



Use of nano- α - Al_2O_3 to improve binary eutectic hydrated salt as phase change material

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ABSTRACT

In this paper, a novel $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ - $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ eutectic hydrated salt (EHS) with melting temperature of 31.2 °C/no phase separation was firstly prepared for thermal energy storage applications at heating solar greenhouses and active solar heating systems in buildings. In order to inhibit supercooling and enhance thermal conductivity of EHS, nano- α - Al_2O_3 at different weight proportions was loaded into EHS. The multi-factors orthogonal test method has been employed to evaluate the nucleation effects of nano- α - Al_2O_3 . Besides, various characterization techniques such as DSC, OM, SEM and FT-IR were adopted to investigate the thermal properties, microstructure and chemical stability. The results showed that nano- α - Al_2O_3 was a highly effective nucleating agent and excellent thermal conductive filler. The supercooling degree was reduced from 7.8 °C to 1.6 °C and the thermal conductivities were improved by up to 61.3% when adding 4.5 wt% nano- α - Al_2O_3 and 1.0 wt% borax. Moreover, the latent heat of 4.5 wt% nano- α - Al_2O_3 modified EHS decreased by only about 8% and its melting point maintained constant as that of pure EHS. In addition, the modified EHS had good thermal and chemical stability after 200 thermal cycles.

1. Introduction

The solid–liquid phase change material (PCM) used for thermal energy storage by absorbing and releasing heat energy during phase transition has become a hot research topic in recent years due to its high energy storage density, smaller volume change and relatively constant phase change temperature [1–4]. Most of the solid–liquid PCMs explored by researchers are organic, such as paraffin [5,6], non-paraffin [7,8], organic binary mixtures [9,10], etc. However, compared with organic PCMs, the inorganic PCMs like hydrated salts show advantages of larger transformation enthalpy, nonflammability, abundant sources, cost effective and so on [3,11,12], which have been showing extensive prospects for use in thermal energy storage.

Hydrated salts can be used as low-temperature heat storage materials at heating solar greenhouses and active solar heating systems in buildings, among which sodium sulfate decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) has received much attention because of its applicable phase change temperature (about 30 °C), high latent heat and low cost [13–15]. Unfortunately, the drawback of phase separation of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ limits its application in heat storage [16]. Among ordinary hydrated salts, disodium hydrogen phosphate dodecahydrate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) rarely has phase separation, but its phase change

temperature of around 40 °C is not compatible with the scope of application above. Nevertheless, the phase change temperatures of many PCMs can be adjusted by mixing with other PCM, and phase separation of a few hydrated salts can be controlled to some degree [17–19].

In addition, the supercooling and low thermal conductivity are the other two serious problems associated with all hydrated salts [20,21]. The supercooling can be avoided by adding suitable nucleating agents into hydrated salts [3,22]. For example, sodium tetraborate (borax) can remarkably reduce supercooling degree of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ [23,24], whereas it does less effective work for reducing supercooling of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$. Therefore, for a multiple system of hydrated salts, the effect of compounded nucleating agents may be superior to a single nucleating agent. Based on heterogeneous nucleation theory, the nucleating agents suspending in hydrated salts system can serve as nucleation sites on which crystals are easier to nucleate and grow. The adsorption of ions and molecules on surfaces of solid particles is a critical step for crystal growth [27]. And when particle size reduces to a nanometer level, adsorption capacity will significantly increase [28]. Hence, the nanoparticles can be considered as proper nucleating agents to diminish supercooling degree of hydrated salts. In previous works, the nucleating agents proposed are virtually hydrated salts and

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inorganic salts [23–26], which make no contributions to the thermal conductivity. M. Hemmat Esfe et al. [29] studied the effects of nano- Al_2O_3 on thermal conductivity of ethylene glycol based Al_2O_3 nanofluids, revealing that the thermal conductivity increased dramatically with Al_2O_3 concentration increasing. Moreover, the same results of thermal conductivity improvement have occurred in the methanol based Al_2O_3 nanofluids and Al_2O_3 - H_2O nanofluids [30,31]. Therefore, the nanoparticles, such as nano-metallic oxide particles, may have a remarkable advantage of enhancing the thermal conductivity of inorganic hydrated salts.

In this work, a new $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ - $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ eutectic hydrated salt (EHS) has been developed as PCM, which supplies a suitable application temperature without phase segregation. The nanoparticle-modified EHS was prepared by dispersing α - Al_2O_3 nanoparticles into EHS to inhibit the supercooling as well as improve thermal conductivity. And the effect of reducing supercooling degree by combining EHS with the compounded nucleating agents of nano- α - Al_2O_3 /borax was evaluated through the significance level of the statistics based on multi-factors orthogonal test. The thermal, crystallographic and morphological characterizations and thermal cycling stability of the nanoparticle-modified EHS were conducted as well.

2. Experimental section

2.1. Materials

Sodium sulfate decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, AR, Tianjin Hengxing Chemical Preparation Co., Ltd.) and disodium hydrogen phosphate dodecahydrate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, purity > 99%, Tianjin BENCHMARK Chemical Co., Ltd.) were employed as the PCMs. Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, AR, Tianjin Zhiyuan Reagent Co., Ltd.) and nano-sized α -alumina (nano- α - Al_2O_3), which was obtained from Shenzhen Jingcai Chemical Co., Ltd., with purity higher than 99.9% and an average size of 100 nm were selected as nucleating agents. Sodium alginate (SA, viscosity=1050–1150 m Pa s, Tianjin Guangfu Fine Chemical Research Institute) and hydroxyethyl cellulose (HEC, viscosity=50000–60000 m Pa s, Henan Datian Food Ingredients Co., Ltd.) used for the mixed surfactants (MS) were also purchased. All chemicals were directly used as received without any further purification.

2.2. Experimental program

2.2.1. Preparation of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ - $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ eutectic hydrated salt (EHS)

The $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ - $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ eutectic mixtures were prepared by replacing $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ with 10, 20, 25 and 30 wt% $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, respectively. Binary hydrated salt mixtures were filled into a small beaker, melting completely at 60 °C in water bath, and the solution under constant temperature was stirred for 5 min at 1000 rpm. Then, during the process of solidification, the real-time temperature of the hydrated salt mixtures was recorded by the multi-channel temperature measuring system with an accuracy of ± 0.1 °C.

2.2.2. Modification of EHS

In order to obtain a high-performance modified EHS with lower supercooling degree and higher thermal conductivity, the amount of nano- α - Al_2O_3 and borax were investigated in terms of different mixed surfactants (MS) ratios (the mass ratio of MS to nano- α - Al_2O_3). MS is comprised of sodium alginate (SA) and hydroxyethyl cellulose (HEC) at the rate of 1:1 in mass. SA serves as an emulsifier to obtain more uniform solution, and HEC plays the role of stabilizer. What's more, SA as anionic surfactant and HEC as nonionic surfactant were mixed together to engender synergism effect of nonideal mixed system of surfactants, which would have a better performance in the high-concentration salt solution of EHS [32,33].

Orthogonal tests designed through Statistical Product and Service

Table 1
Factors and levels for orthogonal experiment.

Factors	Levels			
	1	2	3	4
Nano- α - Al_2O_3 (wt%)	0	1.5%	3.0%	4.5%
Borax (wt%)	0	1.0%		
MS ratio (w/w)	2:3	1:1		

Note: MS ratio (w/w), the mass ratio of mixed surfactants (MS) to nano- α - Al_2O_3 ; Nano- α - Al_2O_3 and Borax (wt%): the mass fraction of nano- α - Al_2O_3 and borax added in EHS.

Solutions software (SPSS) were carried out. The experiment was organized as an L_8 ($4^1 \times 2^4$) orthogonal array, as listed in Table 1. The supercooling degree was chosen to evaluate the influence of the three factors including nano- α - Al_2O_3 , borax and MS ratio. Nano- α - Al_2O_3 was dispersed and stabilized by the mixed surfactants (MS) in accordance with the designed MS ratio.

Sample preparation was as follows: the $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ - $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ eutectic hydrate salt (EHS) was first melted at around 55 °C and then borax and SA were dissolved in molten EHS in order. Solution was stirred by magnetic stirrer at 1000 rpm at around 55 °C for 2 h. Nano- α - Al_2O_3 particles were added into the solution later and stirred at 1500 rpm for 1 h. Then, all the suspensions were ultrasonicated for 30 min at 120 W to obtain a good dispersion. Finally, HEC was added into suspension and mixed at 1500 rpm for another 2 h. The real-time temperature of solidification process of all the samples was recorded by the multichannel temperature measuring system.

2.3. Characterization and testing

Thermal properties of modified EHS were measured using a differential scanning calorimetry (NETZSCH, DSC 200F3). The scanning temperature range was from 15 °C to 55 °C, and the scanning rate was 5 °C/min. The thermal conductivities of modified EHS was tested by a thermal conductivity measuring apparatus (XI'AN XIATECH, TC3000) based on hot-wire method. The estimated uncertainty in the thermal conductivity measurement was $\pm 3\%$. The microstructure of EHS doped with nano- α - Al_2O_3 was examined with environmental scanning electron microscope (SEM, FEI Co., Quanta 200). The crystallography features of before and after modification were observed using the optical microscopy (OM, OLYMPUS, DSX500). FTIR spectrometer (TIANJIN GANGDONG SCI. & TECH., FTIR-650) was used to check functional groups, in which the scanning range was 400–4000 cm^{-1} . The thermal cycling tests were carried out in a thermo-cycling test chamber by heating and cooling the samples between 5 and 60 °C repeatedly.

3. Results and discussion

3.1. Determination of EHS

Fig. 1 shows the cooling curves of pure $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ and binary hydrated salt mixtures. It can be obtained from Fig. 1 that the phase change temperatures of binary hydrate salt mixtures with different $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ replacement percentage (0, 10, 20, 25 and 30 wt%) are 39.6, 34.3, 32.7, 31.2 and 32.3 °C, respectively. With $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ replacement ratio increasing, the phase change temperature decreases firstly and then increases, and the lowest temperature reaches at 31.2 °C when the replacement ratio is 25 wt%. Therefore, the recipe of 25 wt% $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ -75 wt% $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ eutectic hydrate salt (EHS) was determined.

The state of molten $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, EHS and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ is displayed in Fig. 2. It can be observed that $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ has a severe phase separation since the anhydrous salt cannot be entirely dissolved in its solution at the melting point. In contrast, there is nearly no phase

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