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Effect of PEG functionalized carbon nanotubes on the enhancement of thermal and physical properties of nanofluids

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In this study, pristine carbon nanotubes and polyethylene glycol functionalized carbon nanotubes (CNT-PEG) have been used to enhance the heat capacity, viscosity, thermal conductivity, heat transfer rate and pressure drop of nanofluids. Multi-walled carbon nanotubes (MWCNT) were functionalized with polyethylene glycol (PEG) using a Fischer esterification method to improve their dispersion in aqueous media. Three concentrations of 0.01 wt%, 0.05 wt% and 0.1 wt% of pristine and functionalized CNTs in the nanofluids have been used. The heat-transfer rate and pressure drop of these nanofluids have been measured in a shell and tube heat exchanger. Differential Scanning Calorimetry (DSC) was used to study the specific heat capacity of the nanofluids. The specific heat capacity of pristine and functionalized CNTs mixed with water was found to be significantly higher than of the pure water by 10% and 45% respectively. The results of the heat transfer of the nanofluids increased suddenly with the increasing the concentrations of both pristine and functionalized CNTs. It can be concluded that the functionalizing CNT with Polyethylene glycol enhanced the dispersion of the CNTs and increased their heat capacities. The viscosity of the nanofluids was found to be dependent on the concentration of CNTs in solution. The pressure drop of the nanofluid compared with that of pure water was almost unchanged resulting in no extra pumping energy penalty.

1. Introduction

Heat-transfer fluid is one of the critical parameters that affects the cost and size of heat transfer systems [1,2]. Moreover, it has wide industrial applications; in cooling and heating thermal systems, chemical industry, automobile, construction, microelectronics and many other applications [3,4]. However, the heat fluids have limited heat transfer potentialities, due to their limited heat transfer characteristics, the development and the enhancement of the heat transfer systems is also changing. It is the need of the hour to develop and enhance the current heat-transfer fluid capabilities. Different research groups around the world have acknowledged the need to develop new classes of fluids with enhanced heat transfer capabilities [4–7]. They targeted to develop a new generation of heat transfer fluids using nanoparticles, and they have shown a significant enhancement in thermal properties. Due to the high thermal properties of nanoparticles, the addition of these materials can remarkably improve the thermal properties of the base fluid [8]. Hence, a fluid contains homogenously suspended nanoparticles called "*nanofluids*" [9–11]. Nanofluids are a new generation of liquids used for heat energy transport and can be employed as heat transfer fluids in heat exchangers in place of pure single-phase fluids [2,4,5,12–14].

In the last decade, many researchers have developed and generated heat transfer nanofluids using different types of nanomaterials, such as Cu, CuO, Al_2O_3, SiO_2, Fe_2O_3, CNTs, GO and graphene nanoplatelet by dispersing them into base fluids such as water, ethylene glycol, mineral oils and molten salt [13,15–23]. It was found that, the enhancement of thermal conductivity and storage heat capacity of the nanofluids can be effected by many parameters; including the shape and size of the nanoparticles, the concentration of nanomaterials in the base fluid and the temperature of the fluid [24,25]. Recently, carbon nanomaterials have gained significant attention over the last decade since the discovery of

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Nomenclature

List of abbreviations

Q	heat transfer rate in tube (kW)
m_n	mass flow rate for nanofluids (kg/h)
Cp_n	specific heat capacity of nanofluids (J/g C)
$T_{n,in}$	tube inlet temperature (°C)
$T_{n,out}$	tube outlet temperature (°C)
n	subscript for nanofluid
Re	Reynolds's number
Nu	Nussle's number
ΔP	pressure drop (mbar)
η	viscosity of nanofluids (cp)
k	thermal conductivity (W/m K)
f	friction factor

carbon nanotubes (CNTs) in 1991 [8,26]. The most eye-catching features of these structures are their thermal properties, which can permit future applications in thermal science and engineering. CNTs and graphene nanoparticles have unusual heat transfer properties. In the lengthwise direction, they show excellent heat transfer performance. Moreover, it possesses remarkable thermal properties with ultra-high thermal conductivity (2000–3000 W m^{-1} K^{-1}), which higher than water base fluid and engine oil by 3000 times and 10,000 times, respectively [27–29]. Also, their thermal conductivity is much higher than those of the metallic or their oxide nanomaterial used in nanofluids [7,26,30,31]. Therefore, it is expected that thermal conductivity of fluids that contain suspended solid particles could be significantly higher than that of conventional fluids. Recent researches have demonstrated that there is a substantial increase in the thermal conductivities of different CNT nanofluids in comparison to their base fluids in the range of 11–350% enhancement [7,28,32–34]. Hence, the fluids containing suspended carbon nanotubes are expected to have significantly greater thermal conductivity compared to common heat-transfer fluids. The Maxwell's concept of enhancing the thermal conductivity of fluids by dispersion of solid particles is discovered many years before, however, the innovative concept of nanofluid is the idea of using nanometer-sized particles to help it improve the rapid settling of particles in the fluid [12]. Homogenization of nanofluids requires chemical surfactant and sonication to achieve good dispersions of CNTs in these fluids by dispersing nanoparticles into suitable solvents [35–37]. Different types of chemical surfactants have been reported such as Sodium Dodecyl Sulphate (SDS), Polyvinylpyrrolidone (PVP), Arabic Gum (AG) and Cetyl Trimethyl Ammonium Bromide (CITAB) [37,38]. Using these after mentioned surfactants, nanofluids can bed homogenized and stabilized for a long period of time without precipitation [39,40].

The theoretical and experimental studies of effective thermal conductivity of such liquids have been conducted earlier by many researchers [11,41]. Yang et al. [42] found a 30% enhancement in thermal conductivity of MWCNTs/polyisobutylene-based nanofluids for MWCNTs mass fraction of 0.5%. It was also observed that the more uniform MWCNTs being dispersed in nanofluids, the higher thermal conductivity the nanofluids would possess. Xie et al. [29] prepared nanofluids by dispersing CNTs, which had hydroxyl groups on the surface by concentrated nitric treatment, in the water and ethylene glycol. It was noticed the thermal conductivity of ethylene glycol nanofluids was increased by 20% for only a small loading of 1 vol.% CNTs. However, the thermal conductivity of CNTs in axial direction is much higher than that of horizontal direction and the high theoretical thermal conductivity in axial direction still hard to be obtained in nanofluids on the whole. The nanofluids loading CNTs of higher thermal conductivity are obtained depend on strict dispersion conduction which occurs through the interface. Carbon nanoparticles which have a spherical shape and larger specific surface area compared with CNTs may be more favourable for heat transfer and can enhance effectively the thermal conductivity of base fluids [5,7,41,43].

In this study, the effects of pure CNT and functionalized CNT with polyethylene glycol (PEG-CNT) on the thermophysical properties of nanofluids will be investigated. After the CNT was prepared and characterized using SEM and TEM, the CNT was functionalized with PEG using Fischer esterification method. The functionalized CNT has been analysed by FTIR and TGA techniques. The nanofluid was prepared using twos-step method and sonicated to improve the dispersion. The thermophysical properties of nanofluids, such as specific heat capacity (Cp), viscosity, thermal conductivity, heat transfer rate and pressure drop behaviour in turbulent flow regimes were investigated.

2. Experimental work

2.1. Materials

High purity CNTs have been produced by a vertical chemical vapor deposition reactor according to the method described in our previous work [5]. The produced CNTs diameters varied from 20 to 40 nm with 24 nm as an averaged diameter, the length varied from 10 to 30 μm, specific surface area of 200 m^2/g, and a purity of 95%. Polyethylene glycol with high molecular weight (>8000), supplied by Sigma Aldrich, was used to functionalize the surface of CNT.

2.2. Functionalization of CNT with polyethylene glycol

The functionalized CNTs were prepared by oxidizing the CNTs with nitric acid as shown in Fig. 1. The functionalizing process took place through reaction of oxidized carbon nanotubes (COOH-CNT) with functional group in polyethylene glycol and then by applying a Fischer esterification method. The oxidized CNT has active sites enabled to form chemical attached bounds with the surface of the CNT [44].

The experimental procedure was started by mixing an excess amount of polyethylene glycol with certain amount of oxidized CNT in a 500 ml beaker, the mixture was melted to temperature near to the melting point of PEG (~80 °C) using a hot plate while stirring. This melted amount of PEG should be enough to allow submerging all used CNT. After that, a few drops of sulfuric acid were added to the mixture as a catalyst. The reaction beaker was kept on a hotplate with stirring for 2–3 h. The reaction mechanism is illustrated in Fig. 2 [45]. After the reaction is completed, the mixture was dissolved in an excess amount of toluene several times and then filtered by vacuum, to remove any traces of un-reacted PEG and sulfuric acid from the produced CNT-PEG. Finally, a drying process was applied at a temperature of 80 °C using a vacuum oven to evaporate toluene from the produced powder of the CNT-PEG. To ensure the formation of and functionalization of PEG with CNT, the prepared CNT-PEG composite was characterized by Fourier transform infrared spectroscopy (FTIR).