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Emulsifying ability and cross-linking of silk fibroin microcapsules containing phase change materials

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ABSTRACT

The microencapsulation of phase change materials (PCMs) with regenerated silk fibroin (SF) as a shell by means of SF self-assembling was studied. Nonionic, ionic and mixed surfactants were applied to increase the emulsion stability and enhance encapsulating capacity of SF microcapsules. Effects of different types of surfactants on diverse properties of PCM microcapsules including morphology, energy storage density, mechanical strength and thermal stability have been investigated. It was observed that mixed surfactants promoted significantly the formation and stability of n-octadecane/SF emulsion. With the effects of co-emulsifiers, mixed surfactants acted simultaneously as excellent emulsifiers and cross-linkers in SF microencapsulation processing. Adding mixed surfactants to n-octadecane/SF system improved the surface morphology and energy storage density, along with the mechanical strength.

1. Introduction

Phase change materials (PCMs) have been well known for their high latent heat storage [1–3]. They are capable of absorbing or releasing great amount of energy in a form of latent heat during phase transitions between solid–solid or solid–liquid phases over a narrow temperature range. Among the various phase change materials of interest, the use of paraffin waxes is particularly attractive due to non-corrosive and chemically stable merits, little sub-cooling, high latent heat per unit weight and low vapor pressure [1,4,5]. However, paraffin waxes also have disadvantages in low thermal conductivities, flammability and high changes in volume during phase change. Thus, for overcoming the defects and promoting the ease of handling, research groups have developed many encapsulating and storage methods, such as impregnating PCMs into various foams, shape stabilizing by embedding PCMs into a matrix and microencapsulating PCMs with organic/inorganic shells [5–7]. Microencapsulation of PCMs has been shown as effective engulfing method by increasing heat transfer areas and preventing PCMs leakage and the interaction between PCMs with ambient environment [8].

Up to now, there have been many methods for various wall materials to encapsulate PCMs, such as in situ polymerization for melamine–formaldehyde [9,10], interfacial polymerization for urea–formaldehyde [11], suspension-like polymerization for methyl methacrylate-based polymer [2,12,13], sol–gel solution for SiO_2 [14,15] and TiO_2 [16]. Complex coacervation has also received considerable attention in recent years for the microencapsulation of PCMs with natural and biodegradable polymers as shells [8,17–20]. Polysaccharides and proteins are mostly used in literature [20,21], such as gum acacia, hydrophobically modified starch, alginate, carboxymethylcellulose, whey proteins, soy proteins and sodium caseinate. Hawlader et al. [19] prepared paraffin wax/gelatin-acacia microcapsules by spray-drying and complex coacervation. The encapsulated paraffin wax with a thermal energy storage/release capacity of about 145–240 J/g showed a good potential as a solar-energy storage material.

Onder et al. [18] also explored the influence of process parameters on the microencapsulation of paraffin waxes with gum arabic–gelatin mixture as the shell material using complex coacervation method. Regenerated silk fibroin (SF) was firstly used for the microencapsulation of paraffin wax by Basal et al. via complex coacervation method [22]. Span-20, an nonionic surfactant, was introduced to be the emulsifier for the formation of paraffin

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waxes/SF emulsion in their report. SF is an ionic surfactant, not only composing of hydrophobic and hydrophilic segments, but also possessing of negative and positive charges. With the suitable surfactants, the properties of paraffin waxes /SF microcapsules, such as the surface morphology and energy storage density, may be improved. In this manuscript, n-octadecane, one type of paraffin waxes, was used as PCMs. Nonionic, ionic and mixed surfactants were respectively applied to investigate the emulsion stability and SF microencapsulating capacity of n-octadecane. Effects of different types of surfactants on diverse properties of PCM microcapsules including morphology, energy storage density, mechanical strength and thermal stability were discussed.

SF microspheres and microcapsules have been explored in pharmaceutical and medical technology due to their unique combination of self-assembly, mechanical stability, controllable structure and morphology [23–26]. Among various preparation methods, the assembly process of SF particles is relatively simple and avoids the additions required in templating approaches [23]. Some inorganic salts, such as potassium phosphate and sodium chloride, pH variation and organic solvents, such as methanol and ethanol, can induce the conformation transition of SF from Silk I to Silk II, with the result of phase separation [24,27]. In this report, ethanol was applied to induce the assembling of SF walls after the formation of oil-in-water emulsion.

2. Materials and experimental

2.1. Preparation of SF aqueous solution

Cocoons of *Bombyx mori* (Zhejiang province, China) were used to prepare SF aqueous solution as previously described [28]. Briefly, cocoons were boiled twice for 30 min in an aqueous solution of 0.5 wt% Na_2CO_3 solution at 100 °C, and washed with deionized water to remove sericin. After air drying, the degummed fibers were dissolved in a 9.0 M LiBr aqueous solution at 40 °C for 2 h yielding a 10% (w/v) solution. After being centrifuged and filtrated, the solution was dialyzed against deionized water using a cellulose semi-permeable membrane (molecular weight cut-off 14,000, 44 μm in thickness, Yuanju Co. Ltd., Shanghai, China) for 3 days to remove salts. The final concentration of SF aqueous solution was approximately 3 wt%, based on weighing the residual solid of a known volume of solution after drying at 105 °C. The 3 wt% silk solution was stored at 4 °C for further use.

2.2. Preparation of SF microspheres

Self-assembling was applied for the preparation of SF microspheres[24]. 3 mL ethanol was added into 20 mL SF solution (3 wt%) under the stirring rate of 300 rpm at 25 °C over 2 min. Afterwards, the SF solution was incubated in a refrigerator at the freezing temperature of −25 °C for 24 h. Then the frozen sample was defrosted at room temperature. Eventually, SF microspheres could be obtained by lyophilizing with a freezing dryer.

2.3. Preparation of n-octadecane/SF microcapsules (MicroPCMs)

Oil-in-water emulsions must be formed prior to the microencapsulation of PCMs. 3 wt% SF aqueous solution was used as the water phase in oil-in-water emulsion system. n-octadecane (99 wt%, Alfa) was chosen to be the core phase change material at the core-to-coating ratio of 1:1. Firstly, n-octadecane was melted and emulsified into SF aqueous solution under homogenization shearing for 15 min. During the homogenization process, span-80, tween-80, Sodium dodecyl sulfonate (SDS), Cetyltrimethyl ammonium bromide (CTAB) and the mixture of span-80 and CTAB were applied as the emulsifier to achieve the required emulsification, respectively. The emulsion experiments were all performed at 25 °C.

Following the homogenization process, ethanol was added into the emulsion at the volume ratio of 3:20 under the stirring rate of 300 rpm at 25 °C over 2 min. Afterwards, the emulsions were incubated in a refrigerator at the freezing temperature of −25 °C for 24 h. Then the frozen samples were defrosted at room temperature. Eventually, n-octadecane/SF microcapsules could be obtained by lyophilizing with a freezing dryer after the microcapsules were washed with hot ethanol and hot water.

2.4. Characterization of MicroPCMs

The morphology and structure of MicroPCMs were characterized using a HITACHI S4800 field emission scanning electron micro-scope (FESEM). All samples were coated with a layer of gold prior to the observation.

FTIR spectra of n-octadecane, SF shells and MicroPCMs were obtained using a Fourier transformed infrared spectrophotometer (FTIR, VERTEX70, BRUKER)at room temperature.

Thermal properties of MicroPCMs, SF shells and n-octadecane, such as melting/crystallizing points and latent heats, were recorded by a differential scanning calorimetry (DSC 823E, METTLER TOLEDO) in the range of 0–50 °C at a heating/cooling rate of 5 °C/min in an argon atmosphere with the flow rate of 60 ml/min.

Thermal stability of MicroPCMs, SF shells and n-octadecane was measured by a thermal gravimetric analysis (TGA TGA/DSC1, METTLER TOLEDO) in the range of 50–600 °C at a heating rate of 10 °C/min in an argon atmosphere.

3. Results an discussion

n-octadecane/SF MicroPCMs were successfully prepared by SF self-assembly. It was feasible to form microcapsules starting from n-octadecane/SF (aqueous solution) emulsions in the presence of emulsifiers. Ethanol was used to induce the conformation transition of silk fibroins from α-helix/random coil to β-sheets, with the result of phase separation of silk fibroins.

The prerequisite for manufacturing MicroPCMs with good characteristics is the ability to produce stable droplets with a uniform well-controlled size and the surface morphology and thermal properties of MicroPCMs are related to the emulsion stability [29]. Ionic surfactants, CTAB and SDS, and nonionic surfactants, span-80 and tween-80, were chose to be emulsifiers to improve the emulsion stability in this manuscript. For various emulsifiers, parameters of the emulsifying process were identical except for the addition amount of emulsifiers and the homogenization shearing rate. The optimized addition amount of ionic surfactants was 5% of n-octadecane (w/w), while that of nonionic surfactants was 10% of n-octadecane (w/w). The optimum homogenization shearing rates for ionic surfactant system and nonionic surfactant system are 1000 rpm and 12000 rpm, respectively. Long-term emulsion stability was induced by CTAB or span-80 since the appearance of a whitish layer at the top of the emulsion after one day was not observed [29]. However, tween-80 as the emulsifier did little on the emulsion stability of n-octadecane/SF emulsion since a whitish layer at the top of the emulsion appeared after a few minutes even under the homogenization shearing rate of 12000 rpm. The n-octadecane/SF mixture with SDS additive preferred to converting into gels rather than emulsions, and the tendency could not be altered with the decreasing addition of SDS. The similar phenomena also occurred when the content of CTAB was higher than 5% of n-octadecane (w/w).