



# Preparation and characterization of hydrated salts/silica composite as shape-stabilized phase change material via sol–gel process



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## ABSTRACT

A novel shape-stabilized phase change material composite was prepared by impregnating the mixture of hydrated salts ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ – $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ) into porous silica matrix obtained by sol–gel process and further coated with polyvinylpyrrolidone (PVP) to improve the thermal cycling performance. The chemical compatibility, morphology and phase change properties were investigated by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), hot-stage polarizing optical microscope (HS-POM) and differential scanning calorimetry (DSC). Confined in the silica matrix, phase segregation of the hydrated salts was inhibited and subcooling was slightly mitigated. No leakage was observed during the solid–liquid phase transition even when the mass ratio of hydrated salts to silica was as high as 70:30. Results showed that the melting enthalpy of the composite can reach 106.2 kJ/kg with the melting temperature at 30.13 °C and there was no significant enthalpy loss after 30 thermal cycles.

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## 1. Introduction

As one of the most efficient ways for thermal energy storage, latent heat storage has received considerable attentions, since it provides a high energy storage capacity with small temperature swing by using phase change materials (PCMs) [1–4]. PCMs are one kind of energy storage materials that can absorb, store and release latent heat during a phase change process between solid–solid or solid–liquid phases over a narrow temperature range. Due to their good energy storage density, PCMs have been widely used in solar energy storage [5], waste heat recovery [6], and building energy conservation [7]. However, the applications of solid–liquid PCMs are limited by the problems of the leakage of the melted liquid and the corrosion. In order to resolve these problems, the shape-stabilized PCMs are developed with organic or inorganic materials as the supporting networks. To date, there are two main categories of shape-stabilized PCMs, microencapsulated PCMs [8–10] and impregnation of porous materials with PCMs [11,12].

Microencapsulated phase change materials are composed of the core of PCMs and the outer shell formed by polymer or inorganic compounds. Encapsulation of PCMs can effectively resist the leakage when the phase change occurs, while the low thermal conductivity of the organic shell decreases the rate of thermal storage and release. Alternatively, the impregnation of porous

materials with PCMs has attracted a great interest in recent years, since it is easy to use and of low cost. The mostly used inorganic porous materials are porous building materials [13], porous carbon materials [14] and porous silica [15,16], as they have high porosity, high surface area and high thermal conductivity [17]. Sari and Bicer [18] prepared form-stable composite PCMs by absorbing galactitol hexa myristate (GHM) and galactitol hexa laurate (GHL) esters into diatomite, perlite and vermiculite. They found that the maximum mass percentages of GHM absorbed was 67 wt% into the perlite and the thermal conductivity of the PCMs was greatly increased by the addition of expanded graphite. Wang et al. [19] studied the influence of the pore structure of the carbon materials on the phase change behavior of polyethylene glycol. It was revealed that the phase change properties of PCMs were influenced by the pore size, surface functional groups, and pore geometry. Porous silica with a high porosity and a large internal surface area is generally obtained by an extensively studied sol–gel process [20–22], which involves the hydrolysis of silica precursors and the condensation of the resulting hydroxyl groups to form a network structure suitable for confining the phase change materials. Fang et al. [23] used sol–gel method to disperse lauric acid (LA) in  $\text{SiO}_2$  by capillary and surface tension forces. They found that the form-stable LA/ $\text{SiO}_2$  PCMs have a high thermal stability, and can be used repeatedly in a thermal energy storage system. However, introducing a supporting material may inevitably lead to the loss of the energy storage density. Therefore, the porous materials with high PCM load, high shape stability, good thermal conductivity and low cost are the optimal choices.

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Currently, most of the researches about shape-stabilized PCMs focus on organic PCMs. Several organic PCMs, such as paraffin [24,25], fatty acids [26] and PEG [27], have been widely studied due to their little subcooling, non-toxicity, and less volume change during solid–liquid phase transition. In contrast, little is reported about the shape-stabilized PCMs using prospective inorganic heat storage materials, for example, hydrated salts, including  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ . As one of the most promising PCMs for thermal energy storage, hydrated salts enjoy many advantages, such as high energy storage density, relatively high thermal conductivity, nonflammability, and low cost. Nevertheless, two intrinsic drawbacks, including phase segregation and serious subcooling, hinder them from being widely used in practice. In order to overcome these problems, significant efforts have been made in developing various thickening and nucleating agents [28–31]. However, the results reported by different researchers are inconsistent due to the difficulty for accurate control of the amounts of these additives. Moreover, the rigorous conditions are essential for the crystallization of hydrated salts [32,33]. All of these mentioned above make it difficult to prepare shape-stabilized PCMs using hydrated salts. To the best of our knowledge, only one literature has reported about the preparation of shape-stabilized PCMs by encapsulating  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  into silica matrix using the method of in situ synthesis [34]. Although the phase segregation of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  was inhibited, the subcooling was still serious.

In this work, a novel shape-stabilized PCM composite was prepared, adopting a mixture of hydrated salts,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ – $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , as phase change material and  $\text{SiO}_2$  as the supporting material, via sol–gel process. The binary mixture of hydrated salts was intended to promote the crystallization as well as the thermal performance. In addition, polyvinylpyrrolidone (PVP) was used to adsorb onto the surface of silica to improve the thermal cycling performance. The structure and properties of the composite were investigated by scanning electronic microscope (SEM), Fourier transform infrared spectroscopy (FT-IR), and differential scanning calorimetry (DSC).

## 2. Experimental

### 2.1. Materials

Sodium metasilicate nonahydrate ( $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ , analytical grade), sodium sulfate decahydrate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , analytical grade) and sodium phosphate dibasic dodecahydrate ( $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , analytical grade) were obtained from Beijing Modern Eastern Fine Chemicals, China. Polyvinylpyrrolidone (PVP, K-value 30) was supplied by Sigma–Aldrich, Germany.

Na-type cation exchange resin (732) was supplied by Beijing Modern Eastern Fine Chemicals, China. It was treated by sodium hydroxide (3 wt%) and hydrochloric acid (5 wt%) before transforming into the H-type cation exchange resin used for ion exchange with  $\text{Na}^+$ .

### 2.2. Preparation of hydrated salts/silica composite

The procedure for the preparation of hydrated salts/silica composites consisted of three steps: preparation of  $\text{SiO}_2$  hydrogel, penetration and PVP coating. The preparation of  $\text{SiO}_2$  hydrogel was started by adjusting the pH of 20 mL of  $\text{Na}_2\text{SiO}_3$  solution (0.5 mol/L) to 6.5 by introducing the H-type cation exchange resin to exchange  $\text{H}^+$  for  $\text{Na}^+$ . Then, 10 mL of  $\text{NH}_4\text{HCO}_3$  (0.01 g/mL) solution was added into  $\text{Na}_2\text{SiO}_3$  solution at 30 °C to promote the hydrolysis of silica precursors into silanols. After aging for 5 h, the generated hydrogel was washed three times with deionized water to remove the remaining  $\text{NH}_4\text{HCO}_3$ . Subsequently, the mixture of molten hydrated salts containing 0.467 g  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and 0.467 g  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , which was firstly heated by using a thermostat

water bath at 40 °C, was poured into the hydrogel and kept at 30 °C for 48 h to guarantee that the penetration of hydrated salts into the hydrogel was complete. After that, the PVP coating proceeded. The hydrogel was placed into a beaker with 20 mL of PVP aqueous solution (10 wt%), followed by ultrasonication for 3 h and subsequent vigorous stirring (500 rpm) overnight at room temperature. Finally, the hydrogel was separated by centrifugation and dried at 10 °C for 48 h. Thus, the hydrated salts/silica composite with the mass ratio of hydrated salts to silica 70:30 were obtained as white powder and studied in the following researches.

### 2.3. Analysis

The morphology of the composite was investigated by a scanning electron microscope (SEM, JSM7401, Shimadzu, Japan). Samples were coated with gold and observed with an accelerating voltage of 3.0 kV. The FT-IR spectra were obtained by Fourier transform infrared spectroscopy (FT-IR, Tensor27, Bruker, Germany) in the wavenumber range of 400–4000  $\text{cm}^{-1}$  at room temperature. Samples were mixed with KBr and pressed to be a pellet before analysis. The shape stability of the composite was observed by a hot-stage polarizing optical microscope (HS-POM, Olympus BX51, Japan). Samples were heated from 25 to 55 °C at a rate of 5 °C/min and HS-POM images were taken every 10 °C.

Phase change properties were determined using a differential scanning calorimetry (DSC, Q2000, TA, USA). Samples of approximately 10 mg were sealed in an alumina pan and heated from –20 to 50 °C at a rate of 5 °C/min in purified nitrogen atmosphere. The thermal cycling tests were carried out as follows: samples were heated from –5 to 50 °C at a rate of 5 °C/min, and subsequently cooled to –5 °C at a rate of –5 °C/min and kept at –5 °C for 1 min. The cycles above were repeated in an oven. Thermal stabilities were investigated by thermal gravimetric analysis (TGA, STA409PC, Netzsch, Germany). Samples of approximately 15 mg were heated from 20 to 800 °C at a rate of 10 °C/min under a constant stream of nitrogen at a flow rate of 20 mL/min.

## 3. Results and discussion

### 3.1. Chemical compatibility of the composite

Chemical compatibility between the hydrated salts and the silica was investigated by the Fourier transformation infrared spectroscopy (FT-IR). Fig. 1 shows FT-IR spectra of the hydrated

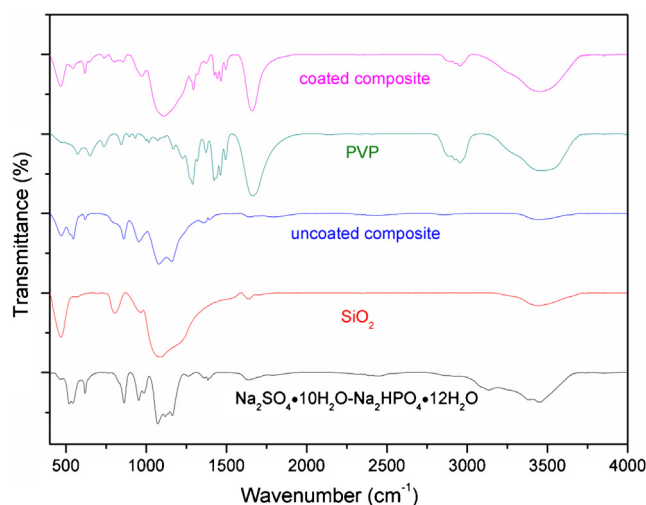


Fig. 1. FT-IR spectra of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ – $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{SiO}_2$ , uncoated composite, PVP, and coated composite.

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