STABILITY AND CHARACTERIZATION OF CNT NANOFLOUIDS USING POLYVINYL ALCOHOL DISPERSANT

S. W. TAM¹, W. RASHMI¹*, S. RASHIDI², L. C. ABDULLAH², M. KHALID³

¹School of Engineering, Taylor's University, Taylor's Lakeside Campus, No. 1 Jalan Taylor's, 47500, Subang Jaya, Selangor DE, Malaysia
²Department of Chemical and Environmental Engineering, University Putra Malaysia, 43400 Serdang, Selangor, Malaysia.
³Manufacturing and Industrial Process Division, University of Nottingham Malaysia Campus, 43500 Semenyih, Selangor, Malaysia.

*Corresponding Author: RashmiGangasa.Walvekar@taylors.edu.my

Abstract

In this research, CNT-water nanofluids are synthesized using polyvinyl alcohol (PVA) dispersant where each of the CNT concentration ranging from 0.01 to 0.1 wt% is tested with 0.25 to 3.00 wt% of PVA to optimize the dispersion and stability of nanofluids. The nanofluids are sonicated for 4 hours using ultrasonic water bath and the stability is analyzed using UV-Vis spectrophotometer. The dispersion state of the CNT-water nanofluid is further examined using optical microscope. The stable nanofluids of each CNT concentration identified were then tested for their thermo-physical properties such as thermal conductivity and viscosity with respect to temperature ranging from 25 to 70 °C. The results revealed that 0.5 to 1.5 wt% of PVA dispersant give the optimum stability to the entire range of CNT concentration studied. It was found that the thermal conductivity enhancement of CNT-water nanofluid stabilized by PVA increased non-linearly with temperature. Although PVA suppressed the thermal conductivity of water, the addition of CNT is able to surpass its effect and the results showed that there is approximately 1 to 44 % enhancement for the range of CNT concentration and temperature studied. It was also observed that the viscosity for 1.5 wt% of PVA aqueous solution at 25 °C is approximately 7.5 mPa.s, which is significantly greater than water. However, the presence of CNT nanoparticles is able to reduce the viscosity of its respective optimum PVA solution by 2 to 6% for the entire range of CNT concentrations investigated, showcasing self-lubrication effect of CNT. Moreover, the viscosity of the nanofluids decreases significantly with increasing temperature.

Keywords: Nanofluid, Carbon Nanotube, Polyvinyl Alcohol, Stability, Thermal Conductivity
1. Introduction
Heat transfer fluids such as water, ethylene glycol (EG) and mineral oils are commonly used in the industries as the medium to exchange the thermal energy in heat exchanger, engines, electrical devices, transformer, etc. A fluid with excellent heat transfer properties such as thermal conductivity will significantly enhance the rate of heat transfer and thus the efficiency of the equipment. However, these conventional fluids often have poor thermal properties which limit their performances and thus the size of the heat transfer equipment need to be increased in order to compensate for its efficiency. Therefore, the approach is to utilize the superior thermal characteristics of solid nanoparticles by dispersing them into the traditional heat transfer fluids. The stable colloidal suspensions with nano-size particles are known as nanofluids. This is due to the facts that the thermal conductivity of solid particle is greater than the water and the nanoparticles have high surface to volume ratio which increases the effective heat transfer surface area [1]. For instance, the thermal conductivity of copper (Cu) nanoparticle is 390 W/mK, which is considerably greater than the thermal conductivity of water of 0.6 W/mK [2].

Different types of metal, metal oxides and carbon based nanoparticles such as are Cu, aluminium (Al), silver (Au), aluminium oxide (Al2O3), copper oxide (CuO), titanium oxide (TiO2), silicon oxide (SiO2), carbon nanotube (CNT), etc. have been studied extensively to maximize the heat transfer performance of the conventional base fluids. Based on the research done by Choi et al. [3], the dispersion of 1 vol% of CNT nanoparticles in oil without the addition of dispersant is able to enhance the thermal conductivity of oil by 2.5 times. Assael et al. [4] and Wang et al. [5] studied the effect of CNT and CuO nanoparticles in the thermal conductivity of water respectively. The findings reported by Assael et al. [4] showed that the addition of 0.6 vol% of CNT in water is able to show 34% enhancement in thermal conductivity. On the contrary, Wang et al. [5] discovered that 9.7 vol% of CuO is required to produce the same value of thermal conductivity enhancement. This shows that CNT has better thermal performance due to its high aspect ratio which allows them to arrange in three dimensional networks that promote rapid heat flow, thus small fractions of CNT is sufficient to show a significant enhancement in the thermal conductivity of nanofluid [6]. Moreover, the thermal conductivity of CNT is approximately 3000 W/mK, which is remarkably greater than the thermal conductivity of metal oxides nanoparticles with the values ranging from 10 to 50 W/mK [7].

However, CNT nanoparticles are more prone to agglomerations compared to other nanoparticles when there are dispersed in polar base fluids such as water. This is due to the large surface area and high van der Waals forces between the hydrophobic surfaces of the CNT [8]. Therefore, CNT nanoparticles are insoluble in most of the base fluids as they cannot interact with the polar molecules to overcome the large inter-tube attractive forces. Besides causing clogging and erosion in the piping systems and micro-channels, the formation of clusters also increases the sedimentation rate of nanoparticles and thus reducing its heat transfer efficiency [1]. Till now, many efforts have been conducted to maximize and maintain the stability of nanofluid. In general, there are two methods used to disperse the nanoparticles, namely physical and chemical methods. Physical
methods involve the usage of mechanical stirrer, homogenizer and ultrasonic agitation to break the agglomerates under high shear rate. However, the suspension will settle down after a short period of time, thus it is normally accompanied by chemical methods to strengthen the stability [9].

Chemical methods can be further divided into surface modification and surface coating. In terms of surface modification, the nanoparticle such as CNT will be oxidized under the presence of acid at high temperature to attach the functional group such as hydroxyl (OH), carboxyl (COOH) or amine (NH2) to its surface via covalent bond [8]. The polar functional group will increase the interaction of the functionalized CNT with the water molecules. However, the structures of CNT are often damage due to the extreme pH and temperature during the oxidation [10]. Hence, surface coating offers a simpler procedure where surfactants or dispersant are added to act as a barrier between the nanoparticles. In CNT-water nanofluid, the hydrophobic tail of dispersant will adsorb onto its non-polar surface, while the hydrophilic head extends to the water to provide repulsion between the nanoparticles. Previous researches shown that the addition of dispersant such as Gum Arabic (GA) [8, 11], sodium dodecyl sulfate (SDS) [12, 13], sodium dodecyl benzene sulphate (SDBS) [13, 14], etc. are able to improve the stability of CNT nanofluid remarkably. To date, GA is the best dispersing agent for CNT nanofluids due to its high hydrophobic polysaccharides content which increases the chances of adsorption onto the nanoparticle surfaces [15, 16]. However, GA has low decomposition temperature where the protein compounds tend to precipitate at approximately 90 °C. This will limit the application of the nanofluid dispersed with GA as it cannot be used for high temperature applications.

Therefore, this research involves the study of alternative dispersing agent, which is polyvinyl alcohol (PVA) on the stability of CNT-water nanofluids. The long hydrocarbon chain of PVA with hydroxyl groups is able to withstand temperature up to 200 °C, which makes it a good candidate for dispersing the nanofluids in heat transfer application [17]. The hydroxyl group is responsible for the formation of hydrogen bond with water and thus increasing the solubility of CNT in water. Although the effect of PVA on nanofluids have been studied by Wang et al. [18] and Singh et al. [19], none of it involves the application of PVA on CNT-water nanofluid. Also, the effect of PVA on the stability, thermal conductivity and viscosity of CNT-water nanofluid are still unknown. The viscosity of nanofluid plays an important role in the applications involving fluid flow as it will affect the pumping cost and pressure drop in pipes. This objective of this study is to optimize the amount of PVA dispersant (0 to 3 wt%) in different concentrations of CNT nanoparticles (0.01 to 0.10 wt%) in order to synthesize the nanofluids with maximum stability. This is because excess dispersant will have adverse effect on the stability, thermal conductivity and viscosity of the nanofluid [20]. Moreover, the effect of PVA and CNT on the thermo-physical properties of stable CNT-water nanofluids such as thermal conductivity and viscosity are investigated with respect to temperature.
2. Research Methodology

2.1. Materials

The multi-wall carbon nanotube (MWCNT) with the purity ≥ 95% is obtained from Laboratory and Scientific Enterprise, Malaysia. The average dimensions of the individual tube in terms of outer diameter and length is 25 nm and 20 µm respectively. The PVA dispersant is obtained from Ever Gainful Enterprise Sdn. Bhd., Malaysia. The thermal conductivity of CNT and PVA is 3000 W/mK and 0.2 W/mK respectively, while the decomposition temperature of PVA is 200 °C.

2.2. Preparation of samples

A low range of CNT concentrations, 0.01 wt%, 0.02 wt%, 0.04 wt%, 0.08 wt% and 0.10 wt% are used in this study to minimize the tendency of agglomeration as the stability of nanofluids tend to decrease due to the formation of dense solution as CNT concentration increases [21]. Each CNT concentration is tested with a wide range of PVA concentrations which are 0.25 wt%, 0.50 wt%, 1.0 wt%, 1.5 wt%, 2.0 wt%, 2.5 wt% and 3.0 wt% respectively so that the optimum PVA concentration required to produce a CNT-water nanofluid with maximum stability can be obtained [8, 22]. The amount of CNT, PVA and water are measured using a four decimal point electronic weighing balance (BEL M164A, Italy) to make up a total weight of 40 grams. Then, the nanofluids are sonicated for 4 hours at temperature and frequency of 60 °C and 35 kHz respectively using ultrasonic bath (Elma Transsonic T1-H-15, USA) to detangle the CNT for the adsorption of PVA dispersant on the surface. The sonication temperature is set at 60 °C to improve the diffusional rates and the frequency of collision between the individual tubes and PVA molecule. It must be noted that the temperature of water bath must not exceed 80 °C as it may change the properties of nanoparticles [23, 24]. Based on previous studies, 4 hours sonication time at 35 kHz is the optimum duration to maximize the adsorption of dispersant on the CNT [8]. Prolonged sonication can lead to dislocation of carbon structure and reduces the aspect ratio of CNT which will affect the thermal properties of CNT [25].

2.3. Stability study of nanofluids

The stability of each sample is analyzed for a period of 20 days using UV-vis spectroscopy (Shimadzu UV-1800, Japan). The nanofluids and their respective blanks are transferred into the cuvette cells immediately after sonication. The function of blanks which consist of water and PVA is to eliminate the absorbance of both water and PVA in the nanofluid so that the absorbance value obtained is purely based on CNT. One of the samples and its respectively blank containing the same PVA concentration are used to determine the absorbance spectrum of the CNT. Based on the absorbance curve shown in Fig. 1, CNT nanoparticles absorbed most of the light energy at the peak of the spectrum, which is 267 nm. The wavelength obtained is used throughout the stability study. Note that the applicable wavelength of the cuvettes used is 220 to 900 nm. Hence, the peaks and fluctuations of the absorbance below 220 nm are not taken into account. A linear calibration curve of absorbance versus CNT concentration as shown in Fig. 2 is constructed to convert the absorbance value into concentration of CNT. Therefore, the optimum concentration of PVA required to produce the most stable
nanofluid for each CNT concentration can be determined based on the graph of CNT concentration against sedimentation time.

![Absorption spectrum of CNT](image1.png)

**Fig. 1.** Absorption spectrum of CNT.

![Calibration curve of CNT-water nanofluid at 267 nm](image2.png)

**Fig. 2.** Calibration curve of CNT-water nanofluid at 267 nm.

### 2.4. Characterization of nanofluid

The five stable samples of different CNT concentrations with its optimum amount of dispersant identified from the stability study were further characterized using optical microscope (Swift M10D, USA) at 40X magnification. This is to estimate the dispersion characteristic of the nanofluid by examining the size of the cluster formed in the range of micrometres because stable nanofluid will have lesser and smaller agglomerates [22].
2.5. Thermo-physical properties of nanofluids

The thermo-physical properties such as thermal conductivity and viscosity of stable nanofluids are measured with respect to temperatures at 25 °C, 40 °C, 55 °C and 70 °C.

2.5.1. Thermal conductivity

The thermal conductivity of stable nanofluids are measured using a transient line source (TLS) thermal conductivity meter (Decagon KD2 Pro Thermal Analyzer, USA) with a 6 cm needle sensor (KS-1) for water based fluid that display the results up to 3 decimal points. The thermal conductivity meter is calibrated with a standard glycerin solution at room temperature each time before measurement and the samples are placed in an enclosed water bath to control the temperature throughout the experiment. Due to the high sensitivity of the thermal conductivity meter to slight changes in the surrounding such as temperature, vibrations and air flow, the experiment was conducted in a quiet and still environment to reduce fluctuations. First few readings were ignored until equilibrium in temperature was reached. Further, at least 10 readings were recorded at 15 minutes interval with error value smaller than 0.01 and averaged.

2.5.2. Viscosity

The viscosity of stable nanofluids for 0.01, 0.04 and 0.10 wt% are measured using a viscometer (Brookfield DV-II+ Pro, USA) with UL adapter which is suitable for viscosity range of 1 to 10 cP. 20 mL of the samples are transferred into the adapter and the rotational speed of the cylindrical spindle is set at 100 rpm (122 s⁻¹), which is the optimum speed for low viscous and water based fluid. A circulating water bath is used to flow the water across the adapter in order to maintain the temperatures of the samples throughout the experiment. The experimental results up to 2 decimal points were repeated 3 times and averaged.

3. Results and Discussion

3.1. Stability study of nanofluids

Figure 3 show the effect of dispersant concentration on the stability of CNT-water nanofluid with respect to sedimentation time. Lack of dispersant might have little or no effects on the stability of nanofluid as the hydrophobic surface of CNT is not fully coated with dispersant. On the contrary, too much dispersant will have adverse effect on the stability of nanofluid because it will weight down the CNT particles and increases the rate of sedimentation [22]. Therefore, it is essential to determine the optimum concentration of PVA dispersant in CNT nanofluid in order to maintain the long term stability of CNT-water nanofluid. Based on the graphs, there were slight sedimentations observed at the beginning of the study period as the concentration of CNT in the suspension decreases with time. This is due to the agglomeration and settlement of uncoated CNT nanoparticles when the dispersion is not agitated [26]. However, the sedimentation rate decreases and reaches a constant value after the suspension and the bonding between the CNT and PVA is stabilised.
Fig. 3. Effect of PVA dispersant on different amount of CNT, (a) 0.01 wt%, (b) 0.02 wt%, (c) 0.04 wt%, (d) 0.08 wt%, (e) 0.10 wt%.
It is observed that the optimum PVA concentration needed to stabilize the nanofluid increases with CNT concentration. As the CNT concentration increases, more amount of PVA is required to adsorb onto the hydrophobic site in order to fully separate the individual tube during ultrasonication. However, increasing the concentration of PVA beyond its optimum value will have adverse effect on the nanofluid dispersion. The PVA molecules will tend to self-aggregate and form reverse micelles due to the presence of additional dispersant molecules which is not adsorbed onto the CNT [20, 27]. In this study, it is proven that PVA dispersant is able to maintain the dispersion of CNT nanoparticles in the water by overcoming the Van der Waals forces between the neighboring tubes via steric repulsion as the hydrophobic hydrocarbon chains of PVA molecules are able to adsorb onto the non-polar surface of CNT. On the other hand, the hydrophilic hydroxyl group of the PVA molecules formed hydrogen bond with water molecules. The optimum concentration of PVA dispersant for each CNT concentration is summarized in Table 1.

<table>
<thead>
<tr>
<th>CNT Concentration (wt %)</th>
<th>PVA Concentration (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.5</td>
</tr>
<tr>
<td>0.02</td>
<td>1.0</td>
</tr>
<tr>
<td>0.04</td>
<td>1.0</td>
</tr>
<tr>
<td>0.08</td>
<td>1.0</td>
</tr>
<tr>
<td>0.10</td>
<td>1.5</td>
</tr>
</tbody>
</table>

### 3.2. Characterization of nanofluid

The optical images of stable nanofluid samples with its optimum amount of PVA are shown in Fig. 4.

Based on Fig. 4, it is observed that 0.01 wt% CNT has the largest size of agglomerates compared to the rest. This might be due to the low concentration of CNT in water which reduces its chances of collision with the PVA dispersant during the sonication process. Hence, the individual nanotubes which are not attached to the dispersant molecules are most likely to re-aggregate [28]. It is further observed that 0.02 wt% and 0.04 wt% of CNT has the smallest size of agglomerates. However, the size of the agglomerates appears to be larger as the CNT concentration increases. This is because the high concentration of CNT in the base fluid gives rise to a more dense nanofluid, which reduces the stability of the suspension as dense particles are more prone to sedimentation [29]. Thus the settled particles will re-aggregate once they accumulated at the bottom of the tube. Note that all the optical microscope images are taken after 2 months where the fresh samples of nanofluids are more likely to have smaller size of agglomerates.
3.3. Thermo-physical properties of nanofluids

3.3.1. Thermal conductivity

The effect of PVA on the thermal conductivity of water is shown in Fig. 5. It can be seen that the addition of PVA suppresses the thermal conductivity of water due to the lower thermal conductivity of PVA (0.2 W/mK) compared to the water (0.6 W/mK). On the other hand, Fig. 6 shows the effect of temperature and CNT concentrations with its optimum amount of PVA on the thermal conductivity of water. The percentage of enhancement in the thermal conductivity of nanofluids is shown in Fig. 7 where it is calculated using Eq. 1, where $k_{eff}$ and $k_f$ is the...
effective thermal conductivity of nanofluid and the thermal conductivity of base fluid (water) respectively.

\[ \text{Percentage Enhancement} = \left( \frac{k_{\text{eff}} - k_f}{k_f} \right) \times 100\% \]  

(1)

---

**Fig. 5.** Thermal conductivity of PVA aqueous solution with respect to temperature.

**Fig. 6.** Effective thermal conductivity of CNT-water nanofluids with its optimum PVA concentrations with respect to temperature.
Fig. 7. Percentage enhancement in thermal conductivity of nanofluids with its optimum PVA concentrations with respect to temperature.

It can be observed that the effective thermal conductivity and the thermal conductivity enhancement of the stable nanofluids with its optimum amount of PVA increases with increasing CNT concentration. At 25 °C, the enhancement increases from 1 to 8.3 % at CNT concentration of 0.01 to 0.10 wt%. Although PVA suppress the thermal conductivity of water, the addition of CNT enhances the thermal conductivity of water. This is attributed by the excellent thermal conductivity of CNT nanoparticles where the increasing amount of CNT in water base fluid raises the resulting thermal conductivity of the nanofluids [8]. In short, the greater the amount of CNT suspended in the solution, the higher the thermal conductivity of nanofluid. The CNT-water nanofluid stabilized with optimum amount of GA studied by Rashmi et al. [21] showed a greater percentage enhancement, which is 4 to 37% at 25 °C for the same range of CNT concentration tested. This is because GA further enhances the thermal conductivity of water by 1.2% at 1.0 wt% of GA aqueous solution instead of suppressing it. However, this study showed greater enhancement in CNT-water thermal conductivity compared to other literatures due to the high stability of nanofluids with optimum amount of dispersant.

Moreover, the thermal conductivity of nanofluids also increases with temperature and the effect is much pronounced at 40 °C. This is due to the Brownian motion of the nanoparticles where the nanoparticles are able to gain more kinetic energy at higher temperature. The CNT with high energy content will tend to move faster and bombard with each other, leading to a substantial increase in the thermal conductivity of nanofluids [30]. Overall, the CNT-water nanofluids stabilized with its optimum PVA concentration respectively are able to show 1 to 44% enhancement in thermal conductivity for the range of CNT concentration and temperature studied.
3.3.2. Viscosity

Figure 8 shows the effect of PVA and CNT-water nanofluids with optimum amount of PVA on the viscosity of water. It is observed that the addition of PVA increases the viscosity of water significantly. This is due to the high molecular weight and long polymeric chain of PVA molecules where the hydroxyl groups will form inter and intra hydrogen bonding with each other as well the hydrogen bonding with water molecules [31]. The presence of such linkages leads to the enhancement of viscosity of water. However, the addition of CNT into their corresponding optimum PVA solution decreases the viscosity of PVA aqueous solution by approximately 2 to 6%. This is can be explained by the self-lubricating effects of the CNT where the nanotubes are able to arrange themselves in the same orientation along the flow direction and slide against each other when forces are applied, causing the viscosity to decrease [32].

In addition, the increase in temperature reduces the viscosity of PVA aqueous solution and nanofluid due to the increase in kinetic energy and movement of the molecules where it will weakens the hydrogen bonds and thus reducing the viscosity [31]. The viscosity of CNT-water nanofluids stabilized with its corresponding PVA dispersant is remarkably greater than the water base fluid. Although high viscosity is undesirable as it will increase the pressure drop along the pipes and pumping cost, the rheological behavior can be further tested in the future as the CNT-water nanofluid stabilized by PVA may exhibit shear thinning behaviors where the viscosity will decrease with increasing shear rate. This parameter is important as the heat transfer fluid in real life application will be constantly subjected to different forces and shear rates under certain circumstances where it will alter the viscosity of nanofluid.

![Fig. 8. Viscosity of PVA aqueous solution and CNT-water nanofluid stabilized with optimum PVA at different temperature.](image-url)
4. Conclusion

In conclusion, nanofluid has a promising potential to enhance the heat transfer properties of the conventional base fluid, given that the appropriate dispersant is used to stabilize the nanoparticles. In this case, PVA is able to maintain the stability of CNT-water nanofluid for 3 months. Although PVA suppresses the thermal conductivity of water, the effect is being counterbalanced by the addition of CNT. The CNT-water nanofluid stabilized with optimum amount of PVA showed 1 to 44% enhancement in thermal conductivity for 0.01 to 0.10 wt% CNT at temperatures of 25 to 70 °C. Also, the nanofluids studied possess high viscosity at low shear rate of 122 s⁻¹. Hence, detail investigations on the rheological properties and nanoparticle Brownian motion should be performed in the future to understand the effect of shear rate on the viscosity of nanofluids and the non-linear behavior of thermal conductivity enhancement of nanofluids as a function of temperature respectively.

References


