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A novel method to predict thermal conductivity of NaCl/water based MCNT nano-suspesnion for cold energy storage

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Abstract

As a typical cold storage media working at sub-zero temperature, NaCl-water solution as a phase change material (PCM) with -21 °C melting point has been selected in this study. 0.0625 vol.%-0.5 vol.% multi-wall carbon nanotube (MCNT) was dispersed in the NaCl-water basefluid via ultra-sonicating to make nano-suspension. The viscosity of MCNT-NaCl-water was measured and the experimental results fitted well with the modified Krieger-Dougherty (K-D) model. The structure of MCNT cluster was derived from the fitting of viscosity data, showing that the lower the temperature, the larger the cluster size could be. Benefited from the MCNT cluster parameter, the thermal conductivity of MCNT-NaCl-water was predicted by modified Hamilton-Crosser (H-C) model, in which the MCNT cluster was considered as a whole part with its equivalent thermal conductivity. In addition, thermal conductivity experiment was also conducted to compare the measured value with the calculated value. The results indicated that the traditional H-C model underestimates the measured thermal conductivity by a large margin while the approach proposed in this paper shows good accuracy. Moreover, it is also found that MCNT will improve the thermal conductivity more significantly at low temperature than at high temperature.

Keywords: nano-suspension, MCNT, thermal conductivity, viscosity, phase change materials, cold storage.

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1. Introduction

Cold storage has become more and more attracting for both academia and industry in last decade due to the increasing demand of low temperature applications, including cold chain transport, air conditioning, biomedicine and so on[1][2][3][4]. In such applications, the desirable temperature is the most important parameter and needs to be well monitored and controlled. To achieve the efficient and economical thermal management in cold storage fields, phase change material (PCM) has been proposed as an promising candidate due to its feature of keeping self-temperature constant while melting and freezing. In aspect of cold storage, the desirable temperature varies a lot in different processes where the most common range is from -30 oC to 0 oC, such as frozen transportation, food preservation, air conditioning and so on. As a result, to meet the sub-zero temperature requirements of above applications, salt-water mixtures have been considered as a promising class of PCM due to their corresponding melting point and high latent heat[5].

In spite of phase changing temperature, thermal conductivity as another very important criteria of selecting PCM is being widely studied, particularly, the topic on enhancing thermal conductivity by adding nanoparticles. For instance, Wang[6] et al. dispersed 0.2 wt.% to 1 wt.% carbon nanotube(CNT) into the palmitic acid to make a stable nano-composite PCM. Then the thermal conductivity of CNT/palmitic acid was measured in both liquid and solid state. It is observed that by adding only 1 wt.% CNT, the thermal conductivity increased over 30 %. Moreover, larger thermal conductivity enhancement were found at solid state, which is 46 % compared with 38 % at liquid state. Also, Jana[7] et al. prepared both Cu/water and CNT/water nanofluids and their thermal conductivity were measured. They found a linear relationship between the nanoparticle concentration and the enhancement of thermal conductivity in Cu/water suspension. But in the CNT suspension, enhancement was non-linearly dependent on the fraction of CNT. Although they contributed the non-linear behaviour of thermal conductivity to the geometric anisotropy caused by large aspect ratios of CNT and the effect of shape and size due to agglomeration, a theoretical model to match the experimental value is still lacking. To further explore the effect of cluster of nanoparticle on the thermal conductivity, Gao[8] et al. designed a contrast experiment to focus on the influence of cluster specifically. Firstly, they mixed Al_2O_3 nanoparticle in to two different types of PCM, which are hog fat and hexadecane and the difference is that hog fat is amorphous and hexadecane is polycrystalline when they are frozen. Based on this knowledge, the morphology of Al_2O_3 nanoparticle in the solid state in the two hosts are very different, consequently, the thermal conductivity enhancement as well. The thermal conductivity results of both frozen samples showed the enhancement is higher in hexadecane than in hog fat, which is even much higher than predicted by Maxwell-Garnet model. They claimed the notable enhancement of thermal conductivity is caused by the formation of rod –type clusters of Al_2O_3 nanoparticle during crystallizing of hexadecane.

Besides that, in terms of sub-zero temperature, papers reporting thermal conductivity of nano-composite PCM can be also found. For example, He[9] et al. used $BaCl_2$-H_2O solution (22.5 wt.%) as the low temperature PCM of which the melting point is -8 ^oC. Then, they suspended a small amount of TiO_2 nanoparticle into the $BaCl_2$-H_2O solution, the size of the nanoparticle is 20 nm and the volume fraction is 0.167 % to 1.130 %. The experimental results of thermal conductivity shown that the relative thermal conductivity increases with TiO_2 concentration linearly. And the enhancement of thermal conductivity is larger at higher temperature. For instance, when particle concentration is 1.13%, thermal conductivity increased by 16.74 % at 25 ^oC, while at -5 ^oC, the increase is 12.76 %.

As listed above, although many of the existent research works invested the enhanced thermal conductivity of PCMs containing nanoparticles, discussion on the mechanism of the heat conduction in nano-composite PCMs at low temperature is still not sufficient. In our present investigation, an novel approach was proposed to explain the thermal conductivity enhancement of MCNT-NaCl-water at low temperature. Specifically, MCNT clustering condition was numerically illustrated via rheology study of salt-water with MCNT. Then, the clustering information was applied to conventional thermal conductivity model to explain the varying degrees of enhancement at different temperature.

In this paper, NaCl-water mixture was prepared as the cold storage PCM which has great potential for temperature sensitive products preservation due to its melting point of -21 ^oC and high latent heat. And to study the thermal conductivity enhanced by adding nano-additives, MCNT-NaCl-water nano-composite PCM was formulated by dispersing MCNT into NaCl-water basefluid with the help of surfactant and ultrasonication. Then, the thermal conductivity of nano-composite samples were tested at different temperatures by laser flash equipment and the viscosity were measured against shear rate at different temperatures by a rheometer. Based on the experimental results, a theoretical model was applied to explain the viscosity of samples containing MCNT. After that, the parameters in the viscosity model related with MCNT cluster structure were substituted into a thermal conductivity model to calculate the predicted value. Finally, the predicted thermal conductivity value were compared with the experimental results to validate the approach of linking rheology with thermal conductivity.

2. Experimental methods

2.1.Materials and preparation

In this work, MCNT with >98% carbon basis, 10 nm outer diameter, 4.5 nm inner diameter and 3~6 μm length (CAS 308068-56-6) and NaCl with purity of 99.5% (CAS 7647-14-5) were purchased from Sigma Aldrich. Distilled water was obtained from an lab water still (Calypso water still, Fistreem International Ltd). To maintain the stability of the nano suspension, Gum Arabic (CAS 9000-01-5, Sigma Aldrich) was used as surfactant.

The two-step method for preparing nano suspension is a process by dispersing nanoparticles into base fluids and it was applied in this work[10]. Firstly, NaCl and water were mixed at the ratio of 22.4/77.6 as basefluid. Then, a certain amount of MCNT corresponding to volume fraction and the same amount of Gum Arabic was dispersed into the mixture of NaCl and water and stirred by a magnetic stirrer for 10 min. After that, the pre-processed nano composites were further treated continuously for 1 h using an ultrasonication probe. The sample preparation procedure is shown in Fig.1. The volume fraction of MCNT were 0.0625%, 0.125%, 0.25% and 0.5% respectively and the mass of added MCNT were calculated correspondingly as following:

$$\varphi = \frac{m_{MCNT}/\rho_{MCNT}}{(m_{MCNT}/\rho_{MCNT})+(m_b/\rho_b)} \tag{1}$$

where φ represents the volume fraction of nano-suspension, m_{MCNT} and m_b are the mass of MCNT and base fluid respectivel, ρ_{MCNT} and ρ_b determine the density of the MCNT and base fluid respectively.

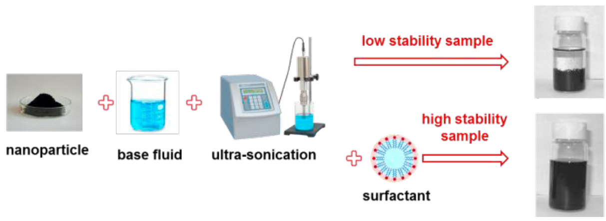

Fig.1. schematic of sample preparation.

2.2. Method of characterization

An Anton Paar MCR 502 rheometer was used in this work to measure the dynamic viscosity of the NaCl-water based MCNT nano suspension. The viscosity was measured at a linear increasing shear rate from 100 s^{-1} to 800 s^{-1} at 25 ºC,-10 ºC and -20 ºC respectively. Value of 1 mPas was obtained at 25 ºC for distilled water, and it kept constant with shear rate from 100 to 1000 s-1, this indicates the good accuracy of rheological properties measured by this rheometer. Thermal conductivity was measure by a transient method called laser flash method, the laser was generated by STARWELD 40, ROFIN, Germany and the laser signal was detected and recorded by LFA 427, Netzsch, Germany. Value of 0.6 W/m·k was measured at 25 ºC for distilled water, this indicates the good accuracy of thermal conductivity measurment.

3. Results and discussion

3.1. Rheology to cluster structure

As studied in other previous works on viscosity of nanofluids, viscosity models like Einstein model, Batchelor model were reported to underestimate the experimental data a lot[11-13], thus original Krieger-Dougherty(K-D) model[14], modified Krieger-Dougherty (K-D) model[11] was selected here to fit the experimental data. Fig.2 shows the measured viscosity of MCNT-NaCl-water nano-suspension and the measurement was taken when the shear rate was given at 100 s^{-1}, along with the temperature was set at 25 ºC, -10 ºC and -20 ºC respectively.

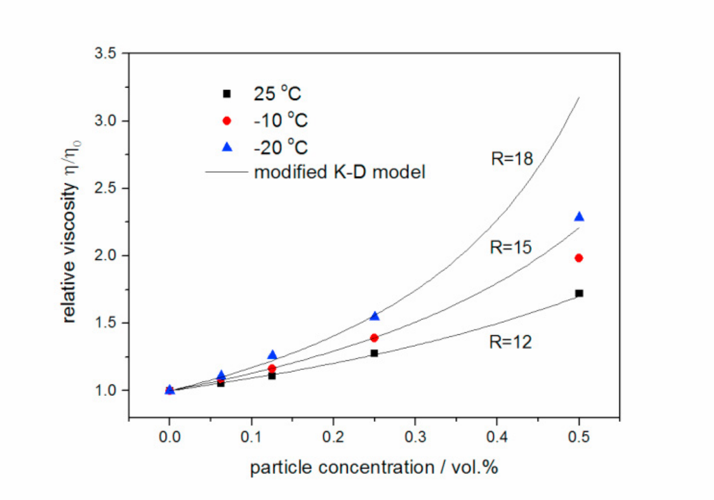

Fig.2. relative viscosity as a function of MCNT volume concentration.

It is obvious that the measured viscosity data has the similar trend with the calculated value, and all of them lie within the range between R=10 and R=17, in which R is the ratio of r_a and r. One can also find that the trend line with only one parameter R cannot fit every point with different particle concentration. As a complement, the fitting value of D, φ_m together with R of our samples by using modified K-D model is listed in Table 1, covering all particle concentration and temperature in this study.

Table 1 fitting value of D, φ_m and R in modified K-D model.

MCNT /vol.%	Temperature /ºC											
	25				-10				-20			
	η/η0	R	D	φ_m	η/η0	R	D	φ_m	η/η0	R	D	φ_m
0.0625	1.05	12	1.65	0.400	1.09	15	1.65	0.400	1.11	18	1.65	0.400
0.125	1.11	12	1.65	0.400	1.16	15	1.65	0.400	1.26	18	1.65	0.400
0.25	1.28	12	1.65	0.400	1.38	15	1.65	0.400	1.54	18	1.65	0.400
0.5	1.72	12	1.65	0.400	1.98	15	1.69	0.400	2.28	18	1.73	0.400

3.2. Cluster structure to thermal conductivity

The well-known Hamilton-Crosser (H-C) model[22] is shown in equation (1), it can be modified by introducing Nan's[23] approach is given in equation (2):

$$\frac{k_{eff}}{k_b} = \frac{k_p+(n-1)k_b-(n-1)(k_b-k_p)\varphi}{k_p+(n-1)k_b+(k_b-k_p)\varphi} \tag{1}$$

$$\frac{k_a}{k_b} = \frac{3+\varphi_{in}[2\beta_x(1-L_x)+\beta_z(1-L_z)]}{3-\varphi_{in}[2\beta_x L_x+\beta_z L_z]} \tag{2}$$

Where k_b and k_a is the thermal conductivity of basefluid and MCNT cluster respectively. φ_{in} is the MCNT volume fraction in one cluster expressed $\varphi_{in}=(r_a/r)^{D-3}$, φ_a is the effective volume fraction of MCNT clusters expressed as $\varphi_a=\varphi/\varphi_{in}$.

Fig.3 only shows the increment of thermal conductivity at -10 ºC together with the calculated data by traditional

H-C model and modified H-C model in our study. One can see that the traditional H-C model predicted data does not vary with temperature and underestimates the measured data by a large gap. This is because the H-C model assumes that all nanoparticles are well isolated from each other, no aggregation forming during sample preparation, which is only applicable in well dispersed ideal suspension. On the other hand, the modified H-C model shows much better matching to the measured data, also agrees very well with our previous expectation that cooling of the sample would promote the MCNT cluster to form high heat conduction pathway.

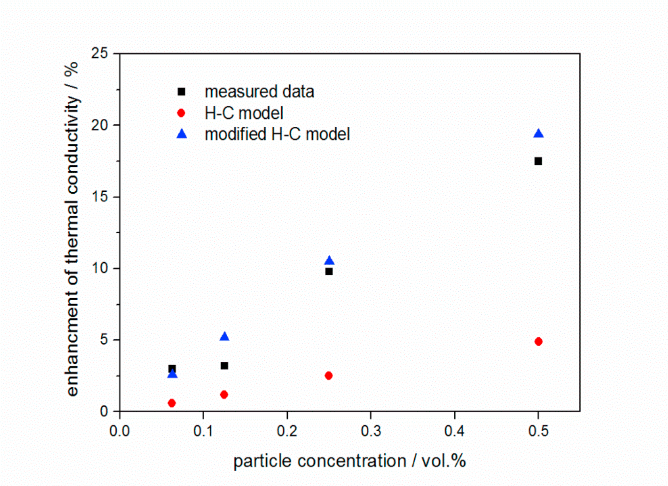

Fig.3. enhancement of thermal conductivity of MCNT-NaCl-water at -10 ºC

4. conclusions

In this paper, an approach to predict thermal conductivity of suspension containing MCNT by measuring viscosity of it was proposed. Firstly, the structure of MCNT cluster was obtained by fitting the measured viscosity data with modified K-D model. Secondly, the solid volume fraction in cluster is derived using the fitting parameter, which then was substituted to Nan's model to calculate the effective thermal conductivity of MCNT cluster. Thirdly, the traditional H-C model was modified by changing the thermal conductivity and concentration term of original MCNT to the equivalent value of cluster to get the predicted thermal conductivity of our suspension. At last, the thermal conductivity was measured experimentally and compared the results with both traditional H-C model and modified H-C mode and found that the former one failed to predict the thermal conductivity, while as the later one presented a quite accurate prediction and followed very well with the increasing thermal conductivity enhancement when temperature is reducing.

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References

[1] Z. Liu, D. Zhao, Q. Wang, Y. Chi, and L. Zhang, "Performance study on air-cooled household refrigerator with cold storage phase Étude sur la performance d ' un réfrigérateur domestique refroidi par air utilisant des matériaux à changement de phase pour l ' entreposage frigorifique," *Int. J. Refrig.*, vol. 79, pp. 130–142, 2017.

[2] M. De Falco, M. Capocelli, G. Losito, and V. Piemonte, "LCA perspective to assess the environmental impact of a novel PCM- based cold storage unit for the civil air conditioning," *J. Clean. Prod.*, vol. 165, pp. 697–704, 2017.

[3] L. Miro, "Improving thermal performance of freezers using phase change materials ´ lioration de la performance thermique des conge ´ lateurs Ame ` l ' aide de mate ´ riaux a ` changement de phase a," vol. 5, pp. 0–7,

2012.

[4] Y. M. Li and Y. A. Chen, "Assessing the thermal performance of three cold energy storage materials with low eutectic temperature for food cold chain," *Energy*, vol. 115, pp. 238–256, 2016.

[5] G. Li, Y. Hwang, R. Radermacher, and H.-H. Chun, "Review of cold storage materials for subzero applications," *Energy*, vol. 51, pp. 1–17, Mar. 2013.

[6] "Enhancing thermal conductivity of palmitic acid based phase change materials with carbon nanotubes as fillers." .

[7] S. Jana, A. Salehi-khojin, and W. Zhong, "Enhancement of fluid thermal conductivity by the addition of single and hybrid nano-additives," vol. 462, pp. 45–55, 2007.

[8] J. W. Gao, R. T. Zheng, H. Ohtani, D. S. Zhu, and G. Chen, "Experimental investigation of heat conduction mechanisms in nanofluids. Clue on clustering," *Nano Lett.*, vol. 9, no. 12, pp. 4128–4132, 2009.

[9] Q. He, S. Wang, M. Tong, and Y. Liu, "Experimental study on thermophysical properties of nanofluids as phase-change material (PCM) in low temperature cool storage," *Energy Convers. Manag.*, vol. 64, pp. 199–205, Dec. 2012.

[10] Z. Haddad, C. Abid, H. F. Oztop, and A. Mataoui, "International Journal of Thermal Sciences A review on how the researchers prepare their nano fl uids," vol. 76, pp. 168–189, 2014.