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Synthesis, characterization and thermal properties of novel nanoencapsulated phase change materials for thermal energy storage

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Abstract

In this paper, nanocapsules containing *n*-octadecane with an average 50 nm thick shell of poly(ethyl methacrylate) (PEMA) and poly (methyl methacrylate) (PMMA), and a core/shell weight ratio of 80/20 were synthesized by the direct miniemulsion method, respectively. The average size of the capsules is 140 nm and 119 nm, respectively. The chemical structure of the sample was analyzed using Fourier Transformed Infrared Spectroscopy (FTIR). Crystallography of nanocapsules was investigated by X-ray diffractometer. The surface morphology was studied by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The thermal properties and thermal stability of the sample were obtained from Differential Scanning Calorimeter (DSC) and Thermal Gravimetric Analysis (TGA). The temperatures and latent heats of melting and crystallizing of PEMA nanocapsule were determined as 32.7 and 29.8 °C, 198.5 and -197.1 kJ/kg, respectively. TGA analysis indicated that PEMA/octadecane nanocapsule had good thermal stability. The nanocapsules prepared in this work had a much higher encapsulation ratio (89.5%) and encapsulation efficiency (89.5%). Therefore, the findings of the work lead to the conclusion that the present work provides a novel method for fabricating nanoencapsulated phase change material, and it has a better potential for thermal energy storage. © 2012 Elsevier Ltd. All rights reserved.

Keywords: n-octadecane; PEMA; Nanocapsules; Miniemulsion; Thermal physical property

1. Introduction

Latent thermal energy storage using phase change materials (PCMs) is the most important thermal energy storage technology due to the PCMs can absorb or release a large amount of heat while undergoing phase changes, with small temperature variations. However, most organic PCMs have problems in low thermal conductivity, instability and flammability; and inorganic PCMs are corrosive to most metals and suffer from decomposition and sub-cooling. Therefore, encapsulation of PCMs is an attractive solution for above problems in both organic and inorganic PCMs.

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The encapsulation cannot only provide a space to control the volume changes during the phase change, but it can also protect PCMs from the outside environment in their applications.

In recent research, various kinds of microencapsulated phase change materials (MPCMs) have been fabricated by in situ polymerization (Li et al., 2007; Salaün and Vroman, 2008; Yu et al., 2009; Yuan et al., 2008), interface polymerization (Liang et al., 2009; Pascu et al., 2008; Zhang and Wang, 2009), suspension like polymerization (Chang et al., 2009; You et al., 2009) and other polymerization methods (Yuan et al., 2008; Zhang et al., 2007). Nevertheless, in some fields especially in latent functionally thermal fluids, MPCMs did not performance very well under repeated cycling due to the large particles of the MPCMs

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Nomenclature

d, D	diameter (m)	Greek letters	
ΔH_c	heat of crystallization (kJ/kg)	R	the encapsulation ratio (%)
ΔH_f	heat of fusion (kJ/kg)	Ε	the encapsulation efficiency (%)
k	Thermal conductivity (W/(m °C))		
T_m	melting temperature (°C)	Subscripts	
T_c	crystallizing temperature (°C)	С	nanocapsule core
		р	particle
		W	wall
$k T_m$	Thermal conductivity (W/(m °C)) melting temperature (°C)	Subscr c p	<i>ipts</i> nanocapsule core particle

not only increased the fluid's viscosity, but also were often crushed during pumping, and this would resulting the blocking of the pipe system (Fang et al., 2008). Therefore, there is a trend to develop nanoencapsulated PCMs with smaller particle size as compared with microencapsulated PCMs. In addition, nanocapsules have higher surface-area-to-volume ratio than microcapsules which provides a stronger "driving force" to speed up thermodynamic processes. In recent years, several kinds of nanoencapsulated PCMs synthesized by mini-emulsion polymerization method have been studied. Fang et al. (2008) fabricated a kind of nanocapsule with polystyrene as the shell and *n*-octadecane as the core. Sari et al. (2009) investigated the nanoencapsulation of *n*-octacosane with poly(methyl methacrylate) (PMMA) shell. They reported that the nanocapsule had energy storage and release capacity (86.4-88.5 kJ/kg) during its phase change. Less than 100 nm size nanocapsules of *n*-octadecane were prepared by Kwon et al. (2010). Alay et al. (2010) prepared PMMA/n-hexadecane nanocapsule as a fiber additive in textile application. Black et al. (2010) fabricated nanocapsules of *n*-hexadecane within a 4-40 nm thick shell of poly(alkyl methacrylate).

According to the literature review above, there is no work has been done on nanoencapsulated of *n*-octadecane by poly(ethyl methacrylate) (PEMA). Therefore, the aim of this work is to fabricate nanocapsules of *n*-octadecane with PEMA shell. Since PS is a rigid plastic and PMMA and PEMA are more softer (PEMA is softer than PMMA), it is suggesting that the soft shell material is favorable for the preparation of microcapsules (Yang et al., 2003). The chemical structure, morphology, diameter and its size distribution, thermal properties of the nanocapsules were obtained from experimental measurements.

2. Method and materials

2.1. Materials

N-octadecane, the methyl methacrylate monomers (MMA) and the ethyl methacrylate (EMA) monomers with a purity of 99 wt.% were purchased from Sigma–Aldrich, respectively. Sodium dodecyl sulphate (SDS) and 2,2-azob-isisobutyronitrile (AIBN) were commercially supplied by

VWR international Ltd., UK. All chemicals were of reagent quality and used without further purification.

2.2. Synthesis of nanocapsules

The PEMA/octadecane nanocapsules and the PMMA/ octadecane nanocapsules were synthesized by the direct mini-emulsion polymerization method. In one beaker, a stock of surfactant solution was prepared by dissolving 0.3 g of SDS in 30 g of deionised water. Then 2 g n-octadecane was added to 0.5 g monomer solution with the desired core/shell ratio: 80:20, and 5 mg of AIBN initiator per gram of monomer was added to the oil/monomer mixture. The mixture solution was added to the surfactant solution and stirred for 0.5 h at 40 °C. The solution was then sonicated with a tip sonicator (Branson Digital Sonifier) in a water bath at 70% amplitude for 3 min while the solution was gently stirred. Then the sonicated solution was poured into a 50 mL flask. The flask was sealed with a rubber septum, and the solution was stirred gently under nitrogen flow for 0.5 h at room temperature to remove oxygen. Polymerization was initiated by heating the solution with approximately 600 rpm stirring rate in an oil bath at 70 °C for 24 h to complete the process. The nanocapsules suspension was then dialyzed with dialysis tubing cellulose membrane in the deionised water (keep changing water once a day) for a week to remove any impurities, unreacted monomers and surfactant for characterization. The yield of polymerization reaction of PEMA and PMMA nanocapsules were 50.04% and 61.26%, respectively.

2.3. Characterization

Fourier Transform Infrared Spectra (FTIR) of the nanocapsules were obtained using an AVATAR-380 FTIR spectrophotometer with the KBr sampling method. XRD patterns of the samples were obtained using an X-ray diffractometer in the 2θ ranges from 10° to 50° (Philips 1820 diffractometer with 20 position sample changer). Morphologies were obtained by using a ZEISS SUPRA 55-VP Scanning Electron Microscopy (SEM), and a Jeol 2010F Transmission Electron Microscopy (TEM) at an accelerating voltage of 200 kV. Dynamic Light Scattering

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