Investigation of stability, dispersion, and thermal conductivity of functionalized multi-walled carbon nanotube based nanofluid

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Abstract. In the attempt of preparing multi-walled carbon nanotube (MWCNTs), covalent functionalisation (CF-MWCNTs) were applied. The stable thermal conductivity was measured as a function of temperature. A number of techniques, such as FTIR, FESEM and UV-vis spectrophotometer were employed to characterise both dispersion stability and morphology of functionalised materials. By using ultrasonic test time, the highest stability of nanofluids was achieved at 60 minutes. As a result, the thermal conductivity displayed by CF-MWCNTs was higher than distilled water. In conclusion, improvement in thermal conductivity and stability displayed by CF-MWCNTs was higher, while the best thermal conductivity improvement was recorded at 31%.

1. Introduction

Nanofluid refers to the stable and homogenous suspension exhibited by nanoparticles (NPs) within conventional working fluids such as ethylene glycol, oil, and water [1, 2]. Prior studies reported that addition of small weight concentration of NPs can improve the efficiency of heat transfer and thermal conductivity in base fluid, hence the suitability for a wide range applications, such as solar collectors, cooling appliances, and heat exchangers [3, 4]. Nanoparticles (NPs) are made of either metal oxide (e.g. Al2O3, SiO2, CuO, and TiO2) [5 – 7], carbon-based particles such as carbon nanotube (CNT) [8, 9], graphene oxide (GO) [10], or graphene nanoplatelets (GNPs) [11, 12]. Numerous types of NPs have been proposed since past decades to generate nanofluids; wherein CuO, Al2O3, ZnO, and SiO2 are more commonly employed than nanomaterials based on metal oxide [13 – 15]. Both graphene and carbon-based NPs (e.g. CNT) [16] have been assessed empirically [12, 17, 18]. Simply put, nanofluids have garnered much attention due to its chemical and physical properties, as well as its nanometre size. More importantly, nanofluids have improved thermal conductivity, hence its suitability to serve as heat-exchanging fluid. Upon inclusion of NP base fluid, a number of empirical studies have also improved convective heat transfer, in comparison to pure base fluid.
However, due to its large surface area with strong attraction force of van der Waals, the preparation of these nanofluids suffered from lack of colloidal stability and agglomeration followed by sedimentation of the nano additives [19]. Therefore, this work aims to improve the suspension stability, dispersibility and thermal conductivity of nanofluid based MWCNTs using chemical functionalization approach by introducing carboxyl (-COOH) and hydroxyl (-OH) functional groups to MWCNTs surfaces.

2. Experimental methodology

The pristine MWCNTs used in this study was purchased from, XG Sciences, Lansing, MI, USA with a diameter of 15 nm, length of 5 μm and purity of 95%. Sulfuric acid 95-97% (H₂SO₄) and nitric acid 65% (HNO₃) were purchased from Sigma-Aldrich Co., Selangor, Malaysia, and were used as the functionalization media. Following description focuses on the nanofluid preparation and method used and also the measurement for analysis of the nanofluid.

2.1. Nanofluid preparation and methods

Pristine MWCNTs is a hydrophobic material and it cannot be dispersed in any solvent which is polar like distilled water. The suitable way to make MWCNTs hydrophilic is by introducing functional groups of carboxyl (-COOH) and hydroxyl (-OH) on its surface via acid treatment. This process also known as functionalization process, as shown in figure 1. This process was achieved by dispersing pristine MWCNTs in a solution of HNO₃ and H₂SO₄ at ratio of (1:3) (strong acid medium) through three steps. In the first step, the pristine MWCNTs was added into H₂SO₄ solution and mixed properly using magnetic stirrer for 30 minutes. In the second step, HNO₃ was gradually added to the mixture while the mixture container was placed in an ice bath to control the reaction temperature and avoid solution evaporation. The mixture solution was then stirred for 30 minutes followed by 3 h in ultra-sonication bath at (60 °C). In the final step, CF-MWCNTs were collected and washed thoroughly for 3 times with distilled water then centrifuged at 6000 rpm for 15 minutes to remove excess acid and then dried under drying oven for 24 h at 80 °C. Samples with different concentrations of CF-MWCNTs (0.02, 0.05, 0.08, and, 0.1wt %) were prepared by adding the CF-MWNTs into distilled water and mix them properly using probe sonicator for 60 minutes.

![Figure 1. Schematic of functionalization and sonication process to making nanofluid.](image-url)
2.2. Measurement devices

2.2.1. Evaluation of suspension stability and dispersibility. The evaluation of the FTIR spectra was done within a wavenumber range of 400-4000 cm\(^{-1}\) for FTIR spectroscopy. Ultraviolet-visible spectrophotometry analysis (UV-vis) was utilized to assess the dispersion quality of CF-MWCNTs in the aqueous suspension. To make available a quantifiable characterization of the stability can measurement of light absorbance of a suspension by UV-vis spectroscopy. The use of UV-vis is Lambda operating in the range of 200-800 nm wavelengths (UV-800/900, Lambda Company, USA). Light absorbance was measured by special quartz cuvettes suitable for UV region since all samples were at certain time intervals for an extra 30 days. A 1:20 ratio diluted in distilled water to allow suitable light transmission for all samples. The morphological characteristics were conducted by Field Emission Scanning Electron Microscopy (FESEM, SU8000, Hitachi), to characterize both the pristine-MWCNTs and the CF-MWCNTs nanofluids.

2.2.2. Thermal conductivity measurement. Thermal conductivity of the prepared nanofluids was measured using KD2 Pro thermal properties analyzer device (Decagon devices, Inc., USA), which has an accuracy of about 5%. Its operation principle is based on the transient hot wire method using the KS-1 probe which consists of a single needle sensor with 1.3 mm diameter and 60 mm long. To keep the samples at the preferred temperature during measurements, a water baths “Memmert WNB 7-45” (Daihan Scientific Co., Ltd., Korea) with 1.4 kW and an accuracy of 0.1 °C was used.

2.2.3. Thermal conductivity measurement. Thermal conductivity of the prepared nanofluids was measured using KD2 Pro thermal properties analyzer device (Decagon devices, Inc., USA), which has an accuracy of about 5%. Its operation principle is based on the transient hot wire method using the KS-1 probe which consists of a single needle sensor with 1.3 mm diameter and 60 mm long. To keep the samples at the preferred temperature during measurements, a water baths “Memmert WNB 7-45” (Daihan Scientific Co., Ltd., Korea) with 1.4 kW and an accuracy of 0.1 °C was used.

3. Results and discussion

3.1. Characterization of CF-MWCNTs nanoparticles

3.1.1. Fourier transform infrared spectroscopy. The FTIR spectra of pristine-MWCNTs and CF-MWCNTs are illustrated in figure 2. Figure 2 displays the absorbance peaks of CF-MWCNTs at 2850, 1650, 1383 and 1100 cm\(^{-1}\), which are attributed to C-H, C=O, C-O and C-O-C bonds, respectively. The bonds reflect the attachment of acid treatment molecules on the surface and edge of MWCNT walls. Both bonds of C=O and C-O signify the successful direct esterification reaction. The CF-MWCNTs showed a broad absorbance peak at wavenumbers between 3450 cm\(^{-1}\); attributable to -OH chains from acid treatment [20]. The CF-MWCNTs peaks indicate the success of CF procedure.

3.1.2. Scanning electron microscopy (SEM). FESEM images for CF-MWCNTs confirm the existence of broken tubes of MWCNTs after functionalization process as shown in figure 3 (a) and (b). Though, these tubes provide better dispersion stability, it may cause a small reduction in thermal conductivity [14]. On the other hand, the functionalization treatment illuminated the upper surface roughness of the P-MWCNTs. The partial damage of graphitic carbon indicates higher roughness, which is mostly due to the effect of carboxyl groups.
3.1.3. Suspension stability and dispersibility. Individual MWCNT are active in the UV-vis region and exhibit characteristic bands corresponding to additional absorption due to ID van Hove singularities [21]. Further, it is possible to establish a relationship between different concentrations of CF-MWCNT dispersed in water and the intensity of the corresponding absorption spectrum. Moreover, UV-vis spectroscopy was used to monitor the dynamics of the dispersion process of MWCNT. After refluxation, the absorbance of MWCNT solutions show a maximum between 250 and 300 nm and gradually decreases from UV to near-IR, which is partly due to scattering, especially in the lower wavelength range. Initially, MWCNT exist as big aggregates and bundles in solution that are strongly and no absorption is evident in the UV-vis spectrum figure 4. After acid treatment, the provided mechanical energy overcomes the van der Waals interactions in the MWCNT bundles and leads to their disentanglement and improved dispersion. The increasing amount of dispersed CF-MWCNT results in an increasing area below the spectrum lines representing the absorbance.
3.1.4. Thermal conductivity. Figure 5 shows the thermal conductivity of water-based nanofluids including CF-MWCNTs with different weight concentrations of 0.02, 0.05, 0.08 and 0.1wt% at different temperatures. It can be clearly seen that the thermal conductivity of water based CF-MWCNTs nanofluids with all concentrations are higher than that of water. In addition, the thermal conductivity increases as the concentrations of MWCNTs in the water-based nanofluids increases. In, the main mechanism of thermal conductivity enhancement can be attributed to the Brownian motion of the suspended particles as it is one of the most dominating functions of temperature [22]. Figure 5 also shows adding 0.1wt% of CF-MWCNTs to the distilled water gives the highest the thermal conductivity of 0.83 W/m.K at 60 °C, which is 31% higher than that of distilled water (DW).
4. Conclusion
The preparation of homogenous and stabilized suspension of functionalized multi-walled carbon nanotube (CF-MWCNTs) in water based thermal fluid was achieved successfully. By proper chemical functionalization approach we managed to introduce some carboxyl and hydroxyl functional groups to pristine MWCNTs surfaces which significantly help to overcome the van der Waals interactions forces between pristine MWCNTs bundles and lead to their disentanglement and improved dispersion. These results were further confirmed using UV-vis, FTIR and FESEM characterization tools. Thermal conductivity measurement showed remarkable enhancement after functionalization treatment, whereas by adding 0.1 wt% of CF-MWCNTs to the distilled water, thermal conductivity increased up to 0.83 W/m.K at 60 °C, which is 31% higher than that of distilled water (DW).

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