Synthesis and thermal properties of novel sodium nitrate microcapsules for high-temperature thermal energy storage

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ABSTRACT

Perhydropolysilazane (PHPS), a ceramic precursor resin with outstanding high-temperature resistance, was used as the shell material to prepare novel sodium nitrate microcapsules (MCP-NaNO$_3$) for high-temperature thermal energy storage. The microstructure and thermal properties of the MCP-NaNO$_3$ were investigated by DSC-TG, SEM, FTIR, EDS, etc. The MCP-NaNO$_3$ presented a melting point of 306.19 ± 0.10 °C and latent heat of 159.2 ± 2.4 J/g. The MCP-NaNO$_3$ had a thin shell, and the weight percentage of NaNO$_3$ in the MCP-NaNO$_3$ was calculated to be about 85 wt%. The melting point of MCP-NaNO$_3$ almost had no change, and the supercooling of MCP-NaNO$_3$ only had a small increase of about 2.69 °C compared with that of NaNO$_3$. The thermal decomposition temperature of NaNO$_3$ in the MCP-NaNO$_3$ was enhanced more than 36 °C, up to 647.60 °C. The PHPS shell was able to ensure the MCP-NaNO$_3$ to be still granular after heated at 350 °C, and the melting point and freezing point of the MCP-NaNO$_3$ were almost invariable. The MCP-NaNO$_3$ developed in this study has great promise in future energy and chemical processes. The method that using ceramic precursor resins as microcapsule shells paves a new way to prepare various high-temperature phase change micro-capsules.

1. Introduction

Inorganic salt high-temperature phase change materials (SH-PCMs), with the melting point of 200–1000 °C, are widely used for high-temperature thermal energy storage [1–3], such as in the fields of concentrating solar energy plant and industrial waste heat utilization. SH-PCMs mainly include chlorides, fluorides, hydroxides, nitrates, carbonates, vanadates, and molybdates, and their binary or ternary eutectic composites [4]. The advantage of SH-PCMs is the low cost, and the disadvantage is the high corrosivity of liquid SH-PCMs that is a critical consideration in the thermal energy storage system designed to run at high temperature for a long time. The microencapsulation of SH-PCMs is an effective way to solve the corrosive problem.

The microencapsulation of PCMs is to engulf small solid or liquid PCM particles with a solid wall of inert polymeric or inorganic materials, which is able to prevent the leakage of liquid PCMs from their location and meanwhile increase the heat-transfer surfaces of PCMs. In the current studies on the PCM microcapsules, the core materials of PCM microcapsules mainly focus on numerous organic PCMs and some hydrated inorganic salts, most of whose melting points are below 100 °C. The corresponding shell materials are mainly carbon-carbon chain polymer [5–19] and inorganic sols [20–23]. These PCM microcapsules are applied for thermal conserving and insulation in buildings, thermal comfort and thermal regulation for intelligent fibers and textiles, transportation packaging for temperature-sensitive products, cooling of electronic chips and devices [24]. There are only limited studies on the high-temperature phase change microcapsules using metal particles of zinc and Al-Si alloy as the core materials that have low corrosivity. Zinc particles (0.6 μm and 5 μm) were coated with an organo-phosphorus shell to improve chemical stability [25]. The Al-Si alloy microcapsules were prepared by the first formation of an AlOOH shell on the PCM particles using a boehmite treatment, and then a heat-oxidation treatment in an O$_2$ atmosphere to form a stable α-Al$_2$O$_3$ shell [26].

To our knowledge, there are no studies on the SH-PCM microcapsules due to the lack of suitable shell materials that have a stable shell structure at high temperature. The carbon-carbon chain polymer does not have enough high-temperature resistance as the shell material of SH-PCM microcapsules. The inorganic sols, as the shell materials of SH-PCM microcapsules, can endure high temperatures but meanwhile have the disadvantage of low shell mechanical strength, resulted from the weak curing cross-linked ability of inorganic sols.

Ceramic precursor resins such as polyborosilazane, polyborosilox-ane, perhydropolysilazane (PHPS), have excellent curing cross-linked

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ability to form a compact bulk which can transform into ceramic at high temperature with a small weight loss and are widely applied for functional composites and coatings [27,28]. Among these ceramic precursor resins, PHPS is able to solidify at room temperature with small amount of curing agent and finally transforms to silica or silicon nitride [29,30], which is convenient for the application as the shell material.

In the present work, the objective is to prepare microcapsules made of PHPS as the shell material and sodium nitrate ($NaNO_3$) as the core. $NaNO_3$ is a typical and important high-temperature PCM due to stable thermal performances. Microcapsules were prepared through solvent extraction and ultrasonic dispersing processes and the properties such as microstructure, particle shape, diameter distribution, latent heat, thermal endurance, and supercooling degree were investigated in detail.

2. Experimental

The microcapsule consisted of $NaNO_3$ (99%, Sinopharm Chemical Reagent Co. Ltd., China) and PHPS (99%, Institute of Chemistry Chinese Academy of Science, China), being used as the core material and the shell material, respectively. The $NaNO_3$ was first milled into powders in an agate mortar by hand and then sieved through a 100 mesh sieve to remove large particles. The weight percentage of PHPS in its dichloromethane solution was 50%. Microcapsules were prepared through a novel method of solvent extraction and ultrasonic dispersing. In a typical synthesis process as illustrated by Fig. 1: 1.6 g of $NaNO_3$ powders was completely mixed with 0.8 g of PHPS solution in a beaker to form a homogeneouss mixture. Afterward, 80 g of tridecane was added into the beaker with standing for 20 min, and during this time the dichloromethane was extracted from the mixture and the PHPS resin that is insoluble in tridecane was more closely coated on the surface of the $NaNO_3$ particles. Subsequently, the above mixture was dispersed into particles in the tridecane by an ultrasonic processor (GEX 750-5C, USA) to form microencapsulated $NaNO_3$ (MCP-$NaNO_3$) powders. Finally, the MCP-$NaNO_3$ powders were filtered out and heated in a forced air oven at 200 °C for 3 h to remove the residual tridecane. Three batches of MCP-$NaNO_3$ were prepared and characterized to verify the reproducibility. The $NaNO_3$ and MCP-$NaNO_3$ powders were piled in the glass-surface vessels, and heated in a muffle furnace at 350 °C for 1 h in an air atmosphere. The dispersed $NaNO_3$ and MCP-$NaNO_3$ particles on the glass slides were heated on a heating stage at 350 °C for 1 min and then quickly transferred to the stage of the microscope for observation.

The micrograph images of $NaNO_3$ and MCP-$NaNO_3$ particles on the glass slides were measured by an optical microscope (DM2500P, Leica, Germany). Scanning electron microscopy (SEM) images were obtained using a scanning electron microscope (QUANTA 650, FEI, USA), and all the specimens were directly observed by the scanning electron microscope and not sputter-coated with any conductive layer. The element composition was measured by an energy-dispersive X-ray spectroscopy (EDS) equipped in the scanning electron microscope. The particle size distributions of $NaNO_3$ and MCP-$NaNO_3$ were determined by a laser particle size analyzer (Master sizer 2000, Malvern, USA) using alcohol as dispersion medium. The latent heat and supercooling degree of $NaNO_3$ and MCP-$NaNO_3$ were measured in the temperature range of 0−500 °C by a differential scanning calorimeter (DSC, 204F1, Netzsch, Germany) with both heating speed and cooling speed of 10 °C/min, and three times repeated measurements for each batch of MCP-$NaNO_3$ were done for the DSC measurement. The thermal stability of $NaNO_3$ and MCP-$NaNO_3$ was measured between room temperature and 1000 °C by a simultaneous thermal analyzer (STA, 449F3, Netzsch, Germany) with a heating speed of 10 °C/min. The FTIR spectra of PHPS, $NaNO_3$, and MCP-$NaNO_3$ heated before and after 350 °C were obtained by a Fourier-transform infrared spectrometer (FTS3000, BIO-RAD, USA) with a resolution of 4 cm^{-1}.

3. Results and discussion

The SEM images and particle size distributions of $NaNO_3$ and MCP-$NaNO_3$ powders are shown in Fig. 2. The particle sizes of $NaNO_3$ powders were observed to be non-uniform, including three particle size distribution peaks, one big distribution peak of 10−140 μm and two small distribution peaks of 0.4−0.8 μm and 1.0−2.0 μm. After the $NaNO_3$ particles were microencapsulated using PHPS as the shell material, the particle size of MCP-$NaNO_3$ became bigger and more uniform. There is only one distribution peak of 10−300 μm for the MCP-$NaNO_3$ (Fig. 2c), which is due to the small $NaNO_3$ particles agglomerating together to form a big particle or adhering to the surface of the bigger $NaNO_3$ particles. So it is reasonable that the volume average particle diameters of $NaNO_3$ and MCP-$NaNO_3$ were measured to be 51.8 μm and 95.6 μm, respectively.

In order to observe the element composition of $NaNO_3$ and MCP-$NaNO_3$ particles, the EDS analysis was done. The EDS results of $NaNO_3$ and MCP-$NaNO_3$ particles are presented in Fig. 3. Fig. 3a shows that the $NaNO_3$ contains N, O, Na elements. Fig. 3b-d shows that the MCP-$NaNO_3$ particles with different appearances all contain the Si element, although the intensities of Si peaks are different, which implies that the shell thickness of the MCP-$NaNO_3$ particles is different. This result indicates that all the $NaNO_3$ particles have been encapsulated by the PHPS, and the particles formed by the small $NaNO_3$ particles agglomeration contain more PHPS (Fig. 3d). The above results also shows that the fabricating method of MCP-$NaNO_3$ is facile and effective, and has no harsh restrictions to the species, shape and size of core materials, which means various high-temperature phase change microcapsules can be prepared by this method. In contrast, the fabricating methods mentioned in the references of [25,26] have some limitations. The organo-phosphorus shell material of Zn microcapsules [25] is more suitable for metal microcapsules, and the fabricating method of a boehmite treatment and heat-oxidation treatment is mainly for Al-Si alloy microcapsules [26].

Three batches of MCP-$NaNO_3$ were prepared and characterized by DSC, SEM and EDS to verify the reproducibility and each batch of MCP-$NaNO_3$ was measured by three times with DSC to make an average. The DSC curves and corresponding thermal properties of $NaNO_3$ and the 1st batch of MCP-$NaNO_3$ are shown in Fig. 4 and

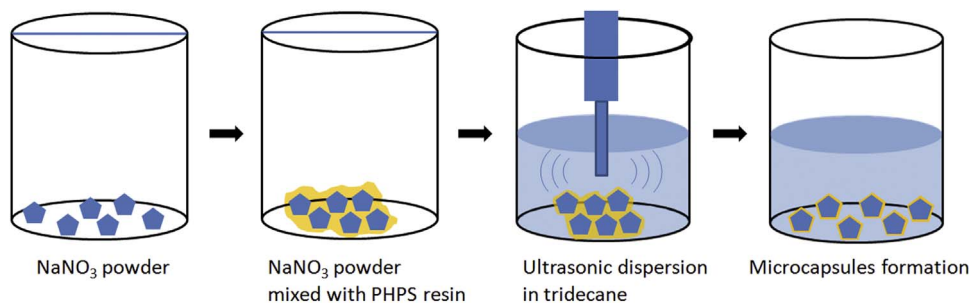**Fig. 1.** Scheme of the solvent extraction and ultrasonic dispersion microencapsulation method

NaNO₃ powder

NaNO₃ powder mixed with PHPS resin

Ultrasonic dispersion in tridecane

Microcapsules formation