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Effective dispersion of multi-wall carbon nano-tubes in hexadecane through physiochemical modification and decrease of supercooling

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ABSTRACT

Prevention of supercooling is essential for phase change material (PCM) utilization. In this study, multi-wall carbon nano-tube (MWCNT) particles were dispersed in an organic liquid n-hexadecane used to decrease supercooling. Various surfactants were tested as additives to overcome the rapid aggregation and sedimentation of the nanoparticles in the organic liquid. Stable and homogenous dispersion was attained through surface modification of the MWCNT particles with strong acids H_2SO_4 and HNO_3, plus the addition of 1-decanol as a surfactant to the organic liquid. Thermal analysis of the n-hexadecane with well dispersed MWCNT particles at concentrations ranging from 0.1% to 10% w/w by differential scanning calorimeter (DSC) indicated that the supercooling of n-hexadecane was significantly decreased with the concentration of 0.1% and 0.5% but only slightly with the concentrations over 1.0%. It appears that well dispersed nanoparticles provided stable foreign nuclei of proper size to promote the heterogeneous nucleation process and accelerate crystallization process, thus the supercooling was significantly reduced. The obvious effects of MWCNT particles on the decrease of supercooling of n-hexadecane provide promising way of improving the performance of system energy efficiency in building cooling and heating applications.

1. Introduction

In recent years, microencapsulated phase change material (MPCM) slurry and PCM emulsion have been investigated for building heating and cooling applications in view of their potential thermal performance and utilization flexibilities [1–3]. However, one of the major problems in using the PCM as thermal storage material is supercooling, i.e., when a PCM liquid is cooled, freezing usually occurs at a lower temperature than the melting point. As the latent heat is only released below the supercooled temperature, large temperature difference between charging and discharging is needed to fully utilize the latent heat, which is undesirable for the energy efficiencies of energy storage applications [4].

As suggested by some researchers [5], an effective approach for decreasing supercooling is the addition of liquid or solid nucleating agents to the PCM liquids as the seeds and catalysts for nucleation and crystal growth. A liquid nucleating agent has a higher melting point than that of the main heat storage material, and is first solidified upon cooling to act as a nucleus of crystal formation. Several studies have been conducted on liquid nucleating agents in various liquids, such as 1-Tetradecanol (2 wt%) for microencapsulated n-Tetradecane [6], 1-octadecanol (10 wt%) for microcapsulated n-octadecane [4], and paraffin wax (0.8–10 wt%) for tetradecane and hexadecane paraffin-in-water emulsion [7]. Solid nucleating agents, such as nanoparticles and impurity particles, acting as nucleation centers to enhance the nucleation progress have shown promising application potentials. As proposed by Oliver and Calvert [8], the crystallization processes of most PCM liquids are controlled by the heterogeneous nucleation mechanism. The phase-transition behavior of the PCM liquids is complicated and very sensitive to small amounts of impurities. He et al. [9] showed that the addition of TiO_2 nanoparticles into pure water effectively reduced the supercooling of water. Zhang et al. [10] reported that the effects of nanoparticles on supercooling of pure water are strongly dependent on their surface wettability. Among the three additive candidates, α-Al_2O_3 had more effect than γ-Al_2O_3 and SiO_2, and the effect was more notable at a lower concentration of 0.3% than at 0.5%. However, up to now, there is no systematic method to select additive for reducing the supercooling. This is because the essential factors affecting the nucleation have not been clarified.

A major problem with the use of nanoparticles as nucleating agents is the poor dispersibility of nanoparticles in the liquid. Because of their high aspect ratios, large specific surface area, and substantial van der Waals attractions, carbon nano-tubes tend to self-aggregate into bundles spontaneously. In addition, the high

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flexibilities increase the possibility of nano-tubes entanglement and close packing [11,12]. The structure of MWCNT particle plays an important role on its poor solubility and dispersivity in either water or organic solvents [11]. The carbons on the tubular part are joined with three neighbor carbons (120°) to form the hexagonal structure hence the hybridization state is sp^2, while the carbons on the end caps are pentagons and heptagons, which are sp^3 hybridized. The sp^2 hybridized carbons stay in the pz orbital and are responsible for π–π interactions causing aggregation between MWCNT particles. But these π-electrons also promote adsorption of various chemicals on the MWCNT particle surface via π–π stacking interactions [11,13]. Two common approaches are available for dispersion of MWCNT: the use of external mechanical forces and physicochemical modification of the particle surface properties [14]. Mechanical approach can only temporarily break the interactions between MWCNT particles and the particles will aggregate again after the force is removed. Physicochemical approaches can be classified into physical and chemical methods. Physical methods mostly involve the adsorption of chemical surfactants onto the MWCNT surface, which do not change the chemical properties of the MWCNT surface. Chemical methods involve the surface modification or functionalization of the particles with various chemical reagents to improve their dispersibility in the liquid and to increase the resistance to aggregation.

Our previous study [15] has investigated the effects of supercooling on the effective MPCM thermal storage capacity and the impact on building cooling utilization. This study is to evaluate the use of MWCNT nanoparticles as nucleating agent to decrease supercooling in the organic liquid PCM n-hexadecane. Addition of various chemical surfactants and chemical modification of the particle surface were attempted to attain a stable and well dispersed suspension of nanoparticles in the organic liquid. The effectiveness of well dispersed MWCNT particles as nucleating agent for decreasing of supercooling was evaluated at various concentrations.

2. Experimental

2.1. Materials

In this study, n-hexadecane $C_{16}H_{34}$ (99%) was chosen as the PCM liquid (purchased from International Laboratory USA), and multi-walled carbon nano-tube (MWCNT) as the nucleating agent, which had an outer diameter 10–20 nm, length 0.5–2 μm and >95% purity (purchased from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences, China). Several surfactants were tested as additives for dispersing the MWCNT particles in hexadecane, including sodium dodecyl sulfate (SDS), cetyl trimethylammonium bromide (CTAB), polyvinylalcohol (PVA), polyethylene glycol (PEG), tetramethylethylenediamine (TEMED), Triethylamine (TEA), glacial acetic acid (AcCOOH), 1-decanol (decan-1-ol), salicylic acid (SA), Tween-80 (polysorbate 80), and Triton X-100 ($C_{14}H_{22}O(C_2H_4O)_n$), which were all of analytical grade.

2.2. Dispersion of MWCNT nanoparticles in hexadecane

Two methods were attempted to improve the dispersion of MWCNT particles in the PCM liquid, the addition of a chemical surfactant into the PCM liquid and the surface-modification of the nanoparticles plus the addition of a surfactant. All dispersion experiments were performed in glass test tubes using the ultrasonication technique. For the dispersion with surfactants, the MWCNT particles were added at 30–50 mg/L to hexadecane in each test tube, and one of the surfactants mentioned above was added to the tube at 1% (w/v). The tubes were ultrasonicated by an ultrasound probe (Sonics Vibra-Cell^{TM}, model VCX130) for 5 min at 30% amplitude of power.

Surface modification of the MWCNT particles was performed in a mixture of two strong acids, concentrated H_2SO_4 (98%) and HNO_3 (70%) at 3:1 volume ratio. MWCNT particles was added to H_2SO_4–HNO_3 in a test tube and sonicated in an ultrasonic bath for 6 h and then heated with reflux at 65 °C for 4 h. After cooling down to room temperature, the acid liquid was diluted with deionized water and the MWCNT particles were spun down at 18,000 rpm for 2 h. After removal of the liquid, the solid particles were dried at 80 °C in an oven for about 24 h.

The surface-modified MWCNT particles were re-dispersed in hexadecane by ultrasonication using an ultrasound probe with 30% amplitude of power for 5 min. Each of the surfactants was added to the dispersion and the dispersion was sonicated in an ultrasound bath for 20 min. Based on the experimental results as shown later in Section 3.1, surface-modification plus the addition of 1-decanol to the PCM liquid was the most effective method for the stable dispersion of the nanoparticles. Therefore, the surface-modified MWCNT particles were dispersed in 1-decanol by ultrasonication for 10 min to attain an excess amount of 1-decanol being coated on the MWCNT particles. This yield a stock of 1-decanol-coated, surface-modified MWCNT particles, which was applied to generate the final MWCNT-hexadecane slurry at various concentrations from 0.1 wt% to 10 wt% for the following studies.

2.3. Characterization and analysis of nanoparticles

Surface properties of the modified MWCNT particles were analyzed by Fourier transform infrared (FTIR) spectrometry on a Nicolet Avatar 360 FTIR instrument using the KBr pellet method.

The size distribution of nanoparticles dispersed in hexadecane was measured by dynamic light scattering analysis using a Malven Zetasizer (model 3000 HSA) at 90° scattering angle and 25 °C. Each sample was scanned 100 times and the average particle size (nm) and the polydispersity index were computed by the Zetasizer 3000HSA-Advanced Software 15.

The morphology of original and modified MWCNT particles was examined with transmission electron microscopy (TEM) using a JEOL 2011 instrument at a high voltage of 200 kV and point resolution 0.23 nm. The TEM was operated by the Jeol Fas TEM software and the images were processed by Gatan Digital Micrograph.

2.4. Thermal analysis of PCM

Thermal analysis of the PCM with the modified MWCNT as the nucleating agent was performed on a differential scanning calorimeter (DSC) (METTLER TOLEDO DSC-822e) equipped with a thermal analysis data station. Samples (10 mg each) were placed into hermetically sealed aluminum pans and treated with the following temperature program: the sample was first cooled to the initial temperature of −5 °C for at least 15 min for stabilization, and then heated from −5 °C to 30 °C at a rate of 5 °C/min, held for 5 min at 30 °C, and finally cooled from 30 °C to −5 °C at a rate of 5 °C/min. STARe software was used to analyze and plot the thermal data.

3. Results and discussion

3.1. Dispersion of MWCNT in hexadecane

3.1.1. Dispersion of original MWCNT by surfactants

Table 1 shows the suspension time, i.e. the period for complete sedimentation of the original MWCNT particles in hexadecane supplemented with the eleven surfactant chemicals. A longer time