs with smaller particle size as compared with microencapsulated PCMs.

Although the concept of nanocapsule was presented out by Narty in the 1970s and the nanocapsulation technology has been widely utilized in medicine dye and perfume [15–16], there is limited precedence for producing nanoencapsulated PCMs. Zhang et al [17] synthesized a kind of nanoencapsulated PCM by the in-situ polymerization, which melaming-formaldehyde resin was used as the shell, *n*-octadecane and cyclohexane as the core. However, the particle size of the nanoencapsulated PCM was as large as 770 nm. Miniemulsion polymerization was a convenient one-step encapsulation technique for preparing nanocapsules. Luo and Zhou [18] studied the nanoencapsulation of hydrophobic compounds by miniemulsion polymerization in terms of the thermodynamics and kinetics, and it was found that thermodynamic factors (the level and type of surfactant, the level of the hydrophilic comonomer, and the monomer/paraffin ratio), kinetic factors (the level of the crosslinking agent or chain-transfer agent), and nucleation modes all have a great influence on the latex morphology. Park et al. [19] prepared polystyrene (PS) nanoparticles containing paraffin wax as the PCM by miniemulsion polymerization. In the current work, a kind of nanoencapsulated PCM with polystyrene as the shell and *n*-octadecane as the core was synthesized by the ultrasonic-assistant miniemulsion in-situ polymerization. The morphology, structure and thermal properties of the nanoencapsulated PCM were characterized by TEM, FT-IR, XRD, DSC and TG.

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2. Experimental section

2.1. Materials

The materials used in the current work include styrene (Tianjin Damao Chemical Reagent Co. Inc., China), *n*-octadecane (Alfa Aesar Co. Inc., USA), butyl acrylate, 2,2-azobisisobutyronitrile (AIBN, from Tianjin Fuchen Chemical Reagent Co. Inc., China), poly-(ethylene glycol) monooctylphenyl ether (OP-10, from Shanghai Lingfeng Chemical Reagent Co. Inc., China), sodium dodecyl sulfate (SDS, from Guangdong Xilong Chemical Reagent Co. Inc., China) and *n*-dodecyl mercaptoan (DDM, from Guangzhou Chemical Reagent Co. Inc., China). The monomer styrene was washed three times with the 10 wt% NaOH solution and deionized water before used.

2.2. Preparation of nanoencapsulated PCM

The monomer mixture {St (10 g), BA (0.2 g), AIBN (0.1 g) and DDM (0.08 g)} was added to the melted *n*-octadecane (10 g) to obtain Mixture A. The composite surfactant (SDS/OP-10 = 1/1) was dispersed in water (120 g) to obtain Mixture B. Then, Mixture A was added to Mixture B to obtain a clear mixture. After being pre-emulsified by a homogenizer for 10 min, the mixture was sonificated with a sonifier (JYD-900, 75% amplitude) for 10 min while being cooled in an ice-bath. Finally, the miniemulsion obtained was put into a four-necked flask equipped with a stirrer and a condenser. Before the reaction began, the flask was purged with nitrogen for 0.5 h to remove oxygen. The reaction was carried out for 5 h under nitrogen atmosphere at 65 °C of the water bath temperature. After the reaction finished, the latex obtained was cooled at room temperature.

2.3. Characterization of nanoencapsulated PCM

The *z*-average diameter of the nanocapsules was measured by a particle size analyzer (Zetasizer nano S, MALVERN). Before measurement, the latex was diluted to 0.01 wt%. The TEM images of the nanocapsules were obtained using a transmission electron microscope (H-7500) at an accelerating voltage of 80 kV. XRD patterns of the samples were obtained using an X-ray diffractometer (D/max-IIIA, Japan). FT-IR spectra of octadecane, polystyrene and the nanoencapsulated PCM were obtained using a FT-IR spectrophotometer (Bruker TENSON 27, wave-numbers 400–4000 cm^{-1}) at room temperature. DSC measurements of the PCMs were carried out on a differential scanning calorimeter (model STA449C, NETZSCH) under N_2 atmosphere, and the scanning rate was 10 °C min^{-1}. The thermal stabilities of the dried nanocapsules were evaluated using a thermogravimetric analyzer (NETZSCH STA 449 C) under N_2 atmosphere, and the scanning rate was 10 °C min^{-1} in the temperature range of 25 °C to 700 °C. The solid samples were obtained by washing the nanocapsules with petroleum ether and deionized water for three times to remove the *n*-octadecane that had not been encapsulated.

3. Results and discussion

3.1. Particle size and morphology of the nanoencapsulated PCM

Fig. 1 displays the particle size distribution of the nanoencapsulated PCM. It can be seen that the particle size varied from 50 nm to 200 nm, exhibiting a narrow size distribution. The *z*-average particle size of the nanoencapsulated PCM was about 124 nm. The TEM image of the nanoencapsulated PCM is shown in Fig. 2. It can be seen that, most of the nanocapsules were regular spherical, and the core of *n*-octadecane (pale part) was located in the shell of styrene (dark part). The diameter of the nanocapsules ranged from 100 nm to 123 nm, consistent with the result from the particle size analyzer.

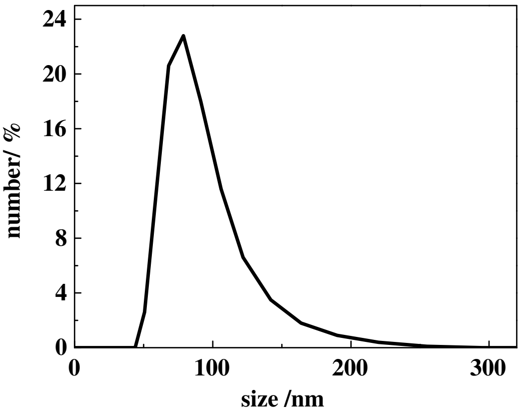

Fig. 1. Size distribution of the nanoencapsulated PCM.

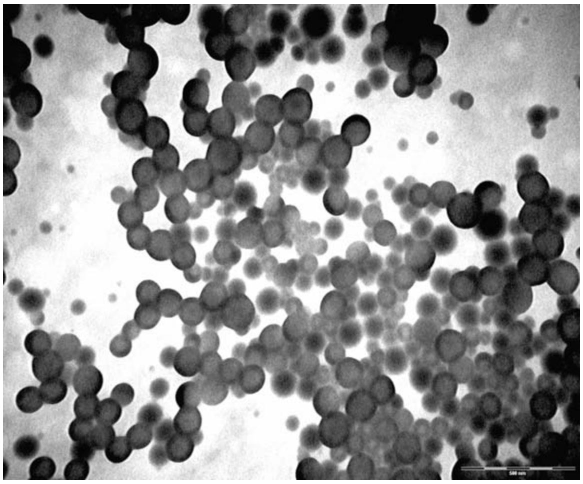

Fig. 2. TEM image of the nanoencapsulated PCM.

3.2. FT-IR analysis

The FT-IR spectra of *n*-octadecane, styrene and the nanoencapsulated PCM are displayed in Fig. 3. It can be seen from Fig. 3a that,

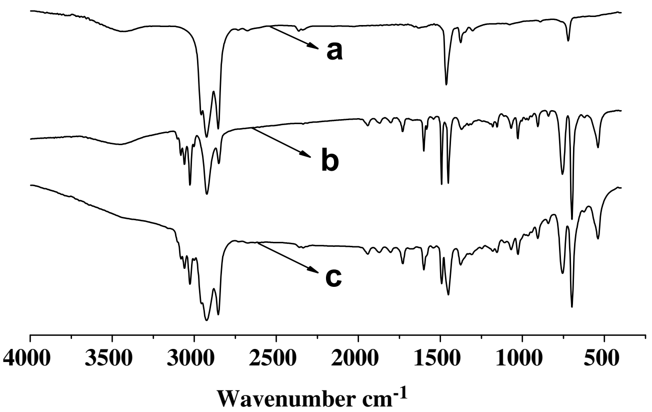

Fig. 3. FT-IR spectra of *n*-octadecane (a), polystyrene (b) and the nanoencapsulated PCM (c).