Preparation and enhanced heat capacity of nano-titania doped erythritol as phase change material

Luo Zhichao [a], Zhang Qiang [a,b,*], Wu Gaohui [a,b]

[a] School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, PR China
[b] National Key Laboratory of Material Behaviors & Evaluation Technology in Space Environments, Harbin 150001, PR China

ARTICLE INFO

ABSTRACT

In this paper, novel nano-enhanced phase change materials (NePCMs) were prepared by two step method. Nano-titania and erythritol were chosen as nano material and phase change material (PCM), respectively. Among many dispersants, triethanolamine (TEA) was proved the most effective one due to its low molecular weight and the carried hydroxide radical. The results showed that the heat capacity of NePCMs was enhanced by the doping of nano-titania. The enhancement was about 40% and 14% in solid and liquid state, respectively, when the volume fraction of nano-titania was only 0.2 vol%. We argued that the increased fraction of atoms located in the metastable interfaces contributed to the increase of specific heat capacity in solid state. While in liquid state, the enhancement of heat capacity was due to the increased interfacial thermal resistance caused by high surface area of nanoparticles.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The unpredictability of the output of renewable energy systems demands robust, reliable and efficient phase change materials (PCM) to integrate into such systems [1]. Unfortunately, an undesirable property of PCM is their relatively low thermal conductivity, which strongly suppresses the energy charging/discharging rates [2,3].

The nano-enhanced phase change materials (NePCMs) were recently proposed by Khodadadi and Hosseinizadeh [4], for improving thermal energy storage by increasing heat conductivity. It was noteworthy that nanoparticles had been formerly utilized, by Choi [5], to develop advanced heat transfer fluids, i.e., nanofluids [6–8]. Mechanisms for the enhanced heat transfer of nanofluids have intensively been investigated [9–11]. Among them, effective conductive cluster was considered as the mechanisms most probably responsible for the enhancement of heat conduction [6]. However, researches showed that the heat conductivity enhancement of PCM caused by nano additives was rather limited [12,13]. When higher dose was used, the sacrificed fusion heat could not be negligible any more.

Fortunately, recent researches [14–17] proved that specific heat capacity of PCM could also be enhanced by doping quite small amount of nanoparticles. The enhanced heat capacity of PCMs would directly improve their thermal energy storage performance. In these studies, different nanofluids with phase change behavior were developed by mixing molten salt (selected as phase change material) with nanoparticles. The enhancements were considerable, 19.9% by doping 0.063 wt% of alumina nanoparticles [16], 57% in solid phase and 22% in liquid phase by 1.0 wt% of a mix of silica-alumina (SiO_2–Al_2O_3) [17], etc. The specific heat capacity of the NePCM would be further enhanced with increase of nanoparticle size [18], strongly depend on the dispersal condition of nanoparticle [16]. Three mechanisms were proposed by Donghyun Shin [14] to explain this anomalous enhancement of specific heat capacity. However, the real mechanism responsible for the enhancement of heat capacity for NePCM was still unclear. Besides, the PCMs selected above were limited to molten salts.

In this work, we chose erythritol and nano-titania as PCM and nano additive, respectively. Erythritol possesses a high fusion heat of 340 J/g (much higher than most of molten salts and waxes) at a melting point of about 119 °C. It is always used for recovering waste heat. Nano-titania particle is one of the cheapest and most common used nanoparticles, which also has good compatibility with many solvents. By introducing nano materials into PCM presented us a new horizon about nano composites. However, few literatures detailedly investigated the preparation process of NePCM. The aim

---

* Corresponding author at: School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, PR China. Tel.: +86 451 86402373 5052; fax: +86 451 864122164.

E-mail addresses: luozhichao1989@gmail.com (L. Zhichao), zhang_tsiang@hit.edu.cn (Z. Qiang).

of this paper was to study the mechanism of dispersion by preparing a stable erythritol suspension with nano-titania particle. Further, to get an insight into the enhancement of specific heat capacity mechanism by utilizing the knowledge of crystallography and surface chemistry.

2. Experimental details

2.1. Nanofluid synthesis

The nano-titania particle (with an average size of 20 nm) was provided by NanoChina (at Nanjing, Jiangsu Province). Fig. 1 showed the morphology and size distribution of nano-titania. Erythritol (purity $\geqslant$ 99.8%) was bought from Sanyuan, Shandong province, China. Conventional two-step method [19] was adopted to prepare the suspensions, as showed in Fig. 2(a). The volume fraction of nano-titania was 0.5 vol%. The dispersants we used included polyvinyl pyrrolidone (PVP), cetyltrimethyl ammonium bromide (CTAB), sodium dodecyl benzene sulfonate (SDBS), sodium tyipolyphosphate (STPP), triethanolamine (TEA) and oleic acid (OA).

Erythritol was melted at 130 °C, then poured into beaker. The beaker was put on the magnetic stirring apparatus (equipped with heat system) for 30 min. A certain amount of dispersant and nano-titania particle (0.5 vol%) were added to the PCM successively. The mass of dispersants were half of the added particles. The most effective dispersant was selected after the suspensions were kept at 130 °C in a drying oven for 24 h of standing. Then NePCMs with different volume fraction of Nano-titania were prepared by using this selected dispersant.

For heat capacity testing, the specimens were solidified at room temperature on a glass slide. Then the solid erythritol was grinded into fine powder and dried at 60 °C for 12 h, in order to eliminate the influence of water on heat properties. The optical micrograph observation was conducted on ZEISS-40MAT. FT-IR spectrophotometer (SPECTRUM ONE B, SHIMADZU) was used to check the functional groups. The range of FT-IR spectra was set in the range of 400–4000 cm^{-1}.

2.2. Heat capacity measurement

The specific heat of the samples was measured by sapphire method (in Q2000, TA Instruments) according to standard DSC measurement protocol ASTM-E1269. The measurement uncertainty of this method is less than 5%. The standard aluminum hermetic pan and lid were used to mount the samples. The temperature is held at 20 °C for 5 min to thermally stabilize the instrument. Then, the temperature is ramped to 170 °C at a rate of 10 °C/min and held at this temperature for another 5 min. For each sample, an empty pan, the pan with the reference material (25.412 mg of sapphire, heat capacity C_r), and the same pan with the sample material were subjected to the temperature cycles

mentioned above and the heat transfer was recorded by the instrument. Then the heat capacity can be calculated based on the true value of heat capacity of sapphire.

3. Results and discussion

3.1. Disperse of titania in erythritol

Fig. 2(b) displayed the suspensions which were prepared by different dispersants after 24 h of standing at 130 °C. As revealed in Fig. 2(b), the suspension stability was obviously improved by the introduction of dispersants. However, not all these dispersants were suitable. TEA and OA were proved the only effective dispersants for this TiO$_2$–erythritol system. But because of the effumability of OA, we did not take this dispersant for further consideration.

Fig. 3 showed the suspensions with different volume fraction (up to 2.0 vol%) of nano-titania particle, which were prepared by using TEA as dispersant. As displayed in Fig. 3, the suspensions were stable after 120 h of standing, slightly layered after 240 h. The dispersion of nanoparticles in a certain solvent involves a series of events, the properties of solvent molecule and surface state of particle. There are two basic mechanisms for the stabilization of nanoparticles in suspensions, as showed in Fig. 4(a) and (b), electrostatic repulsion and steric hindrance [20,21]. Electrostatic repulsion in a suspension system involves absorbed ionic polymers building up a charged layer around the nanoparticles. The formed charged layer enhanced the repulsion force between nanoparticles. While steric hindrance depends on two factors [20]: (a) volume restriction component, (b) mixing or osmotic component, involving compression of the absorbed layer. Some dispersants can provide both electrostatic and steric hindrance stabilization mechanism. An example of which was (SDBS), as showed in Fig. 4(d).

The mechanisms for well dispersion of nano-titania in molten erythritol by TEA can be explained with three aspects as below:

(1) TEA molecules were easier to form the functional nanolayer compared to other dispersants. The mass transport of dispersant is controlled by convection and diffusion [22]. So that it was related to the viscosity of solvent and the molecule weight of dispersant. The viscosity of molten erythritol was higher than that of aqueous solvent. Thus some effective dispersants (perhaps possess high molecular weight) in aqueous solvent may be useless in molten erythritol. Among the many dispersant used, TEA has the smallest molecular weight of about 149. Thus the adsorption process of TEA molecule into the surface of nano particle was quicker.

(2) Second, TEA can take proton from alcohol molecule due to the lone pair electron on the nitrogen atom [23]. While nano-titania act as acid at high pH environment and releases H$^+$ into alcohol [24]. Therefore, the negatively charged nano-
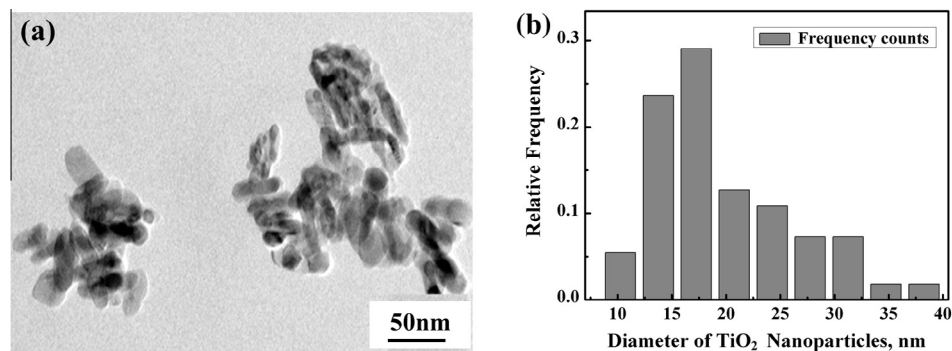

Fig. 1. (a) Morphology of nano-titania in transmission electron microscopy (TEM); (b) size distribution of nano-titania.