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Synthesis, stability, and thermophysical properties of aqueous colloidal dispersions of multi-walled carbon nanotubes treated with beta-alanine

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ABSTRACT

In the present study, multi-walled carbon nanotubes (MWCNTs) with outside diameters of < 8 nm and 20 – 30 nm were covalently functionalized with β-Alanine using a novel synthesis procedure. The functionalization process was proved successful using Raman spectroscopy, FTIR, and TEM. Utilizing the two-step method with ultrasonication, the MWCNTs treated with β-Alanine (Ala-MWCNTs) with weight concentrations of 0.025%, 0.05%, 0.075%, and 0.1% were dispersed in distilled water to prepare water-based nanofluids. The aqueous colloidal dispersions of pristine MWCNTs were unstable. While for Ala-MWCNTs and after > 50 days from preparation, higher colloidal stability was obtained up to relative concentration of 0.955 and 0.939 for the 0.075-wt% samples of Ala-MWCNTs < 8 nm and Ala-MWCNTs 20 – 30 nm, respectively. The measured values of thermal conductivity were in very good agreement with the model of Nan, Birringer, Clarke and Gleiter and increased as temperature, specific surface area (SSA), and weight concentration increased, up to 14.74% for Ala-MWCNTs < 8 nm and 12.29% for Ala-MWCNTs 20 – 30 nm. The viscosity increased as weight concentration increased, up 25.69% for 0.1-wt% Ala-MWCNTs 20 – 30 nm, and decreased with the increase in temperature. Since the matching between the measured values of viscosity and the classical models of Batchelor, Brinkman, and Einstein was bad, a correlation was developed and revealed good agreement. The density and specific heat decreased as temperature increased. As weight concentration increased, the density slightly increased up to 0.065% for Ala-MWCNT < 8 nm while the specific heat decreased down to 0.95% for Ala-MWCNTs 20 – 30 nm, in comparison with water. The equations of (Pak and Cho) and (Xuan and Roetzel) were in good agreement with the measured values of density and specific heat, respectively. The aqueous colloidal dispersions of Ala-MWCNTs that were prepared in this work displayed robust candidature as successful substitutes for the conventional heat transfer fluids in different engineering applications for enhanced thermal performance.

1. Introduction

To enhance the heat transfer yield of different heat exchangers, nanofluids with superior thermal conductivity and selectable rheological and functional properties have recently introduced [1–5]. After introduction of nanofluid by Choi and Eastman [6] in 1995, different types of nanofluids in accordance with different applications were synthesized, e.g., fouling mitigation, drug delivery, improved heat transfer rate, and antimicrobial properties [7–10]. Among all the applications, a majority of nanofluids are employed in heat transfer apparatuses in order to enhance the heat transfer rate in comparison with the conventional heat transfer fluids. To this end, different additives such as metal oxides nanoparticles, metals nanoparticles, and carbon-based nanostructures were applied. The main problems with metal and metal oxide nanoparticles are their weak colloidal stability and the lack of chemical treatment in the presence of these nanoparticles [11–13]. Alternatively, carbon-based nanostructures are great candidates that can be used as additives due to the promising properties, e.g., excellent thermal conductivity; capability for different chemical manipulations such as functionalization, purification and decoration; and favorable potential for enhancing the solubility/hydrophilicity to the desired level [10,14]. Among all carbon-based nanostructures, some of the

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highest thermally-conductive nanomaterials are carbon nanotubes (single-, double-, and multi-walled) [10,15], mono-layer graphene [5,16], fullerene [17], graphene oxide [18], and graphene nanoplatelets [1,14]. While graphene sheets have higher specific surface area (SSA) on a weight basis, multi-walled carbon nanotubes (MWCNTs) seem to be more cost-effective. Moreover, mass production of mono-layer graphene is generally time-consuming, complex, and comprising multiple steps [16]. Accordingly, owning to their outstanding properties, such as high sp^2-hybridized carbon and SSA, MWCNTs have recently attracted a lot of interest for different applications [15]. However, many of the applications were not fully realized due to trivial interaction between MWCNTs and other materials. To improve the interactivity of the MWCNTs, covalent and non-covalent functionalizations were suggested as the main solutions [19,20].

The unwanted effects of non-covalent functional groups have sourced some new problems, such as changing the rheological behavior, formation of excessive foam, and changing pH [19,21]. The highly branched molecules such as surfactants and polymers are responsible for these problems because of their adhesion to the main backbone of the carbon-based nanostructures and acting as insulation. Therefore, covalent functionalization is a great solution to avoid facing the above-mentioned problems [10,14,19]. As an example of covalent functionalization, Aravind, Baskar, Baby, Sabareesh, Das and Ramaprabhu [10] prepared a stable water-based MWCNTs dispersion with the addition of carboxylic groups to the surface of MWCNTs. Although they reported a great colloidal stability and good enhancements in the thermal conductivity and convective heat transfer coefficient, the additive was acidic, imposing this acidity to the base fluid. Also, to reach high degree of colloidal stability with this method, a long period of oxidation time is needed, which can defect the main structure of the nanotubes, unzip tubes, shorten their length, and consequently diminish their thermal properties [4]. The same problems also happened wherever a carboxylic group is used as a bond for decorating with additional functional groups. To avoid these problems, poly ethylene glycol [22] and diamines [2], as non-corrosive functional groups, were added to the main structure of the carbon nanotubes through rapid radical reactions. As another advantage of these methods is the lack of the acid-treatment phase.

Among the numerous functional groups decorated on the surface of MWCNTs, aminoacids can be attached in a quick and simple process. In fact, both the carboxylic acids groups and the nitrogen atoms of the amino group ($-NH_2$) are active chains, which are simply accessible for reacting with other molecules. Due to this reactivity, the various aminoacids-functionalized MWCNTs are commonly employed in the fabrication of nanofluids [23]. Between all the functionalization procedures with hydrophilic amino acids, arginine-treated MWCNTs [24], lysine-treated MWCNTs [25], and aspartic acid-treated MWCNTs [23] showed a great colloidal stability in aqueous media. However, most of the reported procedures were time-consuming and expensive. In fact, amino group ($-NH_2$) in the main structure of aminoacids possess a lone valence electron that can easily react with other molecules using a diazonium reaction.

Here, a one-pot procedure through initiating an active diazonium ion is employed to functionalize MWCNTs with β-Alanine. The colloidal stability of β-Alanine-treated MWCNTs (Ala-MWCNTs) in aqueous media was experimentally investigated for > 50 days. In addition, thermophysical properties were studied and compared with the available correlations and models. Moreover, a valid correlation for nanofluid viscosity was developed based on the experimental results.

2. Methodology

The materials, methods, and devices that were used in this research for the synthesis, evaluation of colloidal stability, measurement of thermophysical properties, and the characterization of the nanomaterials and water-based Ala-MWCNTs nanofluids are presented in this section.

Table 1
Specifications of the pristine multi-walled carbon nanotubes (MWCNTs) used in this research.

Item	Specification	
Supplier company	Nanostructured & Amorphous Materials, Inc., USA.	
Appearance	Powder	
Color	Black	
Purity	$> 95\%$	
Outside diameter	< 8 nm	20 – 30 nm
Inside diameter	2 – 5 nm	5 – 10 nm
Length	10 – 30 μm	10 – 30 μm
True density	2.1 g/cm^3	2.1 g/cm^3
Average specific surface area (SSA)	> 500 m^2/g	> 110 m^2/g

2.1. Materials

Pristine MWCNTs with purity higher than 95%, length of 10 – 30 μm, and two different outside diameters of < 8 nm and 20 – 30 nm were used in this work and procured from Nanostructured & Amorphous Materials, Inc., USA. Detailed specifications are presented in Table 1. The covalent functionalization process was performed using several analytical grade chemicals from Sigma-Aldrich: hydrochloric acid (HCl), *N*,*N*-dimethylacetamide (DMA), beta-alanine (β-Alanine), *N*,*N*-dimethylformamide (DMF), acetone, ethanol, and Sodium nitrite ($NaNO_2$).

2.2. Experimental devices

The devices that were used in this work for characterizing the nanomaterials and nanofluids, measuring the thermophysical properties, and evaluating the colloidal stability are illustrated in the following sections.

2.2.1. Characterization and preparation

The covalently functionalized MWCNTs that were prepared in this work were characterized by different methods: Fourier transform infrared spectroscopy (FTIR) using (Bruker IFS 66/S), Raman spectroscopy using (Renishaw confocal spectrometer at 514 nm), and transmission electron microscopy (TEM) using (LEO 912 AB electron microscope). A precision balance (OHAUS PA214) was used to measure the accurate weight of nanoparticles. An ultrasonication probe (Vibra-Cell, Sonics, VC 750) was used for dispersing the nanomaterial in the base fluid and also for preparing the covalently functionalized MWCNTs.

2.2.2. Evaluation of colloidal stability

The long-term colloidal stability of the nanofluids is considered to be essential for their successful use as new generation heat transfer fluids in different applications. A quantitative characterization of colloidal stability can be made using UV–vis spectroscopy by measuring the light absorbance of the dispersion. UV–vis spectrometer was used for evaluating the colloidal stability of the water-based nanofluids that were prepared in this research. Utilizing special quartz cuvettes, the light absorbance was measured for all the samples using Shimadzu UV-spectrometer (UV-1800) at various time periods for > 50 days. In order to allow for applicable light transmission through the sample in the cuvette, distilled water was used to dilute all the samples at a ratio of 1:20 [18,26–29].

2.2.3. Measurement of thermophysical properties

The thermophysical properties of water and water-based Ala-MWCNTs nanofluids were measured using the following devices: KD2 Pro thermal properties analyzer from (Decagon devices, Inc., USA) was