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Thermal Conductivity Enhancement in Aqueous Suspensions of Carbon Multi-Walled and Double-Walled Nanotubes in the Presence of Two Different Dispersants

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Carbon multi-walled nanotubes (C-MWNTs) and alternatively carbon double-walled nanotubes (C-DWNTs) were added in water, following our previous work, in order to enhance the thermal conductivity of this traditional heat transfer fluid. Hexadecyltrimethyl ammonium bromide (CTAB) and Nanosperse AQ were employed as dispersants. The transient hot-wire technique was used for the measurement of the thermal conductivity with an instrument built for this purpose. The absolute uncertainty is better than 2%. The maximum thermal conductivity enhancement obtained was 34% for a 0.6% volume C-MWNT suspension in water with CTAB. All measurements were made at ambient temperature. In an attempt to evaluate and explain the experimental results, information about the microstructure of the suspensions is needed. The findings of these investigations are presented here along with the analysis.

KEY WORDS: CTAB; DWNT; MWNT; nanofluid; Nanosperse; thermal conductivity; transient hot-wire method.

1. INTRODUCTION

Carbon nanotubes are a relatively novel material, and the scientific community shows much interest in them. Since their discovery by Iijima [1]

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in 1991, many different uses have been proposed because of their unique properties. Suggestions have been made for a wide range of applications, such as nanothermometers [2], transistors [3], hydrogen storage [4], introduction in biologically relevant systems [5], low-friction nanoscale linear bearings [6], electromechanical nanotweezers [7], and more.

The low thermal conductivity of conventional fluids has held back the development of heat transfer applications. Since carbon nanotubes exhibit a very high thermal conductivity [8], it is interesting to disperse small amounts of them in traditional fluids. The effective thermal conductivity of the resulting nanofluid shows considerable enhancement compared to that of the heat transfer fluid. It should be noted that, although nanofluids are multiphase systems, from a practical point of view it is possible to speak of the property of the assembly. Hence, in this paper, the property referred to as thermal conductivity is correctly the effective property of the complex system.

This work follows previous studies [9, 10] in the area of nanofluids. It was shown that the dispersion of Carbon multi-walled nanotubes (C-MWNTs) is possible using sodium dodecyl sulfate (SDS) as a surfactant. Ultrasonic homogenization was employed, in order to achieve a uniform dispersion. The maximum enhancement of the thermal conductivity, 38%, was measured for a 0.6 vol% suspension of C-MWNTs water with 0.1 mass% SDS (sample subjected to 30 min of ultrasonic homogenization). The aim of this work, following previous studies [9], was the investigation of the thermal conductivity increase of water when C-MWNTs or C-DWNTs are added. Hexadecyltrimethyl ammonium bromide (CTAB) and Nanosperse AQ were employed as dispersants.

2. CARBON NANOTUBE CHARACTERIZATION

The C-MWNTs employed in this work were produced by MER Corporation, U.S.A., by the catalytic decomposition method. ILJIN Nanotech Co. Ltd., Korea produced the C-DWNTs, using the chemical vapor deposition (CVD) method. The nanotubes were characterized, following the practice of our earlier work [9], by means of transmission electron microscopy (TEM), scanning electron microscopy (SEM), and micro-Raman spectroscopy.

2.1. Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) observations were performed with JEOL 120UX and JEM-2010 electron microscopes operating at 100 and 200 kV, respectively.

2.1.1. TEM for C-MWNTs

Typical selected area diffraction (SAD) images of this type of material show discrete spots in the 0002 graphite ring, which confirm the existence of C-MWNTs. Conventional transmission electron microscopy (C-TEM) and high resolution transmission electron microscopy (HR-TEM) were also employed, in order to get details of the structural characteristics of the nanotubes.

Careful examination of the photographs revealed the following. The length of the nanotubes exceeded 10 μm, and the outer diameters ranged from 100 to 250 nm, with an average value of 130 nm. The thickness of the walls was also measured, and the results showed that the main part of the C-MWNTs consists of nanotubes with nearly 90 graphitic layers. The sheets are closed at the end of the nanotube. Furthermore, it is pointed out that the pictures showed the systematic presence of graphitic onions.

2.1.2. TEM for C-DWNTs

The main characteristic of this sample was the presence of closely packed groups of nanotubes. It was impossible to resolve these formations in a finest distribution. Bright field (BF) and dark field (DF) C-TEM images were taken. They confirm the appearance of long and flexible nanotubes intertwined in thicker modules. The average outer diameter of the C-DWNTs was found to be about 5 nm, and the inner diameter was at least 2.5 nm. The SAD images taken from different regions of the samples reveal the existence of a considerable, but not dominant, amount of a second type of nanotube. In this type the graphite ring corresponding to 0002 reflection consists of distinguishable spots, thus confirming the existence of nanotubes with more than 10 graphitic layers. This observation is verified by BF C-TEM images. Rigid C-MWNTs coexist together with the dominant phase of flexible C-DWNTs. The outer and inner diameters of the C-MWNTs were measured from DF images. The average values were 40 and 15 nm, respectively. The aforementioned results suggest that the nanotubes are composed of 10–25 graphitic layers.

2.2. Scanning Electron Microscopy (SEM)

Scanning electron microscopy, SEM, (Model JEOL JSM-6300, 20 keV) was also employed. This method was used in order to obtain information about the morphology of the specimens.

2.2.1. SEM for C-MWNTs

It was found that the specimen consists of well-defined nanotubes gathered in bundles, and average lengths over 40 μm were revealed. Further examination verified the presence of graphitic onions, which were observed by TEM, as well as nanotubes in a wide range of diameters. It is pointed out that the nanotubes appear to be distinguished from one another.

2.2.2. SEM for C-DWNTs

The C-DWNTs were also studied by SEM. Photographs taken showed nanotubes with different diameters. This observation leads to the conclusion that the sample consists of compact aggregates and that it may not contain double-walled nanotubes exclusively. These observations are in agreement with the results obtained by TEM. The nanotubes are tangled in bundles, and they form packed agglomerates. Additionally, they are curved and not oriented. Nanotubes with lengths over 20 μm can be found. It is clear that the specimen is not uniform and that the existing close-packed C-DWNTs cannot be considered as nano-dimensional material in their bulk form.

3. DISPERSION OF NANOTUBES IN WATER

Water is a widely used heat transfer fluid, and it is of particular interest due to its presence in biological systems. Nanotubes cannot be directly dispersed in water, since there is no chemical affinity between the two compounds. Mixing these materials directly leads to unstable, non-uniform suspensions. Sedimentation starts almost instantly. In order to obtain a homogeneous and relatively stable solution, two procedures were combined. A dispersant was added, and the mixture was homogenized by ultrasonic vibration (Model HD 2200 Bandelin Electronics). This procedure has been successfully used in the first part of our research [9]. The existing agglomerates can be broken to smaller sizes by ultrasonic homogenization, but the nanotubes are broken to smaller lengths as well. An optimum homogenization time is considered.

In previous studies [9] C-MWNTs were dispersed in water (Riedel-de Haën, CHROMASOLV) with the aid of SDS. The thermal conductivity enhancement achieved for a 0.6 vol% C-MWNT suspension in water was 38%. In this work hexadecyltrimethyl ammonium bromide (Fluka, Biochemica), CTAB, and Nanosperse AQ (NanoLab Inc.) were employed as dispersants. CTAB is a known cationic surfactant [11], while Nanosperse AQ is one of the first dispersants for carbon nanotubes in water made available commercially.

This study is also one of the first attempts to study aqueous suspensions of C-DWNTs. The double-walled nanotubes could not be dispersed directly into water. It was first attempted to prepare samples with SDS, but they were not uniform. The addition of CTAB and Nanosperse AQ alternatively resulted in equally homogeneous suspensions. It is pointed out that the synthesis of the latter is not known. This is the reason why CTAB was chosen to enable the dispersion for this series of experiments.

The following type of suspensions were finally prepared and measured:

(1) *Group A suspensions*. These were prepared by first adding CTAB in water and then C-MWNTs. The resulting mixture was placed in an ultrasonic homogenizator for a period of time ranging from 5 to 50 min.

(2) *Group B suspensions*. These were formed by first adding Nanosperse AQ in water and then C-MWNTs. The resulting suspension was again homogenized by ultrasonic vibration for a period of time ranging from 5 to 80 min.

(3) *Group C suspensions*. The dispersant CTAB was first added in water and then C-DWNTs. The ultrasonic homogenization time ranged from 5 to 120 min.

Optical observation showed that the increase of the CTAB concentration in the C-MWNT suspensions produced samples with slightly better homogeneity. The increase of the ultrasonic treatment duration led to more uniform specimens. Hence, in addition to the measurement of the actual enhancement of the thermal conductivity of these suspensions, the impact of the effects of the concentration of the dispersant CTAB and of the homogenization time need also to be investigated.

The addition of Nanosperse AQ in water initially led to unstable suspensions, but this changed with increasing duration of ultrasonic vibration. The effect of the homogenization time needs to be taken into account.

Furthermore, suspensions of C-DWNTs were studied. It was decided to employ CTAB as the dispersant, since it to helped prepare more stable samples with small duration of ultrasonic homogenization. The influence of several parameters on the enhancement of the thermal conductivity was examined. The concentration of C-DWNTs and CTAB, as well as the duration of ultrasonic homogenization, were investigated.

4. CHARACTERIZATION OF THE SUSPENSIONS OF NANOTUBES

In order to characterize the suspensions, whose thermal conductivity was to be measured, SEM and micro-Raman spectroscopy were employed. The aforementioned techniques were selected, because it has been shown [9] that they can generate valuable information about the structure of the dispersions and the interactions between the substances constituting the samples.

4.1. SEM Results

Scanning electron microscopy, SEM (Model JOEL JSM-6300, 20 keV), was employed in order to derive information about the morphology of the suspensions. Typical results for the different groups of suspensions are:

(1) 0.6 vol% C-MWNT with 6 mass% CTAB (Group A), homogenization for 12 min.

(2) 0.6 vol% C-MWNT with 0.7 mass% Nanosperse AQ (Group B), homogenization for 60 min.

(3) 0.75 vol% DWNT with 1 mass% CTAB (Group C), homogenization for 10 min.

4.1.1. Suspension of 0.6 vol% C-MWNT with 6 mass% CTAB (Group A), 12 min Homogenization

This is a uniform suspension of well-defined C-MWNTs. The sample contains nanotubes more than 20 μm long, as can be seen in Fig. 1. It is pointed out that formations of carbonaceous material are found throughout the specimen. They are probably the graphitic onions observed by TEM. Further observation of the photographs reveals a uniform distribution of diameters with a mean size of about 120–130 nm. This result is in agreement with the findings of the TEM analysis.

4.1.2. Suspension of 0.6 vol.% C-MWNT with 0.7 mass% Nanosperse AQ (Group B), 60 min Homogenization

In this suspension Nanosperse AQ was used as a dispersant for the first time. Macroscopically, the sample is a uniform black liquid. The SEM photographs verified the observed uniformity and revealed a compact network of nanotubes surrounded with a “coating”, which is believed to be the dispersant. No conclusion could be drawn for the lengths of the nanotubes. Nevertheless, as it can be seen in Fig. 2, the outer diameter is about 130 nm, as was measured by TEM.

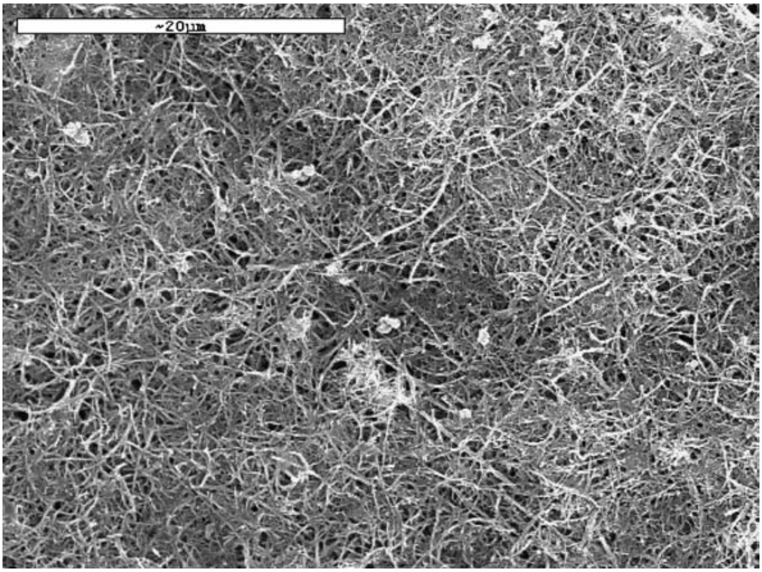

Fig. 1. Suspension of 0.6 vol% C-MWNT with 6 mass% CTAB (Group A), 12 min, magnified 2500 times.

4.1.3. Suspension of 0.75 vol.% DWNT with 1 mass% CTAB (Group C), 10 min Homogenization

The particular form of this sample is notable. Macroscopically it is a uniform suspension of relatively coarse-grained powder. The SEM analysis shows that the nanotubes are tangled firmly together, in a way that it makes it difficult to talk about a "nanofluid", as is shown in Fig. 3. Configurations of nanotubes of various diameters can be seen (from less than 10 to 70 nm). It is noted that this observation is in agreement with the TEM measurements, which showed presence of C-MWNTs in the C-DWNT bulk form. Furthermore, the evaluation of a mean length for this sample was not possible due to the form of the nanotube network. Nevertheless, nanotubes more than 7 μm long were found.

4.2. Spectroscopic Results – Micro-Raman Spectroscopy

The micro-Raman spectroscopic technique was also employed in this work in order to investigate the effect of the dispersant and the homogenization on the aqueous suspensions of C-MWNTs and C-DWNTs. The Raman spectra were recorded using a triple monochromator (DILOR XY)

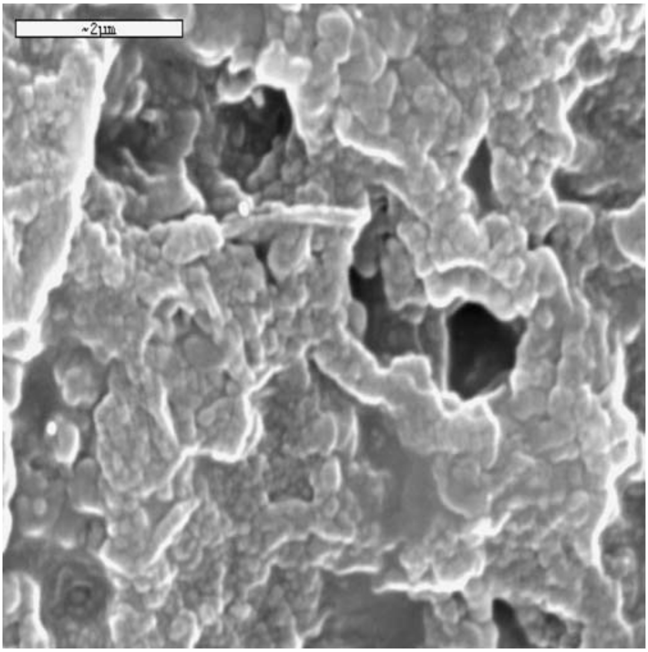

Fig. 2. Suspension of 0.6 vol% C-MWNT with 0.7 mass% Nano sperse AQ (Group B), 60 min - magnified 15000 times.

equipped with a CCD liquid-nitrogen-cooled detector system. The 514.5 nm line of an Ar^+ laser was used for excitation with the laser power kept below 0.05 mW, measured before the sample and focused with a 20× magnification lens, in order to eliminate the thermal-induced softening of the observed Raman peaks [12]. The spectra were calibrated by means of a neon lamp.

4.2.1. Micro-Raman Spectroscopy for C-MWNT and Their Suspensions

In the Raman spectrum of the starting C-MWNT material (not presented here), three main peaks can be resolved, located at 1354(2), 1582(2) and 1614(4) cm^{-1}. The strongest Raman peak at 1582 cm^{-1} is related to the E_{2g} mode of graphite, corresponding to carbon stretching vibrations and is the so-called G band of the carbon nanotubes (tangential band) [13]. The weaker peak at 1354 cm^{-1} is a disorder-induced mode in carbon nanotubes that also appears in graphite (D peak) [13]. Moreover, the peak having the highest frequency is also a defect-related peak (ω peak) [14].

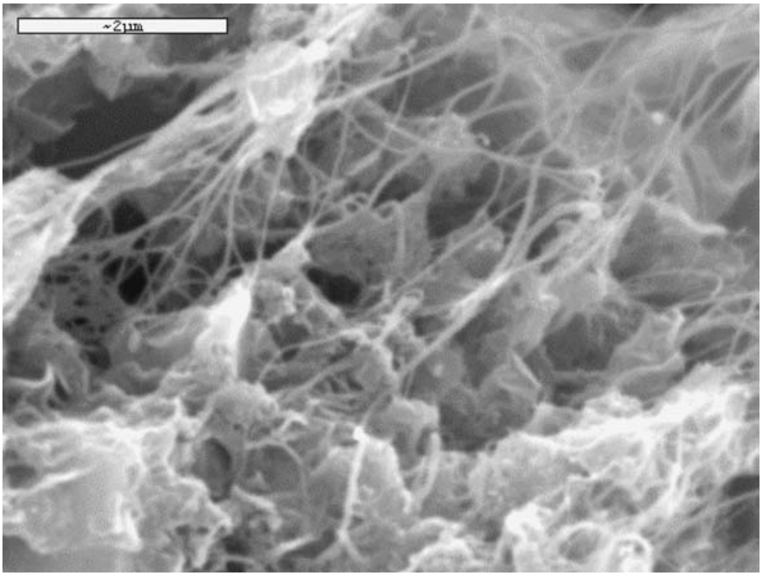

Fig. 3. Suspension of 0.6 vol% C-DWNT with 1 mass% CTAB (Group C), 10 min, magnified 16000 times.

The study of various C-MWNT suspensions after relatively short times of homogenization (5–12 min) indicates that, as the dispersant concentration increases, the Raman spectra preserve their main characteristics [15]. The ratio of the relative intensities$I_{\mathrm{D}}/I_{\mathrm{G}}$ remains almost constant. Only a relatively small broadening of the C-MWNT Raman peaks in the suspensions is observed, which can be associated with increased disorder. The almost unaffected$I_{\mathrm{D}}/I_{\mathrm{G}}$ ratio in the case of the C-MWNT suspensions, compared to the pronounced changes observed in the C-DWNT suspensions (discussed in the next section), could be explained on the basis of the significant contribution of inner carbon tubes in the measured Raman signal. This contribution smoothes out any changes in the spectrum caused by the possible modification of the surface of the outer tubes due to the presence of the CTAB. A quite small, and within the estimated error, hardening of the D, G (1–2 cm^{-1}), and ω (4–5 cm^{-1}) bands is observed in the various suspensions studied in comparison to those of the pristine material. This result is similar to earlier observations for C-MWNT suspensions in water, using SDS as the dispersant [9]. This hardening may be attributed to a moderate shortening of the C–C covalent bonds in the surface of the outermost carbon nanotubes resulting

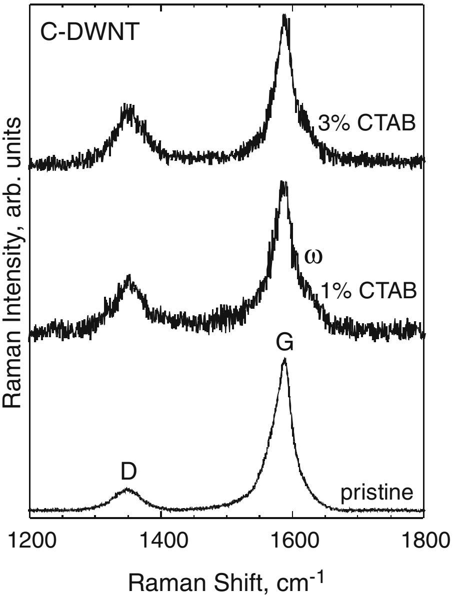

Fig. 4. Raman spectra in the frequency region 1200–1800 cm^{-1} of the pristine C-DWNT material and its suspensions with 1 and 3 mass% CTAB. The intensity of the suspension spectra in the "G" Raman peak region has been scaled to that of the starting material.

from the interaction between the nanotubes and the dispersant. Consequently, there is an indication that C-MWNTs interact with CTAB.

4.2.2. Micro-Raman Spectroscopy for C-DWNT and Their Suspensions

The Raman spectrum of the starting C-DWNT material was taken, and it was similar to that of C-MWNT. The G and the D bands can be clearly observed in the high-frequency region (bottom spectrum in Fig. 4). The former band appears to be asymmetric on the low-frequency side, reflecting the existence of both the inner and outer tubes constituting a C-DWNT. In addition to the high-frequency modes, relatively weak Raman peaks appear with frequencies lower than 400 cm^{-1} [15]. These low-frequency peaks were attributed to radial breathing modes (RBM) of the rolled graphene sheets [13].

The high-frequency Raman spectra of two representative C-DWNT suspensions, with 1 and 3 mass% CTAB, are also illustrated in Fig. 4. The D and G Raman peaks appear to be broader in the suspensions, while their frequency positions remain almost constant. Moreover, a relative – to the main G peak and to the defect-related ω peak – intensity enhancement of the low-frequency shoulder is observed in the suspensions. However, the most prominent effect found in the Raman spectra of the C-DWNT suspensions in the frequency region included in Fig. 4 is the significant increase of the integrated intensity ratio$I_D/(I_D + I_G)$, from$\sim$0.19 in the starting material to$\sim$0.37 in the water suspension containing 3 mass% of CTAB. These relative intensity changes are also accompanied by the disappearance of the RBM band and clearly suggest the distortion of the rolled graphene sheets and the modification of their C–C bond lengths, due to the presence of the dispersant in their neighborhood and/or to the sonication procedure of the suspensions [15]. It is important to note the similarity of the Raman spectra of the two C-DWNT suspensions containing different dispersant concentrations. This similarity is compatible with the comparable thermal conductivities of the 1 and 3 mass% CTAB C-DWNT samples (Section 5). Hence, it is concluded that the type of nanotubes used here interact with the dispersant employed in this study.

5. THERMAL CONDUCTIVITY MEASUREMENTS

The thermal conductivity of the nanofluids studied in this work was measured with the transient hot-wire method. The instrument developed for this purpose is described elsewhere [9]. The maximum thermal conductivity enhancement observed was 34%.

5.1. Suspensions of C-MWNTs

The suspensions of C-MWNTs in water consist of two groups. Group A is formed by aqueous 0.6 vol% C-MWNT samples with CTAB as the surfactant. For group B, Nanosperse AQ is used to disperse the nanotubes in water. The results of the thermal-conductivity measurements for the aforementioned suspensions are shown in Fig. 5. The y-coordinate is the enhancement ratio with respect to the thermal conductivity of water, and the abscissa is the total homogenization time.

Group A showed the largest increase of the thermal conductivity. The maximum thermal conductivity enhancement measured was 34%. This was observed in two samples of 0.6 vol% C-MWNT aqueous suspensions, with 1 and 3 mass% of CTAB, after subjecting both of them to 10 min of ultrasonic homogenization. This result is comparable with the ones reported in former studies [9]. Furthermore, the following observations are made.

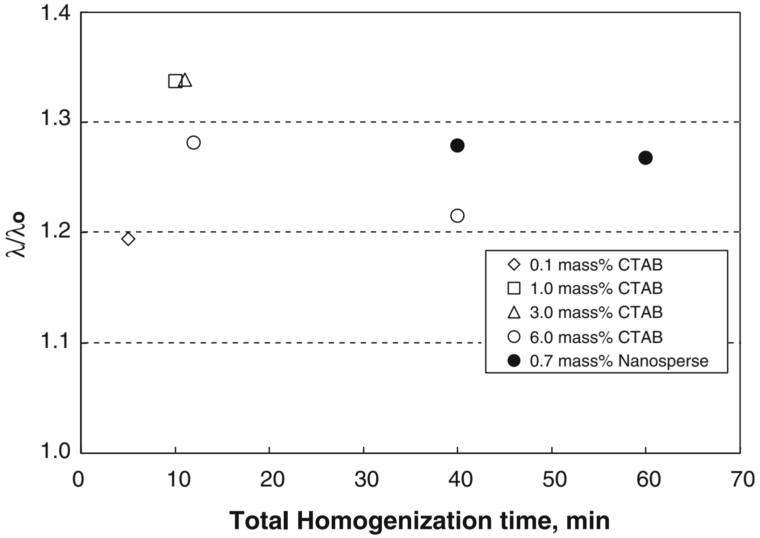

Fig. 5. Thermal conductivity measurements of 0.6 vol.% of C-MWNT suspensions in water (Group A samples – open symbols, Group B – closed symbols).

5.1.1. Effect of CTAB Concentration

It can be seen that the CTAB concentration has minor effects on the thermal conductivity of the suspension. It is noted that the presence of CTAB in water alone over a range of concentration from 0.1 to 6 mass%, leads to a small decrease in thermal conductivity (from 0.3 to 5%). At small concentrations and small homogenization times, the dispersed nanotubes form large agglomerates that have not yet been broken down. It is plausible to say that the nanotube network is not yet well defined. At medium CTAB concentrations, there is no significant impact on the studied property. For the highest CTAB content, it is apparent that the enhancement is smaller. It further decreases with an increase in homogenization time, as expected from the observations made in earlier studies [9].

It should be noted that, initially, an effort was made to disperse the nanotubes in water, without adding any other substance. The C-MWNTs could not be dispersed directly in the solvent. This behavior was expected, because water has no chemical affinity with carbon. Thus, it is necessary to add CTAB as the dispersant, in order to disperse the nanotubes in water, and to form stable samples. It is noted that the increase of the content of the surfactant (CTAB) leads to more uniform suspensions.

5.1.2. Effect of the Type of Dispersant

It is noted that a solution with the same amount of Nanosperse AQ in water as the one used in the C-MWNT suspensions leads to 1% decrease of the thermal conductivity. It is pointed out that for the same homogenization time, the enhancement is larger for the samples with Nanosperse AQ, rather than for the ones with CTAB. This fact could be attributed to the chemical composition of the commercially available product, which was not known to us. The suspensions prepared with the two types of dispersants were equally uniform, but the ones containing CTAB were more stable, as explained in the next section.

5.1.3. Effect of Homogenization Time

The homogenization time plays a key role in the stability of the suspensions. When the sonication time is very low (<5 min), the bundles of the nanotubes are not yet untangled. The subjection to ultrasonic homogenization for about 10 min leads to uniform, stable suspensions that still contain aggregates of considerable size. Further sonication breaks down the size of the agglomerates. It also decreases the length of the nanotubes [9, 16].

At this point it should be noted that C-MWNT suspensions with SDS have been reported to be relatively stable even after 8 h of sonication [9]. This is not the case for the samples either with CTAB or with Nanosperse AQ. The dispersions containing CTAB are not stable after homogenization for more than 60 min. Observations of samples using the commercial surfactant revealed stable dispersions for ultrasonic treatment from 30 to 60 min. Smaller or larger sonication times led to C-MWNT suspensions that precipitated quickly.

Possible explanations for the aforementioned observations are given below. At smaller sonication times the large aggregates of the nanotubes have not yet "interacted" with Nanosperse AQ and this is the reason why the nanotubes precipitated quickly. Furthermore, the subjection of the sample to ultrasonic homogenization is accompanied with heating of the suspension for the same amount of time. The sonicated dispersion was cooled with a water jacket, but the temperature reached 60^{o}C. The intensive sonication and the mild heating could have affected the bonds of the surfactant with the nanotubes. Should this be the case, the nanotubes have been deprived from the protective layer of the dispersant and, since they are no longer kept in suspension, they precipitate forming a separate phase.

The results presented here are in agreement with other studies [9, 17, 18]. The enhancement of the thermal conductivity due to the presence of nanoparticles has gained considerable interest [10, 19–27]. It was only

4 years ago that the study of the thermal conductivity of nanofluids containing C-MWNTs was initiated.

It should be mentioned that Choi et al. [17] studied the increase of the thermal conductivity of synthetic poly(a-olefin) oil caused by the addition of C-MWNTs (mean outer diameter, D, of about 25 nm and length, L, of about 50 μm, containing an average of 30 annular layers) and found a 2.6-fold increase at 1 vol% of nanotubes. It is noted that the length-to-diameter ratio was in this case about $L/D = 2000$. The thermal conductivity was measured with a bare-platinum transient hot-wire instrument. The enhancement that was observed for a 0.6 vol% suspension was about 60%. The results of this work are consistent with this value. It should be kept in mind that the nanotubes used in this study have a mean outer diameter of 130 nm (ranging from 100 to 250 nm) and a length of more than 20 μm, containing an average of 90 layers ($L/D = 154$). The greater length-to-diameter ratio and, perhaps, the narrower outer diameter range are believed to be responsible for the larger enhancement reported by Choi et al. [17]. Furthermore, the different procedure for the formation of the suspensions, as well as the dispersion of the C-MWNTs in a different continuous phase (water or poly(a-olefin) oil), have also affected the transport property studied.

Moreover, it is noted that the present results are comparable with our earlier work [9]. A 38% enhancement was previously measured for a 0.6 vol% C-MWNT suspension in water, containing 0.1 mass% SDS, subjected to 30 min of ultrasonic homogenization. It should be kept in mind that the dimensions of the carbon nanotubes employed in our previous studies ($D = 120$ nm, $L = 70 \mu$m, $L/D = 583$) are comparable to those of this work. This fact accounts for the similar enhancements for the aqueous suspensions studied.

The enhanced thermal conductivity of nanofluids containing C-MWNTs was also studied by Xie et al. [18]. The measurements were preformed with a Teflon-coated platinum transient hot-wire instrument. Nanotubes were dispersed in water, ethylene glycol, and decene. The authors observed a 19.6% enhancement for a 1 vol% suspension in decene with oleyamine as the surfactant. For a 0.6 vol% loading of nanotubes in decene, ethylene glycol, and water, the increase would be about 11, 8 and 5%, respectively. It is clear that the continuous phase employed for the dispersion of the nanotubes influences the studied property. This behavior is in agreement with our observations and the results of Choi et al. [17]. Moreover, the preparation method of the samples in this case involves intensive sonication, which has been found to shorten the dispersed nanotubes [9, 16]. It is feasible to say that the C-MWNTs used in the study of Xie et al. [18] were broken down to smaller pieces, compared to

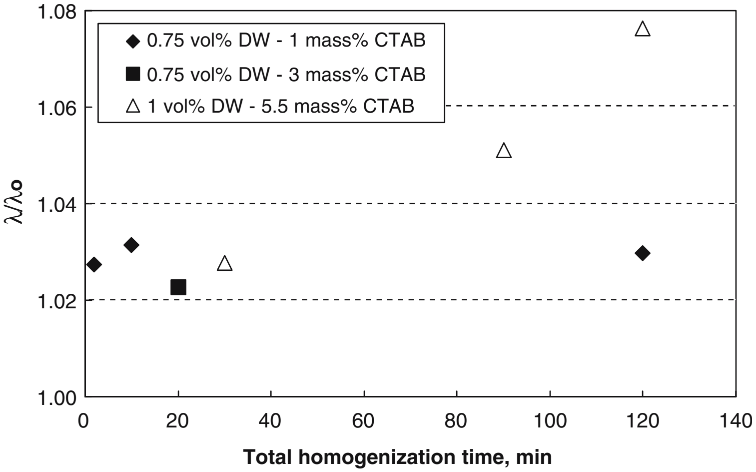

Fig. 6. Thermal conductivity measurements of C-DWNT suspensions in water (Group C samples).

the 30 μm of length in their bulk phase. This arrangement accounts for the smaller increase obtained by this group, and it is consistent with our former [9] and present results. It has been shown that the thermal conductivity enhancement increases with increasing L/D ratio.

Summarizing the points made above, the increase of the thermal conductivity observed in this work is consistent with other studies. It is influenced by the length-to-diameter ratio of the nanotubes(L/D), the type and content of the employed surfactant, the duration of ultrasonic homogenization, and the type of the continuous phase in which the C-MWNTs are dispersed.

5.2. Suspensions of C-DWNTs

The double-walled nanotubes were suspended in water with the aid of CTAB. Two concentrations of nanotubes were employed to account for the effect of this factor on the thermal conductivity of the dispersions. Different surfactant contents were also used. The resulting thermal conductivity enhancements are shown in Fig. 6 as a function of the total homogenization time.

The largest increase, 7.6%, was observed for a 1 vol% suspension of C-DWNTs in water with 5.5 mass% CTAB and 120 min of homogenization. The following results are noted

5.2.1. Effect of C-DWNT Concentration

The thermal conductivity enhancement appears not to be influenced by the C-DWNT concentration at lower homogenization times, even though the CTAB content also ranges from 1 to 3 mass% (Fig. 6). The unique form of these samples should be kept in mind. Although they are macroscopically uniform, the SEM analysis reveals closely packed nanotube bundles, up to medium homogenization times (approximately 30 min). It is clear that the dispersed phase (twined nanotubes) does not have dimensions in the range of nanometers. The dispersed phase is, in reality, micrometer-sized. This observation explains the small increase of the thermal conductivity. At higher homogenization times, the enhancement increases with greater C-DWNT content. This fact is attributed to the arrangement of the nanotubes in the suspension, and it is further explained in the following sections.

5.2.2. Effect of CTAB Concentration

Careful observation of the results in Fig. 6 for low and medium homogenization times demonstrates that the surfactant concentration has no apparent effect on the thermal conductivity enhancement. Nevertheless, the suspensions were more stable and more homogeneous with the augmentation of CTAB content.

The suspensions subjected to sonication for 120 min should be analyzed more carefully. It is possible that for higher homogenization times, the CTAB content affects the thermal conductivity enhancement, along with the amount of C-DWNTs added. The greater surfactant concentration is translated into a different orientation of the CTAB molecules in water and along the nanotubes. It is believed that this helps in the formation of stronger bonds with the double-walled nanotubes, thus aiding in the structure of a nanotube network. The increased uniformity of the samples is consistent with this observation.

5.2.3. Effect of Homogenization Time

The overall duration of sonication strongly affects the thermal conductivity of the suspensions. Subjection of the sample to ultrasonic homogenization for up to 30 min did not result in considerable untangling of the nanotube bundles. As the sonication time increased, the aggregates were progressively broken down and this phenomenon was more obvious after treating the dispersions for 90 min and more. Further homogenization (up to 4 h) reduced the size of the agglomerates and helped the untwining of the nanotubes.

Nevertheless, the samples that were vibrated for more than 2 h were not stable. The intensive sonication along with the elevation of the temperature probably influenced the binding of CTAB with the C-DWNTs. Hence, it is believed that the nanotubes were left without a surrounding coating of dispersant. This constitutes a possible explanation for the precipitation of the nanotube phase.

The results obtained in this work are comparable with those obtained by Choi's group [28]. The thermal conductivity enhancement observed for C-DWNT suspensions in their case was 2–3%. It should be noted that the nanotubes dispersed by both groups were purchased from ILJIN Nanotech Co. Ltd. The use of the same raw material facilitates the comparison of the measured enhancements. Both groups anticipated a greater increase, taking into account the length-to-diameter ratio of the double-walled nanotubes. Nevertheless, the form of the bulk sample should be carefully considered. It is suggested that the close-packed bundles of nanotubes, which are twined, do not constitute a nanometer-sized material. Thus, it is difficult to consider the prepared samples as 'nanofluids', and the obtained results are fully understood.

6. CONCLUSIONS

The thermal conductivity enhancement of suspensions of C-MWNTs and C-DWNTs in water was investigated. The nanotubes were dispersed with the aid of CTAB and Nanosperse AQ. Two main conclusions were drawn from the experiments and verified by the SEM and Raman analysis:

(a) The enhancement of the thermal conductivity increases with an increase in the length-to-diameter ratio in the nanometer scale range.

(b) CTAB is probably a suitable dispersant, since there is a strong indication that it interacts with both C-MWNTs and C-DWNTs, modifying the surface of the outermost nanotubes.
The largest thermal conductivity enhancement observed was 34%. In order to avoid intensive sonication, which shortens the nanotubes, a dispersant is needed. It seems that CTAB is a good choice.

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