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Consolidated microcapsules with double alginate shell containing paraffin for latent heat storage

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ABSTRACT

Double-shell alginate microcapsules containing paraffin phase change material (PCM) were prepared for latent heat storage by a method of repeated interfacial coacervation/crosslinking. The proposed process consisted of three main steps: (1) preparation of paraffin containing core particles by dripping an O/W emulsion of melted paraffin and aqueous sodium alginate into a calcium chloride ionic cross-linking solution, (2) encapsulation of the core particles into double alginate shell by ionic gelation/crosslinking by repeated interactions between the sodium alginate and calcium chloride solutions, and (3) consolidation of the capsule shells by contact heat treatment. The effects of process parameters such as the sodium alginate concentration, the calcium chloride concentration in certain stages of the process, and the contact time between the formed core particles and the surrounding alginate solution on the paraffin content and the mean diameter of capsules were studied by experimental design and statistical evaluations. The prepared PCM capsules had uniform sizes, core/shell structure, double-walled non-porous alginate coating, tunable void space inside the core, and suitably high paraffin content at properly selected process conditions, corresponding to 95.0 J/g melting and 91.7 J/g freezing latent heat capacity. Thermogravimetric analysis and repeated thermal cycling evidenced good thermal stability, and proper mechanical strength for leakage free microcapsules.

1. Introduction

Thermal energy storage has received more and more attention due to the endeavor of energy saving. Latent heat storage is one of the most efficient ways of thermal energy storing [1]. Phase change materials (PCMs) are used for latent heat storage. Most promising fields of application of PCMs are waste heat recovery systems, solar heating systems, building energy conservation systems and air-conditioning systems [2,3]. Using PCMs in solar heating systems heat energy can be stored with much higher energy storage density with a smaller temperature swing when compared with the sensible heat storage. The volume of heat storage tank can be reduced, thus the cost of the solar heating system becomes lower. The operation of air-conditioning systems can be shifted to nighttime hours when the cooling load is low [4].

Most of the organic PCMs are non-corrosive and chemically inert, stable, recyclable and compatible with numerous building materials. They have desirable cohesion, high latent heat capacity per unit weight, low vapor pressure, no supercooling, and offer congruent melting and self-nucleation. They have disadvantages such as low thermal conductivities, flammability and relatively higher changes in volume during phase change.

Paraffins are versatile PCMs, since they are chemically inert and reliable, non-corrosive, non-toxic and commercially accessible at rational cost. They have large latent heat capacity, negligible supercooling, low vapor pressure, good thermal and chemical stability, self-nucleating behavior, high latent heat of fusion and wide range of solid–liquid phase change temperatures for many latent heat energy storage applications [5,6]. However, they have some drawbacks such as low thermal conductivity, flammability and high volume change during phase change [7,8]. To overcome

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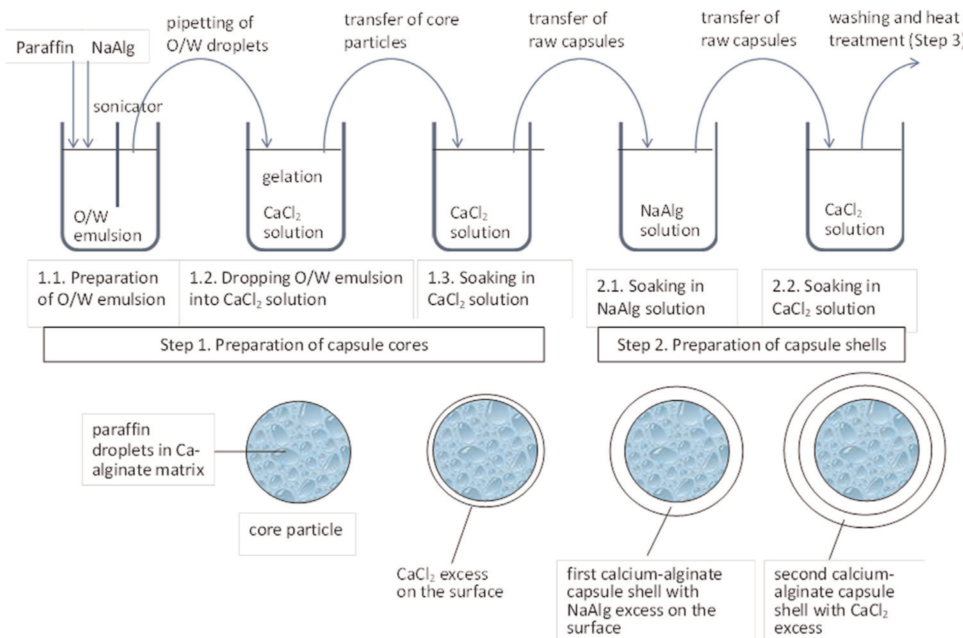

Fig.1. Schematic illustration of the capsule preparation method.

these drawbacks, microencapsulation can be an efficient tool. By this way the heat transfer surface area can be increased, the volume change problem can be eliminated, leakage of PCM during its phase changing from solid to liquid can be prevented, moreover, the reactivity of PCM with its close environment might be lessened [7]. The microencapsulated PCMs, suspended in a heat transfer fluid phase, form heat storing solid–liquid slurry [8]. Due to the embedment of PCM particle in a plastic shell, the core material is always separated from the heat transfer or carrier fluid, which makes the slurry behave like a liquid, while the latent heat effect substantially increases the heat capacity of the carrier fluid [9]. In addition, the heat transfer coefficient and surface may be greatly increased because of the latent heat effect and the particle to particle interactions.

Calcium cross-linked alginate hydrogels with its natural origin and environmental friendly character have been used in many biomedical applications, such as cell transplantation and drug delivery [10]. Alginate typically has the physical form of a hydrogel with small or large pores which is advantageous in some utilization. However, porosity and capability of absorbing large quantities of water are obstacles of its use in PCM microencapsulation. Nevertheless, in a few work alginate was used as shell material in PCM incorporation. E.g. Wang et al. [11] prepared alginate macrocapsules containing n-octadecane phase change material shape-stabilized with high-density polyethylene by using a traditional coating pan. Lan et al. [12] stabilized an inorganic phase change material, disodium hydrogen phosphate dodecahydrate by a novel gelling method by polymerizing sodium alginate grafted sodium acrylate in its molten salt. In another approach shape stabilized PCMs ranging from 1 to 5 mm with calcium alginate matrix were formed, and then were coated with calcium complex compound as shell in order to obtain microPCMs [13]. Macrocapsules containing acrylic-based copolymer microPCMs were also prepared through the piercing-solidifying incuber method. PCM microcapsules were prepared by using a co-extrusion minifluidic device with melted paraffin wax Rubitherm RT27 as the inner fluid and sodium alginate solution as the outer fluid, and the capsules were collected in a container with $CaCl_2$ solution [14]. Although none of these processes considered all of the disadvantages of alginate materials mentioned above.

Our aim was to prepare microcapsules containing paraffin as PCM incorporated into double alginate shell which was then treated by heat. The contact heat treatment resulted in the loss of water, and the formation of a non-porous, glassy coating on the surface of the capsules. Due to the heat treatment the alginate shell shrank, reducing its wall thickness, hence void space formed inside the capsules, which was advantageous allowing the volume change during phase change without harmful stress in the capsule wall. As for the process of preparation, the effects of most important variables were analyzed by a 3-level 3 factors Box-Behnken experimental design.

2. Material and methods

2.1. Materials

Sodium alginate (NaAlg) and $CaCl_2 \cdot 2H_2O$ were purchased from Sigma-Aldrich, paraffin of melting temperature in interval 55–57 °C was kindly provided by the MOL Plc, Hungary. Petroleum ether (boiling temperature 60–62 °C) was purchased from Lach-Ner s.r.o., Nercetovice, Czech Republic. All chemicals were of analytical grade and were used as purchased. For all aqueous solutions distilled water was used.

2.2. Methods

The objective of the work was to produce uniform capsules containing paraffin for latent heat storage in non-porous alginate shell of suitable mechanical and thermal stability. The process, schematically shown in Fig. 1, consisted of three main steps: (1) preparation of core particles, (2) encapsulation of core particles into double alginate shell by repeated ionic gelation/crosslinking, and (3) consolidation of capsule shells by heat treatment.

2.2.1. Preparation of capsules

Step1. Preparation of core particles

Step 1.1. First 50.0 g O/W emulsion was prepared by emulsifying melted paraffin (O) in aqueous sodium alginate solution (W).