THE EFFECT OF SURFACTANT ON STABILITY AND THERMAL CONDUCTIVITY OF CARBON NANOTUBE BASED NANOFLUIDS

by

Kin Yuen LEONG*, Nurfadhillah MOHD HANAFI, Risby MOHD SOHAIMI, and Noor Hafizah AMER

Department of Mechanical Engineering, National Defence University of Malaysia, Kuala Lumpur, Malaysia

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The addition of highly conductive substance such as carbon nanotubes into a traditional heat transfer fluid will enhance the fluids' thermal conductivity. However, dispersion process of carbon nanotubes into base fluids is not an easy task due to hydrophobic characteristic of its surface. This study attempts to investigate the stability and thermal conductivity of carbon nanotube based ethylene glycol/water nanofluids with and without surfactants. Stability investigation was conducted through observation and zeta potential measurement methods. As for the thermal conductivity, the samples were measured based on transient line heat source. The results showed that 0.01 wt.% of carbon nanotube based nanofluid, containing 0.01 wt.% hexadecyltrimethylammonium bromide possess highest zeta potential value compared to the other tested samples. The 0.5 wt.% of carbon nanotube based nanofluids with gum Arabic exhibit 25.7% thermal conductivity enhancement.

Key words: *nanofluids, carbon nanotubes, ethylene glycol, water, surfactants, thermal conductivity*

Introduction

Heat transfer performance of a thermal system can be improved through several methods. They are: maximizing heat transfer area, increasing temperature difference between the fluids, and improving thermal conductivity of the heat transfer fluid. However, the first method is not preferable especially in the field of microelectronic and microprocessor as compact and small cooling system is required. The second method is complex to be implemented due to the constraints in material and thermal system's operation. Therefore, most of the thermal scientists and researchers have focused on improving thermal conductivity of traditional heat transfer fluids. Mahmoodi [1] stressed that heat transfer rate of the industrial thermal systems can be improved by increasing the fluids' thermal conductivity.

The efforts to improve heat transfer fluids' thermal conductivity through nanoparticles were initiated by Argonne National Laboratory [2]. This novel heat transfer fluid, known as *nanofluid*, is defined as a mixture of nanoparticles and base fluid. Carbon

* Corresponding author; e-mail: leongkinyuen@gmail.com

nanotube (CNT) is one of the particles that can be added into the base fluid. The CNT offers attractive performance in terms of its mechanical strength, chemical stability, electric, and thermal conductivity. Marquis and Chibante [3] reported that CNT thermal conductivity is about 1800-2000 W/mK.

Inclusion of CNT into base fluid will improve its thermal conductivity and lead to better thermal performance of a thermal or energy system [4]. Nevertheless, it is noted that CNT posses hydrophobic surface in nature. This increases the tendency of nanoparticles to aggregate and precipitate in a base fluid. Therefore, this paper investigates the stability and thermal conductivity characteristics of CNT based ethylene glycol/distilled water nanofluids, subjected to three types of surfactants. The surfactants considered were polyvinylpyrrolidone (PVP), gum Arabic (GA) and hexadecyltrimethylammonium bromide (CTAB). To the best of authors' knowledge, there are limited studies which are focused on comparing the CNT based ethylene glycol/distilled water added with these types of surfactants.

There has been numerous studies carried out to understand the thermal conductivity and stability behaviours of CNT based nanofluids. Chen *et al.* [5] stabilized the CNT based nanofluids through cationic Gemini surfactant. Their results from the zeta potential measurements indicated that nanofluids without any surfactant tend to aggregate compared to that of nanofluids with Gemini surfactant. Meibodi *et al.* [6] used fractional factorial design approach to propose suitable condition for CNT/water nanofluids' production. Chen and Xie [7] revealed that higher concentration of Gemini surfactant gives adverse effect on the thermal conductivity enhancement of multiwalled CNT (MWCNT) based nanofluids. Authors explained that the decrease of the thermal conductivity enhancement is attributed to the increase of space chain length of the surfactant. Nasiri *et al.* [8] studied the effect of dispersion method on thermal conductivity and stability of five different CNT based nanofluids. Functionalization, ultrasonic probe/SDS surfactant and ultrasonic bath/SDS surfactant, were used to disperse the CNT. Nanofluids formulated via CNT functionalization process showed the best thermal conductivity enhancement compared to other dispersion method.

Lamas *et al.* [9] evaluated the stability of functionalized MWCNT based nanofluids. Measurement of particles settling velocity was conducted in their investigation. It is also revealed that the settling velocity of MWCNT based nanofluids decreases with the increase of nanoparticles loading and aspect ratio. Kumaresan and Velraj [10] found that the thermal conductivity of 0.45 vol.% MWCNT based ethylene glycol (30%)/deionised water (70%) nanofluids is enhanced about 19.73% at 40 °C operating temperature. Sodium dodecyl benzene sulphonate (SDBS) was used as surfactant in their study. Authors explained that thermal conductivity enhancement is due to the kinetics of nanoparticles aggregation and interfacial liquid layering effects.

Preparation of the nanofluids

The MWCNT >95% purity used in this study were purchased from Chengdu Organic Chemicals, China. From the observation via NANO NOVASEM 240 (FEI), the diameter of the MWCNT is less than 30 nm. Typical field emission scanning electron microscopy (FESEM) image of the MWCNT is depicted in fig 1.

According to the vendor, chemical vapour deposition (CVD) method was used to produce the MWCNT. As for the base fluid, authors used mixture of distilled water (60%) and ethylene glycol (40%). Ethylene glycol and surfactants were purchased from Sigma Aldrich. The samples are prepared based on concentration detailed in tab. 1.

Table 1. Concentration of carbon nanotube based nanofluids

No.	Samples without surfactant*	Samples with surfactant
1	0.01 wt.% CNT + ethylene glycol /water	0.01 wt.% CNT + 0.01 wt.% surfactant + + ethylene glycol /water
2	0.05 wt.% CNT + ethylene glycol/water	0.05 wt.% CNT + 0.05 wt.% surfactant + + ethylene glycol/water
3	0.1 wt.% CNT + ethylene glycol/water	0.1 wt.% CNT + 0.1 wt.% surfactant + + ethylene glycol/water
4	0.3 wt.% CNT + ethylene glycol/water	0.3 wt.% CNT + 0.3 wt.% surfactant + + ethylene glycol/water
5	0.5 wt.% CNT + ethylene glycol/water	0.5 wt.% CNT + 0.5 wt.% surfactant + + ethylene glycol/water

* Surfactants used are PVP, GA or CTAB

Initially, the base fluid and surfactants were mixed through magnetic stirrer. Then, the MWCNT were added into the base fluid and subjected to ultrasonication process. During ten minutes of ultrasonication process, the sample (beaker) was immersed into ice bath. This is to minimize the temperature rise during the ultrasonication process. Ten minutes was chosen to avoid breakage of the CNT. It is noted that excessive ultrasonication process will reduce the CNT length and aspect ratio [11].

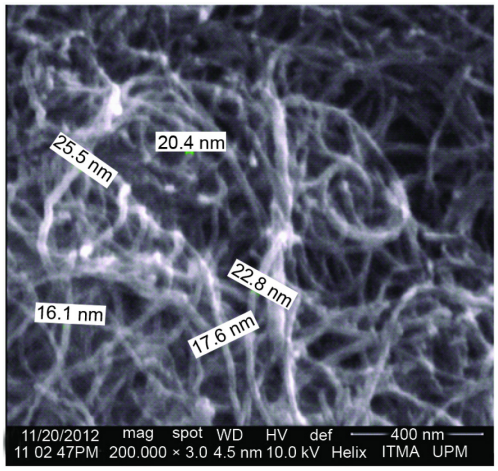

Figure 1. The FESEM image of MWCNT

Thermal conductivity and stability of the nanofluids

The stability of the CNT based nanofluids was investigated through two approaches: observation and measurement of zeta potential. In the observation method, the prepared samples (put in the measuring cylinders) were observed in terms of the particles' sedimentation. It was done within the duration of four weeks. For the particles' agglomeration characteristic, zetasizer nano (mavern nano Z) was used to investigate the samples' zeta potential values. Zeta potential represents the tendency of the nanoparticles to flocculate in the base fluid.

The KD2-Pro thermal analyzer was used to investigate the CNT based nanofluids' thermal conductivity at room temperature (~25 °C). It works on the principle of transient line heat source. In order to minimize the errors during measurements and repeatability of results, an average reading from ten measurements was taken from each the samples. In addition, the measurement was taken only after thermal equilibrium between the sensor and sample was achieved. This instrument has a specified accuracy of ±5%.

Results and discussions

Figure 2 illustrated the condition of various weight percentages of the CNT based nanofluids four weeks after the ultrasonication process.

From fig. 2, it is obvious that particles coagulation happened on the nanofluids containing 0.01 and 0.05 wt.% of CNT. This phenomenon is attributed to the hydrophobic surface of the CNT itself. Van der Waal's attractive force is stronger, and consequently the CNT tend to be attracted to each another. However, there is no obvious particles coagulation or sedimentation observed for CNT based nanofluids with surfactant for the same period as shown in fig 3.

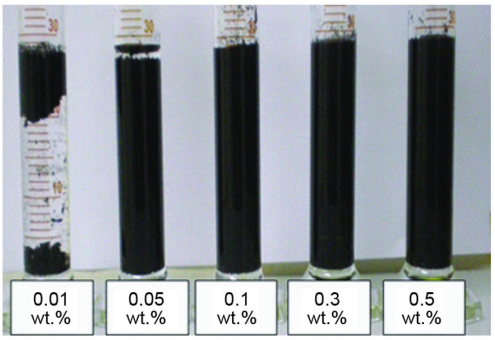

Figure 2. Condition of CNT based nanofluids without surfactant

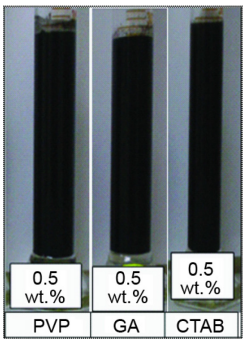

Figure 3. Condition of CNT based nanofluids with surfactant

The inclusions of surfactants in the nanoparticles samples are modifying the CNT surface from hydrophobic to hydrophilic. The CNT nanoparticles tend to repulse each other due to the surface modification. Moreover, Garg *et al.* [11] reiterated that surfactant is able to change the wetting and adhesion behaviours of CNT particles, thus reducing the tendency of these particles to agglomerate. The stability of the samples is further examined through zeta potential measurements. As expected, the zeta potential values for samples with surfactant are higher (deviates from zero) than the values for sample without surfactant, as shown in fig 4.

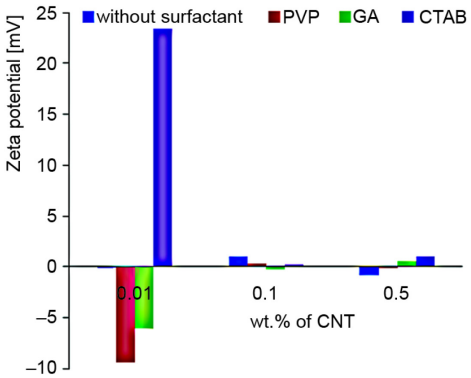

Figure 4. Stability of CNT based nanofluids

Figure 4 also depicts that 0.01 wt.% of CNT based nanofluids added with CTAB (23.4 mV) is the most stable among the tested nanofluids, followed by nanofluids with PVP (–9.37 mV), GA (–6.09 mV), and lastly the nanofluids without surfactant (–0.178 mV). It can be seen that nanofluids added with surfactant exhibited higher zeta potential value compared to the nanofluid without surfactant. Higher absolute zeta potential value indicates that the electrostatic repulsion force between the nanoparticles is high which lead to better stability of the samples. Nanofluids without surfactant which have low zeta potential value tend to coagulate as seen in fig 2. Chen *et al.* [5], Hwang *et al.* [12], and Murshed *et al.* [13] in their experiment agreed that addition of surfactant into the nanofluid will increase its zeta potential value.

However, as the particles loading increases, zeta potential values for all samples are relatively similar. It is known that CNT have very low density (2.1 g/cm^3). The quantity of CNT added into base fluid increases as the weight percentage increase. Consequently there is

less space for the nanoparticles to disperse and the nanoparticles are closer to each others. This contributes to the smaller zeta potential values. However, it must be noted that there is no obvious nanoparticles sedimentation or flocculation observed in these samples.

Figure 5 depicts the comparison of thermal conductivity values measured from experiment and from Incroprea *et al.* [14].

Thermal conductivity of water and ethylene glycol are obtained from Incropera *et al.* [14]. Experiment implies that 6.1% and 0.6% deviations were observed for water and ethylene glycol, respectively. This shows that the instrument used in the present study is reliable and accurate especially for highly viscous fluid. The effect of CNT on the thermal conductivity of the ethylene glycol/water based fluids is depicted in fig. 6.

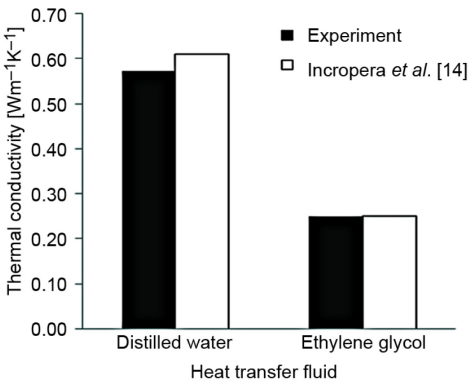

Figure 5. Validation of the measured experiment data

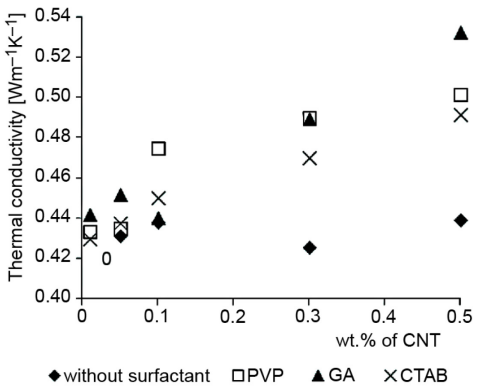

Figure 6. Effect of CNT concentration with and without surfactant

It is noticed that there is no substantial thermal conductivity augmentation for the base fluids without surfactant. Thermal conductivity of 0.01 wt.% CNT was not measured because the nanoparticles started to agglomerate right after the sonication process. At 0.5 wt.% of CNT, there is only 3.8% thermal conductivity enhancement compared to that of base fluid. In this study, the thermal conductivity of base fluid (ethylene glycol/water mixture) is found to be 0.4234 W/mK. However, the percentage of thermal conductivity of CNT based nanofluids with surfactants show convincing thermal conductivity improvement. It is found that 25.7%, 18.4%, and 16.0% enhancement were observed for 0.5 wt.% of CNT based nanofluids with GA, PVP, and CTAB, respectively. The thermal conductivity also shows an increasing trend when the weight percentage of CNT increases. This proves that samples with higher values of zeta potential are not necessary to produce higher thermal conductivity. Kumaresan and Velraj [10] reported that, the thermal conductivity enhancement is due to the intrinsic thermal conductivity of the CNT.

Figures 7-9 compare thermal conductivity of base fluid (ethylene glycol/water mixtures) containing surfactant only and base fluid added with CNT and surfactants.

The purpose of this comparison is to investigate the effect of surfactant on the nanofluids' thermal conductivity. These figures clearly show that thermal conductivity of base fluid containing surfactant only exhibits lower thermal conductivity than the sample with CNT and surfactant. This proves that thermal conductivity enhancement as shown in fig. 6 is not solely due to the effect of surfactant. It is the combination effect of surfactant and CNT particles which contributing to the thermal conductivity enhancement. When the effect of

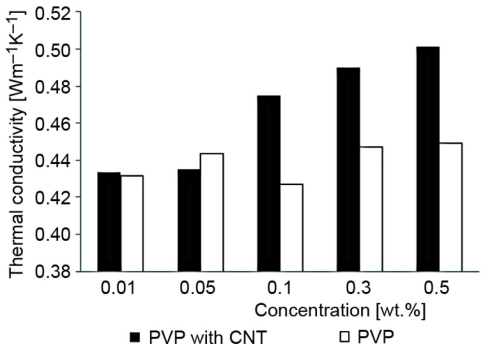

Figure 7. Thermal conductivity of CNT based nanofluids and base fluids containing PVP

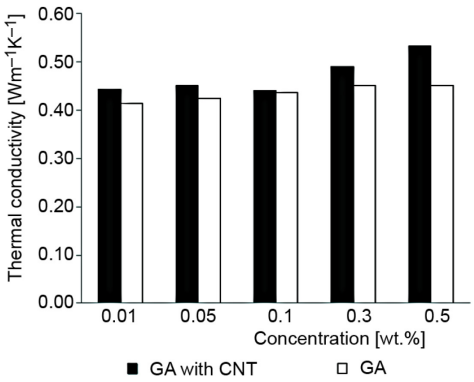

Figure 8. Thermal conductivity of CNT based nanofluids and base fluids containing GA

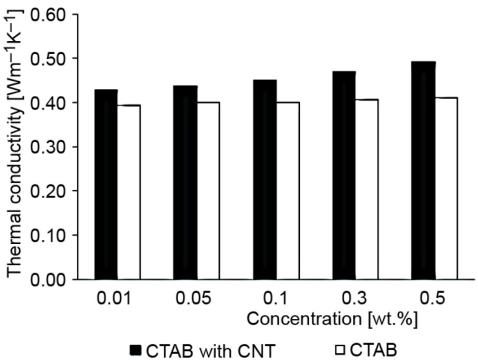

Figure 9. Thermal conductivity of CNT based nanofluids and base fluids containing CTAB

PVP surfactant was examined closely as shown in fig. 7, there is no specific trend on the thermal conductivity of the base fluid when the PVP surfactant weight percentage is being increased. However, thermal conductivity of base fluid containing GA progressively increases when the GA loading increase (fig. 8). About 6.6% thermal conductivity increment is observed for base fluid containing 0.5 wt% of GA. Addition of 0.5 wt.% of CNT into this sample leads to 25.7% thermal conductivity augmentation compared to that of base fluid. Figure 9 illustrated that the addition of CTAB surfactant into base fluid have negative effect on the base fluid thermal conductivity. It is found that thermal conductivity of base fluid containing CTAB is lower than the base fluid (Basefluid's thermal conductivity = 0.4234 W/mK), regardless of its weight percentage. Also, significant thermal conductivity enhancement is observed when the CNT are added into the base fluid.

Figure 10 illustrated the effect of sonication time on the thermal conductivity of 0.5 wt.% of CNT based nanofluids with and without surfactants. The sonication time was varied from 5 to 30 minutes.

There is only slight increase on thermal conductivity compared to that of base fluid for samples subjected to only five minutes sonication time. It can be said that five minutes sonication time is not enough to disperse nanoparticles into the base fluid. However, when the sonication time increases to up to ten minutes, CNT nanofluids with surfactants showed substantial thermal conductivity augmentation. Thermal conductivity of nanofluids with surfactants, except for PVP surfactants increases with the increase of sonication time. Longer sonication time might break the CNT into smaller particles, thus increasing the nanofluids' thermal conductivity. The thermal conductivity of nanofluids will decrease if the optimum ultrasonication time is exceeded. As for nanofluids without surfactant, only a slight increase in thermal conductivity can be observed. From fig. 10, study implies that the thermal conductivity of samples with GA remain stable when the sonication time reaches twenty minutes.

Conclusions

In this study, the effect of surfactant on the stability and thermal conductivity of CNT based nanofluids has been investigated. The following conclusions can be derived from the present study.

- The CNT based nanofluids containing surfactant exhibit better stability compared to that of nanofluids without surfactant through observation approach. At 0.01 wt.% of CNT, ethylene glycol/water mixture base fluid containing CTAB exhibits highest zeta potential value compared to that of other tested samples.
- Thermal conductivity of CNT based nanofluids with surfactants exhibit higher enhancement compared to nanofluids without surfactant. At 0.5 wt.% of CNT, there is only 3.8% thermal conductivity enhancement compared to that of base fluid. The 0.5 wt.% of CNT based nanofluids containing GA demonstrated 25.7% thermal conductivity enhancement. This is the highest enhancement compared to that of other surfactants.
- The combined effects of CNT and surfactants are required to produce sample with high thermal conductivity.

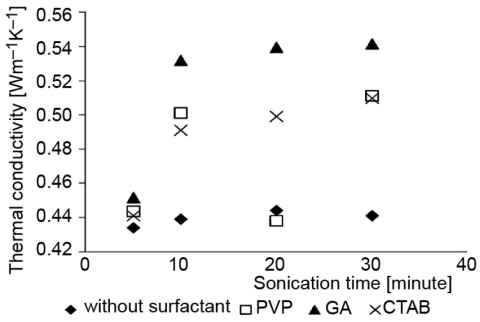

Figure 10. Effect of sonication time on thermal conductivity of CNT based nanofluids with and without surfactants

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Acronyms

CNT – carbon nanotube
CTAB – hexadecyltrimethylammonium bromide
CVD – chemical vapour deposition
FESEM – field emission scanning electron microscopy
GA – gum Arabic
MWCNT – multiwalled CNT
PVP – polyvinylpyrrolidone
SDS – sodium dodecyl sulphonate
wt.% – weight percentage

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