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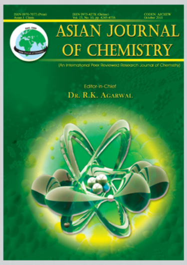

Enhancement of Dispersion, Thermophysical and Electrical Properties of Metals (Na, Al, Li) Treated Water Based Carbon Nanofluids

LEI ZHU[1], ZE-DA MENG[1], MING-LIANG CHEN[1], JONG-GEUN CHOI[1], CHONG-YEON PARK[1],
SHI-CHOON LEE[2], DAE-SEUNG HONG[2], JEONG-GEOL LEE[2] and WON-CHUN OH[1,*]

[1]Department of Advanced Materials Science & Engineering, Hanseo University, Seosan, Chungnam 356-706, South Korea
[2]N-Barotech Co. Ltd., Ulsan 681-802, South Korea

*Corresponding author: Fax:+82 41 6883352; Tel: +82 41 6601337; E-mail: wc_oh@hanseo.ac.kr

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Nanofluids have been paid attention because of the intriguing heat transfer enhancement performances as one kind of promising heat transfer media. This paper reports an experimental work on the enhancement of dispersion, thermophysical and electrokinetic properties of aqueous suspensions of metal treated carbon nanoparticles (nanofluids). In this study, a simple route used to synthesize metal (Na, Al, Li) treated carbonaceous nanomaterials was studied. The dispersion effect, electrical conductivity, thermal diffusivities of the metal-carbon-nanofluids system were introduced and discussed. The results show that these properties were significantly enhanced, which could be due to not only the outstanding physical and electrical properties of the carbon nanomaterials but also to the introduction of metal ions.

Key Words: Carbon materials, Metal, Dispersion effect, Thermal and electrical properties, Nanofluids.

INTRODUCTION

Nanofluid is envisioned to describe a fluid in which nanometer-sized particles are suspended in conventional heat transfer basic fluids. Conventional heat transfer fluids, including oil, water and ethylene glycol mixture are poor heat transfer fluids, since the thermal conductivity of these fluids play important role on the heat transfer coefficient between the heat transfer medium and the heat transfer surface. Development of advanced heat transfer fluids is clearly essential to improve the effective heat transfer behaviour of conventional heat transfer fluids. Nanomaterials have been extensively researched in recent years. Emerging nanotechnology shows promise in every aspect of engineering applications. Recently, there has been interest in using nanomaterials as additives to modify heat transfer fluids to improve their performance[1-7].

The new class of heat transfer fluid is termed nanofluids, which are formed by combining nanomaterials with heat transfer fluids. The nanofluids are shown to improve thermal conductivity and heat transfer considerably. Dispersion or suspension of nanomaterials of high thermal conductivities into base fluids gives rise to higher thermal conductivity of the mixtures[1-3]. Researchers have used different types of solid nanoparticles like: (1) metallic particles (Cu, Al, Fe, Au and Ag); (2) nonmetallic particles (Al_2O_3, CuO, Fe_3O_4, TiO_2 and SiC); and (3) nano droplet with high thermal conductivity as additives of nanofluid. There are mainly two techniques used to produce nanofluids; (i) the single-step direct evaporation method represents the direct formation of the nanoparticles inside the base fluids and (ii) the two-step method represents the formation of nanoparticles and the subsequent dispersion of the nanoparticles in the base fluids. In either case, the preparation of a uniformly dispersed nanofluid is essential for obtaining stable reproduction of physical properties or superior characteristics of the nanofluids. The single-step process was developed by Akoh *et al.*[8] and is called the vacuum evaporation onto a running oil substrate (VEROS) technique. A modified vacuum evaporation onto a running oil substrate process was proposed by Wagener *et al.*[9]. The processes of drying, storage, transportation and the dispersion of nanoparticles are avoided, so the agglomeration of nanoparticles is minimized and the stability of the fluids is increased. However, only low vapour pressure fluids are compatible with this process. This disadvantage limits the application of this method. Whereas, the two-step process is extensively used in the synthesis of nanofluids considering the available commercial nanopowders supplied by several companies. Eastman *et al.*[10], Lee *et al.*[11] and Wang *et al.*[12] used this method to produce Al_2O_3 nanofluids. Murshed *et al.*[13] also prepared TiO_2 suspension in water using the two-step method. In this process, nanoparticles were produced and then dispersed with the base fluids. Generally, ultrasonic treatment, control of pH or addition of surface active agents are some techniques, which are used to attain stability of the suspension of the nanofluids against sedimentation by suppressing formation of particle cluster. But, the addition of surface active agents can affect the heat transfer performance of the nanofluids, especially at higher temperature. However, these efforts to improve the thermal conductivity have been interfered with the stability of particle size. When the heat transfer particles were dispersed in solvents, nanoparticles tend to aggregate into large clusters [14-16].

The colloidal suspensions and emulsions are important parts of everyday life. In recent years, some studies have highlighted the significance of aqueous colloidal dispersions of carbon materials. carbon nanotube[17] was successfully dispersed by the addition of ionic surfactants such as sodium dodecyl sulfate, NaDDBS and Dowfax. Hyung *et al.*[18] found that natural organic matter served to stabilize carbon nanotube aqueous suspensions. In Sh *et al's.* work[19] the dispersion and stability of carbon black nanoparticles was studied and it was found that the optimum conditions could be achieved in colloidal mixture containing CB and Triton X-100 in a weight ratio of 2:1. Yu *et al.*[20] reported that the ethylene glycol based nanofluids containing graphene nanosheets was developed *via* a facile technique. The thermal conductivity of the base fluid was increased significantly by the dispersed graphene: up to 86 % increase for 5.0 vol % graphene dispersion.

Literature survey reveals that nanofluids dispersing copper[21], aluminium[22], tin[23], iron[24] and their oxide, titania[25] and gold[26] nanoparticles have been widely investigated with water, ethylene glycol, toluene, engine oil, poly oil, decene and FC-72 as base fluid and their results are published in the peer reviewed journals. However, very few reports are available on sodium[27,28] aluminium[22] lithium[29,30] based carbon nanofluids, which has excellent chemical and physical stability, even though it is not widely investigated. Therefore, in the present study, the chemical reduction method, which is simple two-step process involving simultaneous formation of metal treated carbon nanoparticles and the subsequent dispersion of the nanoparticles in the base fluids with an aim of obtaining an effective water-based carbon nanocolloid which have good dispersion effect, excellent electrical conductivity and improved thermal conductivity and could used for thermal and electrical transport applications.

EXPERIMENTAL

The carbonaceous materials (active carbon, activated carbon fibers, carbon black) were kindly provided by Carbon Nano-material Technology Co. Ltd., Korea and used as received. To oxidize the surface of the carbonaceous materials, *m*-chloroperbenzoic acid (MCPBA) was used as an oxidizing reagent and was purchased from Acros Organics, New Jersey, USA. Lithium hydroxide monohydrate, aluminum hydroxide, sodium bicarbonate were used as the dopant source, which was purchased from Daejung Chemicals & Metals Co. Ltd., Korea. Distilled water was used in all studies.

Preparations of nanoscaled pristine carbon materials: A three-roll mill is an alternative dispersing method commonly used in ink and electronic industry and was already successfully used to disperse carbon nanotubes in epoxy[31,32]. Shear forces are applied to the agglomerates while they are passing through the gap of two rolls rotating in opposite directions with different velocity. Unlike stirring, that can cause breakage of individual tubes[33], this method has only little destructive effect on the carbon nanotubes. Relevant processing parameters are the viscosity of the fluid and the gap width and velocity of the rolls. So in this study, in order to obtain nanoscaled carbon materials the preparation of carbonaceous nanofluids including: milling the activated carbon to the optimal size by ball milling and mono-planetary high energy milling. Activated carbon (AC), activated carbon fiber (ACF) and carbon black (CB) were selected as the starting carbonaceous materials. In a typical treatment, 8 g of carbonaceous materials was ball milled for 48 h at room temperature in a laboratory tumbling ball mill. The mechano-chemically carbon materials were obtained using a laboratory Pulverisette 6 mono-planetary high energy mill (Idar-Oberstein, Frisch, Germany) for 1 h with ZrO_2 ball (1 mm × 300 g). Nanoscaled activated carbon fiber and carbon black were also obtained using the same method.

Preparations of water based carbon nanofluids: Carbonaceous materials present remarkable intrinsic properties, but for many applications in which they have to interact with or to be integrated in a given system, it is necessary to functionalize their surfaces to obtain higher performance. Schierz *et al.*[34] reported that there was a pronounced influence of surface treatment on the behaviour of the carbon nanotubes in an aqueous suspension. In particular, although no specific study has yet appeared on the subject, it has been shown that functionalization should be performed to produce well dispersed supported catalysts[35]. For example, among the main processes for carbon nanotube surface functionalization[36], fluorination or the introduction of oxygenated groups are used most frequently, due to the simplicity of the relevant reactions involved and the feasibility of further reactions after these treatments. The purpose of these oxidative treatments is as follows: (i) to improve the carbon nanotube and graphene interactions with the solvents and dispersion; (ii) to allow the grafting of nanoparticles; (iii) to modify the carbon nanotube and graphene adsorption properties; or (iv) to perform chemical treatments on the carbon nanotube and grapheme[37,38]. In the present study, *m*-chloroperbenzoic acid (*ca.* 2 g) was suspended in 80 mL benzene as a solvent. Subsequently, 0.2 g of activated carbon, activated carbon fiber and carbon black were placed into the agent solution. The mixture was treated by magnetic stirring for 6 h at 343 K. Furthermore, the resulting solution was washed continuously with deionized water and ethanol before drying at 363 K. Finally, the oxidized activated carbon, oxidized activated carbon fiber and oxidized carbon black were obtained and named OAC, OACF and OCB, respectively.

The milled and treated carbon materials (OAC, OACF, OCB) were ultrasonicated in 200 mL of distilled water containing 0.05 mol $LiOH·H_2O$, 0.05 mol $Al(OH)_3$) and 0.05 mol $NaHCO_3$ respectively, using a VCX750 Ultrasonic Probe CV33 at 1.3×10^5 J power. After the intensive sonication treatment for 1 h, thus different stable metal treated carbon materials in water-based nanofluids was obtained.

Characterization: The composites were characterized by scanning electron microscopy using a JSM-5200 JOEL equipped with an X-ray detector for energy dispeisive X-ray analysis. The dispersion effect of the carbon nanofluids were examined by UV-VIS spectroscopy (Optizen POP, Mecasys Co. Ltd., Korea) with the absorbance change in the nanofluids, which was measured as function of the concentration and time. In this study, a transient hot-wire method was used to measure the thermal conductivity of the nanofluids. Every sample was tested by 5 times and obtained their mean value. For comparison, the base fluid (water) was used and their thermal conductivity was 0.604 W/m K (THW). The hot wire method is a standard transient dynamic technique based on the measurement of the temperature rise in a defined distance from a linear heat source (hot wire) embedded in the test material. If the heat source is assumed to have a constant and uniform output along the length of test sample, the thermal conductivity can be derived directly from the resulting change in the temperature over a known time interval[39]. The hot wire probe method utilizes the principle of the transient hot wire method. Here the heating wire as well as the temperature sensor (thermocouple) is encapsulated in a probe that electrically insulates the hot wire and the temperature sensor from the test material[40].

The ideal mathematical model of the method is based on the assumption that the hot wire is an ideal, infinite thin and long line heat source, which is in an infinite surrounding from homogeneous and isotropic material with constant initial temperature. If q is the constant quantity of heat production per unit time and per unit length of the heating wire (W m^{-1}), initiated at the time t = 0, the radial heat flow around the wire occurs. Then the temperature rise ΔT (r, t) at radial position r from the heat source conforms to the simplified formula:

$$k = [q/4\pi\Delta T(r, t)] \ln (4 a t/r^2 c) \qquad (1)$$

where, k is the thermal conductivity (W m^{-1} K^{-1}), a thermal diffusivity (m^2 s^{-1}) ($a = k/\rho c_p$, with ρ is the density (kg m^{-3}) and c_p the heat capacity (J kg^{-1} K^{-1}) of the test material and C = exp(γ), γ = 0.5772157 is the Euler's constant. A WalkLAB digital conductivity pro meter (Trans Instruments (S) Pte Ltd., Singapore) was used to obtain a precise measurement of the electrical conductivity.

RESULTS AND DISCUSSION

Morphology and structure analysis: The typical micro-surface structures and morphology of the as-prepared metal treated ACF nanofluids samples were characterized by SEM (Fig. 1). From Fig. 1(a) and 1(b), it can be observed that although there are signatures of agglomeration present in the micrograph, the particles are truly nanometric. It can be attributed that when the metal treated carbon nanofluids was milled and ultrasonicated, almost of the ACF structure was interrupted. However, since the carbon nanofluids was treated by $NaHCO_3$ and ultrasonicated, a few of ACF could be clearly ascertained from the figure and the surface of ACF was coated with some white particles which can be considered as $NaHCO_3$ materials. From the results it was observed that these suspension included micrometer and nanometer particles and even size of about 100 nm was obtained. It was beneficial for the enhancement of the dispersion effect of these composites.

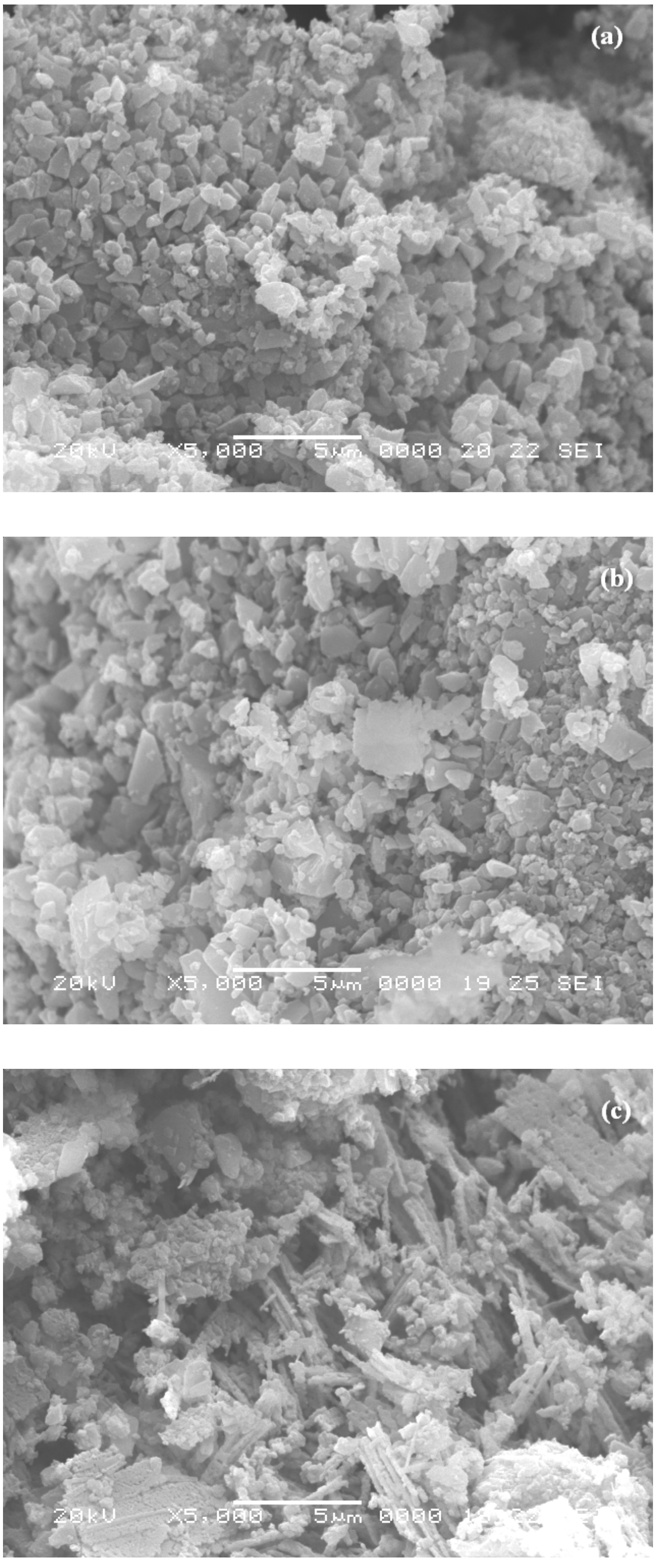


Fig. 1. SEM micrographs of metal treated ACF composites samples. (a) AlOACF, (b) LiOACF (c) NaOACF

Energy dispeisive X-ray is conducted on several zones of the composite. The main elements and wt. % found in a representative analysis are shown in Fig. 2. As observed in Fig. 2, four kinds of composites have not only the peaks for C and O but also the peaks of Na and Al. However, for LiACF smaple, the Li element was not existed which may be considered the very low amount of $LiOH{\cdot}H_2O$ used in this study.

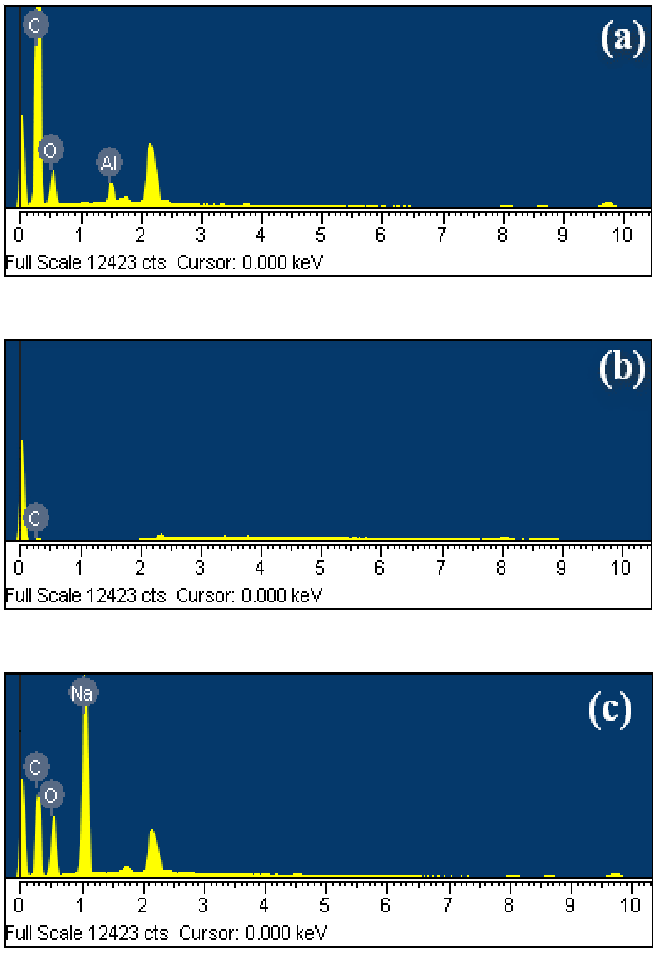


Fig. 2. EDX elemental microanalysis for metal treated ACF composites samples. (a) AlACF, (b) LiACF, (c) NaACF

Dispersion effect: One important characteristic of metal treated carbon nanofluids is that they have good dispersibility in water. In this study, the dispersion test was carried out by placing 0.2 g of OAC, OACF and OCB each into 200 mL of distilled water containing 0.05 mol $LiOH{\cdot}H_2O$, 0.05 mol $Al(OH)_3$) and 0.05 mol $NaHCO_3$ and ultrasonicated for 1 h respectively. The metal treated carbon nanofluids were then diluted to 10 wt. % with distilled water. As shown in Fig. 3, after the OAC, OACF and OCB were dispersed in distilled water by ultrasonication for 1 h, all the samples were kept stable in distilled water for weeks. This suggests that all the prepared Li ion treated carbon materials have good dispersibility in water. Taking into consideration all the process parameters and their possible influences on the particle properties, we chose one kind of typical sample (AC) before sonication as a process-testing example. As seen in Fig. 4, an average diameter of 1 μm was obtained by laser particle size analyzer (model: analysette 22 Nano Tec). The particle size primarily ranged from 0.1 to 10 μm.

The prepared oxidized carbon nanofluids, which contained 10 wt % and their dispersion effect with a function time (0, 1, 2, 5 and 10) was measured by their absorbance using UV-VIS spectroscopy. Fig. 5 shows the absorbance of the as-prepared metal treated carbon nanofluids as a function of time for different contents of carbon materials (OAC, OACF, OCB). After 10 h, the absorbance of OAC and OACF were similar to that observed at 0 h, suggesting that OAC and OACF had good dispersibility in water. For OCB, the absorbance was lower than observed at 0 h, indicating that the dispersibility of OCB was lower than that of OAC and OACF. These results indicate that oxidized activated carbon has the best dispersibility in water. After treatment of three kinds of metal ions, the absorbance for NaAC, AlACF and LiCB shown us this three kinds of smaples have very good dispersibility. And the dispersion effect of carbon nanofluids was improved after treated with metal ions.

Fig. 3. Photographs of the typical Li treated carbon nanofluids (containing 10 wt % carbon materials (Li-OAC, Li-OACF, Li-OCB)) dispersed in distilled water

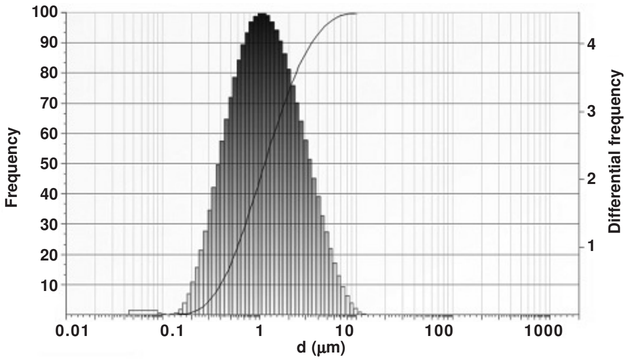
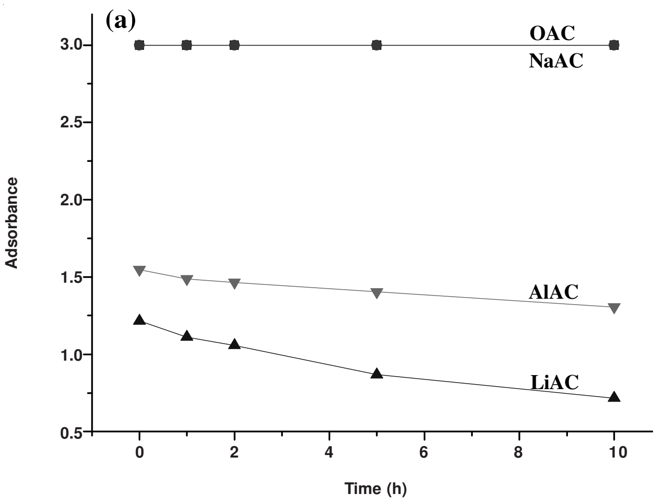


Fig. 4. Partical size distribution of typical carbon material (activated carbon) before sonication



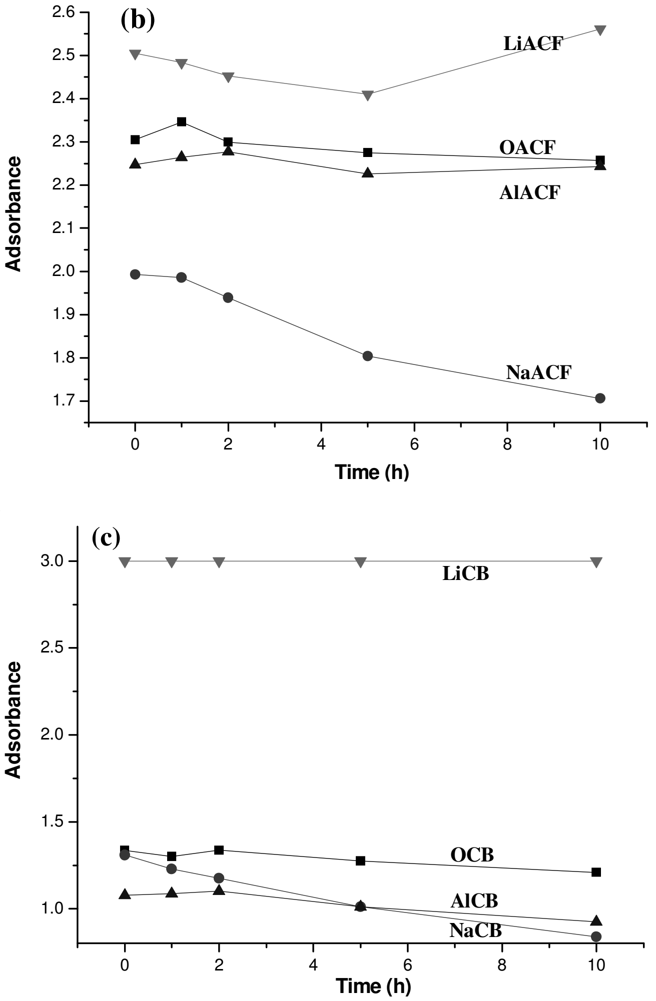


Fig. 5. UV-VIS absorption of metal-carbon materials (AC, ACF,CB) composites dispersed in distilled water as a function of time (10 wt % carbon materials). (a) metal-AC, (b) metal-ACF and (c) metal-CB

Thermal diffusivity: Theoretically speaking, the thermal diffusivity of metal-carbon nanofluids is only dominated by three factors including the density ρ, specific heat c_p and thermal conductivity k. Their product, namely $a = k/\rho c_p$, stands for the thermal diffusivity of metal-carbon nanofluids. Fig. 6 shows the results of the histogram experiments for the thermal diffusivity test. The results were compared with the technical indicator of new-type materials. Here their thermal diffusivity is worth to emphasize. From these results, it is clearly observed that in comparison of pristine carbon materials its thermal diffusivities were increased inordinately after oxidizing process, after the carbon nanofluids were treated with different metal ions, there were some changes to thermal diffusivity. Among these smaples, the Al treated oxidized carbon nanofluids (AC, ACF, CB) showed the best thermal diffusivity and their thermophysical properties were enhanced to 0.112, 0.088 and 0.106 mm^2/s compared with pristine carbon. This might be estimated that special electronical property of these metal ions might play an important role to the increase in thermal diffusivity of as-prepared nanofluids.

Electrical conductivity: Fig. 7 shows the changes in the electrical conductivity of different nanofluids. The electrical conductivity of the Li treated carbon nanofluids increased more than that of primary carbon nanofluids. For the carbon nanofluids (OAC, OACF, OCB), the electrical conductivity of the products on sample OAC was slightly higher than those on sample OACF but lower than those on sample OCB. This indicates that the oxidized carbon black showed the highest electrical conductivity after the acid treatment.

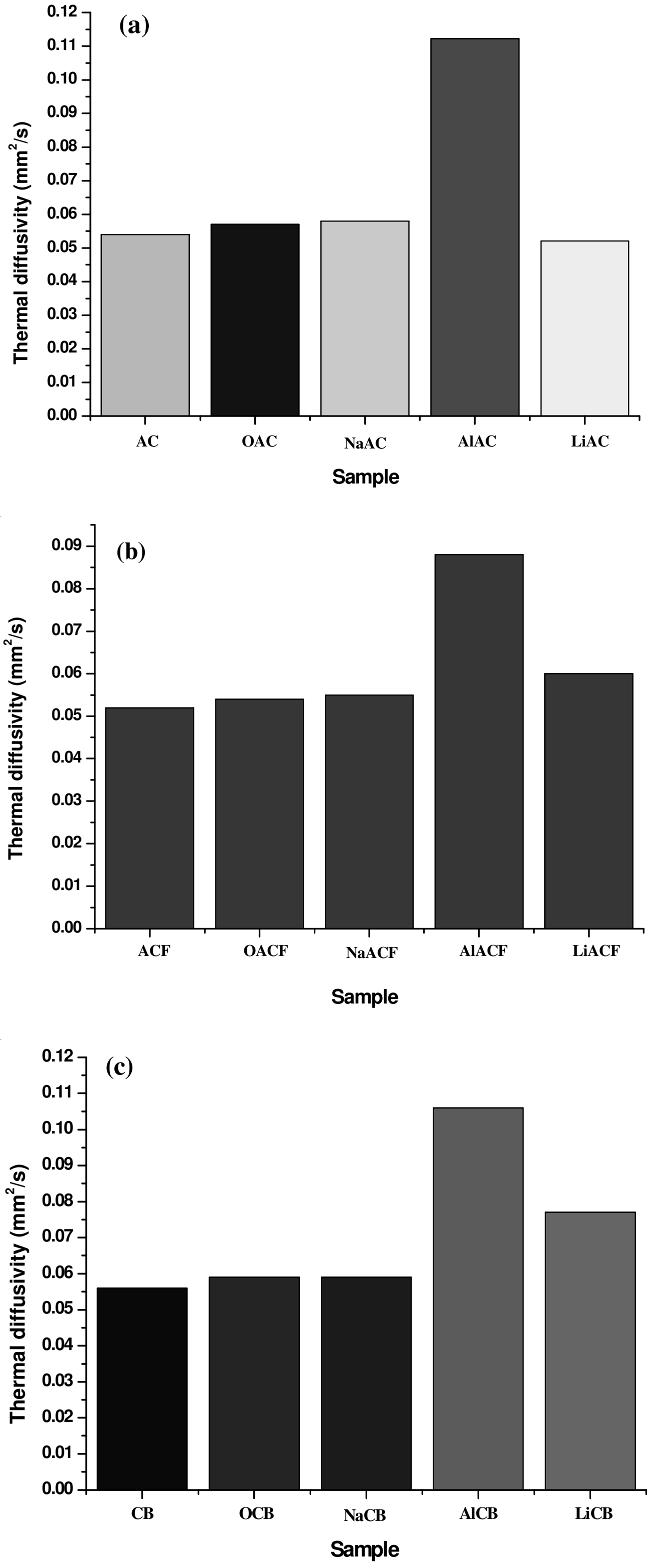


Fig. 6. Thermal diffusivity of metal-carbon materials (AC, ACF,CB) composites in the presence of water. (a) metal-AC, (b) metal-ACF and (c) metal-CB

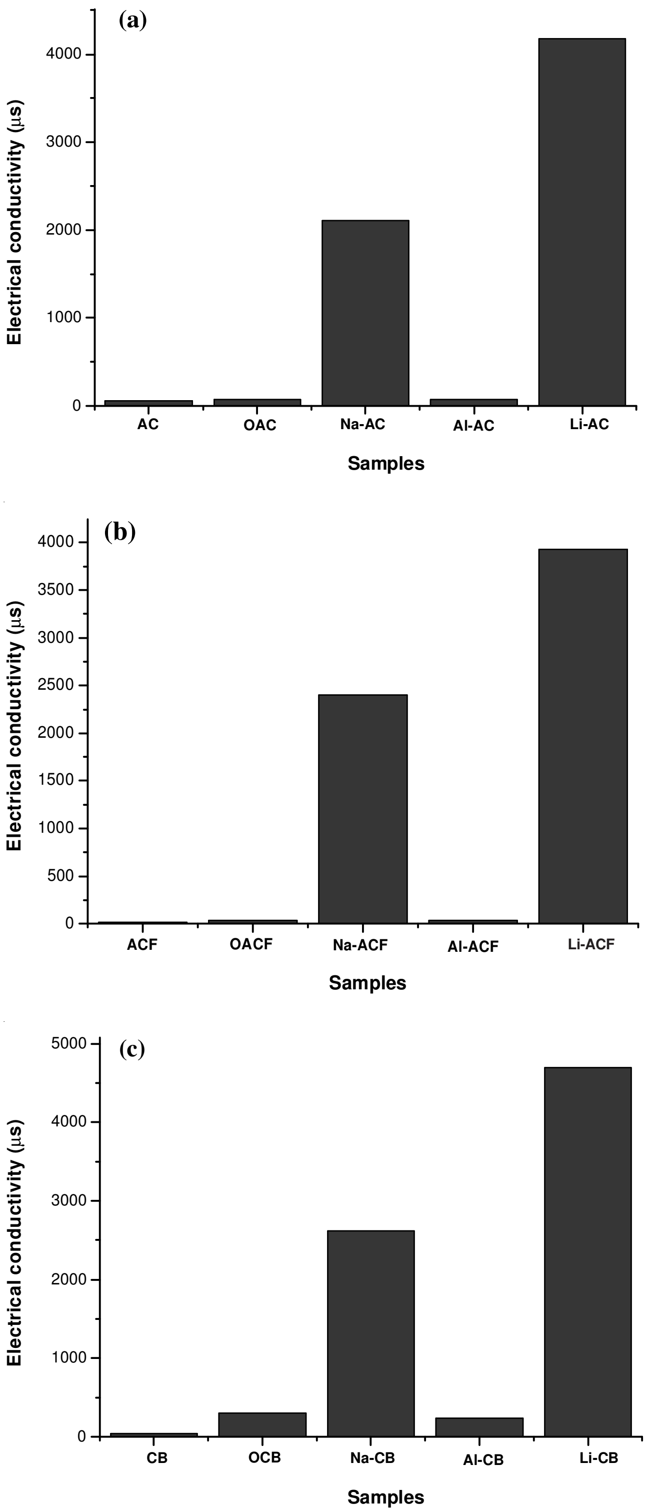


Fig. 7. Electrical conductivity of metal-carbon materials (AC, ACF, CB) composites in the presence of water. (a) metal-AC (b) metal-ACF and (c) metal-CB

The electrical conductivities of the Li treated carbon nanofluids (Li-AC, Li-ACF, Li-CB) largely increased after the different metals treatment. The electrical conductivity of all Li treated carbon nanofluids was larger than those carbon nanofluids, which were 4180, 3930 and 4700 μS/cm for Li-AC, Li-ACF and Li-CB, respectively. And the sodium treated AC, ACF, CB nanofluids also shown good electrical conductivities compared with pristine carbon materials, which were 2110, 2400 and 2620 μS/cm for Na-AC, Na-ACF and Na-CB, respectively.

Conclusion

Activated carbon (AC), activated carbon fiber (ACF) and carbon black (CB) were chosen as carbon sources to examine the typical effects of metal treated water based carbon nanofluids. After the *m*-chloroperbenzoic acid treatment and mono-planetary high energy milling, the particle size of AC, ACF and CB decreased and these carbon materials had good dispersibility in distilled water. After different metal ions treatment, some significant changes in dipersion effect, electrical conductivity and thermophysical properties of the Na, Al, Li ion treated OAC, OACF and OCB nanofluids were observed. In particular, the electrical conductivity of the Li and Na treated carbon nanocolloid showed remarkable improvement due to the optical properties of carbonaceous nanomaterials and the added electrical properties of lithium and sodium ions.

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