# FEDSM-ICNMM2010-' 0( \$&

# PREPARATION OF STABLE SILICONE OIL BASED NANOFLUID CONTAINING MULTI-WALLED CARBON NANOTUBE BY USING HEXAMETHYLDISILOXANE AS DISPERSANT

Lifei Chen/School of Urban Development and Environmental Engineering Shanghai Second Polytechnic University Shanghai, 2360 Jinhai Road, China/Ifchen@eed.sspu.cnl

Yang Li/School of Urban Development and Environmental Engineering Shanghai Second Polytechnic University Shanghai, 2360 Jinhai Road, China/liyang@eed.sspu.cn

# ABSTRACT

Stable and homogeneous silicone oil based nanofluids of multi-walled carbon nanotubes (MWNTs) were prepared by using hexamethyldisiloxane as surfactant. The used MWNTs were cut by mechanical ball-milling approach following strong acid treatment. Scanning electronic microscopy results show that the MWNTs disperse well in the silicone oil. The addition of hexamethyldisiloxane reduces the viscosity of silicone oil greatly in all the studied temperatures. It is different from some water based nanofluids with surfactant. The minor viscosity augmentation of silicone oil based MWNT nanofluid with high thermal conductivity make it the ideal media in high burden of heat transfer and heat transfer enhancement in special condition. As expected, the viscosity of the nanofluid increases with MWNT volume fraction, but decreases with temperature. The 0.54 vol% MWNT dispersions with the addition of 0.6 wt % hexamethyldisiloxane show no MWNT precipitation for a couple of weeks.

#### **1. INTRODUCTION**

Nanofluids have been proposed as novel heat transfer fluids for their high thermal conductivity enhancement at a very low volume fraction [1]. The enhancement has relation to the nanoparticles' properties including the size [2, 3], morphology[4], intrinsic thermal conductivity, and the dispersion in the base fluids [5, 6]. Carbon nanotubes (CNTs) have been verified to be the excellent additives to enhance the

Huaqing Xie/School of Urban Development and Environmental Engineering Shanghai Second Polytechnic University Shanghai, 2360 Jinhai Road, China/hqxie@eed.sspu.cn

Wei Yu/School of Urban Development and Environmental Engineering Shanghai Second Polytechnic University Shanghai, 2360 Jinhai Road, China/yuwei@eed.sspu.cn

> thermal conductivity of base fluids because CNTs have very high thermal conductivity [7-9]. However, the preparation of homogeneous CNT suspensions remains a technical challenge since the CNT always form aggregates due to its non-reactive surfaces, the intrinsic Von der Walls forces [10], and the very large specific surface areas and aspect ratios [11]. To obtain stable CNT suspensions, physical or chemical treatment have been conducted such as an addition of surfactant [12, 13], surface functionalization by concentrated acid treatment [14, 15] or through a wet-mechanochemical reaction with potassium hydroxide using ethanol as solvent [16,17]. Studies have demonstrated that CNTs treated only by using a concentrated acid are still very long. Long and slender CNTs are usually curving and self-entangled. Curl and self-entanglement of CNTs will be a primary obstacle to the thermal conductivity enhancement and the stability of nanofluids [18, 19]. Silicone oil can be continuously used in higher temperature with slight property changes. It is not erosive due to the intrinsic chemical non-reactive, in addition, its thermal conductivity are more stable in very broad temperature region. Therefore, silicone oil would be the preferred heat transfer media in high temperature. However, silicone oil can not always satisfy the need of high burden of heat transfer and heat transfer enhancement in special condition. To solve this problem, the preparation of silicone oil based nanofluid containing CNTs would be the promising choice. To the best of our knowledge there is no literature on the preparation of silicone oil bases nanofluids due to the poor dispersion of CNTs in silicone oil.

In this work, multi-walled carbon nanotubes (MWNTs) were treated by a concentrated acid mixture in order to modify the affinity between the MWNT surfaces and the dispersant. Mechanical mill method was further employed to cut the MWNTs treated by concentrated acid. Hexamethyldisiloxane (HMDS) was selected as dispersant in the preparation of silicone oil based nanofulids containing MWNTs. The dispersion of MWNTs in silicone oil was studied by scanning electric microscope (SEM). Viscosity measurements have been conducted to study the effect of the addition of HMDS and MWNTs on the viscosity of the nanofluids.

# 2. Materials and methods

#### 2.1. Materials

Multi-walled carbon nanotubes (purity: 95%, the length is ~20um and the diameter is 30~50nm) were purchased from Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences. Silicone oil was used as base fluid in all studied. HMDS, nitric acid and sulfuric acid are all analytic agents.

#### 2.2. Treatment of MWNTs

MWNTs were mixed with concentrated nitric acid and sulfuric acid (1:3 in volume ratio) and refluxed at 90°C for 20 min. After washing with deionized water to attain a pH around 7, the samples were dried in vacuum at 100 °C for at least 24 h. The hydrophilic functional groups such as C-O-C, C=O, and O-H have been introduced on the MWNT surfaces. The dried samples were ball-milled with different ball-milling times.

#### 2.3. Dispersibility observation

Dispersibility of MWNTs in silicone oil was observed by using SEM (Hitachi S-4800 Scanning Electron Microscope). A drop of the suspension containing MWNTs was settled on a sample platform, filter paper was used to absorb the silicone oil until suitable for the subsequent SEM analysis.

#### 2.4. Determination of viscosity

Viscosity of MWNT suspensions was measured as a function of temperatures using a Brookfield LV DV-II Pro viscometers (measurable scope  $1.5 \sim 30 \text{KmPa} \cdot \text{s}$ ). About 6.0 milliliter sample was needed in the measurements.

# 3. Results and Discussion

#### 3.1. Stability of MWNT dispersions



Fig.1 Stability comparison of nanofluids containing MWNTs with different milling times (a: 0h; b: 5 h; c: 38 h)

The effect of the MWNT length on the stability of silicone oil based nanofluids was studied. The mixture of silicone oil with the addition of 0.6 wt % HMDS was mixed equably by using ultrasonic. Different length MWNTs with functionalized surfaces were dispersed to silicone oil in 0.54% volume fraction by using shearing equipment. Three samples were obtained and kept stationary. Fig. 1(a) shows that the MWNTs with functionalized surfaces precipitate quickly when they were not milled. However, as can be seen from Fig. 1(b), when the MWNTs were milled for 5 h the MWNTs could form stable dispersions in silicone oil without MWNTs precipitation for several days. As shown in Fig. 1(c), when the milling time is increased to 20 h, the silicone oil based dispersions containing MWNTs show no MWNT precipitation for a couple of weeks. The stability of the silicone oil based dispersions containing MWNTs can be controlled by adjusting the length of functionalized MWNTs. After being milled the change of the functionalized MWNT length can also be got from the following results of dispersibility observation.

# 3.2. Dispersibility of MWNTs in silicone oil

The dispersion micrographs were presented in Fig. 2. The length of the MWNTs turned short with the increase of the milling time. The fractions of MWNTs and HMDS in the two samples are 0.54 vol% and 0.6wt%. Fig. 2(a) shows that the MWNTs with short milling time still appear entangled. The entanglement of MWNTs will contribute to the sediment of MWNTs in silicone oil. As can be seen from Fig. 2(b) there is no MWNT aggregation in silicone oil when the milling time is increased to 20 h and the MWNTs disperse well in the silicone oil. Good dispersion plays the dominant role for improving the stability of the nanofluids.



Fig. 2 Dispersibility comparison of nanofluids containing MWNTs with different milling time (a: 5 h, c: 38 h)

3.3. Viscosity of MWNT suspensions



Fig. 3 Viscosity of silicone oil (a), Viscosity of silicone oil based nanofluids (b) ( $\phi$ : Volume fraction of MWNTs)

The effect of HMDS addition on the viscosity of silicone oil has been studied. The results presented in Fig. 3(a) reveal that the viscosity of the silicone oil, with or without addition of HMDS, decreases greatly with the increase of temperature. Addition of HMDS (0.6 wt%) greatly reduces the viscosity of silicone oil in all the studied temperatures. Fig. 3(b) presents the viscosity of silicone oil based nanofluids with the addition of MWNTs. The mass fractions of HMDS in these three samples are all 0.6wt%. The addition of 0.6wt% HMDS resulted that the viscosity of the nanofluid containing 1.0vol% MWNTs almost has no augmentation compared with that of pure silicone oil. Thermal conductivity measurements revealed that the thermal conductivity enhancement of the silicone oil based nanofluid with 1.0vol% MWNT loading is up to 27.8%. The minor viscosity increase of silicone oil based MWNT nanofluid with high thermal conductivity make it very suitable to be used in the high burden of heat transfer and heat transfer enhancement in special condition. Furthermore, it can be observed that in general, the viscosity of the silicone oil based nanofluids increases considerably with MWNT volume fraction. This effect is due to the fact that increasing concentration would have a direct effect on the fluid internal shear stress.

# 4. Summary

Silicone oil based MWNT nanofluids stabilized by HMDS have been obtained. Before dispersing MWNTs in silicone oil, the MWNTs have been treated by concentrated acid followed by mechanical ball-milled technology. The stability of the silicon oil based nanofulids containing MWNTs increases with decrease of MWNT length. The 0.54 vol% MWNT dispersions with the addition of 0.6wt % HMDS show no MWNT precipitation for a couple of weeks. And the short MWNTs also can disperse well in the silicone oil. The addition of HMDS reduces the viscosity of silicone oil greatly in all the studied temperatures. It is different from some water based nanofluids with surfactant. The silicone oil based MWNT nanofluid with minor viscosity augmentation resulted from the addition of HMDS will be the ideal media in the high burden of heat transfer and heat transfer enhancement in special condition. As expected, viscosity of silicone oil based nanofluid containing MWNTs increases considerably with increasing MWNT volume fraction.

# ACKNOWLEDGMENTS

This work was supported by the National Science Foundation of China (50876058), Shanghai Educational Development Foundation and Shanghai Municipal Education Commission (07SG56), Innovation Program of Shanghai Municipal Education Commission (08ZZ99), and Program for Excellent and Yong Scholar Selected and Cultivated by Shanghai Municipal Education Commission (EGD-07006).

#### REFERENCES

[1] Choi, S. U. S., 1995, "Developments and Applications of Non-Newtonian Flows" (ASME, New York,), FED-Vol. 231, pp.99-102.

[2] Lee, S., Choi, S. U. S., Li, S., and Eastman, J. A., 1999, "Measuring thermal conductivity of fluids containing oxide nanoparticles," J. Heat Transfer., 121[2], pp. 280-289.

[3] Das, S. K., Putra, N., Thiesen, P., and Roetzel, W., 2003, "Temperature dependence of thermal conductivity enhancement for nanofluids," J. Heat Transfer., 125[8], pp. 567-574.

[4]Xie, H., Wang, J., Xi, T., and Liu, Y., 2002, "Thermal conductivity of suspensions containing nanosized SiC particles," Int. J. Thermophys., 23[2], pp. 571-580.

[5] Keblinski, P., Phillpot, S. R., Choi, S. U. S., and Eastman, J. A., 2002, "Mechanisms of heat flow in suspensions of nanosized particles(nanofluids)". Int. J. Heat Mass Transfer., 45[4], pp. 855-863.

[6] Prasher, R., Phelan, P. E., and Bhattacharya, P., 2006, "Effect of Aggregation Kinetics on the Thermal Conductivity of Nanoscale Colloidal Solutions (Nanofluid)," Nano Lett., 6, pp. 1529-1534.

[7] Berber, S., Kwon, Y. K., Tomanek, D., 2000, "Unusually High Thermal Conductivity of Carbon Nanotubes," Phys. Rev. Lett., 84[20], pp. 4613-4616.

[8] Kim, P., Shi, L., Majumdar, A., and McEuen, P. L., 2001, "Thermal Transport Measurements of Individual Multiwalled Nanotubes," Phys. Rev. Lett., 87[21], pp. 215502/1-215502/4.

[9]Fujii, M., Zhang, X., Xie, H., Takahashi, K., Abe, H., and Shimizu, T., 2005, "Measuring the Thermal Conductivity of a Single Carbon Nanotube," Phys. Rev. Lett., 95, pp. 065502/1-065502/4.

[10] Lin, T., Bajpai, V., Ji, T., and Dai, L., 2003, "Chemistry of Carbon Nanotubes," Aust. J. Chem., 56 [7], pp. 635-651.

[11]Park, C., Qunaies, Z., Watson, K., Crooks, R., Smith, J., Lowther, S., Connell, J., Siochi, E., Harrison, J., and Clair, T., 2002, "Dispersion of single wall carbon nanotubes by in situ polymerization under sonication" Chem. Phys. Lett., 364[3-4], pp.303-308.

[12]Sophie, H. W., and Philip, P., 2001, "Adsorption of anionic surfactant by activated carbon: effect of surface chemistry, ionic strength, and hydrophobicity," J. Colloid. Interf. Sci., 243[2], pp. 306-315.

[13]Kunio, E., 2001, "Interactions between surfactants and particles: dispersion, surface modification, and adsolubilization," J. Colloid. Interf. Sci., 241[1], pp. 1-17.

[14]Esumi, K., Ishigami, A., Nakajima, A., Sawada, K., and Honda, H., 1996, "Chemical treatment of carbon nanotubes," Carbon., 34[2], pp. 279-281.

[15]Li, Y. H., Xu, C. L., Wei, B. Q., Zhang, X. F., Zheng, M. X., and Wu, H., 2002, "Self-organized ribbons of aligned carbon nanotubes," Chem. Mater., 14[22], pp. 483-485.

[16]Chen, L. F., Xie, H. Q., Yang, L., Wei, Y., 2009, "Carbon nanotubes with hydrophilic surfaces produced by a wetmechanochemical reaction with potassium hydroxide using ethanol as solvent," Materials Letters., 63, pp. 45-47.

[17]Chen, L. F., Xie, H. Q., Yang, L., Wei, Y., "Surface Chemical Modification of Multi-walled Carbon Nanotubes by a Wet-Mechanochemical Reaction," Nanomaterials, doi:10.1155/2008/783981.

[18]Xie, H., Lee, H., Youn, W., and Choi, M., 2003, "Nanofluids containing multiwalled carbon nanotubes and their enhanced thermal conductivities," J. Appl. Phys. 94[8], pp. 4967-4971.

[19]Sano, M., Kamino, A., Okamura, J., Shinkai, S., 2001, "Ring Closure of Carbon Nanotubes," Science., 293[17], pp. 1299-1301.