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# A facile hydrothermal preparation for phase change materials microcapsules with a pliable self-recovering shell and study on its thermal energy storage properties

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ABSTRACT

A facile method to prepare phase change materials (PCM) microcapsules containing paraffin was developed, through in-situ polymerization combined with hydrothermal process. Paraffin melting at 20 °C was used as PCM. The hybrid microcapsules' shell was prepared by copolymerizing styrene (St), acrylic acid (AA), n-butyl acrylate (BA), and pentaerythritol triacrylate (PETA) which were employed as crosslinking agents. The initiator could be spared because the synthesis reaction was carried out in high temperature hydrothermal reaction. Microcapsules with well-defined core–shell structure were obtained, and their morphologies were studied by (scanning electronic microscope) SEM and (transmission electron microscopy) TEM. Under hydrothermal conditions, the flexibility and strength of the shells were enhanced by PETA added, which made it possible to form a more uniform thickness of shell materials, and bigger expansion volumes inside the microcapsules than the traditional in-situ polymerization. The expansion space was very important for the stability of PCM microcapsules, which could allow PCM expand and shrink inside the microcapsules, and the flexible shells could keep themselves intact in repeated absorbing–releasing thermal transmittance process. Innovatively, the deformations of these shells caused by the expansion and shrinkage in this process could recover to a certain extent after being soaked in water without loss of enthalpy values. The results of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) indicated that the PCM microcapsules have high heat storage capability and good thermal stability.



## 1. Introduction

PCM perform well on thermal energy storage and can keep temperature stable during the heat storage/release process. When engulfed with a solid matrix as microcapsules, it has better endurance during operation and storage. The latent heat of PCM microcapsules can be applied in many fields as an efficient way of storing energy [1]. The stability of the PCM microcapsules is crucial for the application of thermoregulated materials [2]. Therefore, studies have been conducted to select an appropriate shell in order to improve the thermal stability of PCM microcapsules 3,4. Previous experimental results [5] show that internal pressure of the microcapsules increased because the PCM core expanded as temperature rose, and cracks were herein formed on the surface of the microcapsules when temperature declined because of the different contract coefficient between the shell and PCM core. The PCM materials escaped by seepage through the crack on the microcapsules shell in repeated absorbing–releasing thermal transmittance process, which is the primary PCM outflow mode [6]. A stress analysis of various shapes of PCM microcapsules has been conducted by Blaney et al. [7], and the effect of an internal air void on the heat transfer phenomenon within PCM microcapsules is examined [8].

To avoid the breakage of the microcapsules, the main method is to leave sufficient void space [9] in the PCM microcapsules to minimize the pressure increase inside and to maintain structural integrity of the microcapsule. A free expansion space inside the microcapsules is formed after the volatile solvent added in the core diffused out of the shell by heat treatment [10]. Meanwhile, the duration of heat treatment is a crucial factor to keep the PCM microcapsules integrity, and the rupture and the leakage rate of microcapsules are enhanced as heat treatment prolonged.

The mechanical strength of microcapsules is a key factor to remain intact during manufacturing applications and further processing [11–13]. Especially in construction systems, the compression of the PCM microcapsules inside the wall could result in leakage [14,15]. PCM microcapsules are usually embedded in a polymer matrix, the shells' mechanical properties of which can be enhanced by controlling and modifying the synthesis conditions [16]. Though melamine–formaldehyde shells have high compressive strength and toughness to keep being protective, the ability of resisting deformation of PCM

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microcapsules can still be ruined by repeated thermal absorbing–releasing process, because the different expend-coefficients between the PCM and the shell could cause reversible deformation of the shells [17]. Therefore, it is important to improve both the mechanical strength and the pliable stability of the PCM microcapsules at the same time.

The PCM microcapsules have been prepared by using the suspension polymerization method [18,19], the phase separation [20], the layer-by-layer assembly [21], the simple or complex coacervation [22], the in-situ polymerization method [23,24], the interfacial polycondensation reaction method [25,26] and the emulsion polymerization method [27]. The PCM microcapsules made by the various methods stated above hold less flexible polymer shell which could not maintain its integrity during the repeated process of the temperature variation. And this property hinders its application in latent heat storage technology.

As we know, hydrothermal reaction is remarkably simple and versatile and capable of producing nanoparticles, [28] and nanofibers [29] in large quantities. In producing microcapsules, hydrothermal method is reported to conduct heat-curing process [30] after solvent evaporation, and to produce inorganic hollow microcapsules [31]. However, to our knowledge, there are few related reports about synthesizing microcapsules directly on basis of hydrothermal reaction.

Inspired by the previous work [32] on preparing monodisperse polystyrene particles by hydrothermal process, we attempt to investigate the feasibility of the hydrothermal reaction to produce microcapsules on the basis of in-situ polymerization method after mechanical emulsification. The influence of pentaerythritol triacrylate (PETA, a typical cross-linking agent) on reinforcing the capability of encapsulation was also studied. Using this method, paraffin wax can be encapsulated into copolymer microcapsules of vinyl monomers efficiently. The morphologies of microcapsules were investigated by scanning electron microscopy (SEM), while differential scanning calorimetry (DSC) was employed to investigate the thermal properties of microcapsules. The introduction of hydrothermal condition made the reaction process of PCM microcapsules with hybrid shell becomes more simple and convenient. Also, the initiator can be spared in our present synthetic process. To avoid the shells' rupture caused by frequent phase change, the researchers created reserved expansion space by introducing an expandable agent into the microcapsules. The formation of the expansion space of microcapsules led to a higher thermal stability and lower pressure to the shell [9]. Although the microcapsule shells can be protected efficiently, this method inevitably leads to higher costs and air pollution. Unexpectedly, reserved expansion space was also formed spontaneously when a hydrothermal reaction with high pressure was operated [33]. The cost of an expandable agent was saved and the weight percent of encapsulated materials almost keeps unchanged. In addition, the flexibility of the polymer shell was increased through adding PETA. Then, the deformation of microcapsule shells, because of pressure changes during the synthesis process, could recover to some extent without loss of enthalpy values after soaking. All the above results show that mechanical emulsification combined with a hydrothermal reaction can provide a facile method for the encapsulation of liquid core in a pliable self-recovering polymer matrix to generate microcapsules.

## 2. Experimental part

### 2.1. Materials

Styrene (St), acrylic acid (AA), and n-butyl acrylate (BA) were purchased from Beijing Yili Fine Chemicals Co. Ltd., and used as received. The crosslinking agent, pentaerythritol triacrylate (PETA) was purchased from Tianjin TianJiao Fine Chemicals Co. Ltd., and used as received. Paraffin was purchased from China Petroleum & Chemical Corporation, and used after purification. The emulsifier, polyvinyl pyrrolidone (PVP K30) was used as received. Doubly deionized water was used as aqueous medium.

### 2.2. Synthesis of PCM microcapsules

1.3 g of PVP was dissolved in 50 mL of deionized water. A mixture of 10 g of St, 0.6 g of AA, 3 g of BA, 9 g of paraffin, and 0.2 g of PETA was dispersed in the aqueous solution of PVP with a homogenizer at a stirring speed of 5000 rpm to form an oil-in-water emulsion. Successively, the emulsion was transferred to a 75 mL autoclave. The autoclave was sealed with a Teflon cap, kept at 120 °C and 150 °C for 8 h and then cooled automatically to room temperature. Then the sample was washed repeatedly with distilled water and was dried to the constant weight in an automatic electric oven at 50 °C.

The usual preparation of microcapsules was conducted at 80 °C as the comparative experiment in the same way except with flask instead of autoclave.

### 2.3. Characterization of PCM microcapsules

The dispersion solution of PCM microcapsules was dropped onto a clean silicon wafer and dried in a vacuum oven for 4 h, and the PCM microcapsules were observed directly under a scanning electron microscope (SEM, JSM 7401, JEOL, Japan) with an accelerating electronic voltage of 1 KV and transmission electron microscopy (TEM, JEM-2010, JEOL, Japan) with an accelerating voltage of 80 kV.

The latent heat storage densities of microcapsules were measured with differential scanning calorimeter (DSC; Shimadzu Co., DSC-60). The samples were heated from −30 to 40 °C at 5 °C/min in a nitrogen atmosphere, held at 40 °C for 2 min, cooled to −30 °C at 5 °C/min, held at −30 °C for 2 min, and then heated from −30 to 40 °C at the same rate. The second cooling and second heating DSC traces were performed to estimate the thermal behaviors of the copolymers. TGA was recorded by a Shimadzu DTG-60 from ambient temperature to 600 °C at a heating rate of 20 °C/min in air (40 mL/min).

## 3. Results and discussion

### 3.1. Preparation of PCM microcapsules

Encapsulated paraffin with polymer hybrid shell materials was prepared through a one-pot hydrothermal reaction on the basis of in-situ polymerization, as shown in Scheme 1. A stable oil-in-water (O/W) emulsion which was stabilized by PVP as an emulsifier was firstly formed by intensive stirring. After the emulsion was transferred to a 75 mL autoclave for a hydrothermal reaction, the stirring stopped and was replaced by intense disturbance owing to a high temperature up to 150 °C and a high pressure in autoclave [33]. The internal pressure was speculated higher than 3.5 MPa [34]. As the reaction proceeds, the copolymer precursors migrated to the oil/water interface continuously. Eventually, the copolymer shell consisted of St, AA, BA and PETA which was successfully fabricated onto the surface of the paraffin droplets through such an in-situ polymerization aided by hydrothermal reaction. The special inner state of hydrothermal reaction ensured the preparation of PCM microcapsules successful. In the hydrothermal process, the volume of PCM in shell expended while it was resisted by the shells. When the environment temperature dropped to room temperature, its volume was decreasing faster than the shell. Then, a deformation without cracks occurred in the shells because of the different contract coefficient between the PCM and the shell. However, the shell of PCM microcapsules was pliable enough to recover from deformations to spheres after soaked in water, so no cracks were observed.

### 3.2. Morphology of PCM microcapsules by hydrothermal reaction

Before using the hydrothermal method, an in-situ polymerization of PCM microcapsules was firstly carried out at 80 °C. The oil droplets always float on the emulsion surface even though a cross-linking agent is added. As a result, the encapsulation of paraffin wax in microcapsules