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Nanoencapsulation of n-alkanes with poly(styrene-co-ethylacrylate) shells for thermal energy storage ☆

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HIGHLIGHTS

- Four series of nanocapsules containing n-alkanes were synthesized in poly(styrene-co-ethylacrylate).
- The emulsion co-polymerization technique was used.
- Influence of core:shell ratio on encapsulation and thermal properties reported.

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ABSTRACT

In this work, we synthesized a series of four nanocapsules containing n-alkanes (C_nH_{2n+2}), namely tetradecane, pentadecane, hexadecane, and heptadecane, in poly(styrene-co-ethylacrylate) using an emulsion copolymerization method. The nanocapsules were characterized according to their geometric profiles, phase transition temperatures, phase transition heats, mean particle sizes, and chemical stabilities by means of scanning electron microscopy, differential scanning calorimetry, thermal gravimetric analysis and Fourier transform infrared spectroscopy. Furthermore, we also focused on the effect of the core/shell mass ratio on the phase change properties of the nanocapsules. We found that microcapsules were synthesized successfully and that the best core/shell mass ratio was 3:1 for this study. These results indicate that encapsulated n-alkanes with poly(styrene-co-ethylacrylate) have an excellent potential for energy storage.

1. Introduction

In our world today, energy conservation is as important as energy production. For energy conservation, it is imperative to try new alternatives. Recently, the study of phase change materials (PCMs) and their applications for thermal energy storage has been an area of extensive research [1–5]. Furthermore, in order to increase the efficiency of thermal energy storage applications, we can use microencapsulated n-alkanes. n-Alkanes (C_nH_{2n+2}) are saturated aliphatic hydrocarbons and consist of $(CH_2)_n$ chains. Alkanes, which were used as core materials in this study, are appropriate for many thermal energy storage applications due to their suitable melting temperatures and they fact that they do not have toxic properties. Alkanes and their mixtures (paraffins) have been extensively used as phase change materials (PCMs) for thermal energy storage applications.

Microencapsulation can be defined as a process in which tiny particles or droplets are surrounded by a coating or embedded in a homogeneous or heterogeneous matrix. This process gives many useful properties to small capsules. Microencapsulation can provide a physical barrier between a core compound and other components of the products [6]. The main goal of microencapsulation of phase change materials is to produce active materials that are easy to synthesize, safer to handle, and possess improved thermal properties as a result of an increased heat transfer area [7].

Microencapsulation processes are usually categorized into two groups: chemical and physical. Physical methods mainly include spray drying or centrifugal and fluidized bed processes. Chemical processes mainly include interfacial polymerization, in situ polymerization, simple or complex coacervation, phase separation, suspension-like polymerization, and other fabrication methods.

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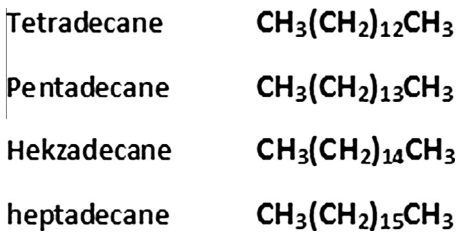
PCM microcapsules are primarily synthesized by chemical methods due to their properties and applications [8]. In recent years, there has been growing interest in the fabrication of microPCMs containing phase change materials using chemical processes [7,9–15]. Styrene-ethyl acrylate copolymer, which is used as a shell material in this study, is an acrylate polymer that is modified by styrene. In the last few years, styrene and styrene copolymers have been utilized in a wide range of experiments as shell materials for micro-nanocapsules. For example, paraffin wax, tetradecane, Rubitherm RT27, Rubitherm 20, and nonadecane were encapsulated with polystyrene using a suspension, free-radical polymerization process. The results revealed that polyethylene glycol (PEG) could not be encapsulated due to its hydrophilic nature. Microcapsules that are created with 50% (by weight) capsules are PCMs [16]. In another study, microcapsules of polystyrene with encapsulated paraffin wax and a narrow size distribution were prepared using a suspension-like polymerization process [17]. Paraffin wax was microencapsulated by Sanchez et al. based on a suspension-like polymerization method using a shell based on a copolymer of methyl methacrylate (MMA) and styrene (St). These authors found that an MMA/St ratio of 4 and a monomer to paraffin mass ratio of 3.0 gave rise to microcapsules with characteristics that are appropriate for industrial applications [18]. Hexadecane was microencapsulated with a narrow size distribution in a poly(styrene-co-N,N-dimethylaminoethyl methacrylate) shell by a Shirasu porous glass emulsification technique and a subsequent suspension polymerization process [19]. Otto et al. [20] two sets of copolymers comprised of styrene and either methyl or ethyl methacrylate as comonomer were conveniently synthesized by microemulsion copolymerization as drug-releasing films. Yang et al. [21] microencapsulated n tetradece with acrylonitrile-styrene copolymer and acrylonitrile-styrene-butadiene copolymer for obtain good mechanical properties and prevent the leakage of the core. Fang et al. [22] nanoencapsulated polystyrene/n-dotriacontane composite as phase change material for thermal energy storage. Nanocapsules were synthesized by a facile and time-saving ultrasonically initiated miniemulsion polymerization method. Based on our knowledge, among all available microencapsulation and nanoencapsulation studies, no study has been reported on the preparation of nanocapsules of n-alkanes with poly(styrene-co-ethylacrylate) (PScEA) shells. This work presents and discusses the micro-nanoencapsulation of n-alkanes in PScEA using an emulsion copolymerization method. The structure and thermal properties of the prepared nanoPCMs are characterized. Nanocapsules with different core/shell ratios were prepared to optimize a stable ratio with the greatest phase change enthalpy.

2. Experimental

2.1. Material

Tetradecane (99%, Merck, Germany), pentadecane (99%, Merck, Germany), hexadecane (99%, Alfa Aesar, Germany) and heptadecane (99%, Sigma Aldrich Company, USA) were used as core materials. All of them consist only of hydrogen and carbon atoms are shown in Fig. 1. Styrene (>99, Sigma Aldrich Company, USA) and ethyl acrylate, $C_5H_8O_2$, (>99, Meck, Germany) were used as shell material; ethylene glycol dimethacrylate, $C_{10}H_{14}O_4$, (Meck, Germany) was used as a crosslinking agent and it was distilled before use. The initiator of ammonium peroxodisulfate (Merck, Germany) and other analytical reagents such as; tert-butylhydroperoxide (70%, Merck, Germany), Triton X-100 (Merck, Germany), iron (II) sulfate 7-hydrate ($FeSO_4{\cdot}7H_2O$) (Panreac, Spain) and sodium thiosulfate ($Na_2O_3S_2$) (Merck, Germany) were used without further purification.



Tetradecane	$CH_3(CH_2)_{12}CH_3$
Pentadecane	$CH_3(CH_2)_{13}CH_3$
Hekzadecane	$CH_3(CH_2)_{14}CH_3$
heptadecane	$CH_3(CH_2)_{15}CH_3$

Fig. 1. Chemical composition of core materials.

2.2. Preparation of nanoencapsulated PCMs

In this study, an emulsion polymerization method was used to prepare the nanoPCMs. A typical emulsion polymerization method [10,14] includs the following nine steps:

Step 1: Preparation of the first phase, A1 (deionized water, core material, and surfactant).

Step 2: Stirring and heating, A1 was mixed in a glass reactor with a mechanical stirrer and heated until 40 °C.

Step 3: Preparation of the second phase, B1 (consisting of ethyl acrylate, a cross linker, and iron (II) sulfate 7-hydrate ($FeSO_4{\cdot}7H_2O$) and ammonium peroxodisulfate).

Step 4: Preparation of an emulsion: B1 was added to A1.

Step 5: After stirring for 20 min, C1 (sodium thiosulfate and tert-butylhydroperoxide) was added to A1 + B1.

Step 6: A1 + B1 + C1 was mixed until 4 h at 70–80 °C.

Step 7: The suspension of the emulsion was cooled to room temperature.

Step 8: When the emulsion cooled to room temperature, the suspension of microcapsules was left for 48 h in a water bath in order to obtain more stable microcapsules.

Step 9: Filtration, rinsing, and drying. The suspension was separated under vacuum with filter paper. The nanocapsules were rinsed with deionized water and dried for 72 h at room temperature. The reaction scheme of PScEA is shown in Fig. 2.

2.3. Analyses

2.3.1. Scanning electron microscope (SEM) observation

The particle size and the morphological features of nanocapsules were evaluated using a scanning electronic microscope (SEM, JEOL JSM-6400). The samples for SEM observation were prepared by coating a thin gold film in vacuum conditions.

2.3.2. Differential Scanning Calorimeter (DSC) analyses

The measurements were taken with a Perkin Elmer Diamond DSC Differential Scanning Calorimeter with IntraCooler and Pyris Software. Samples of about 5 mg in aluminum pans were heated from −30 °C to 60 °C at a heating rate of 10 °C/min.

Furthermore, PCM content in nanoPCMs was determined according to the formula:

$$\mathrm{PCM\%} = (\Delta H_{nanoPCMs}/\Delta H_{PCM}) * 100$$

where $\Delta H_{nanoPCMs}$ is the enthalpy for the analysed nanocapsules (J/g) and ΔH_{PCM} is the enthalpy of the noncapsulated PCMs (J/g).

2.3.3. Thermo-gravimetric analyzer (TGA)

Seiko SII TGA 7200 was used for the observation of thermal decomposition behavior of the microcapsules in order to determine the thermal stability of the samples. The analyses were carried out at 20 ml/min flow and 10 °C/min heating rates under inert nitrogen atmosphere from 40 to 800 °C