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Short communication

A novel gelling method for stabilization of phase change material $Na_2HPO_4 \cdot 12H_2O$ with sodium alginate grafted sodium acrylate

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Abstract

To stabilize phase change material, disodium hydrogen phosphate dodecahydrates ($Na_2HPO_4 \cdot 12H_2O$), a novel gelling method by polymerizing sodium alginate grafted sodium acrylate in its molten salt was investigated. The optimum synthesis conditions to obtain product with stable heat storage performance were 2.8% (w/w) sodium acrylate, 0.3–0.4% (w/w) sodium alginate, 0.1–0.19% (w/w) *N*,*N*′-methylenebisacrylamide and 0.06% (w/w) $K_2S_2O_8$ and Na_2SO_3, at 50 °C. $Na_2HPO_4 \cdot 12H_2O$ was dispersed in the as-synthesized gel network as tiny crystals less than 0.1 mm. Melting points were in the range 35.4 ± 2 °C. Short-term thermal cycling proves the effectiveness of the novel gelling method for eliminating phase separation in the gelled salt.

Keywords: Phase change material; Disodium hydrogen phosphate dodecahydrates; Phase separation; Gelling method; Sodium alginate

1. Introduction

Latent heat energy storage based on fusion and freezing of phase change materials (PCMs) is an effective way of storing thermal energy and particularly suitable for solar energy heating, peak-shift of electrical demand and heat recovery [1–9]. Organic phase change materials usually show stable thermal energy capacities; whereas inorganic PCMs, mainly salt hydrates, often show phase separation during thermal cycling, leading to failure of the latent heat storage system. A common practice is to add a thickening agent or by gelling to overcome this phenomenon.

Disodium hydrogen phosphate dodecahydrates has almost the largest mass heat storage capacity among low temperature PCMs [1,2]. The drawback of the material comes from its incongruent melting character during solid–liquid transformation. Thickening agents have been tried to solve the problem, such as starch, sodium alginate, cellulose derivates, silica gel, attapulgite and cross-linked water-absorbing polymer [9–11]. But their effects are not ideal. Gelling by in situ synthesizing a water-absorbing polymer, cross-linked sodium polyacrylate, in the molten salt has been reported for prevention of phase segregation [10,11]. But this method showed poor reproducibility in our experiments. This paper presents a new gelling method by polymerizing sodium alginate grafted sodium acrylate in the solution of $Na_2HPO_4 \cdot 12H_2O$ and the effectiveness of the method.

2. Experimental

Sodium alginate, all the inorganic salts (Shanghai Chemical Reagents Co.) and *N*,*N*′-methylenebisacrylamide (MBA, Tianjin Kermel Chemical Reagent Development Center) were of analytical grade. Acrylic acid (CP) was purified through reduced pressure distillation and prepared as a storage solution of 20% (w/w) with pH 7.

$Na_2HPO_4 \cdot 12H_2O$ was prepared by cooling a solution of 40 g Na_2HPO_4 and 100 g H_2O below 35 °C [12]. The crystals were filtered out and dried before use.

A typical synthesis of gelled $Na_2HPO_4 \cdot 12H_2O$ was: 13.5 g $Na_2HPO_4 \cdot 12H_2O$ and 1.5 g H_2O mixed in a closed vial and stirred at 50 °C till a clear solution was obtained. Then 0.085 g sodium alginate was introduced and stirred for 30 min. After which, under nitrogen, an aqueous sodium acrylate solution 2.5 g, 0.017 g of MBA and 0.01 g potassium peroxodisulfate were added and dissolved sequentially; 15 min later, 0.01 g of sodium sulfite dissolved in 0.67 g water was dropped into the

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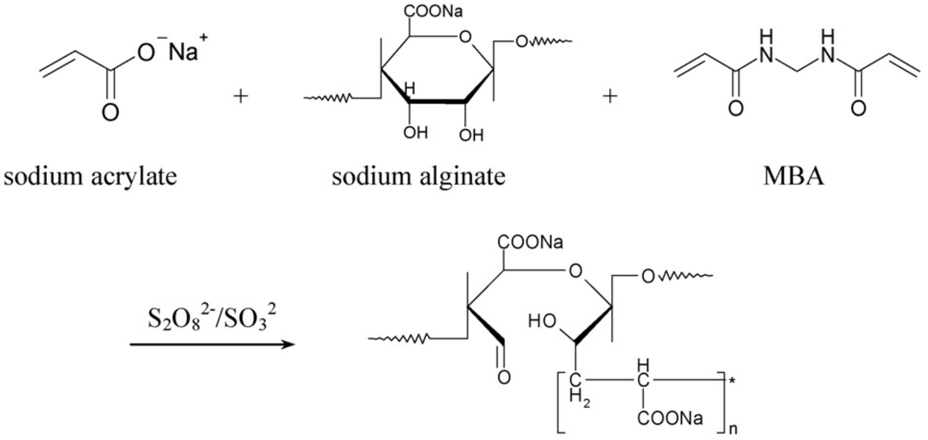

Scheme 1. Radical polymerization for synthesizing water-absorbing polymer.

solution. A jelly-like product was obtained in a few minutes and was cooled down after 2 h (Scheme 1).

Acrylate was not detected in the product by FT-IR since C=C stretching ions 1640 cm^{-1} in sodium acrylate and 1660 cm^{-1} in MBA are not observed (figure not shown).

Evaluation of heat performance of the samples was performed on a DSC (141, SETARAM, France, calibrated with indium, aluminum, tin, of standard material, 99.99% pure) under high purity nitrogen atmosphere, within 0–50 °C. The 3–5 mg sample was sealed in a 30 μL aluminum crucible. TG analysis was performed on Setsys 16/18 (Setaram, France) and FT-IR was by Nicolet Impact 400D spectrophotometer (ThermoNicolet, USA).

3. Results and discussion

Extra water is added to help dissolve $Na_2HPO_4 \cdot 7H_2O$, to produce $Na_2HPO_4 \cdot 12H_2O$ on melting. A molar ratio of $Na_2HPO_4:H_2O = 1:18$ was adopted in our experiments.

TG analysis shows the loss of water for pure $Na_2HPO_4 \cdot 12H_2O$ (60.1%) and the gelled salt (63.7%) up to 160 °C. DTG curves show different states of water: free water, lattice water and water bonded to gel network, which are lost in this sequence.

Influence of synthesis conditions on the heat storage performance is shown in Fig. 1(a)–(d). The influence of sodium acrylate was studied in our previous work [13]: ∼3% (w/w) is desirable. More sodium acrylate leads to a very short gelation time, <30 s, which may cause inhomogeneity in the gel network; if less, the solution dose not gel. Fig. 1 also presents the initial sizes of $Na_2HPO_4 \cdot 12H_2O$ crystals dispersed in the water-absorbing polymer, which were measured with a microscope and expressed as length × width ($a \times b$, mm).

From the results, optimum synthesis conditions of the gelled $Na_2HPO_4 \cdot 12H_2O$ were (w/w): sodium acrylate 2.8%, sodium alginate 0.3–0.4%, MBA 0.1–0.19%, $K_2S_2O_8$ and Na_2SO_3 0.06%, reaction temperature 50 °C. In addition, the initial particle size distribution relates to heat storage performance of the gelled salt: the smaller sizes, the more stable heat storage performance. Most of the crystals in gelled salt with stable heat storage performance were less than 0.1 mm.

The reproducibility of the synthesis method was confirmed by three parallel tests. All three samples exhibited stable heat storage performance, narrow initial particle size distribution (<0.1 mm for the most part) and small variations of melting point (35.4 ± 2 °C) during thermal cycling.

A short-term thermal cycling test was performed to further evaluate the gelling method. Two samples (each about 25 ml) taken from the parallel tests had initial heat of fusion of about 180–190 J g^{-1}. After a 50-run freeze-thaw cycling, the samples maintained both homogeneity and heat storage capacities. At the 100th cycle, one sample was homogeneous in appearance and possessed the same heat of fusion. But another sample had about 10% volume coming out of the gel network. The remaining part of sample still had heat of fusion within 180–190 J g^{-1}. It illustrated that the synthesis process needs to be carefully controlled to obtain uniform products. In addition, melting points varied in the range 35.4–37.5 °C.

In our series of work, heat storage performance has been evaluated for pure $Na_2HPO_4 \cdot 12H_2O$ and the salt gelled by sodium polyacrylate, amylose-g-sodium acrylate and sodium alginate-g-sodium acrylate [13,14]. The severe phase separation of pure $Na_2HPO_4 \cdot 12H_2O$ is constrained to some extent when the salt is dispersed in sodium polyacrylate. But only ∼30% of samples synthesized at the optimum conditions showed stable heat storage capacities. After amylose and sodium alginate are introduced into the gel frame of sodium polyacrylate, the gelled $Na_2HPO_4 \cdot 12H_2O$ then exhibits stable heat storage performance when synthesized at optimum conditions. So the stabilization of $Na_2HPO_4 \cdot 12H_2O$ needs not only a water-absorbing polymer to homogenize the salt but also a suitable composition of the polymer acting as a habit modifier so as to obtain tiny salt particles and to maintain small particle sizes during thermal cycling.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2007.04.008.

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