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Technical Notes

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Heat Transfer Nanofluids Based on Carbon Nanotubes

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I. Introduction

CONVENTIONAL heat transfer fluids such as water, mineral oil, and ethylene glycol play an important role in many industries including power generation, chemical production, air conditioning, transportation, and microelectronics. However, their inherently low thermal conductivities have hampered the development of energy-efficient heat transfer fluids that are required in a plethora of heat transfer applications. It has been demonstrated recently that the heat transfer properties of these conventional fluids can be significantly enhanced by dispersing nanometer-sized solid particles and fibers (i.e., nanoparticles) in fluids [1,2]. These new heat transfer fluids are known as nanofluids.

Nanoparticles of various materials have been used to make heat transfer nanofluids including copper, aluminum, copper oxide, alumina, titania, and carbon nanotubes [3]. Of these nanoparticles, carbon nanotubes show the greatest promise due to their excellent chemical stability and extraordinary thermal conductivity. Carbon nanotubes are nanometer-sized particles with high aspect ratios in the shape of a cylinder. There are two main types of carbon nanotubes: single-walled nanotubes (SWNT) and multiwalled nanotubes (MWNT). The structure of a single-walled carbon nanotube can be described as a single graphene sheet rolled into a seamless cylinder whose ends either open or are capped by either half fullerenes or more complex structures including pentagons. Multiwalled carbon nanotubes comprise an array of such nanotubes that are concentrically nested like rings of a tree trunk with a typical distance of approximately 0.34 nm between layers.

Carbon nanotubes conduct heat better than any material known. Research over the past decade has shown that carbon nanotubes could have a thermal conductivity value of 3000 $W/m \cdot K$ for multiwalled carbon nanotubes and 6000 $W/m \cdot K$ for single-walled carbon nanotubes, which is an order of magnitude higher than copper. Therefore, the thermal conductivities of nanofluids containing such solid particles would be expected to be significantly enhanced when compared with conventional fluids. Experimental results have demonstrated that carbon nanotubes yield by far the highest thermal conductivity enhancement ever achieved in a fluid: a 150% increase in conductivity of oil at about a 1% by volume loading of multiwalled carbon nanotubes [2].

Several additional studies of carbon nanotube suspensions in various heat transfer fluids have since been reported. However, only moderate enhancements in thermal conductivity have been observed. Xie et al. measured a carbon nanotube suspension in an aqueous solution of organic liquids and found only a 10–20% increases in thermal conductivity at 1% by volume of carbon nanotubes [4]. Similarly, Wen and Ding found about a 25% enhancement in the conductivity at 0.8% by volume of carbon nanotubes in water [5]. Hong et al studied the dispersion of carbon nanotubes in the polyalphaolefin oil and observed a 10% thermal conductivity (TC) increase with only 0.1 wt % loading [6].

Despite the extraordinarily promising increases in thermal conductivities exhibited by these carbon nanotube suspensions, it remains a serious technical challenge to effectively and efficiently disperse carbon nanotubes into aqueous or organic mediums while obtaining the stability that is needed for consistent thermal properties. Because of the hydrophobic nature of the graphitic structure, carbon nanotubes are not completely soluble in any known solvent. They also have a very high tendency to form aggregates and extended structures of linked nanoparticles, thus leading to phase separation, poor dispersion within a matrix, and poor adhesion to the host. These properties are essential for the fluids use in practical industrial applications. Without these properties, the thermal characteristics of the fluid will constantly change as the solid nanoparticles gradually separate from the fluid. Unfortunately, these early studies on carbon nanotubes containing nanofluids have primarily focused on the enhancement of thermal conductivity, and very little experimental data are available regarding the stability of these nanoparticle suspensions.

In this paper, we report on the effort to prepare a stable suspension of carbon nanotubes in a hydrophilic thermal transfer fluid with the intention of increasing the fluids thermal conductivity while also lowering its freezing point.

II. Experiment

Carbon nanotubes (multiwall and single wall) were purchased from Helix material (Richardson, Texas), Carbolex (Broomall, Pennsylvania) and Carbon Nanotechnologies Inc. (CNI, Houston, Texas).

Prestone (PAC) is a commercial antifreeze/coolant. The chemical surfactant sodium dodecylbenzene sulfonate (SDBS) was purchased

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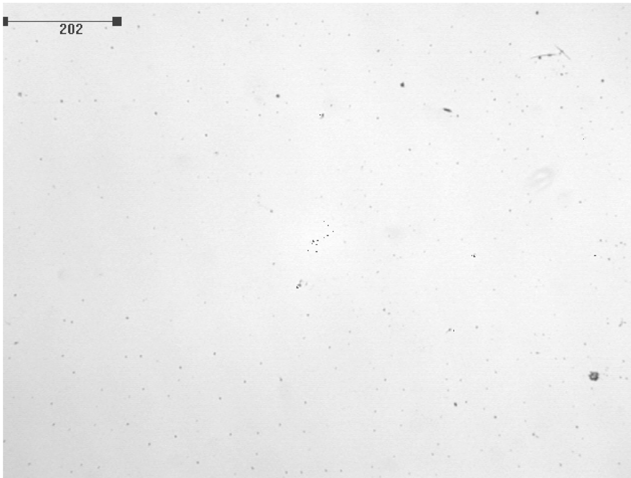

Fig. 1 Microscope picture of 0.2 % wt F-SWNT dispersed in the PAC solutions.

from Sigma Aldrich. Sonication was performed using a Branson digital sonifier, model 450.

The microscope picture was taken using an Olympus VANOX-T microscope. The magnification was 500×.

The pH values were measured using a Denver instrument UP-10 pH/mV meter. The thermal conductivity data were obtained using the Hot Disk™ thermal constants analyzer.

Dispersion and stability are observed with the naked eye. We put the nanofluids in the transparent glass beaker and observed if there was any precipitation at the edge and/or bottom of the glass beaker.

III. Results and Discussion

Figure 1 is the microscope picture of 0.2 wt % fluorinated SWNT (F-SWNT) dispersed in the Prestone antifreeze/coolant (PAC) solution using sodium dodecylbenzene sulfonate (SDSB) as the chemical dispersant. It is clearly seen that the nanoparticle is dispersed well and no agglomeration is observed. The nanofluids are stable when exposed to air for a relatively long time. The measured pH value of the fluid was 10.05.

To better understand how the pH value influenced the nanofluid stability and physical performance, we have tested two samples, both containing 0.05 wt % F-SWNT-CNI dispersed in a PAC solution, but with different pH values. The pH value of sample A is 9.95 whereas the pH value of sample B is 10.73. Freezing points were determined according to ASTM D1177. The current experiment was carried out as follows: the fluids were first frozen, the frozen samples were then thawed at room temperature, and after thawing, the samples were poured into a 250 ml beaker so that the extent of sedimentation or agglomeration could be determined qualitatively through visual inspection of the beaker. Before and after the freezing and thawing process, the two samples appeared stable and no precipitations were observed on either the side or the bottom of the beaker. As shown in Table 1, there is no pH effect on the stability and freezing point of the PAC sample containing carbon nanoparticles. Interestingly, however, the carbon nanotube lowered the freezing point of the PAC solution 4 or 5°. The normal freezing point of the PAC solution is −35–36°C.

Table 1 0.05 wt % F-SWNT-CNI dispersed in the PAC solution with different pH values

Sample	pH value	Refractometer reading °C	Freeze point °C	Visual stability	
				Before	After
A	9.95	−40.6	−39.5	Clean	Clean
B	10.73	−41.1	−39.8	Clean	Clean

Fig. 2 The diagram of the Hot Disk™ thermal constant analyzer and sensor.

To further investigate the changing of the freezing point in the PAC solutions, we prepared three nanofluids in PAC with different carbon nanotube loadings, including 0.05%, 0.10%, and 0.20 wt %. Freezing points for these samples were then measured and summarized in Table 2. Clearly, the carbon nanotube loading has a significant effect on the freezing point of the nanofluid. The freezing point decreases as the loading increases. Similar effects were also observed with nanofluids containing double walled carbon nanotubes (DWNT) in ethylene glycol (EG). These results also indicate that this effect is independent of the type of nanotube and solvent (fluid).

Of course, our ultimate goal of the research work was to increase the TC (or heat transfer properties) of the nanofluid. We have measured the TC of many nanofluid samples at room temperature using the Hot Disk™ thermal constant analyzer. Figure 2 is the diagram of the hot disk analyzer and sensor that was used to measure the nanofluids.

Table 3 shows the thermal conductivity of several nanofluids with 0.05 wt % carbon nanotube loading. It is indicated that an increase in TC of about 10% for the 0.05 wt % nanotube loading was seen. We expected that the TC would increase more with a higher carbon nanotube loading. We have tried 0.1 and 0.2 wt % loading and have not observed the significant TC increase expected. We are working hard to understand the reason behind this phenomenon. It is well known that this field is very challenging, and people have observed many contradictory phenomena [7].

It is very interesting to point out that recently we have observed 20% heat transfer coefficient increase using 0.2 wt % of a soluble carbon nanotube derivative [8,9]. The results are very encouraging because to reach a 20% TC increase, people have needed loadings of 0.8–1 vol % carbon nanotubes. At this high of a percentage of carbon nanotube loading, the nanofluid loses its fluidity and becomes very viscous. The increased viscosity of the sample would make it impossible to use in any current coolant system. These new test results may open a new route and possibility towards real commercial application.

Table 2 Freezing point of different concentrations of carbon nanotubes in PAC and EG solutions

Nanofluid composition	Freezing point, °C
PAC solution	−35.6
0.05 wt % F-SWNT-CNI in PAC solution	−40
0.10 wt % F-SWNT-CNI in PAC solution	−41.1
0.20 wt % F-SWNT-CNI in PAC solution	−42.8
0.10 wt % D-SWNT-CNI in EG solution	−40.6
0.20 wt % D-SWNT-CNI in EG solution	−42.2

Table 3 The thermal conductivity (TC) of some nanofluids

Nanofluid composition	TC, W/m · K
0.05% SWNT-CNI in PAC solution with 1.00 wt % SDBS	0.50
0.05% acid treated SWNT in PAC solution with 1.00 wt % SDBS	0.49
0.05% SWNT-HiPco in PAC solution with 1.00 wt % SDBS	0.48
PAC solution with 1.00 wt % SDBS	0.45

IV. Conclusion

Dispersion is the key issue for obtaining good nanofluids based on carbon nanotubes. No improvement in physical properties such as TC can be expected without stable and homogeneous fluids. This is why soluble carbon nanotube derivatives may become the best candidate in obtaining these fluids. However, by chemically modifying the carbon nanotube to make it more soluble, we may change the structure of the carbon nanotube, thereby changing some of its properties such as thermal conductivity. It is hoped that more effective heat transfer fluids can be created when some of these challenging obstacles are overcome.

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References

[1] Eastman, J. A., Choi, S. U. S., Li, S., Yu, W., and Thompson, L. J., "Anomalously Increased Effective Thermal Conductivities of Ethylene Gycol-Based Nanofluids Containing Copper Nanoparticles," *Applied Physics Letters*, Vol. 78, No. 6, 2001, pp. 718–720.

[2] Choi, S. U. S., Zhang, Z. G., Yu, W., Lockwood, F. E., and Grulke, E. A., "Anomalous Thermal Conductivity Enhancement in Nanotube Suspensions," *Applied Physics Letters*, Vol. 79, No. 14, 2001, pp. 2252–2254.

[3] Keblinski, P., Eastman, J. A., and Cahill, D. G., "Nanofluids for Thermal Transport," *Materials Today*, Vol. 8, No. 6, 2005, pp. 36–44.

[4] Xie, H., Lee, H., Youn, W., and Choi, M., "Nanofluids Containing Multiwalled Carbon Nanotubes and Their Enhanced Thermal Conductivities," *Journal of Applied Phyisics*, Vol. 94, No. 8, 2003, pp. 4967–4971.

[5] Wen, D. S., and Ding, Y. L., "Effective Thermal Conductivity of Aqueous Suspensions of Carbon Nanotubes (Carbon Nanotubes Nanofluids)," *Journal of Thermophysical Heat Transfer*, Vol. 18, No. 4, 2004, pp. 481–485.

[6] Hong, H., Wensel, J., Peterson, S., and Roy, W., "Disperse the Carbon Nanotube into Polyalphaolefine Oils for Heat Transfer Application," *Polymeric Materials: Science & Engineering*, 2006 (to be published).

[7] Eastman, J. A., Phillpot, S. R., Choi, S. U. S., and Keblinski, P., "Thermal Transport in Nanofluids," *Annual Review of Materials Research*, Vol. 34, March 2004, pp. 219–246.

[8] Johnson, J. E., "Evaluation of Nanofluid Coolants and Lubricants: Development of Coolants," SWRI Project No. 08-10813, March 2006.

[9] Liang, F., Beach, J. M., Rai, P. K., Guo, W., Hauge, R. H., Pasquali, M., Smalley, R. E., and Billups, W. E., "Highly Exfoliated Water-Soluble Single-Walled Carbon Nanotubes," *Chemistry of Materials*, Vol. 18, No. 6, 2006, pp. 1520–1524.