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A thermally stable phase change material with high latent heat based on an oxalic acid dihydrate/boric acid binary eutectic system

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ABSTRACT

An oxalic acid dihydrate/boric acid (OCD-BA) binary eutectic mixtures containing 88 wt% OCD and 12 wt% BA was investigated as a novel phase change material (PCM) with high latent heat and thermal stability. The solid-liquid phase diagram of binary systems is established, and the phase change temperature of OCD-BA binary eutectic mixture is 87.3 °C and the latent heats of the melting and crystallization process are 344 J g^{-1} and 262 J g^{-1}, respectively. Its thermophysical properties and thermal stability were studied using differential scanning calorimetry (DSC), Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), and Scanning electron microscopy-Energy dispersive spectroscopy (SEM-EDS). Its thermal stability was investigated in situ through 100 cycles using DSC and 1000 thermal cycling tests using Refrigerated and heating circulators (RHC). The latent heat of melting still exceed 280 J g^{-1} after 1000 heating/cooling cycles. The heat release platform sustained 5 h at more than 70.0 °C, and the degree of supercooling was only 1.0 °C according to T-history method. These results indicate that the newly prepared OCD-BA binary eutectic mixture is a potential PCM for thermal storage tanks.

1. Introduction

With the rapid growing demand for electricity from industry and society in recent years, it is increasingly imperative for electricity utility companies to reduce the peak demand on their generation and distribution systems [1–3]. Latent heat thermal energy storage using phase change materials (PCMs) has been applied in various areas such as solar energy systems [4], waste heat recovery [5], building energy conservation [6], temperature-regulating textiles [7], and thermal storage tanks [8,9]. Storage tanks are one of the best-known thermal energy storage technologies and are used to accumulate hot water for domestic use. Large thermal storage tanks have been widely utilized in both industrial and domestic applications by allowing the accumulation of heat for use at a later stage. The improvement of the thermal energy storage capacity using PCMs in storage tanks is currently being studied to reduce the consumption of energy by taking advantage of the large heat storage capacity of PCMs [10–12].

Over the past decade, various hydrous inorganic salts including sodium acetate trihydrate, calcium chloride hexahydrate, barium hydroxide octahydrate, and sodium sulfate decahydrate have been studied as PCMs and extensively applied in thermal energy storage materials because of advantages such as large latent heat, numerous species, and low cost [13–15]. However, most salt hydrate PCMs suffer from poor recycling ability. The main problems are that the salt hydrates themselves participate in the phase separation, greater supercooling, and instability [16,17]. In addition, some researchers have been focusing on a large number of organic PCMs such as fatty acids, amides, and polyhydric alcohols [18]. However, because organic PCMs have shortcomings such as low thermal conductivity, liquid leakage during the phase change processes, and they can be explosive and toxic, their application in many fields has been limited [19,20].

In general, PCMs that are intended for latent thermal energy storage can be categorized into three types, namely, inorganic phase change materials, organic phase change materials, and eutectic mixtures [21]. In order to meet requirements for various phase change temperatures, two or three PCMs can be mixed to form binary or ternary eutectics which contain organic-organic eutectic PCMs, inorganic-inorganic eutectic PCMs and organic-inorganic eutectic PCMs [22–24]. Nevertheless, the organic-inorganic eutectic PCMs have been few reported because many organic compounds cannot be dissolved in inorganic salt hydrates when they are liquids. The following were specific reports about organic-inorganic eutectic PCMs.

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For instance, Tang, et al. investigated the thermal energy storage performance and phase change stability of mixture PCMs consisted of stearic acid and $Na_2PO_4 \cdot 12H_2O$. It is speculated that they complement each other on the basis of organic/inorganic characteristics in itself for these two component materials of the mixture [25].

Shahbaz et al. reported that choline chloride (ChCl) and $CaCl_2 \cdot 6H_2O$ as the deep eutectic solvents, which is the molar ratios of 1:6 and 1:8 (ChCl: $CaCl_2 \cdot 6H_2O$), have the potential to be utilized as PCMs in building applications with large latent heat (127–135 J g^{-1}) and suitable phase change temperature at 20.6–23.0 °C [26].

In our previous studies, the cyclic stability of OAD was determined by using ordinary aluminum pans and high pressure gold-plated pans in DSC measurement [27]. The OCD and 9 wt% NaCl composite as eutectic PCMs improved the cyclic stability of OCD, and reduced the melting point by 12.5 °C, while maintaining a relatively high heat of fusion of 328 J g^{-1} [28].

Among the PCMs that have been studied, the eutectic mixtures are particularly promising candidates for use in thermal energy storage applications due to their broad range of melting temperatures, high heat capacity, little or no super-cooling, low vapour pressure, melting congruency, good chemical and thermal stability, non-toxicity, low cost and small volume change [29,30].

It is well known that OCD is a potential PCM for thermal energy storage [31]. Owing to its phase change temperature of 101.5 °C, widespread use, large heat storage capacity, and low investment cost, this kind of materials has been of great interest in many fields. However, OCD itself has a phase transition temperature of 101.5 °C, and when the heat is stored and the OCD is directly heated and melted in an airtight device, the vapour pressure of water is rapidly increased and can result in the explosion of the device. This situation can be avoided by adding another compound to the OCD system to reduce its melting point. Furthermore, adding another compound could be of benefit through the formation a eutectic system [32–34]. However, it is not easy to find an appropriate eutectic compound. In fact, OCD and BA have an enormous hydrogen bond network like a spider web, which leads to the storage of more bond energy. The bond energy was clearly higher when the OCD and BA form a binary eutectic system.

In this study, an OCD-BA binary eutectic system containing 88 wt% OCD and 12 wt% BA was prepared as a novel thermally stable PCM with high enthalpy and used in a thermal storage tank. The OCD-BA binary eutectic system successfully solved the problem of the high vapour pressure of OCD-BA caused by insecurity. Compared with other PCMs reported in the literature, this PCM has one of the biggest latent heats at 87 °C used in a heat storage tank. To differentiate the novel PCM prepared in this work, it was named Institute of Salt Lakes 87 PCM according to the place of discovery and its phase change property (abbreviated as ISL-87 PCM).

Herein, we report the preparation of an OCD-BA binary eutectic system for use as a thermal energy storage material. The eutectic point parameters were determined by FT-IR, XRD, SEM-EDS and DSC [35,36]. The thermal physical properties including the phase change temperature, enthalpy, degree of supercooling, and cycling stability after 100 cycles were investigated by DSC [37,38]. The thermal stability of ISL-87 PCM after 1000 cycles was also investigated.

2. Experimental section

2.1. Eutectic system preparation

A binary eutectic system based on OCD-BA was prepared and named ISL-87 PCM. The pre-dried raw materials of OCD (99%, Aladdin) and BA (99%, Aladdin) were mixed well for 2 min by grinding in the weight proportion of OCD: BA = 88.00:12.00. The mass ratio was at the eutectic point of the OCD-BA binary system as determined from the phase diagram. The binary mixture was melted in a round-bottom flask and allowed to equilibrate at 90 °C for 10 min. The mixture was naturally cooled to room temperature and then ground into a powder, dried, and preserved for experiments.

2.2. Thermophysical properties measurements

A differential scanning calorimetry thermal analyzer (DSC 2, STARe system, METTLER TOLEDO) was used to measure the thermophysical properties of the eutectic binary system of ISL-87 PCM including its onset melting temperature, solidification point, latent heat, and specific heat. For a standard measurement, a maximum of 10 mg of the PCM was loaded into a 40 μL aluminum crucible for analysis. The binary system of ISL-87 PCM was measured with a heating rate of 1 °C min^{-1} in the temperature range of 40 °C to 120 °C under a constant flow of dry nitrogen at a rate of 100 mL min^{-1}. This program was repeated three times for each sample. The melting temperatures and latent heats of fusion were obtained from the second heating cycle. The DSC was calibrated once two weeks by Indium and Zinc standard samples, which was hermetically sealed in a 40 μL standard DSC aluminum pan until the system "STARe Software 10.0" displayed "The DSC module is within specifications!". The uncertainties of this DSC system are typically ± 5% for the latent heat, ± 2 °C for the temperature. All experiments were carried out with a heating and cooling rate of 1 °C min^{-1} under a constant flow of dry nitrogen at a rate of 100 mL min^{-1}.

2.3. Thermal cycling

An in situ thermal stability experiment over 100 cycles was performed using DSC, for a more accurate measurement, a sample of approximately 10 mg of the ISL-87 PCM was loaded into a 40-μL gold-plating medium pressure crucible (METTLER TOLEDO) for analysis. Thermal stability testing over 1000 cycles was performed using a melting-freezing method in a refrigerated and heating circulator (RHC, FP50-MA, JULABO). Bulk ISL-87 PCM samples (50 g) were used in the stability tests. The samples were placed in a sealed quartz tube with a volume of 100 mL. The temperature of the oven was controlled to melt and freeze the ISL-87 PCM with a heating/cooling rate of 5 °C min^{-1} in the temperature range of 70–120 °C to ensure complete melting and cooling. In this study, 1000 thermal cycles of the eutectic mixtures were performed, and the resulting sample was analyzed using FT-IR and XRD.

2.4. Sample characterization

The composition of the OCD-BA eutectic mixture after one cycle and one thousand cycles was determined using FT-IR and XRD to confirm whether decomposition or a chemical reaction occurs. Samples were characterized with the help of Nicolet Nexus 670 FT-IR Spectrophotometer (Thermo Nicolet Corporation, Madison, USA), with KBr pellets, in the wave number ranging from 4000 to 400 cm^{-1} for analyzing the chemical compatibility between of 1th cycle and 1000th cycle of ISL-87 PCM.

XRD were carried out to study the composition of samples. Diffraction patterns were obtained by using PANalytical X'PRO Pert diffractometer fitted with Cu Kα radiation (λ = 1.54 Å) and were recorded at a tube voltage of 40 kV and a tube current of 30 mA, applied a step size of 0.017° 2θ in the angular range of 5° to 70° with 21 s per step.

The microstructure morphology was obtained by Scanning Electron Microscopy (SEM, JSM-5610LV, JEOL) and Energy Dispersive Spectrometer (EDS, INCA, OXFORD) was used to calculate the distribution of oxygen and carbon in ISL-87 PCM.