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Microencapsulation of *n*-heptadecane phase change material with starch shell

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ABSTRACT

In this study, *n*-heptadecane as a phase change material was microencapsulated with a starch wall for thermal energy storage applications. The effect of encapsulation parameters including mixing rate, reaction time, starch to *n*-heptadecane mass ratio and starch to water mass ratio were investigated on the microcapsule properties. The chemical compositions of the prepared microcapsules were characterized by Fourier transform infrared spectroscopy. The optical microscopy and scanning electron microscopy observations showed that the spherical microcapsules with a rough and intact shell were formed. The particle size analysis and thermogravimetric analysis were utilized to study the microcapsule structural properties and to explain the microencapsulation mechanism. The mechanism of the microencapsulation involved a multi-stage adsorption of starch components started with the migration of the amylose-lipid complexes onto the *n*-heptadecane droplets. The microencapsulated *n*-heptadecane with the starch wall had high melting and solidifying enthalpies and a proper thermal reliability, according to the results of differential scanning calorimetry. The prepared microcapsules can be used in different matrices, such as surface coatings, sheets, and liquid media.

1. Introduction

Phase change materials (PCMs) have attracted increasing interests for thermal energy storage due to their high heat storage density, reliability, practicability, and a moderate variation of their volumes and temperatures. They can absorb and release a large amount of latent heat when undergoing the phase change, mainly solid to liquid or liquid to solid. Based on this mechanism, PCMs are capable of regulating the surrounding temperature at close to their melting temperatures [1]. The PCM properties, applications, and characterizations have been extensively investigated by numerous researchers [2–6]. The straight chain alkanes (*n*-alkanes) known as paraffin are one of the organic PCMs (OPCMs). Safety, chemical inactivity, non-corrosiveness and good thermal properties are of their advantages as the OPCMs [7]. However, the OPCMs are restricted to direct use for energy storage because of their gradual leakage during the melting state, low thermal conductivity, and flammability. Microencapsulation of the PCMs are developed to increase heat transfer area, control their volume changes as phase change occurs, and limit the environmental impacts on their performance [8,9]. Microencapsulation is a process to coat the micron-sized (1 μm–1 mm) particles with a proper shell. Some of most often used microencapsulation methods are categorized as chemical processes, physico-chemical processes and physico-mechanical processes [10]. The comprehensive studies of the PCM microencapsulation are summarized in several reviews [11–13]. Su et al. [14] fabricated the microencapsulated paraffin by an in-situ polymerization method using methanol-modified melamine-formaldehyde prepolymer to decrease the residual formaldehyde and improve the shell mechanical properties. The impact of wall materials on the microencapsulated caprylic acid was studied by Konuklu et al. [15]. Caprylic acid as an OPCM was microencapsulated with different wall materials, including urea-formaldehyde, melamine-formaldehyde and urea + melamine-formaldehyde using the simple coacervation method. Malekipirbazari et al. [16] produced paraffin wax microcapsules with gelatin/gum Arabic wall through the complex coacervation method. Microcapsules of *n*-octadecane with silica wall were prepared by He et al. [17]. The encapsulation mechanism was based on the sol-gel process by sodium silicate as a silica precursor. Giro-Paloma et al. [18] investigated the properties of microcapsules containing paraffin or palmitic acid as the PCMs. The microencapsulation was carried out using an emulsion polymerization technique with poly(styrene-co-ethylacrylate) for wall material. Zhang et al. [19] synthesized the microencapsulated *n*-eicosane with zirconia shell by the sol-gel process to achieve the thermal energy storage and photoluminescence properties. Zirconia precursor

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induced the phase transition from amorphous ZrO_2 to crystalline one by F^- ion to generate the photoluminescence characterization. Beyhan et al. [20] microencapsulated capric acid-myristic acid mixture with methyl methacrylate co-polymers as the wall materials by a free radical polymerization method to increase the robustness of the shell structure. Among the various shell materials which can be utilized to microencapsulate the paraffin, starch is one of the most proper materials, caused by its capability of the core material protection, feasibility to use, accessibility, inexpensiveness and environmentally friendship. Fanta et al. [21] made a coating of cornstarch on the paraffin wax droplets by passing the aqueous two-phase of materials through a steam jet cooker. The starch adsorption on the water-paraffin interface was investigated using different cornstarch types. Although the morphology monitoring showed that the coating was not sealed enough to prevent the leakage of paraffin. Vitorino et al. [22] prepared a cellular skeleton of graphite/paraffin composite collaborating with starch. Starch helped graphite to self-organize on paraffin particles in an aqueous medium and maintain the continuous cellular skeleton after drying the composite. The effects of stirring rate, mixing time and starch and graphite amounts on the cell size and thermal and electrical conductivities were studied.

The literature survey above revealed that there is no work focused on the facile preparation of microencapsulated PCMs (MPCMs) with the starch wall, analysis of the process mechanisms and investigation the effects of encapsulation parameters on the MPCM thermal and physical properties. In this work *n*-heptadecane as a PCM and starch were used for the core and shell, respectively. The melting temperature of *n*-heptadecane is within the human comfort, 20–22 ° C, and its high latent heat, 240 j/g, making it as a considerable alternative of the PCMs to apply in multifarious areas such as protective garments and buildings. The paraffin core was encapsulated with starch in an aqueous medium by a facile method. The mixing rate, time of reaction and material weight ratios were studied as the encapsulation parameters. The parameter effects on the morphological, dimensional, core to shell ratio and thermal properties of the prepared MPCMs was investigated. The results of this study can be used to comprehend that encapsulation mechanism and optimize the process parameters for any purpose.

2. Experimental

2.1. Materials

n-Heptadecane, $C_{17}H_{36}$, was used as the core materials (Merck, Germany). An unmodified food grade potato starch (Alborz Starch Company, Iran) was utilized as the shell materials.

2.2. Preparation of microcapsules

The microencapsulation of *n*-heptadecane with the starch shell was performed through a multi-stage adsorption of starch components on the paraffin drops in an aqueous medium. Starch was dispersed in deionized water and heated to the boiling temperature. The materials were continuously mixed and boiled for 15 min. After that, this aqueous suspension was added to *n*-heptadecane at 50 °C and stirred vigorously to prepare the microcapsules. The material weight ratios, stirring rates and process times are tabulated in Table 1. The microcapsules were filtered, washed repeatedly with deionized water and dried for 48 h at room temperature.

2.3. Characterization

The microcapsule morphologies were studied by using scanning electron microscope (SEM, LEO 1455VP) and optical microscope (OM, Optika) equipped with a Canon digital camera. For SEM, samples were coated with a layer of gold in vacuum conditions previous to the observations.

Table 1
Preparation variables of the microencapsulation process and the microcapsule mean particle sizes.

Sample	Starch to water mass ratio	Starch to paraffin mass ratio	Mixing rate (rpm)	Time (min)	Size (μm)
MC1	1:20	3:1	11000	30	30 ± 5
MC2	1:20	3:1	11000	60	30 ± 5
MC3	1:20	3:1	1100	30	50 ± 10
MC4	1:20	3:1	1100	60	50 ± 10
MC5	1:20	1:1	11000	30	55 ± 5
MC6	1:20	1:1	11000	60	50 ± 10
MC7	1:20	1:1	1100	30	80 ± 5
MC8	1:20	1:1	1100	60	75 ± 10
MC9	2:20	3:1	11000	30	50 ± 5
MC10	2:20	3:1	11000	60	50 ± 5
MC11	2:20	3:1	1100	30	90 ± 10
MC12	2:20	3:1	1100	60	90 ± 5
MC13	2:20	1:1	11000	30	80 ± 10
MC14	2:20	1:1	11000	60	85 ± 10
MC15	2:20	1:1	1100	30	170 ± 10
MC16	2:20	1:1	1100	60	175 ± 5

Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Spectrum One) was used to study the chemical compositions of the microcapsules.

The mean sizes of the microcapsules were obtained by OM images combined with image analysis (Image J and Digimizer softwares). The averages of 100 measurements were used to determine the particle sizes of samples.

Thermogravimetric analysis (TGA, Pyris Diamond Perkin Elmer) was performed to measure the mass loss of the samples from 25 to 600 °C with a heating rate of 5 °C/min under flowing 100% nitrogen gas.

The melting and freezing temperatures and latent heats of the microcapsule samples and *n*-heptadecane were obtained by differential scanning calorimetry (DSC, TA Instrument, Q100). The thermal reliability of the microcapsules was investigated by DSC after 100 heating/cooling cycles. All measurements were carried out at a heating or cooling rate of 10 °C/min in the nitrogen atmosphere.

3. Results and discussion

3.1. Chemical compositions

The chemical compositions of raw materials and the microcapsules were evaluated by FTIR spectroscopy. FTIR spectra of *n*-heptadecane, starch and MC4 are shown in Fig. 1. Three intensive bands at 2957, 2923 and 2853 cm^{-1} are associated with the C—H stretching vibrations of methyl and methylene groups. The C—H bending vibrations of methylene groups are found at 1467 cm^{-1} and 1378 cm^{-1}. The band at 721 cm^{-1} refers to the in-plane methylene rocking vibrations [17,23]. In the spectrum of starch, the bands at 1018, 1081 and 1161 cm^{-1} are assigned to the C—O stretching vibrations of the glucose unites [24]. The peaks at 3435 cm^{-1} and 1644 cm^{-1} are attributed to the hydroxyl stretching and bending vibrations, respectively [25]. The starch characteristic bands in the MC4 spectrum (Fig. 1c) indicate the formation of the starch wall around *n*-heptadecane droplets. There are no significant shifts in the band wave numbers of MC4 spectrum respect to *n*-heptadecane and starch proving weak interactions between *n*-heptadecane core and the wall of starch.

3.2. Morphology

Fig. 2 shows the OM images of the microcapsules. It can be seen that the prepared MPCMs have spherical shapes with different particle sizes. The SEM surface morphology of MC4 is represented in Fig. 3. The intact