

# EFFECTS OF ADDITION OF MULTI-WALL CARBON NANO-TUBES ON SUPERCOOLING OF N-HEXADECANE

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## 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 (Farid et al. 2004, Zhu, Ma and Wang 2009, Huang, Petermann and Doetsch 2009). 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 (Zhang et al. 2005).

As suggested by some researchers (Sangwal 2007), 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 (Yamagishi et al. 1996), 1-octadecanol (10 wt%) for microcapsulated n-octadecane (Zhang et al. 2005), and paraffin wax (0.8-10 wt%) for tetradecane and hexadecane paraffin-in-water emulsion (Huang et al. 2010). 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 (1975), 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, Tong et al. (2007) showed that the addition of TiO<sub>2</sub> nanoparticles into pure water effectively reduced the supercooling of water. Zhang, Wu et al. (2010) reported that the effects of nanoparticles on supercooling of pure water are strongly dependent on their surface wettability. Among the three additive candidates,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> had more effect than  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, and the effect was more notable at a lower concentration of 0.3% than at 0.5%. However, up to now, there is not a 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 flexibilities increase the possibility of nano-tubes entanglement and close packing (Vaisman, Wagner and Marom 2006, Sun et al. 2009). Two common approaches are available for dispersion of MWCNT: the use of external mechanical forces and physicochemical modification of the particle surface properties (Rastogi et al. 2008). 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 (Zhang and Niu 2010) 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  $\mu\text{m}$  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 ( $\text{AcCOOH}$ ), 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

The surface-modification of the nanoparticles plus the addition of a surfactant was attempted to improve the dispersion of MWCNT particles in the PCM liquid. All dispersion experiments were performed in glass test tubes by 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<sup>TM</sup>, 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  $\text{H}_2\text{SO}_4$  (98%) and  $\text{HNO}_3$  (70%) at 3:1 volume ratio. MWCNT particles was added to  $\text{H}_2\text{SO}_4$ - $\text{HNO}_3$  in a test tube and sonicated in an ultrasonic bath for 6 hours and then heated with reflux at 65 °C for 4 hours. After cooling down to room temperature, the acid liquid was diluted with deionized water and the MWCNT particles were spun down at 18000 rpm for 2 hours. After removal of the liquid, the solid particles were dried at 80 °C in an oven for about 24 hours.

The surface-modified MWCNT particles were re-dispersed in hexadecane by ultrasonication using an ultrasound probe with 30% amplitude of power for 5 min. The surfactant 1-decanol was added to the dispersion and the dispersion was sonicated in an ultrasound bath for 20 minutes 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 FT-IR 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 minutes for stabilization, and then heated from -5 °C to 30 °C at a rate of 5 °C/min, held for 5 minutes 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. The particle size and dispersion of MWCNT-1-decanol

The average hydrodynamic diameter of Modified MWCNT assisted by 1-decanol (MWCNT-1-decanol) in hexadecane was 2761.3 nm or 2.76  $\mu\text{m}$  (Figure 1) as measured by dynamic light scattering analysis (Malven Zetasizer) with the count rate at 200.3 +6.6 kilo count per second (kcps) at 25 °C. The range difference within the repeated measurements was +36.1 nm, therefore the MWCNT particles were well dispersed. The polydisperse index was 0.585, which means the range of particle size distribution was medium. MWCNT-1-decanol were well dispersed in liquid n-hexadecane to form a stable n-hexadecane / MWCNT-1-decanol slurry. The visible aggregation was negligible even after seven days.

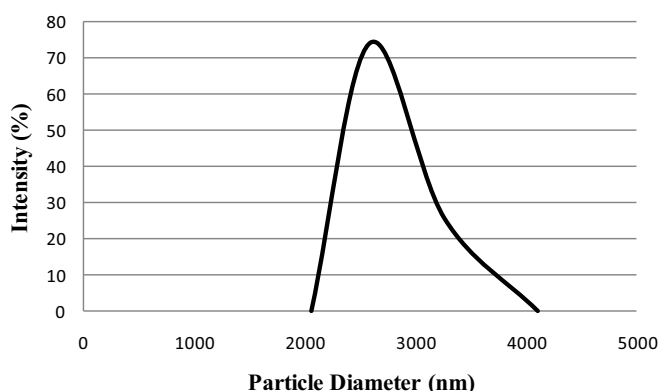


Figure 1. The size distribution of MWCNT-1-decanol in hexadecane

#### 3.2. Morphology of MWCNT

TEM micrographs of the original MWCNT and MWCNT-1-decanol are presented in Figure 2 and Figure 3 respectively. The size and shape of MWCNT particles can be observed clearly and are consistent with the parameters provided by manufacturer, with an outer diameter of 10-20 nm and a length of 0.5-2  $\mu\text{m}$ . Compared with the morphology of original MWCNT, the surface of MWCNT-1-decanol was rougher. There were some masses on the surface of the nano tubes, and the mass may be caused by surfactant modification and the addition of decan-1-ol. These can be observed more clearly in the TEM micrographs (Figure 4), showing the crystal structure of nano tubes.

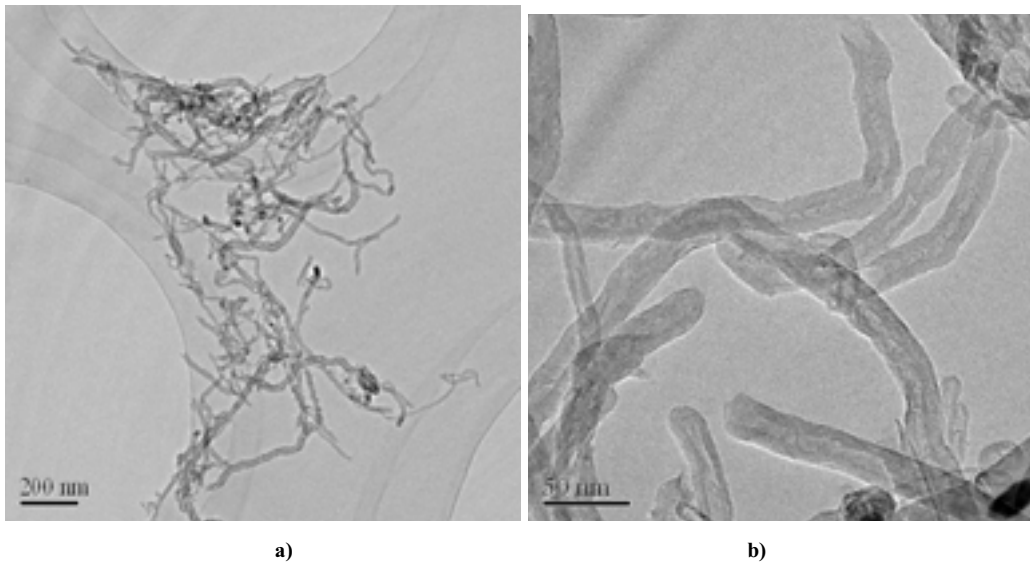


Figure 2. TEM micrographs of original MWCNT on different scales showing the morphology: a) 200 nm and b) 50 nm

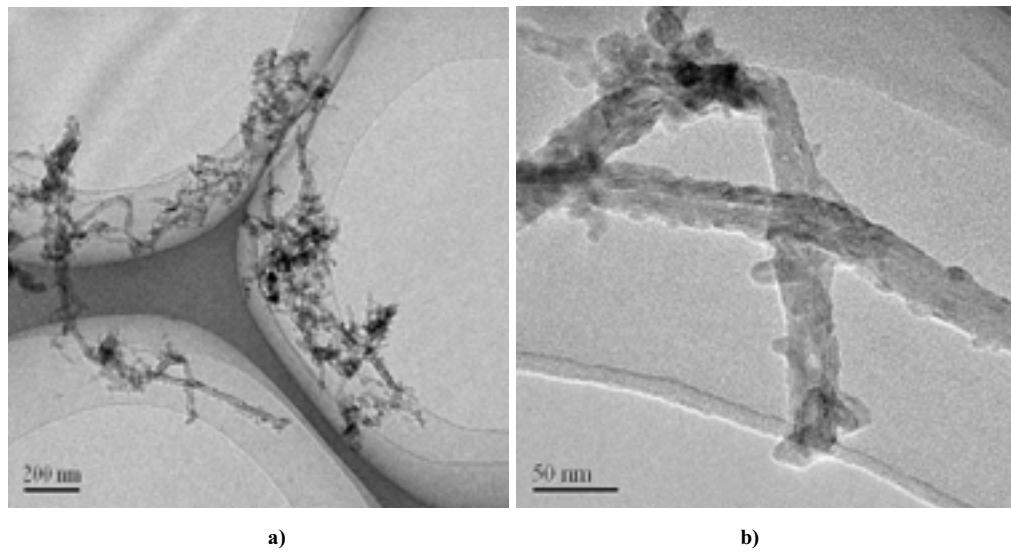


Figure 3. TEM micrographs of well dispersed MWCNT-1-decanol on different scales showing the morphology: a) 200 nm and b) 50 nm

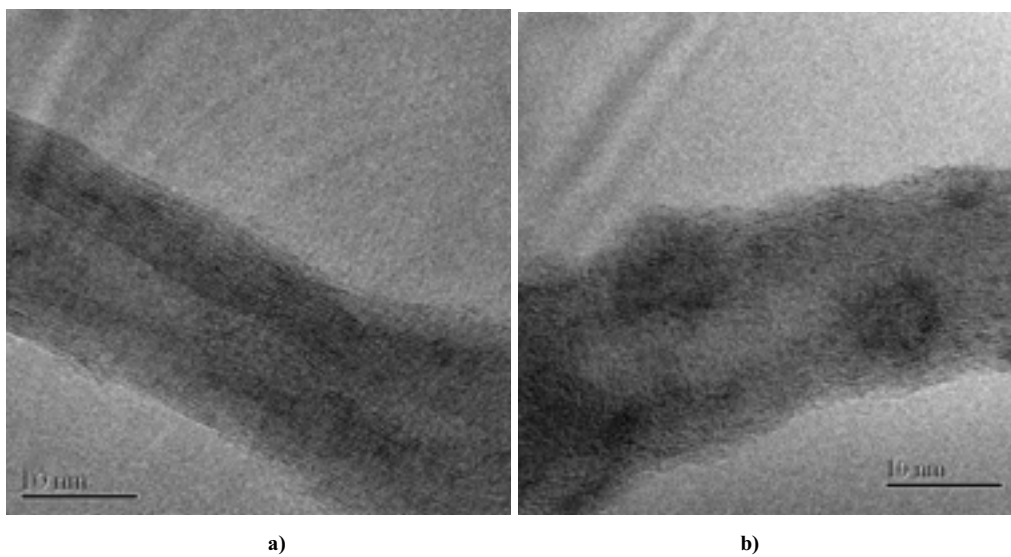


Figure 4. TEM micrographs of different MWCNT showing the crystal structure of MWCNT: a) original MWCNT and b) MWCNT-1-decanol

### 3.3. Supercooling Reduction

In the nucleation process, the formation of the nuclei is associated with a change in the free energy of the system. At a given supersaturation and temperature, there is a critical value of the free energy when stable nuclei of critical size are formed. This behavior of the free energy change,  $\Delta G$ , associated with the formation of the nucleus was shown in Figure 5 as a function of nucleus radius  $r$ . When the radius  $r$  of the nuclei is smaller than  $r^*$ , the nuclei dissolve. However, when  $r > r^*$ , the nuclei are stable and grow.  $\Delta G^*$  is a barrier for nucleation, and only when  $r > r^*$  there is a reduction in the free energy of the nucleus with an increase in its size. The higher the activation barrier  $\Delta G^*$ , the more difficult it is to attain stable nuclei. Nucleation process may be homogeneous or heterogeneous. Homogeneous nucleation is possible when there is no external source, in ideally pure liquids, whereas heterogeneous nucleation occurs when the system contains nanoparticles and/or impurity particles (Sangwal 2007).

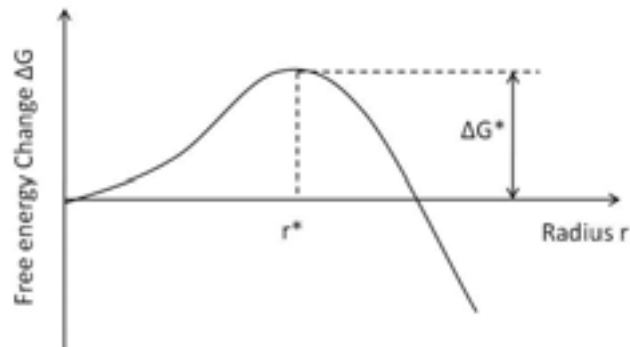


Figure 5. Change in Gibbs free energy  $\Delta G$  as a function of radius  $r$  of nucleus formed in a supersaturated medium (Sangwal 2007)

According to the classical nucleation theory, well dispersed MWCNT particles are expected to act as seeds during the process of crystallization, thus to be used as nucleating agents to reduce the supercooling of hexadecane. DSC technique was used to analyze the thermal property of the hexadecane / MWCNT-1-decanol slurry. Figure 6 showed the DSC melting and freezing curves of the pure hexadecane at 5 °C/min scanning rate and the characteristic temperatures including melting temperature  $T_m$ , melting peak temperature  $T_{m,peak}$ , freezing temperature  $T_f$  and freezing peak temperature  $T_{f,peak}$ . The difference between  $T_{m,peak}$  and  $T_{f,peak}$  is the supercooling  $\Delta T$ . It can be observed that the melting/freezing peak temperature is 22.67 °C and 14.08 °C respectively, so the supercooling is 8.59 °C.

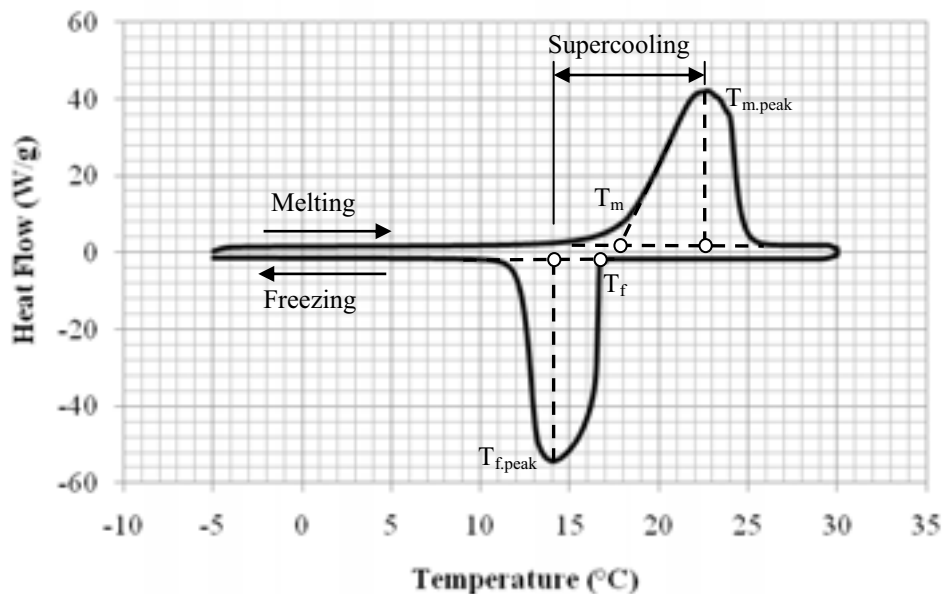
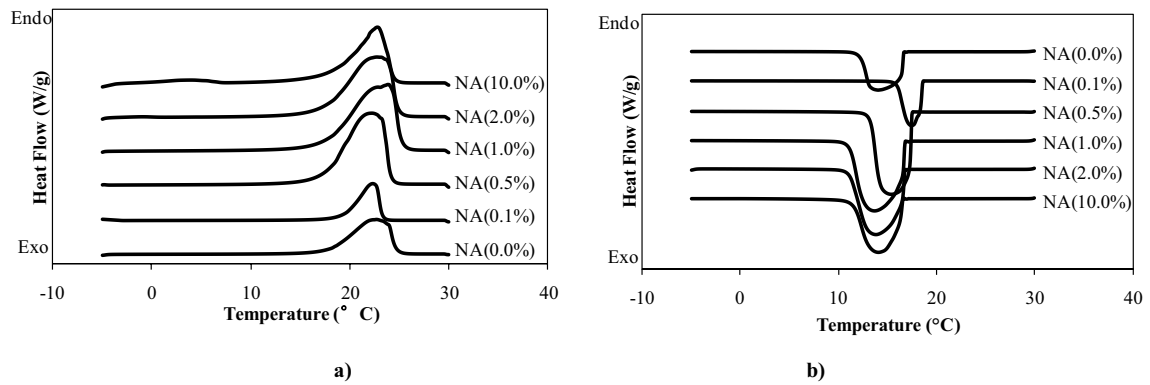


Figure 6. DSC melting and freezing curves of the pure hexadecane at 5 °C/min scanning rate and the characteristic temperatures  $T_m$ ,  $T_{m,peak}$ ,  $T_f$  and  $T_{f,peak}$ .

The DSC heating/cooling curves of the hexadecane / MWCNT-1-decanol slurry obtained at a heating and cooling rate of 5 °C/min are presented in Figure 7, and the melting and crystallization properties calculated from the DSC tests are presented in Table 1. It can be observed that the freezing temperature of the hexadecane / MWCNT-1-decanol slurry varied with the MWCNT concentrations while the melting temperature remained fundamentally unchanged. With the addition of the nucleating agent of 0.1 wt%, the freezing temperature clearly increased from 14.08 °C to 17.42 °C, and the supercooling of hexadecane decreased by 43%, from 8.59 °C to 4.91 °C. With the addition of the nucleating agent of 0.5 wt%, the supercooling reduction effect was also significant but weaker than at the lower concentration. When the concentrations of the nucleating agent exceeded 1.0 wt%, the effect of reducing supercooling was not seen. Judging from these results, it appears that there existed an optimal or a most effective concentration range of the nucleating agent and this agrees with experimental research reported by other researchers (Liu 2005, Tomura and Kawasaki-shi 2010). The fact that the mass concentration required is small has positive practical implications.



**Figure 7.** DSC curves of the hexadecane with MWCNT of different fractions as the nucleating agent (NA): a) heating process and b) cooling process

**Table 1.** Melting and crystallization properties of hexadecane with MWCNT of different fractions as the nucleating agent (NA)

	$\Delta H_m$	$\Delta H_f$	$T_{m,peak}$	$T_{f,peak}$	$\Delta T$
	J/g	J/g	°C	°C	°C
NA (0.0 wt %)	227.13	225.81	22.67	14.08	8.59
NA (0.1 wt %)	196.58	196.33	22.33	17.42	4.91
NA (0.5 wt %)	256.28	250.59	22.25	15.42	6.83
NA (1.0 wt %)	237.90	239.77	23.83	13.67	10.16
NA (2.0 wt %)	244.81	244.22	22.75	13.83	8.92
NA (10.0 wt %)	219.60	223.03	22.70	14.08	8.67

### 3.4. Discussion

The crystal structure of n-hexadecane (even-carbon n-alkanes with  $n < 26$ ) is triclinic structure (Sangwal 2007), and that of MWCNT particles with a diameter of 10-20 nm (more than  $25 \text{ \AA}$ ) is honeycomb structure (Tersoff and Ruoff 1994). The similar crystal structure of MWCNT and n-hexadecane is the basis for MWCNT to be used as the nucleating agent. The experimental results help to confirm this hypothesis. Without any foreign additives, formation of stable nuclei relying on homogeneous nucleation is a “sluggish” process, which is the main cause of large supercooling. In this experimental investigation, the well dispersed nanoparticles provided stable foreign nuclei of proper size to promote the heterogeneous nucleation process and accelerate crystallization process, thus the crystallization temperature was raised and the supercooling was significantly reduced.

The small concentration of additives required has a number of positive implications for the potential engineering application of the technology. Firstly, it will have negligible impact on the volumetric latent heat of the PCM; secondly, the cost of the nano materials can be much reduced.

#### 4. Conclusions

It was difficult to disperse the original MWCNT particles in a hexadecane liquid. The surfactant used to disperse MWCNT must be soluble to the hexadecane, and the results showed that the functional group in the surfactants that are supposed to react with the acid groups in MWCNT should be as exposed as possible, otherwise the branch near the functional group would produce hindrance and lower the dispersion effect. Modified MWCNT particles plus the addition of 1-decanol as surfactant were successfully dispersed in hexadecane. It can be expected that using 1-decanol to disperse MWCNT in other higher molecular alkanes that are similar to hexadecane such as pentadecane and heptadecane is possible; the results may also imply that using other fatty alcohols, such as nonadecan-1-ol and undecan-1-ol, which have similar structures to 1-decanol to assist to disperse MWCNT in hexadecane is also possible.

It is encouraging that well dispersed MWCNT of relatively low concentration had significant effect in reducing supercooling of hexadecane. With the addition of 0.1wt% MWCNT, the supercooling of hexadecane can decrease by 43%, which produced the most significant effect among the test samples. It is also interesting to note that there was an effective concentration range of nanoparticles for supercooling reduction, and better results cannot be obtained by continuously increasing nanoparticle concentration.

For thermal cooling storage in air conditioning system and other building applications, reducing supercooling as much as possible is essential. Large supercooling will decrease the COP of the cooling storage process in electric-driven cooling storage systems, and reduce the utilization hours or the per-volume storage capacities of natural cooling systems such as evaporative cooling system.

#### References

- Farid, M. M., A. M. Khudhair, S. A. K. Razack & S. Al-Hallaj (2004) A review on phase change energy storage: materials and applications. *Energy Conversion and Management*, 45, 1597-1615.
- He, Q., W. Tong & Y. Liu (2007) Experimental study on super-cooling degree of nanofluids for cryogenic cool storage (in Chinese). *Journal of Refrigeration*, 28, 33-36.
- Huang, L., E. Günther, C. Doetsch & H. Mehling (2010) Subcooling in PCM emulsions--Part 1: Experimental. *Thermochimica Acta*, 509, 93-99.
- Huang, L., M. Petermann & C. Doetsch (2009) Evaluation of paraffin/water emulsion as a phase change slurry for cooling applications. *Energy*, 34, 1145-1155.
- Liu, Y. 2005. Study on Preparation and Thermal Properties of Phase Change Nanocomposites for Cool Storage (in Chinese), PhD Thesis. In College of Power Engineering. Chongqing: Chongqing University.
- Oliver, M. J. & P. D. Calvert (1975) Homogeneous nucleation of n-alkanes measured by differential scanning calorimetry. *Journal of Crystal Growth*, 30, 343-351.
- Rastogi, R., R. Kaushal, S. K. Tripathi, A. L. Sharma, I. Kaur & L. M. Bharadwaj (2008) Comparative study of carbon nanotube dispersion using surfactants. *Journal of Colloid and Interface Science*, 328, 421-428.
- Sangwal, K. 2007. Additives and Crystallization Processes: From Fundamentals to Applications. John Wiley & Sons Ltd.
- Sun, G., G. Chen, J. Liu, J. Yang, J. Xie, Z. Liu, R. Li & X. Li (2009) A facile gemini surfactant-improved dispersion of carbon nanotubes in polystyrene. *Polymer*, 50, 5787-5793.

- Tersoff, J. & R. S. Ruoff (1994) Structural Properties of a Carbon-Nanotube Crystal. *Physical Review Letters*, 73, 676.
- Tomura, K. & J. Kawasaki-shi. 2010. Heat storage substance, heat storage agent, heat reservoir, heat transport medium, cold insulation agent, cold insulator, melting point control agent for heat storage agent, supercooling preventive agent for heat storage agent and method for producing main agent of heat storage agent heat transport medium, or cold insulation agent. United States.
- Vaisman, L., H. D. Wagner & G. Marom (2006) The role of surfactants in dispersion of carbon nanotubes. *Advances in Colloid and Interface Science*, 128-130, 37-46.
- Yamagishi, Y., T. Sugeno, T. Ishige, H. Takeuchi & A. T. Pyatenko. 1996. An evaluation of microencapsulated PCM for use in cold energy transportation medium. In *Energy Conversion Engineering Conference, 1996. IECEC 96. Proceedings of the 31st Intersociety, 2077-2083*. Washington, DC, USA.
- Zhang, S. & J. Niu (2010) Experimental investigation of effects of supercooling on microencapsulated phase-change material (MPCM) slurry thermal storage capacities. *Solar Energy Materials and Solar Cells*, 94, 1038-1048.
- Zhang, X.-x., Y.-f. Fan, X.-m. Tao & K.-l. Yick (2005) Crystallization and prevention of supercooling of microencapsulated n-alkanes. *Journal of Colloid and Interface Science*, 281, 299-306.
- Zhang, X. J., P. Wu, L. M. Qiu, X. B. Zhang & X. J. Tian (2010) Analysis of the nucleation of nanofluids in the ice formation process. *Energy Conversion and Management*, 51, 130-134.
- Zhu, N., Z. Ma & S. Wang (2009) Dynamic characteristics and energy performance of buildings using phase change materials: A review. *Energy Conversion and Management*, 50, 3169-3181.