Chapter 2
The Study on Paraffin-Water Emulsion PCM with Low Supercooling Degree

Xiyao Zhang, Jianlei Niu, Jianyong Wu and Shuo Zhang

Abstract This study aims to develop paraffin waxes based phase change material emulsion with low supercooling degree, which can be applied in a Thermal Energy Storage (TES) systems to maximize the use of natural heating and cooling sources via solar thermal collectors or evaporative coolers, and to raise the energy efficiency of the chillers operating at off-peak period. In this study, a kind of hexadecane-water emulsion with small droplet size was prepared and analyzed. The modified Multi-Wall Carbon Nano-Tube (MWCNT) particles were dispersed in emulsion as the nucleating agent to reduce supercooling degree. The MWCNT particles were modified with strong acids H_2SO_4 and HNO_3 to increase the compatibility with the organic liquid. Thermal analysis of the hexadecane-water emulsions with well-dispersed MWCNT particles by Differential Scanning Calorimeter (DSC) indicated that the supercooling degree of emulsion was significantly decreased. The effective ranges of nucleating agent concentration were summarized which provided a promising way of improving the performance of system energy efficiency in TES systems.

Keywords TES · Supercooling · PCM · Emulsion · MWCNT · Nucleating agent

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2.1 Introduction

Thermal Energy Storage (TES), as it deals with energy saving and the optimum use of renewable energy, have obtained considerable attention in the past 20 years. In particular, the energy storage materials applied in TES system is a key factor to maximize the use of the energy sources. Generally, the energy storage materials have a high energy storage density which can store or release a large amount of latent heat during their phase transformation processes, so they are also named Phase Change Materials (PCM).

However, as the thermal conductivity of most PCM is comparatively low, they generally have a low heat transfer rate which is unacceptable in the heat exchange processes. For solving this problem, PCM emulsions and microencapsulated PCM are often used to improve the heat transfer between the PCM and the ambient by increasing the surface to volume ratio of the PCM [1, 2].

Besides, the PCM liquid usually can be cooled below its melting point without occurring in crystallization. This phenomenon is called supercooling which is unexpected in the latent heat storage as it leads to a shift of the controlling temperature range of the systems and even an increase of the energy consumption of the chiller resulted from a low COP. Furthermore, from the nucleation theory, supercooling of PCM in small volumes is expected to be more severe than in large volumes, which indicates that the supercooling in emulsion will be more serious than that in bulk PCM as their small droplet size. Günther et al. studied in detail the supercooling in hexadecane emulsions with droplet size in the range of about 0.1–20 μm. An increased supercooling of at least 10 K for small droplets was observed [3]. For decreasing the supercooling, an effective approach is the addition of liquid or solid nucleating agents to the PCM liquids as the seeds and catalysts for nucleation and crystal growth [4], such as 1-Tetradecanol for microencapsulated *n*-Tetradecane [5], paraffin wax for tetradecane and hexadecane paraffin-in-water emulsion [6], and TiO_2 [7] or α-Al_2O_3 [8] for the pure water.

Our previous study [9] has investigated the effects of Multi-Wall Carbon Nano-Tube (MWCNT) particles as nucleating agent to inhibit supercooling in the PCM liquid, which showed a good performance at low concentration. This study is to evaluate the effectiveness of the MWCNT nano-particles as nucleating agent in emulsions. Hence, in this study, a kind of *n*-hexadecane emulsion was designed and prepared and the MWCNT particles were well dispersed in emulsions at various concentrations. The effectiveness of the nucleating agent for emulsion was evaluated by comparing the DSC results of emulsions.

2.2 Experiment

2.2.1 Materials

In this study, *n*-hexadecane $C_{16}H_{34}$ (99 %) was chosen as the PCM liquid (purchased from International Laboratory USA), and the multi-walled carbon nano-tube (MWCNT) used as raw material of 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). The nitric acid (70 %) and sulfuric acid (98 %) were obtained from Aldrich. 1-decanol (decan-1-ol) and Tween-20 (polysorbate 20) were chosen as surfactants for dispersing the MWCNT particles in hexadecane and the emulsion preparing respectively, which were all of analytical grade.

2.2.2 Modification of MWCNT Particles

The original MWCNT particles were oxidized by the concentrated H_2SO_4 (98 %) and HNO_3 (70 %) at 3:1 volume ratio in a flask with reflux at 65 °C for 4 h. After cooling down to room temperature, the resulting diluted nanotube-acid mixture was then filtered using a 0.2 μm nylon membrane filter (Millipore), and leaving a MWNT filter cake. The nanotubes were then rinsed with water until a pH above 5 was obtained. Final rinsing was done using ethanol and the resulting solid particles were dried at 80 °C in an oven for about one day.

2.2.3 Preparation of PCM Slurry and PCM-Water Emulsion

After furbished, the surface-modified MWCNT particles were re-dispersed in hexadecane with the 1-decanol as the surfactant. In this step, an ultrasound probe (Sonics Vibra-Cell, model VCX130) was used to help the well dispersion with 30 % amplitude of power for 20 min. By repeating the above steps, the PCM slurry with the nucleating agent at various concentrations from 0.05 to 0.5 wt% was yielded for the following studies.

The above different PCM slurries were then mixed with water at 1:2 mass ratio and the Tween 20 (5 wt%) as the surfactant was added into the mixture. A disperser (type ULTRA-TURRAX T25 by IKA-Labor-Technik) was used for the formation of emulsion with a rotate speed at 8,000 rotations per minute for 10 min. The emulsions with different concentration of nanoparticles were prepared by the method above.

2.2.4 Characterization and Analysis of Emulsion Droplets and the Nanoparticles

The size distributions of emulsion droplets and the nanoparticles were determined by using a laser diffraction particle size analyzer of type Malven Zetasizer. This analyzer has a broad measuring range from 0.02 to 5,000 μm. 100 measurements were performed for 20 min at a scattering angle of 90° at 25 °C. The average particle size (in nm) and the polydispersity index were analyzed out by the Zetasizer 3000HSA-Advanced Software.

The morphology of the PCM-water emulsion droplets were examined with an optical microscope type Leica DM4000 under 400x. The images were processed by Leica LAS AF software.

2.2.5 Thermal Analysis

To determine the melting and nucleation temperatures, a DSC type METTLER TOLEDO DSC-822e with aluminum crucibles was used. The temperature and sensitivity calibration were carried out by using the standard materials. The temperature program for each material was created in such a way: The heating/cooling rate was 5 °C/min. The samples were first cooled to the initial temperature of −5 °C for at least 15 min for stabilization, and then heated to 30 °C, held for 5 min at 30 °C, and finally cooled to −5 °C.

2.3 Results and Discussion

2.3.1 The Particle Size Distribution of Modified MWCNT Particles

The average hydrodynamic diameter of MWCNT-1-decanol in hexadecane shown in Fig. 2.1 was 1,762 nm or 1.76 μm by the dynamic light scattering analysis with the count rate at 248 ± 5.2 kilo count per second (kcps) at 25 °C. The range difference within the repeated measurements was ±94.8 nm, therefore the MWCNT particles were well dispersed. The polydispersity index was 1, which means the range of particle size distribution was wide. Besides, it can be seen that the particle size of the MWCNT was obviously increased after the modification. The main reason was the aggregation occurring in the modification process, especially in the drying step. Moreover, in the dispersion procedure, the MWCNT particles were coated by the 1-decanol to enhance the compatibility in liquid [9], which eventually enlarged the average hydrodynamic diameter. However, from our observation, the growing of the particle size did not show an obvious negative affection on the nucleation.

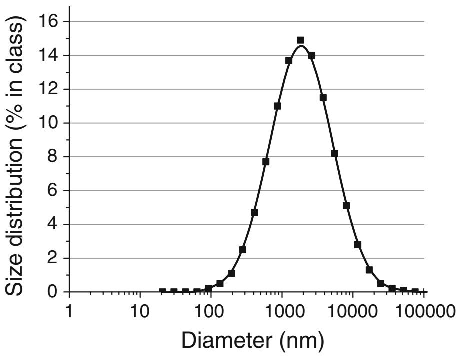

Fig. 2.1 The particle size distribution of the modified MWCNT particles

2.3.2 The Droplet Size Distribution of the PCM-Water Emulsion

After a high-speed stirring of the disperser, the emulsion with small droplets of PCM was obtained. For scaling the droplet size of the emulsion, the nucleating agent was not added in. And also measured by the dynamic light scattering analysis at 25 °C, the average diameter of hexadecane droplets was 2,082 nm with a wide distribution (PDI = 1) shown in Fig. 2.2. The count rate was at 231.2 ± 31.9 kcps.

2.3.3 The Morphology of PCM-Water Emulsion Droplets

Optical photomicrographs of the PCM-water emulsion droplets under 400x are presented in Fig. 2.3. The size and shape of droplets can be observed clearly and are consistent with the results from the DLS, with a centralized outer diameter of 0.1–10 μm. The modified MWCNT particles are hardly observed as their small diameter and low concentration.

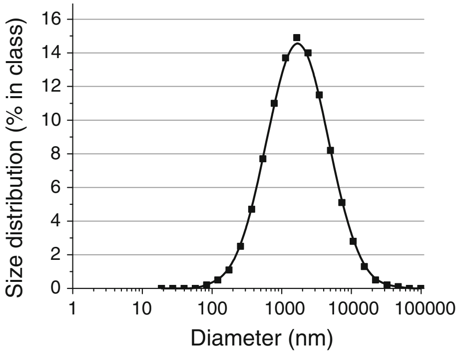

Fig. 2.2 The particle size distribution of PCM-water emulsion

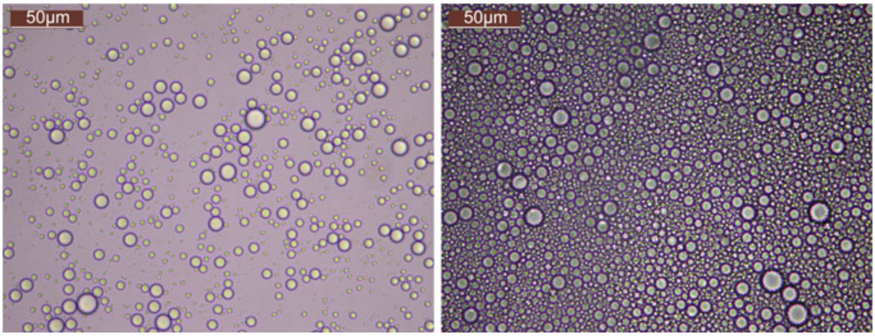

Fig. 2.3 The morphology of the PCM-water emulsion droplets (*left* diluted, *right* undiluted)

2.3.4 The Supercooling in PCM-Water Emulsion

We have observed the capacity of the modified MWCNT as the nucleating agent (NA) to reduce the supercooling of PCM crystallization in previous work [9], especially in relatively light concentrations. The optimal concentration of NA was around 0.1–0.2 wt% versus the *n*-hexadecane. In this section, a detailed investigation in emulsions was conducted to find out an optimum concentration of nucleating agent. The differential scanning calorimetry was used to analyze the thermal property of the *n*-hexadecane-water emulsion. The melting peak point was defined as the melting temperature $T_{\mathrm{m.peak}}$ and the freezing peak point as the nucleation temperature $T_{\mathrm{f.peak}}$. The difference between the melting and nucleation temperature was considered as the supercooling degree.

According to the nucleation theory, the supercooling is expected to increase along with the droplets decline [3]. From the DSC heating/cooling curves of the PCM-Water emulsion shown in Fig. 2.4, when the nucleating agent was absent

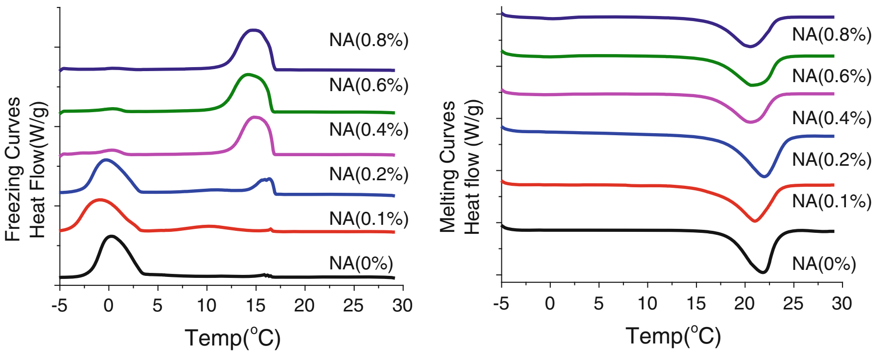

Fig. 2.4 The DSC freezing/melting curves of different emulsion samples with MWCNT as NA (weight concentration vs. the *n*-hexadecane)

Table 2.1 Melting and crystallization properties of PCM-water emulsion with MWCNT as NA

Sample	ΔH_m (J/g)	ΔH_f (J/g)	$T_{m.peak}$ (°C)	$T_{f.peak}$ (°C)	ΔT (°C)
NA (0 wt%)	−73.86	73.61	19.44	1.37	18.07
NA (0.1 wt%)	−98.51	73.71	19.69	0.48	19.21
NA (0.2 wt%)	−82.94	1st: 11.12	20.34	1st: 16.92	3.42
		2nd: 51.82		2nd: 0.76	19.58
NA (0.4 wt%)	−72.53	66.76	19.49	16.00	3.49
NA (0.6 wt%)	−80.56	75.21	19.69	15.49	4.20
NA (0.8 wt%)	−80.51	77.39	19.37	15.97	3.40

(MWCNT at 0 wt%), the PCM droplets hardly occurred crystallization until near the ice point, in despite of tiny energy fluctuations occurring in freezing circle at approximate 15 °C, thus a dramatically large extent of supercooling of 18.07 °C was observed. Associated with the increasing concentrations of the nucleating agent, there are two obvious peaks can be observed on the freezing curves and the extent of the releasing energy at zones above 10 °C enhanced gradually with the other peak going down until the mass ratio of MWCNT and PCM reached to 0.6 wt%. After that, the nucleation effect was also significant but similar to that at 0.6 wt%. And it should also be noticed that the supercooling was controlled to below 4 °C by the effect of modified MWCNT. The detailed melting and crystallization properties calculated from the DSC data are presented in Table 2.1.

Considered that the mass ratio of PCM and water was 1:2, the 'macroscopical' concentration of the nucleating agent should be approximate 1/3 of that in PCM, thus the results coincide with the performance of MWCNT in PCM liquid in our previous work. Moreover, in the microcosmic view, as the PCM was separated into many small volumes, nucleation had to occur in every volume individually [3]. Especially when the nucleating agent particles in a low concentration only existed in some droplets, the heterogeneous nucleation was limited to this part of PCM droplets and the rest PCM volumes could only solidify after homogeneous nucleation, which contribute to the two freezing peaks in some curves. Therefore, there existed an optimal or a least effective concentration of the nucleating agent and it was 0.6 wt% versus the *n*-hexadecane for the emulsion investigated in this work.

2.4 Conclusion

In this study, the experimental results show that, as the nucleating agent, a low concentration of modified MWCNT nano-particles were effective to reduce the supercooling degree in the PCM-Water emulsions. Besides, it is clear that there existed an optimal or a least effective concentration of the nucleating agent for the emulsion and it was 0.6 wt% (weight concentration vs. the *n*-hexadecane) for the emulsion investigated in this work. Eventually, a kind of emulsion which has heat capacity at approximate 80 J/g and freezes around 16 °C was obtained.

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