Effect of Acid Treatments and Surfactant on MWCNTs Nanofluids: Structural, Morphological and Thermal Conductivity

Norshafiqah Mohd Saidi[1], Norli Abdullah[1,*], Nurjahirah Janudin[1,2], Noor Azilah Mohd Kasim[1,2], Mohd Junaedy Osman[1] and Imran Syakir Mohamad[3]

[1]Centre for Defence Foundation Studies, Universiti Pertahanan Nasional Malaysia, Kem Sungai Besi, Kuala Lumpur 57000, Malaysia

[2]Research Centre for Chemical Defence, Universiti Pertahanan Nasional Malaysia, Kem Perdana Sungai Besi, Kuala Lumpur 57000, Malaysia

[3]Faculty of Mechanical Engineering, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, Durian Tunggal 76100, Melaka, Malaysia

* Correspondence: norli.abdullah@upnm.edu.my

Abstract: This study discussed the effect of using three acid treatment methods (Method A, Method B and Method C) to introduce the surface oxygen functional group (SOFG) on multi-walled carbon nanotubes (MWCNTs) for structural, morphological and thermal conductivity performance. The SOFG on the MWCNTs has been characterized by Fourier Transform Infrared (FTIR) spectroscopy, Raman spectroscopy and Field Emission Scanning Electron Microscopy (FESEM). The result shows that the modification with acid treatment significantly affects the degree of defects and surface group functionality of surface oxidized MWCNTs from method B. The preparation of nanofluids using MWCNTs in water-based fluids produced from method B (MWCNT-MB) was prepared using two different parameters: with and without polyvinylpyrrolidone (PVP) as surfactant with variable setting of carbon particle concentration from 0.1 wt.% to 1.0 wt.%, and the amount of PVP is 10% of carbon particles at different temperatures (6°C, 25°C, 40°C). The thermal conductivity performance of nanofluids proved that the surface oxidized MWCNTs with PVP enhanced thermal conductivity compared to the nanofluid containing MWCNTs without PVP due to the stability and homogenization of nanoparticles. These promising properties of MWCNTs in water-based fluids would enable the nanofluids to be utilized in heat transfer fluid and cooling applications.

Keywords: CNT; MWCNTs; nanofluids; polyvinylpyrrolidone; PVP; thermal conductivity

1. Introduction

Nanofluids containing a suspension of carbon-based nanoparticle such as carbon nanotubes (CNTs), carbon nanofibers (CNFs) and graphite in the range 1 to 100 nm in a homogeneous fluid have attracted researchers' attention [1-3]. It has been found that the thermal conductivity of a nanofluid consisting of ethylene glycol and only 0.3 vol.% Cu nanoparticles increased by up to 40% over that of pure ethylene glycol [4]. CNTs have always been the focus of attention due to their amazing power and excellent mechanical, electrical, thermal and magnetic properties [5], and has received notable attention due to its large intrinsic thermal conductivity and low density in comparison to metals or metal oxide nanoparticles [6]. The major weakness of CNTs is that it is hydrophobic in nature and thus difficult to be dispersed in most solvent matrixes. Dispersion is one of the main factors that influence the properties of nanocomposites. Due to the presence of attractive forces (Van der Waals forces), nanomaterials tend to agglomerate from their polarizable, extended π-electron systems [7]. To overcome these limitation, CNT surface are often tailored using two surface modification: covalent [8, 9], and non-covalent modification [10]. Covalent surface modification involves direct incorporation of new element or organic functionalities into the CNT sidewalls. A covalent surface modification is effective in improving the adhesion and chemical properties of the composites but it exhibits the disadvantage of disturbing to some extent the graphitic structure of CNT sidewalls [11]. Hence in this study, commercial MWCNTs were chemically modified using three different methods of acid treatment to introduce SOFG. The presence of SOFG on the carbon materials has been characterized by FTIR spectroscopy. Morphology, structural and thermal properties were performed using FESEM, Raman spectroscopy and thermogravimetry, respectively. Based on the results obtained, modification with acid treatment presented a significant effect on both the degree of defects and surface group functionality of all samples will be proceed for the preparation of nanofluids was followed by using two different parameters: with and without surfactant, PVP. the nanofluids

performance has been characterized through the observation on stability and dispersion analysis of nanofluid and thermal conductivity of nanofluid.

2. Experimental

2.1 Materials

In this study, commercial MWCNTs used is 95% purity, specific surface area is 200 m^2/g, outside and inside diameter with 10 to 20 and 5 to 10 nm, respectively, was purchased from Nanostructured & Amorphous Materials, Inc., United State of America. Whereas, two types of acid were used together with other chemicals for the chemical oxidation modification of nanocarbon are concentrated sulphuric acid (H_2SO_4, 98%), nitric acid (HNO_3, 65%) sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$) and hydrogen peroxide (H_2O_2) purchased from Merck kGaA, Darmstadt, Germany. All the chemicals were of analytical reagent grades and used as received without further purifications. The non-ionic surfactant used, polyvinyl pyrrolidone (PVP) was purchased from R & M Chemicals, Essex, United Kingdom.

2.2 Surface oxidative treatments of MWCNTs

Modification of MWCNTs with acid treatment was employed in this research due to its significant effect on the degree of defect and surface functionality that may provide enhanced thermal properties [9]. Three different acid treatment methods were used. For the first method (Method A), in three neck round bottom, 2 grams of commercial MWCNTs were immersed in mixture of 98% concentrated sulfuric acid (H_2SO_4) and 65% nitric acid (HNO_3) in ratio of 3:1 (v/v). The mixture was placed in an ultrasonication water bath (Fisher Scientific, FB 15057, frequency: 50 to 60 Hz) at 313 K for 30 minutes After that, it underwent reflux treatment at 423 K for 180 minutes. Finally, the modified nanocarbon powder was washed with deionized water several times and filtered through a 0.43 µm cellulose nitrile membrane filter until it reached pH 7. The powder was dried in vacuum oven at temperature of 323 K for 24 hours prior to use. The second (Method B) and the third (Method C) had the same process with Method A, though the reflux process was eliminated. However, different times of ultrasonication were employed with 2 hours for Method B and 6 hours for Method C at 343 K.

2.3 Preparation and formulation of MWCNTs nanofluid

Based on characterization analysis data on surface oxidative treatment of MWCNTs nanoparticles, MWCNTs nanoparticles prepared using method B (MWCNT-MB) were used for the preparation of nanofluid. In this experiment, 40 ml ultrapure water was used as the base fluid for the preparation of nanofluids in a glass container. Two types of nanofluids were prepared: without PVP and with PVP. The amount of MWCNTs used in the formulation was ranged from 0.1 weight percent (wt.%) to 1.0 wt. % in the interval of 0.1. Whereas for the PVP used for the nanofluid formulation is 10% concentration of MWCNTs nanoparticles. The formulation ratio of water, MWCNTs, with and without PVP is presented in Table 2 and Table 3. In order to obtain the total volume of all materials, a formula can be used to calculate the synthesis of nanofluid which can be referred to Equation 1, where V is volume (ml), m is mass (g) and ρ is density. The pure base fluid (standard) used is ultrapure water.

Table 2. Nanofluids formulation using commercial and modified MWCNTs without PVP

Weight Conc. of MWCNTs (wt.%)	Mass of MWCNTs (g)	Volume of ultrapure water (ml)	Total volume of nanofluid (ml)
0.1	0.04	39.96	40.00
0.2	0.08	39.92	40.00
0.3	0.12	39.88	40.00
0.4	0.16	39.84	40.00
0.5	0.20	39.80	40.00
0.6	0.24	39.76	40.00
0.7	0.28	39.72	40.00
0.8	0.32	39.68	40.00
0.9	0.36	39.64	40.00
1.0	0.40	39.60	40.00

Table 3. Nanofluids formulation using commercial and modified MWCNTs with PVP

Weight Conc. of MWCNTs (wt.%)	Mass of MWCNTs (g)	Weight Conc. of PVP (wt.%)	Mass of PVP (g)	Volume of deionized water (ml)	Total volume of n nanofluid (ml)
0.1	0.04	0.01	0.004	39.96	40.00
0.2	0.08	0.02	0.008	39.91	40.00
0.3	0.12	0.03	0.012	39.87	40.00
0.4	0.16	0.04	0.016	39.82	40.00
0.5	0.20	0.05	0.020	39.78	40.00
0.6	0.24	0.06	0.024	39.74	40.00
0.7	0.28	0.07	0.28	39.69	40.00
0.8	0.32	0.08	0.032	39.65	40.00
0.9	0.36	0.09	0.036	39.60	40.00
1.0	0.40	0.10	0.040	39.56	40.00

$$V = \frac{m}{\rho} \text{ (ml)} \qquad (1)$$

The two-step process was used to disperse the MWCNTs nanoparticles in water based nanofluid. This physical dispersion can be accomplished by using D1000 Handheld Homogenizer at a rotation speed of 10000 rpm. Then, the samples underwent ultrasonication process at room temperature (25°C) for 30 minutes at a frequency of 60 Hz with the generation of an output power of 240 W. The nanofluid samples were homogenized once again for 5 minutes at the rotation speed of 10000 rpm.

2.4 Characterizations

The structural analysis was characterized using Perkin Elmer Frontier spectrometer FTIR (BX FTIR (Perkin Elmer, England)) with a scanning range of 500 to 4500 cm^{-1} and 16 scan numbers. The surface morphological analysis and the diameter size distribution of the commercial and after oxidation of nanocarbon were characterized using a FESEM JEOL 7600F, Carl Zeiss Gemini FESEM 500 (Carl Zeiss AG, Jena, Germany). The diameter of the MWCNTs nanoparticles was measured using ImageJ software with 50 points for each sample. For the MWCNTs nanofluids, the stability of MWCNTs nanofluids with and without PVP was observed through sedimentation photograph capturing method. In this study, the nanofluid samples were left for 100 hours after undergoing ultrasonication process. KD2 Pro Analyzed (Decagon, Pullman, WA, USA) with water-based fluid, KS-1 (1.3 mm diameter x 60 mm long) and specific accuracy of 5% was used to investigate the thermal conductivity of the MWCNTs nanofluid samples. In this study, the thermal conductivity was measured at three different temperatures which are 6°C, 25°C and 40°C.

3. Results and Discussion

3.1 FTIR analysis

FTIR of commercial MWCNTs in Figure 1 (a) shows several predominant peaks at 2880 cm^{-1} and in range between 1600 cm^{-1} and 1350 cm^{-1}. The peak at 2880 cm^{-1} and 1350 cm^{-1} region correspond to C-H asymmetric and symmetric stretching vibrational, respectively. The peak around 1600 cm^{-1} corresponds to C=C aromatic ring stretching related to MWCNT in nature [12,13]. Kouklin et al. (2004) studied MWCNTs of 60 nm diameter and reported spectrally uniform IR spectrum with a 100 meV bandgap and IR-active peaks at 1725 cm^{-1} (COOH groups), 1584 cm^{-1} (G band), 1200 cm^{-1} (D band) and several peaks in the range of 3000 cm^{-1} range that were attributed to CHx groups [14]. However, broad peak associated to the O-H stretch of the hydroxyl group around 3500 cm^{-1} are absent from the sample. This might be due to the purification process by the manufacturer. After treatment with acid mixture H_2SO_4/HNO_3, a strong peak appears at wavenumber of 2950 cm^{-1} to 3230 cm^{-1}. This peak is assigned to the vibration of O-H bonds and can be related to hydroxyl groups and carboxyl groups. The peak of O-H bond shown in Figure 1 (d) is very weak due to the structure of MWCNTs was highly damaged. Besides, a new peak appears (Figure 1 (c) in the range 1673 cm^{-1} to 1970 cm^{-1} which is attributed to the C=O groups in the different environments which are carboxylic acid, ketone or quinone [15]. This result clearly indicates that the functional group is successfully attached on the surface of MWCNTs.

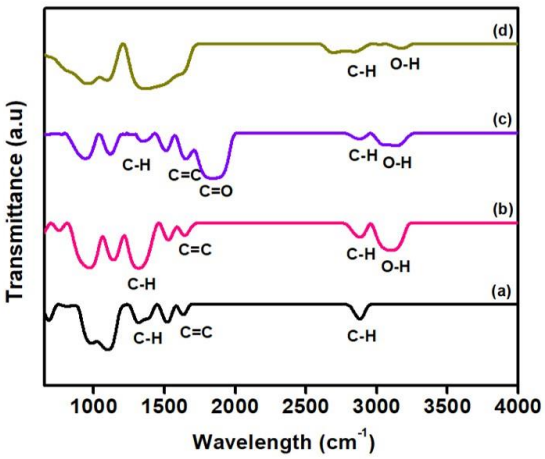

Figure 1. FTIR spectra of commercial and surface oxidized MWCNTs: (a) commercial MWCNTs (b); MWCNT-MA (c); MWCNT-MB and (d) MWCNT-MC

3.2 Raman spectroscopy analysis

Figure 2 presented Raman spectrum of surface oxidized MWCNTs. All samples were observed to have peaks near 1350 cm^{-1} and 1590 cm^{-1} which were designated to D and G band, respectively. MWCNT-MC has higher intensity D-band peak compared to other three samples. This reflected that MWCNT-MC sample had high defects on its MWCNTs wall with there also was an agreement in FESEM images. The G-band has slightly shifted up field about 5 to 6 cm^{-1} compared to commercial MWCNTs. It slightly shifted due to presence of the functional group on the surface of MWCNTs. The values of intensity ratio, I_D/I_G for the commercial and surface oxidized MWCNTs are summarized in Table 2. The higher intensity ration of the nanomaterials indicates higher defect due to the successfully of the oxidation process onto the MWCNTs side wall. The value of I_D/I_G ratio is 0.75 for the commercial MWCNTs. The surface oxidation process that increases the ratio the most, and thus introduces the most defect in the MWCNTs, is the surface oxidized by Method B (MWCNT-MB) (I_D/I_G =0.91). By comparing the ratio I_D/I_G values of surface oxidation and commercial MWCNTs, it is observed that the ratio values increase as expected after surface oxidation. The oxidation of MWCNTs breaks some of its bonds and inserts chemical groups that can be interpreted as defects on the structure. Comparing types of surface oxidation, all processes show a relevant change on the intensity of band D. These results indicate certain insertion of defects and/or break on the structure of MWCNTs.

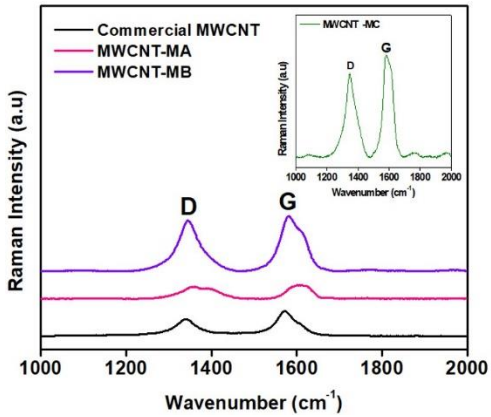

Figure 2. Raman spectrum of commercial and surface oxidized MWCNTs

Table 2. The value of I_D/I_G ratio for commercial and surface oxidation of MWCNTs

Sample	I_D/I_G
Commercial MWCNTs	0.75
MWCNT-MA	0.87
MWCNT-MB	0.91
MWCNT-MC	0.82

3.3 FESEM analysis

Figure 4 (a) to (d) represent FESEM images of commercial MWCNTs, MWCNT-MA, MWCNT-MB and MWCNT-MC and their corresponding diameter size distribution histogram with different resolution. The commercial MWCNTs in Figure 4 (a) clearly shows the surface of walls are smooth with random growth, inhomogeneous diameter distribution and is highly entangled. The van der Waals forces attraction between the tubes cause the formation of bundles and entanglements. The diameter distribution of commercial MWCNTs is in the range of 10 nm to 50 nm with a mean diameter of 26 nm. The arrangement of MWCNTs became debundled and disentangled following chemical and physical treatment using method A and Method B. Some areas show the tubes are exfoliated and become curled. Besides that, the diameter distribution of MWCNTs increased and the mean diameter of MWCNT-MA and MWCNT-MB are in the range of 38 nm and 42 nm, respectively. However, no shortening of tubes length was observed for MWCNTs sample treated using method A. This indicates that the MWCNTs are strong enough to be unaffected with concentrated acids solution used during treatment On the other hand, surface treatment using method C reveals a densely packed structure of MWCNT-MC. This is due to the fact that tubular structure of nanotubes has been significantly destructed and changed. This was caused due to the MWCNTs being exposed to high temperature for longer period of reaction time (6 hours). Therefore, as a result the CNT diameter was unable to be determined. The overall SEM images showed that the acid treatment process performed at different period of time affect the bundling arrangement of nanotubes.

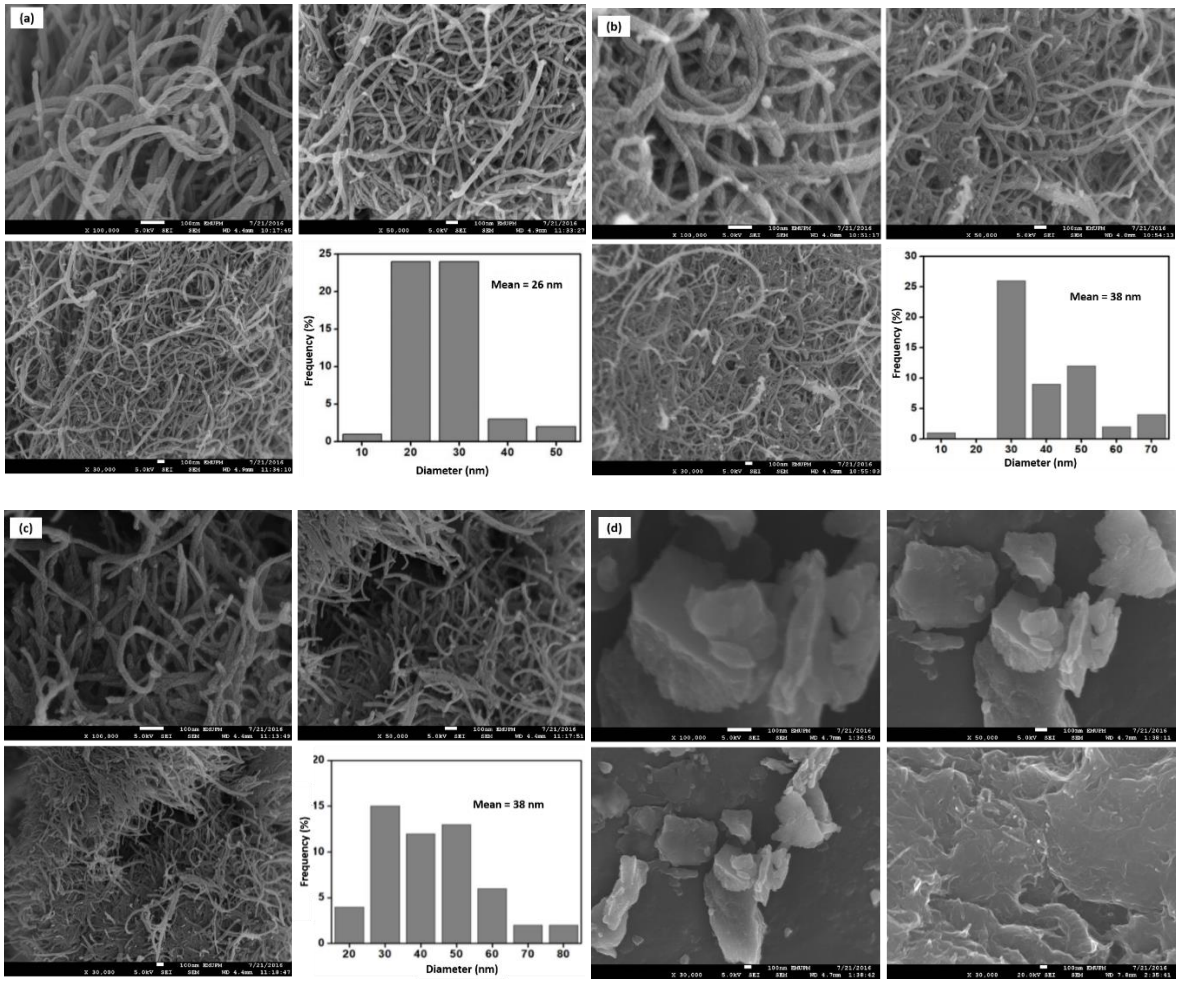

Figure 4. FESEM images of (a) commercial MWCNTs, (b) MWCNT-MA, (c) MWCNT-MB and (d) MWCNT-MC with different resolution and diameter distribution histogram

3.4 Stability and dispersion analysis of nanofluids (MWCNT-MB)

The nanofluids are considered stable when there is no particle sedimentation. The sedimentation of each sample was captured at two different periods which is 0.5 hours after the homogenization and sonication process, and secondly after 100 hours. Producing a stable nanofluid becomes more challenging when it comes to suspensions containing carbon particles. MWCNTs are hydrophobic in nature and usually exist

in bundles and at the same time, MWCNTs have very high aspect ratio which make them easy to agglomerate into different sizes and shapes but the graphite powder directly forms sediment. This means that when MWCNTs nanoparticle were dispersed in base fluid, the agglomeration and sedimentation occur very fast and the suspensions are unstable. Figure 5 (a) and (b) shows the condition of various weight percentage of the commercial MWCNTs based nanofluid (0.1 wt.%, 0.2 wt.%, 0.3 wt.%, 0.4 wt.%, 0.5 wt.%, 0.6 wt.%, 0.7 wt.%, 0.8 wt.%, 0.9 wt.% and 1.0 wt.%) without surfactant for 0.5 hours and 100 hours after the homogenization and sonification process. There were visual rapid sedimentation and coagulation observed 0.5 hours after the homogenization and sonification process except 0.3 wt.% and 0.7 wt.%. According to Phuoc et al. (2011), carbon nanotube based nanofluid without surfactant settled down quickly after ultrasonication process [15-18]. After 100 hours, it can be seen clearly that sedimentation occurred to all the samples of commercial MWCNTs based nanofluids and the height of sedimentation are different. All the weight concentration of commercial MWCNTs are considered unstable but it seen the 0.5 wt.% and 0.7 wt.% have less settle down of particles compare to others. This phenomenon is attributed to the highly hydrophobic surface of MWCNTs itself. The Van der Waal attractive force is stronger, consequently the MWCNTs tend to attract each other. This is consistent with our FESEM images. Besides that, the homogenization and sonication process alone is not enough to produce a stable nanofluid sample.

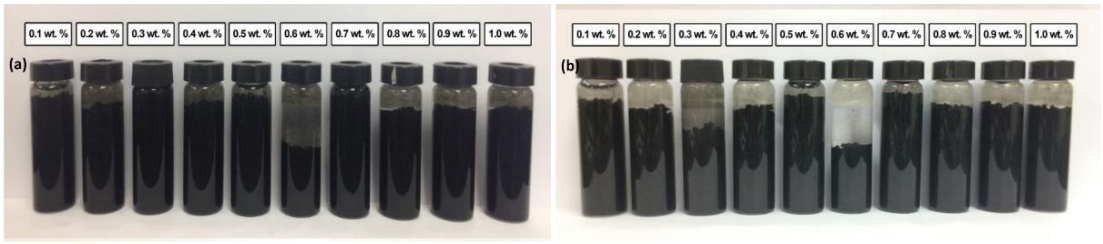

Figure 5. Stability and dispersion condition of various weight percentage of the commercial MWCNTs based nanofluid without surfactant for (a) 0.5 hours; (b) 100 hours after homogenization and sonication process.

Figure 6 (a) and (b) shows the condition of various weight percentages of the commercial MWCNTs based nanofluid with surfactant of PVP. As can be seen, the dispersion stability improved slightly in comparison to nanofluids without PVP with similar settling sedimentation behaviour. Nanofluids contain low concentration of MWCNTs show stability with no sedimentation, however rapid dispersed sedimentation occurred in the samples at 0.4 wt.%, 0.5 wt.%, 0.6 wt.% 0.7 wt.%, 0.9 wt.% and 1.0 wt.% after 0.5 hours. This sedimentation continuously occurred at 0.2 wt.% of commercial MWCNTs based nanofluid after 100 hours. As known, the PVP is added to reduce the surface tension between solid and liquid thus to improve the dispersing of particles and prevent the particles from settling. But in this experimentation, the particles coagulated and the sedimentation occurred. This result can be due to the weight percentage of PVP which is 10% concentration of carbon particle which is not suitable for certain weight percentage of MWCNTs and made the nanofluids unstable. The duration of homogenization and sonication process that is too long also can cause sedimentation to occur [18]. However, there were no sedimentation observed for 0.1 wt.% and 0.3 wt.% of commercial MWCNTs based nanofluids after 100 hours.

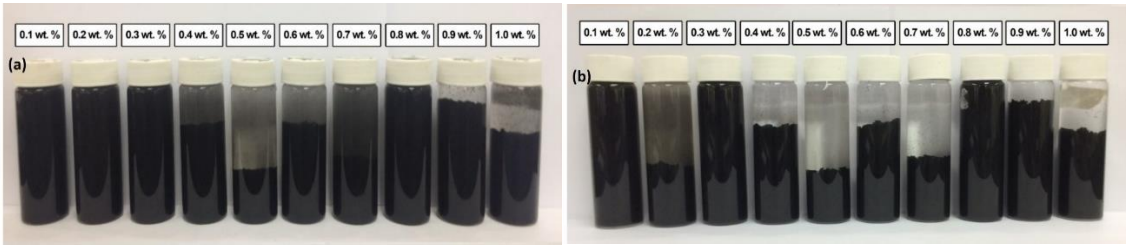

Figure 6. Stability and dispersion condition weight percentage of the commercial MWCNTs based nanofluid with surfactant of PVP for (a) 0.5 hours; (b) 100 hours after homogenization and sonication process

Figure 7 shown the stability and dispersion condition of various weight percentage of the surface oxidized MWCNTs without surfactant for (a) 0.5 hours; (b) 100 hours after homogenization and sonication process. No sedimentation occurred in surface oxidized MWCNTs nanofluids, but has only small amount sedimentation after 100 hours. Therefore, all samples are considered stable. Stable nanofluids was due to the presence of functional groups (-COOH and O-H) on the surface walled of MWCNTs. The presence of

SOFG led to reduction of Van der Waals interaction among them, which promotes their separation and dispersion in the nanofluids compared with commercial MWCNTs nanoparticle. On the other hand, the sonication technique applied during the surface oxidation, as well as in the dispersion process also had an energetic effect in getting the MWCNTs bundles to start to get loose [19].

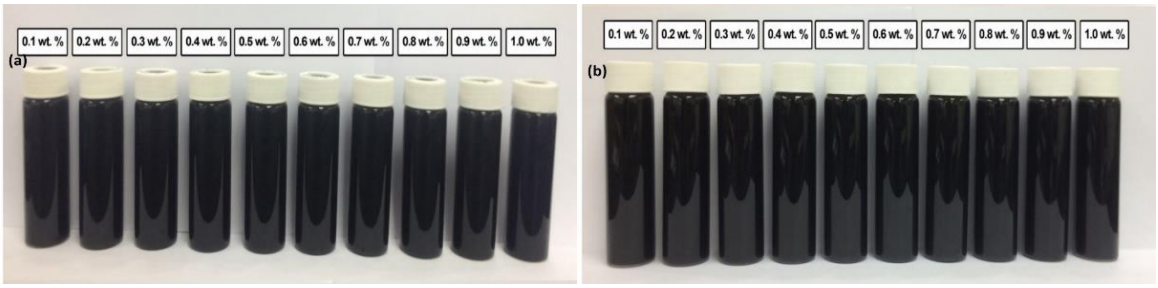

Figure 7. Stability and dispersion condition of various weight percentage of the surface oxidized MWCNTs (MWCNT-MB) based nanofluid without surfactant for (a) 0.5 hours; (b) 100 hours after homogenization and sonication process

3.5 Thermal conductivity of commercial MWCNTs based nanofluids

The result of thermal conductivity of commercial MWCNTs nanofluid without PVP at three different temperatures is represented in Figure 8 in order to identify the patterns of the heat effects on each sample. The thermal conductivity for pure base fluid (standard) was 0.546 W/m.K, 0.570 W/m.K and 0.595 W/m.K at 6°C, 25°C and 40°C, respectively, and presented in a straight line in Figure 8. These values of thermal conductivity are standard values for comparison with the thermal conductivity of commercial MWCNTs based nanofluid without PVP. Based on the graph, the trend of conductivity for this nanofluid is increasing thermal conductivity with increasing temperature. The values of thermal conductivity are above the pure base fluid (standard) as the temperature increases from 6°C to 25°C. However, at temperature of 40°C, there are few samples that record thermal conductivity that is lower than the standard value, which are at weight concentrations of 0.3 wt.% and 0.4 wt.%. While the other samples are continuously increasing as the temperature increases to 40°C.

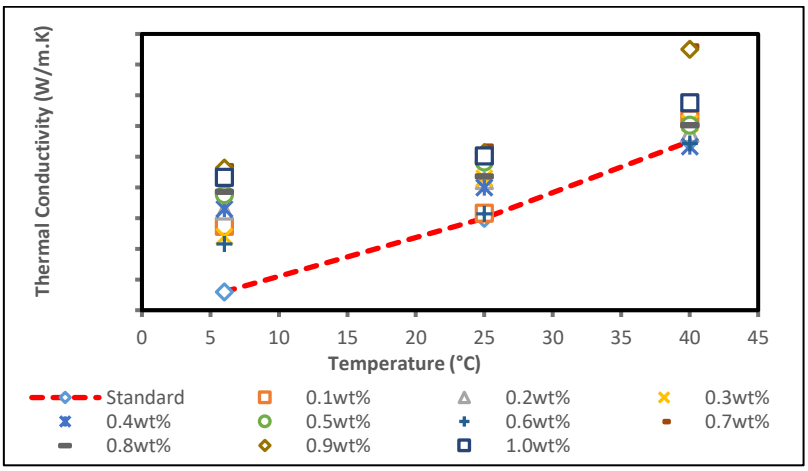

Figure 8. Thermal conductivity of commercial MWCNTs based nanofluid without PVP with various concentration at different temperatures

The percentage enhancement was calculated according to the Equation 2, where K_{nf} and K_f represent the thermal conductivity of the nanofluid and the pure base fluid, respectively.

$$K_{enhancement}\,(\%) = \left[\frac{K_{nf} - K_f}{K_f}\right] \times 100\ \% \qquad (2)$$

Referring to the Table 3 for thermal conductivity enhancement of commercial MWCNTs nanofluid without PVP, an irregular trend was observed in terms of the enhancement at all temperatures. At 0.3 wt.% and 0.4 wt.% weight concentration, there was no enhancement in the thermal conductivity of nanofluid with respect to the pure base fluid. It is noted that well dispersed nanoparticles are a crucial factor in improving the thermal conductivity of nanofluid. Most of the samples of nanofluid exceed the pure base fluid in

thermal conductivity enhancement and the highest percentage enhancement recorded is at temperature of 40°C, which is 10.25%. This enhancement is due to the intrinsic heat transport capacity of the MWCNTs [7]. For overall, at concentration of 0.7 wt.% is optimum weight concentration for commercial MWCNTs based fluid and in line with our stability test observation.

Table 3. Thermal conductivity enhancement of commercial MWCNTs nanofluid without PVP

Weight Concentration of Commercial MWCNTs (wt.%)	Percentage of $K_{enhancement}$ (%) at different temperature		
	6°C	25°C	40°C
0.1	3.91 (0.05)	0.29 (0.06)	1.23 (0.06)
0.2	4.82 (0.04)	2.16 (0.06)	0.45 (0.07)
0.3	3.30 (0.04)	0.25 (0.03)	-
0.4	4.95 (0.06)	1.75 (0.04)	-
0.5	5.80 (0.07)	3.22 (0.07)	0.90 (0.05)
0.6	2.87 (0.07)	2.28 (0.07)	1.01 (0.1)
0.7	7.51 (0.06)	4.09 (0.09)	10.25 (0.09)
0.8	5.98 (0.1)	2.40 (0.09)	0.90 (0.05)
0.9	7.39 (0.9)	3.74 (0.2)	5.60 (0.09)
1.0	6.84 (0.06)	3.57 (0.1)	2.13 (0.1)

(*) = error bar

As shown in Figure 9, the results varied for commercial MWCNTs based nanofluid with the addition of surfactant that will increase the thermal conductivity. By adding 10% of PVP, the thermal conductivity of all weight concentrations of commercial MWCNTs increased linearly with the rise in temperature. The thermal conductivity of each nanofluid increases with increasing temperature with the highest thermal conductivity is at temperature of 40°C, followed by 25°C and 6°C. Based on Figure 9, the highest thermal conductivity at all temperatures was recorded for 0.9 wt.%. The highest reading for the thermal conductivity at temperature 6°C was gained at 0.608 W/m.K, whereas at 25 °C, the highest thermal conductivity reading was 0.628 W/m.K, followed by 0.650 W/m.K at 40 °C. Whilst, the lowest reading of thermal conductivity at 6°C is 0.598 W/m.K at concentration of 0.1 wt.% and at 25°C, the lowest thermal conductivity is 0.608 W/m.K at concentration of 0.4 wt.%. At 40°C, there are two concentrations that have similar values (0.618 W/m.K), which are 0.3 wt.% and 0.4 wt.%. In this study, the thermal conductivity of nanofluid did not depend on weight concentration of commercial MWCNTs and PVP.

The highest percentage enhancements for MWCNTs nanofluid with PVP at 6°C, 25°C and 40°C were obtained at 0.9 wt.%, which is the optimum concentration for this nanofluid. The thermal conductivity percentage enhancement of this concentration was 11.36%, 10.23% and 7.62% at 6°C, 25°C and 40°C, respectively. However, the concentration of 0.3 wt.% at 40°C is the lowest enhancement, which is 3.81%. Although the enhancement is the lowest, at least the presence of MWCNTs in base fluid has enhanced the thermal conductivity rather than the thermal conductivity of standard. In addition, at concentration of 1.0 wt.%, the result is declined where the enhancement of thermal conductivity is 10.50%, 8.07% and 4.65% at 6°C, 25°C and 40°C, respectively. The results show that MWCNTs interact with each other due to their high aspect ratio, even with low MWCNTs loading. Overall, the thermal conductivity enhancement of the commercial MWCNTs nanofluids with surfactant is higher than without surfactant [21].

Table 4. Thermal conductivity enhancement of commercial MWCNTs nanofluid with PVP

Weight Concentration of Commercial MWCNTs (wt.%)	Weight Concentration of PVP (wt.%)	Percentage of $K_{enhancement}$ (%) at different temperature		
		6°C	25°C	40°C
0.1	0.01	7.63 (0.01)	7.78 (0.02)	5.27 (0.04)
0.2	0.02	8.97 (0.04)	7.43 (0.03)	5.21 (0.03)
0.3	0.03	10.38 (0.02)	7.13 (0.05)	3.81 (0.009)
0.4	0.04	8.24 (0.009)	6.67 (0.04)	3.92 (0.04)
0.5	0.05	9.89 (0.01)	8.65 (0.06)	5.38 (0.03)
0.6	0.06	10.44 (0.03)	8.54 (0.05)	6.55 (0.01)
0.7	0.07	10.99 (0.01)	9.12 (0.02)	6.89 (0.04)
0.8	0.08	11.17 (0.05)	9.82 (0.03)	7.34 (0.009)
0.9	0.09	11.36 (0.06)	10.23 (0.07)	7.62 (0.02)
1.0	0.10	10.50 (0.06)	8.07 (0.07)	4.65 (0.02)

(*) = error bar

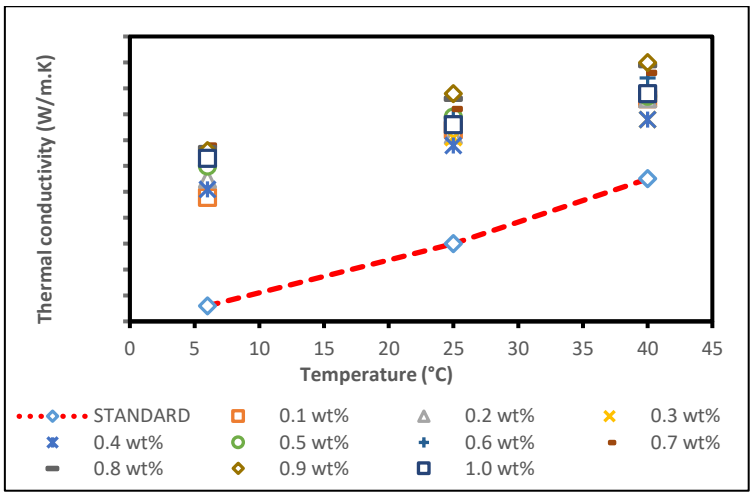

Figure 9. Thermal conductivity of commercial MWCNTs based nanofluid with PVP with various concentration at different temperatures

3.6 Thermal conductivity of surface oxidized MWCNTs based nanofluids (MWCNT-MB)

Thermal conductivity of surface oxidized MWCNTs based nanofluids results with and without surfactant, PVP at different temperature is presented in Figure 10 and Figure 11, respectively. Figure 10 shows the thermal conductivity of the base nanofluid containing surface oxidized MWCNTs clearly shows that the thermal conductivity of base fluid containing surface oxidized MWCNTs had higher thermal conductivity compared to pure base fluid and also on the thermal conductivity of commercial MWCNTs based fluids. The increaments of both properties is about 2 times as the commercial based nanofluids. In Figure 10, it was observed that thermal conductivity enhancements of ultrapure water-based nanofluids containing surface oxidized MWCNTs showed augmentation with respect to temperature for each concentration MWCNTs. Based on Table 5, the weight concentration of surface oxidized MWCNTs is not significant due to the fluctuation in increment of thermal conductivity. The thermal conductivity shows increment until concentration of 0.7 wt.% and then the decrement starts at concentration of 0.8 wt.% to 1.0 wt.%. This is due to when the weight concentration is beyond 0.5 wt.%, surface oxidized MWCNTs tends to agglomerate and reduce the performance of thermal conductivity. But as observed, the effect of temperature is more important due to the thermal conductivity of all weight concentrations increasing when temperature increases. This is because the Brownian motion of nanoparticles and the –OH group on the MWCNTs surface have a tendency to transfer more energy to nanofluids through increments in temperature [22, 23]. While, at 6°C, 25°C and 40°C, the highest thermal conductivity was at concentration of 0.7 wt.%, where the values were 0.619 W/m.K, 0.640 W/m.K and 0.657 W/m.K, respectively. Meanwhile, the lowest thermal conductivity happens at a concentration of 0.1 wt.% at 6°C and 40°C, which is 0.583 W/m.K and 0.614 W/m.K.

Table 5. Thermal conductivity enhancement of surface oxidized MWCNTs nanofluid without PVP

Weight Concentration of Surface Oxidized MWCNTs (wt.%)	Percentage of $K_{enhancement}$ (%) at different temperature		
	6 °C	25 °C	40 °C
0.1	8.61 (0.003)	9.24 (0.002)	4.87 (0.001)
0.2	10.07 (0.006)	9.59 (0.006)	6.78 (0.005)
0.3	8.91 (0.005)	8.71 (0.005)	7.17 (0.004)
0.4	10.26 (0.004)	10.29 (0.007)	8.57 (0.006)
0.5	10.81 (0.006)	10.70 (0.005)	8.46 (0.009)
0.6	11.42 (0.003)	9.36 (0.005)	9.69 (0.008)
0.7	13.31 (0.002)	12.22 (0.006)	10.42 (0.001)
0.8	13.19 (0.01)	11.99 (0.01)	10.25 (0.005)
0.9	10.32 (0.008)	11.35 (0.02)	9.75 (0.004)
1.0	12.76 (0.01)	11.81 (0.007)	10.20 (0.007)

(*) = error bar

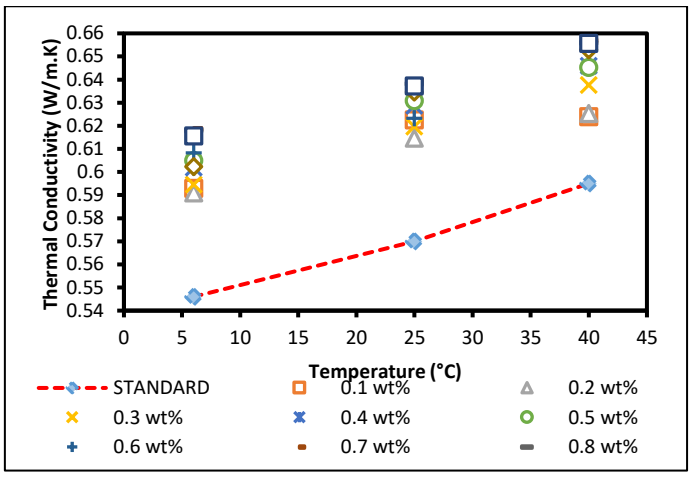

Figure 10. Thermal conductivity of surface oxidized MWCNTs based nanofluid without PVP with various concentration at different temperatures

Figure 11 represents the thermal conductivity of base fluid containing surface oxidized MWCNTs with surfactant. Based on the value of percentage enhancement, surface oxidized MWCNTs nanofluid had higher percentage compared to commercial MWCNTs. This is due the surface oxidation MWCNTs that have very small particles size. Theoretical evidence indicates that the effect of thermal conductivity of nanofluid increased with decreased particle size [23]. Besides that, -OH groups on the surface of MWCNTs tend to transfer more energy to the nanofluid through temperature increase. From the results, it could be seen that the increase in thermal conductivity varies with an increase in the weight percentage of nanoparticles and starts to decrement at concentration of 0.7 wt.% to 1.0 wt.%. The value of thermal conductivity is 0.647 W/m.K at 6°C, 0.675 W/m.K at 25°C and 0.693 W/m.K at 40°C, respectively. It shows that the thermal conductivity increases with increasing temperature. The enhancement analysis was done to observe the trend and is shown in Table 6 by the irregular enhancements in thermal conductivity. The enhancement of thermal conductivity shows increment until at concentration of 0.5 wt.% and then the decrement as started at concntration of 0.6 wt.% to 1.0 wt.%. this is due to when weight concentration beyond 0.5 wt.% surface oxidized MWCNTs tend to agglomerate and reduce the performance of thermal conductivity. However, the enhancement was improved compared to surface oxidized MWCNTs without PVP. It proved that by addition of surfactant improved the thermal conductivity of nanofluid. Based on the Table 6, the nanofluid sample with a concentration of 0.5 wt.% had the highest enhancement in thermal conductivity of 18.50%,18.42% and 16.47% at 6°C, 25°C and 40°C, respectively. This is the optimum weight concentration of this nanofluid. There are two different concentrations that are shown the lowest enhancement of thermal conductivity at all temperatures, which are 0.3 wt.% at 6°C, and 0.1 wt.% at 25°C and 40°C.

Table 6. Thermal conductivity enhancement of surface oxidized MWCNTs nanofluid with PVP

Weight Concentration of Surface Oxidized MWCNTs (wt.%)	Weight Concentration of PVP (wt.%)	Percentage of $K_{enhancement}$ (%) at different temperature		
		6 °C	25 °C	40 °C
0.1	0.01	14.65 (0.001)	13.16 (0.002)	9.24 (0.002)
0.2	0.02	14.10 (0.003)	14.21 (0.001)	10.76 (0.003)
0.3	0.03	11.36 (0.002)	15.26 (0.002)	11.26 (0.006)
0.4	0.04	15.20 (0.001)	16.14 (0.003)	12.77 (0.001)
0.5	0.05	18.50 (0.004)	18.42 (0.004)	16.47 (0.002)
0.6	0.06	17.95 (0.005)	17.72 (0.001)	15.80 (0.004)
0.7	0.07	17.22 (0.003)	17.02 (0.002)	15.46 (0.002)
0.8	0.08	17.40 (0.003)	15.79 (0.001)	13.45 (0.003)
0.9	0.09	17.03 (0.004)	15.61 (0.003)	13.78 (0.004)
1.0	0.10	15.57 (0.004)	16.49 (0.003)	13.28 (0.008)

(*) = error bar

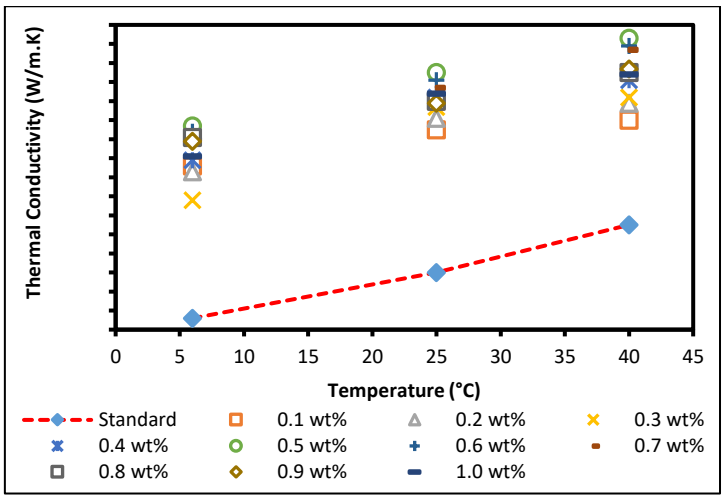

Figure 11. Thermal conductivity of base fluid containing surface oxidized MWCNTs with PVP with various concentration at different temperatures

Conclusions

MWCNTs have been successfully chemically modified using the acid treatment method to introduce the SOFG on the MWCNTs wall structure. The stability of the surface oxidized MWCNT with PVP in water-based nanofluids is more stable than non-oxidized MWCNTs with PVP and commercial MWCNTs with and without PVP by the observation on the particle sedimentation and coagulation. The thermal conductivity performance of nanofluids revealed that the surface oxidized MWCNTs with PVP shows enhancement in thermal conductivity contributed by the improvement of stability and homogenization of nanoparticles. Hence, improved the distribution of MWCNTs in water base media leads to improvement in thermal conductivity. These promising properties of MWCNTs in water-based fluids would enable the nanofluids to be used in heat transfer fluid and cooling applications.

Acknowledgements

The authors would like to express their grateful acknowledgements to the Ministry of Higher Education under Fundamental Research Grant Scheme (FRGS. Code Grant: FRGS/2/2013/ST05/UPNM/03/1). The authors also would like to acknowledge UPNM for their necessary financial support

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