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The influence of decorated multi walled carbon nanotubes with TiO_2 nanoparticles on the thermal conductivity of water based nanofluids

Sedigheh Abbasi[1], Seyed Mojtaba Zebarjad[2], Seyed Hossein Noie Baghban[3], Abbas Youssefi[4]
Esfarayen University of Technology, Esfarayen, North khorasan, Iran

abasi_1362@yahoo.com , s.abbasi@esfarayen.ac.ir

Abstract
In this paper, we report for the first time the thermal conductivity behavior of nanofluids containing MWCNTs which decorated with different amount of TiO_2 nanoparticles. For this purpose we synthesis the TiO_2 nanoparticles and decorated MWCNTs with different amount of TiO_2 nanoparticles using hydrolysis method. The samples are characterized by transmission electron microscopy (TEM). TEM image confirmed that the ends of MWCNTs successfully opened. Meainwhile acid treatment leads to the cutting of MWCNTs to the short length and the outer surface of MWCNTs successfully decorated withTiO_2 nanoparticles. Measurements of thermal conductivity behavior of nanofluids were carried out in the range of temperature varying from 25 to 70 °C. The mass fraction of the TiO_2 nanoparticles, MWCNTs and decorated multi walled carbon nanotubes with TiO_2 nanoparticles in water is 0.25, 0.5, 1 and 1.5 %wt..The results of thermal conductivity behavior of nanofluids revealed that the thermal conductivity and enhancement ratio of thermal conductivity of MWCNTs-TiO_2 at different amount of TiO_2 nanoparticles are higher than those of TiO_2 and MWCNTs nanofluids. Temperature and weight fraction dependence study also show that the thermal conductivity of all nanofluids increases with temperature and weight fraction. However the influence of temperature is more significant than that of weight fraction.

Keywords: MWCNT, TiO_2 Nanoparticles, Decoration, Thermal Conductivity

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[1] Assistant Professor, Esfarayen University Of Technology

[2] Professor, Shiraz University
[3] Professor, Ferdowsi University of Mashhad
[4] Assistant Professor, Par-e-Tavous Research Institute

1- Introduction

Conventional fluids such as water and oil have poor thermal properties that restricted the heat transfer performance compared to most of the solids. Many techniques are available in order to increase heat transfer rates and reduce the size of the heat transfer equipments[1]. The key idea is to exploit the very high thermal conductivities of solid particles that can be several hundreds of times greater than all of the conventional fluids combined. Various types of particles, such as metallic, non-metallic and polymeric, can be added into fluids to form slurries[2].

In a few years ago solid particles of millimeter and micrometer in size were suspended in the conventional fluids to improved thermal behavior but some serious problemsemerged by use of these types of fluids. For example, poor stability of the suspension and high erosion and pressure drop in pipelines and equipments.

With the advent of nanotechnology, nanoparticles in size between 1 nm and 100 nm replaced instead of particles in order of millimeter and micrometer. This type of fluid called nanofluid[3].The stability and heat transfer rate of nanofluids are extraordinary higher than those of suspensions contains particles in the size of millimeter or even micrometer.

Among the various nanoparticles, carbon nanotubes (CNTs) due to their very excellent thermal conductivity and large aspect ratio are a good selection to prepare nanofluids[4]. The presence of van der Waals attraction between tubes lead to hydrophobic nature of CNTs so that the dispersibility of them is very low in water and other organic solvents[5]. Therefore in the preparation of stable suspension, the surfactant addition is an effective way to enhance the dispersibility of CNTs[6]. However, surfactant molecules attaching on the surfaces of CNTs may increase the thermal resistance between the CNTs and the base fluid[7], which limits the enhancement of the effective thermal conductivity.

Modifying the surface of nanotubes with oxygen-containing groups lead to improvement the interaction of CNTs with the solvent matrix these functional groups are formed by chemical treatment such as nitric acid[8]. Zhang et al.[9]investigated the heat transfer performance of TiO_2/water nanofluid. They observed that the effective thermal conductivity and thermal diffusivity increase with an increase in the particle concentration. He et al.[10] studied static thermal conductivity, heat transfer and flow behavior of stable aqueous TiO_2 nanofluid with different particle sizes and concentrations. They found that the convective heat transfer coefficient increased with increasing nanoparticle concentration.

The previous study reported different results about the thermal conductivity of nanofluids containing CNTs. This might be due to the differences in the experimental conditions such as carbon nanotube aspect ratios, dispersants used and the approaches used for preparing the experimental nanofluids.

Garg et al.[11] reported the enhancement of thermal conductivity from 3 to 5% for nanofluids containing 1 wt% MWCNT which measured at 25°C and the ultrasonication from 20 to 80 min, respectively. Chen et al.[12] reported an enhancement of 17.5% at volume fraction of 0.01 for an ethylene glycol based nanofluid containing multi-walled carbon nanotubes.

Meibodi et al.[13] investigated the effects of different factors such as nanoparticle size and concentration on thermal conductivity of CNT/water nanofluids. Their results showed that Thermal conductivity of nanofluid is time dependent immediately after ultrasonication and independent of time at longer time.

Talaei et al.[14]reported the influence of functional group concentration on the thermal conductivity of MWCNT nanofluids. The results show that increasing the functionalized group causes better stability and higher thermal conductivity if the surface of MWCNT does not damage in functionalize process.

Xie et al.[4] have prepared the stable nanofluids of multi-walled carbon nanotubes into ethylene glycol base fluid and studied the influence of mechanical ball milling on the straight and length distribution of CNTs. Their results demonstrate that the nanotube loading, temperature, straightness ratio, aspect ratio and aggregation play a key role in the thermal conductivity of nanofluids.

Raykar et al.[15]investigated the effect of temperature and Brownian motion on the enhancement of effective thermal conductivity of carbon nanotube based nanofluids. Their experiments revealed that the Brownian motion has a significant effect on the effective thermal conductivity. Also they observed that the enhancement of effective thermal conductivity in dilute nanofluids is higher.

Hong et al.[16] studied the effect of external magnetic field on the enhancement thermal conductivity of nanofluids containing 0.01 wt% nanotube and 0.02 wt% Fe_2O_3 in water under the different magnetic strength. Their results showed that the thermal conductivity of nanofluids under uniform magnetic field is higher than that under non-uniform field.

Jha et al.[17] reported the effect of various nanoparticles such as Ag, Au and Pd which dispersed on the outer surface of carbon nanotubes on the thermal conductivity of water and ethylene glycol based nanofluids. Their experiments demonstrated that nanofluids maintain the same sequence of thermal conductivity as that of metal nanoparticles Ag-MWNTs> Au-MWNTs> Pd-MWNTs.

Amiri et al.[18] investigated the dispersion stability and thermal conductivity of multi walled carbon nanotubes in the presence of gum arabic (MWCNT-GA) as well as functionalized MWCNT with cysteine (MWCNT-Cys) and silver (MWCNT-Ag). The effect of temperature and weight concentration on the enhancement of thermal conductivity revealed that the covalent functionalization by Ag is more effective than non covalent functionalization.

Although thermal behavior of CNT nanofluids has been investigated by many researchers, but the effect of decorated MWCNTs with different amount of nanoparticles on the thermal behavior has never been reported so far. Therefore in this study, we want to report for the first time the effect of modified MWCNTs with various amount of TiO_2 nanoparticles on the thermal conductivity of nanofluids.

2- Materials and Experimental

Titanium tetrachloride ($TiCl_4$, M= 189.79, 99%, Merck) without any further purification was used to prepare the TiO_2 nanoparticles using hydrolysis method. The appropriate amount of TiCl4 was dissolved drop wise in distilled water under vigorous stirring. This aqueous $TiCl_4$ solution was stirred for 5h at ambient temperature then heated for 24 h at 80 ℃.Finally TiO_2 nanoparticles separate from the solution using filtration dried at room temperature and calcined at 370 ℃ for 3 h.

In a typical synthesis of MWCNT-TiO_2, 100mg MWCNTs (average diameter of 40-60 nm and lengths ranging from 5 to 15 micrometers) were first dispersed in 50 ml nitric acid (HNO_3, M= 63, 65%, Merck), sonicated at room temperature for 2 h in an ultrasound bath and stirred for 2 h at high speed. The acid-treated MWCNTs were rinsed several times with distilled water until the pH value of the solution close to neutral and then dried at 90 °C for an overnight. Subsequently, a little amount of Hydrochloride Acid (HCl 37 wt. %, Merck) and certain amount of $TiCl_4$ was added drop wise to 100 mL distilled water under rapid stirring, then 75 mg of oxidized MWCNTs were dispersed in this solution using ultrasound bath for 2 h. The mixture was stirred for 22 h at room temperature and then raised temperature to 80 ℃ and the mixture was stirred for 3 h then filtered, dried at 80 ºC for 1 h and calcinated at 370 ºC for 3 h.

The measurement of thermal conductivities was done using KD2 Pro thermal property analyzer purchased from Decagon Devices Inc. The mentioned instrument has three different probes and measures the thermal conductivity according to the transient hot wire technique. In this study we used the single-needle (KS-1) with 60 mm long and1.3 mm diameter and accuracy ±0.01 W/(m· K) from 0.02 - 0.2 W/(m· K).Measurements were carried out in the range of temperature varying from 25 to 70 °C. In order to change and control the temperature, the KD2 Pro device was connected to a constant temperature bath (Thermo Haake K10 TT4310) which has a circulator and was able to maintain temperature uniformity. For more accuracy, we maintained the sample and probe in double walled cylindrical container having liquid circulating facility at constant temperature and wait for about fifteen minutes between readings. Fig. 1 illustrated the using KD2 Pro device. A number of measurements were taken for each sample and only measurements resulted with the mean correlation coefficient r^2> 0.9998 were considered. Transmission electron microscopy (TEM) micrographs of acid-treated and modified MWCNTs with TiO_2nanoparticles were obtained using a LEO 912AB system operating at 120kV.

Fig. 1. Experimental set up (KD2 Pro device) for thermal conductivity measurements.

3. Results and discussion

3.1. Acid treatment of MWCNTs

During the formation of multi walled carbon nanotubes the open ends of them are often closed by catalyst particles. Treatment of MWCNTs in nitric acid mainly removed the catalyst particles. Therefore, the tube ends are opened and largely decorated with oxygen containing groups such as acid carboxylic (-COOH) and hydroxyl (-OH) which could change the sp^2 hybridization of MWCNTs to sp^3 hybridization[19]. Fig. 2 shows the TEM image of acid treatment of MWCNTs in nitric acid. As can be seen, acid treatment leads to the opening and cutting of MWCNTs to the short length.

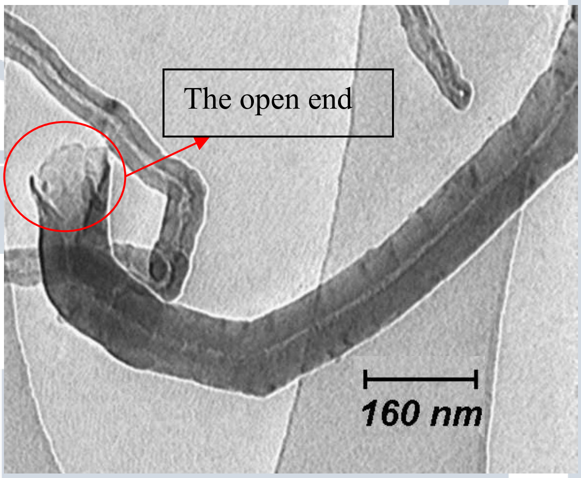

Fig. 2. TEM image of acid treated MWCNTs.

3.2. Decoration of MWCNTs

As a result of oxidation of MWCNTs with HNO_3, oxygen containing groups act as active sites and adsorb titanium ions which are produced by hydrolysis of $TiCl_4$. Adsorption of titanium ions on the outer surface of MWCNTs due to the electrostatic attraction lead to the nucleation of TiO_2 nanoparticles. Then calcination of MWCNT-TiO_2 results the nanocrystalline TiO_2 on the outer surface of MWCNTs. Fig. 3 illustrates the TEM image of decorated MWCNTs. It is observed that the outer surface of MWCNTs was decorated with TiO_2 nanoparticles. The formation mechanism of TiO_2 nanoparticles is as below:

$$TiCl_4+2H_2O \longrightarrow TiO_2+4HCl \quad (1)$$

The amount of TiO_2 nanoparticles which was introduced to the outer surface of MWCNTs affected by the used volume of precursor ($TiCl_4$). Therefore, by increasing the volume of $TiCl_4$, the larger amount of TiO_2 nanoparticles covalently attach on the outer surface of MWCNTs. In this study, we synthesis two kinds of MWCNTs-TiO_2 with 34% and 61% of TiO_2 nanoparticles.

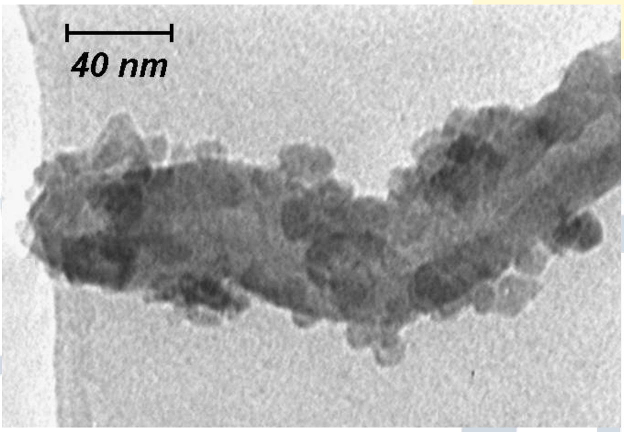

Fig. 3. TEM image of MWCNTs-TiO_2.

3.3. Measurement of thermal conductivity of nanofluids

Fig. 4 depicts the measured thermal conductivity of TiO_2/water nanofluids as a function of temperature at four different mass fractions. Because of influence of temperature on the thermal conductivity of nanofluids, nanofluids may be used under different temperatures. Therefore, we want to investigate the temperature effect on the thermal conductivity and thermal conductivity enhancement ratio of nanofluids. In Fig. 5, it is clear that the thermal conductivities of TiO_2 nanofluids are higher than those of the base fluids at all the tested temperatures. Also it can be observed that the thermal conductivity increases with increasing temperature and TiO_2 concentration. Meanwhile it can be deducted that the temperature has a more significant effect than the mass concentration. For the nanofluid containing sphere metal or metal oxide nanoparticles the strong temperature dependence of thermal conductivity was due to the Brownian motion of nanoparticles

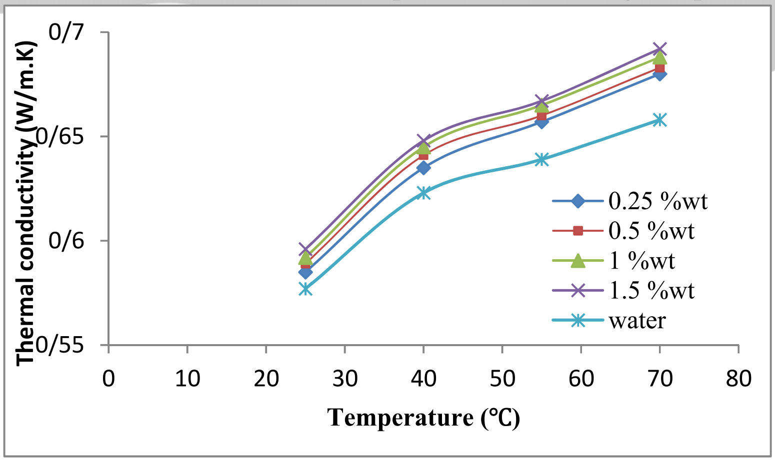

Fig. 4. Dependence of the thermal conductivity of TiO_2/water nanofluids on temperature at different mass fractions.

Fig. 5 depicts the thermal conductivity of the MWCNTs nanofluids as a function of temperatures respectively. The mass fraction of the MWCNTs in water is 0.25, 0.5, 1 and 1.5 %wt. According to the Fig. 7, it is corroborated that the thermal conductivity of water-based nanofluids containing MWCNTs shows augmentation with respect to temperature and weight fraction of MWCNTs. It should be mentioned that in the tested weight fraction rang, the influence of weight fraction is not significant and can be negligible. But as can be observed, the effect of temperature is more important. According to the FTIR analysis, the outer surface of MWCNTs is functionalized with oxygen containing groups such as –OH which introduce during the purification of as prepared MWCNTs (data not shown). Therefore, in the water-based nanofluids containing MWCNTs, in addition to the Brownian motion of MWCNTs, the chemical functionalized groups have a key effect on the amount of energy which transfers into the nanofluids by changing the temperature[23].As we know, by increasing the temperature, the hydrogen bond of water was weakened. Therefore the structure of water molecules was destroyed and the number of free water molecules increased. These free water molecules can be arranged around the MWCNTs surface. This liquid layer which produced due to the chemical surfaces of MWCNTs and van der Waals force between the water molecules has a higher thermal conductivity than the bulk liquid[24].

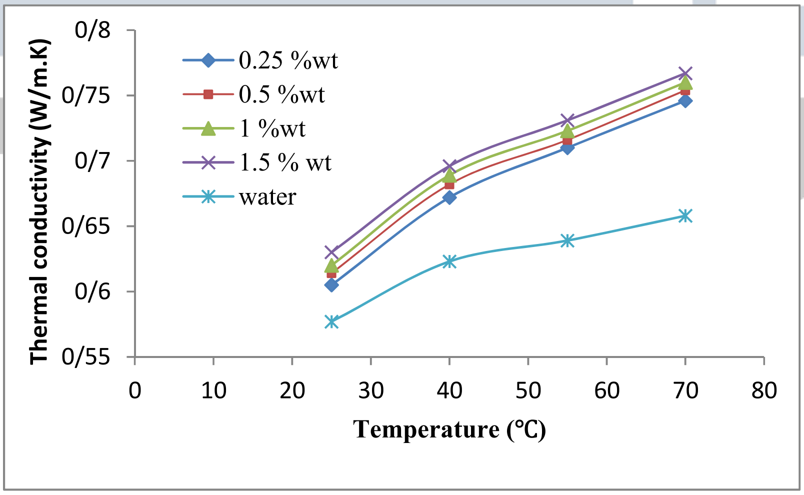

Fig. 5. Dependence of the thermal conductivity of MWCNTs/water nanofluids on temperature at different mass fractions.

Thermal conductivity of nanofluids containing MWCNTs-TiO_2 is presented in Fig. 6. It is clear that the application of MWCNTs-TiO_2 increases the thermal conductivity of nanofluids as with respect to the temperature and weight fraction. From Fig.6 can be inferred that the thermal conductivity of nanofluid containing MWCNTs-TiO_2 is equal to 0.805 at temperature of 70℃ and weight fraction of 1.5 %wt.

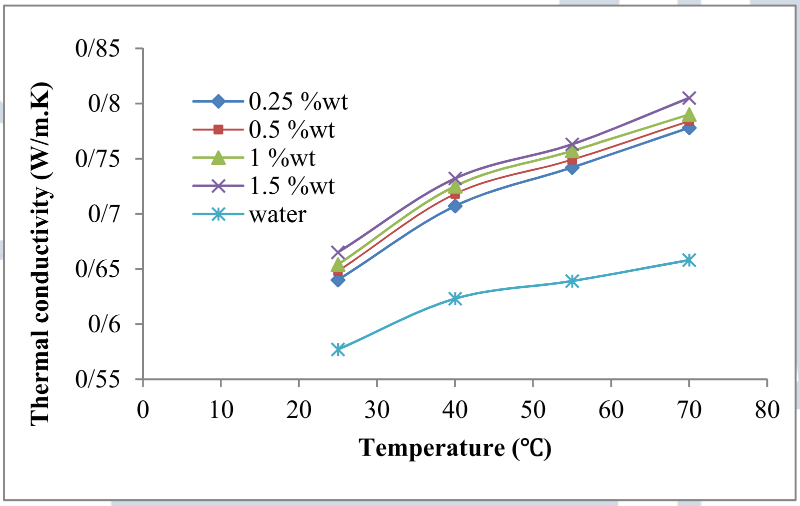

Fig. 6. Dependence of the thermal conductivity of MWCNTs-TiO_2/water nanofluids on temperature at different mass fractions.

The comparison between thermal conductivity of nanofluids containing the TiO_2 nanoparticles, pristine MWCNTs and decorated MWCNTs illustrated in Fig. 7. As can be deducted from this figure, the sequence of sequence of thermal conductivity of nanofluis containing different amount of nanoparticles are the intrinsic thermal conductivity of nanoparticles (the thermal conductivities of the order given by MWCNT-TiO_2 > MWCNTs > TiO_2.

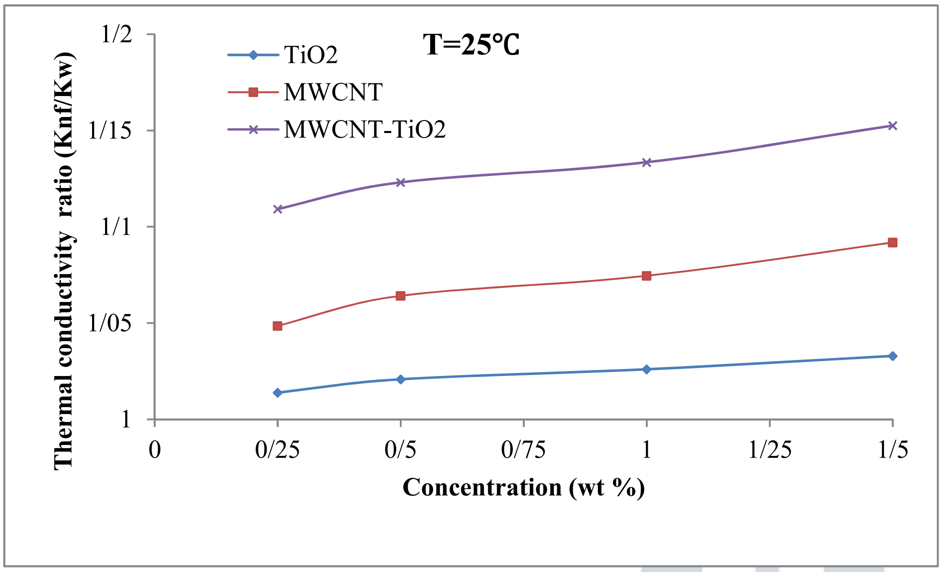

Figure 7. Comparison the thermal conductivity of MWCNT-TiO_2, MWCNTs and TiO_2 at 25℃.

Conclusions

The present study measured the thermal conductivity of nanofluids containing TiO_2 nanoparticles, pristine MWCNTs and decorated MWCNTs with TiO_2 nanoparticles and investigated the effects of weight concentrations and temperature. The results show that the thermal conductivities of all studied nanofluids are higher than those of the base fluids at all the tested temperatures and concentrations and the influence of temperature on the thermal conductivity and enhancement ratio of the thermal conductivity is more significant than the weight fraction. Also it has been observed that the thermal conductivity of nanofluid is the sequence as thermal conductivity that of nanoparticles, i.e., MWCNTs> TiO_2. In addition, the results revealed that the nanofluids containing MWCNTs-TiO_2 have higher thermal conductivity than that of the TiO_2 and MWCNTs nanofluids.

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