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Review on the Preparation and Thermal Performances of Carbon Nanotube Contained Nanofluids

Huaqing Xie* and Lifei Chen

School of Urban Development and Environmental Engineering, Shanghai Second Polytechnic University, Shanghai 201209, China

ABSTRACT: Carbon nanotubes (CNTs) with ultrahigh thermal conductivity and very large aspect ratio have been proposed as excellent dispersions for preparing nanofluids, a new kind of thermal performance enhanced heat transfer media. In the past decade, various techniques have been developed to produce homogeneous and long-term stable CNT contained nanofluids with or without using surfactants. The thermal performances including thermal conductivity, convective heat transfer coefficient, and boiling critical heat flux have been investigated. Efforts have been taken to elucidate the heat transfer mechanism in CNT nanofluids, and theoretical models have been proposed to predict the thermal conductivity enhancement of CNT nanofluids. This article aims to address the preparation techniques and the experimental and theoretical studies on the heat transfer charicteristics of CNT nanofluids.

1. INTRODUCTION

Carbon nanotubes (CNTs) are tubular carbon molecules with remarkable mechanical, chemical, thermal, and electrical properties. They have been paid increasing attention ever since their discovery in 1991[1] because of the unique structure, novel properties, and potential applications. Nowadays, a large quantity of CNTs can be produced by either arc discharge or thermal decomposition of hydrocarbon vapor, which provides the opportunity to utilize CNTs in large-scale production.

Composites with CNTs as additives have been demonstrated to possess enhanced mechanical, electrical, and thermal properties compared to the matrix materials.[2−4] In the cases of thermal transport, CNTs show tremendous potential for applications because of their ultrahigh thermal conductivity. Berber et al.[5] calculated an isolated (10, 10) CNT by equilibrium molecular dynamics simulations and obtained a value of 6600 $W \cdot m^{-1} \cdot K^{-1}$ for the thermal conductivity at room temperature. Che et al.[6] reported a calculated value of 2980 $W \cdot m^{-1} \cdot K^{-1}$ for the room temperature thermal conductivity of a single-walled CNT (SWNT). Kim et al.[7] measured the individual multiwalled nanotubes with a 14 nm diameter and obtained a value over 3000 $W \cdot m^{-1} \cdot K^{-1}$ for the thermal conductivity at room temperature. The experimental results of Fujii et al.[8] showed that the thermal conductivity of CNT at room temperature increased as its diameter decreased, and exceeded 2000 $W \cdot m^{-1} \cdot K^{-1}$ for a CNT with a diameter of 9.8 nm. The temperature dependence of the thermal conductivity for a CNT with a diameter of 16.1 nm appeared to have an asymptote near 320 K. Xie et al.[9] used a laser flash technique to measure the thermal diffusivity along a CNT array and showed that the thermal conductivity of individual CNTs was about 750 $W \cdot m^{-1} \cdot K^{-1}$ at room temperature. It is believed that CNTs are excellent candidates as fillers for preparing thermal conductivity enhanced nanocomposites due to their very high thermal conductivity and very large aspect ratio. Biercuk et al.[10] investigated the effective thermal conductivity of epoxy based composites containing SWNTs and vapor grown carbon fibers (VGCFs) using a comparative method. Results showed 125 % and 45 % improvements for a mass fraction (ϕ_m) of 1.0 % SWNTs and VGCFs, respectively. The experimental study of Choi et al.[11] on thermal properties of SWNTs-epoxy composites demonstrated the similar thermal conductivity enhancement. They proposed that the bundling of nanotubes would be an important factor for thermal transport characteristics.

In the past decade, a new kind of heat transfer enhanced nanoparticle-fluid mixtures, named as “nanofluids” in the community have attracted increasing attention. Nanofluids, produced by dispersing nanoparticles homogeneously in traditional heat transfer fluids,[12] have potential application in many heat transfer areas because of their intriguing properties such as considerable increase in thermal conductivity, long-term stability, and prevention of clogging in microchannels. A variety of physical and chemical factors, including the volume fraction, the size, the shape, and the species of the nanoparticles, pH value and temperature of the fluids, the Brownian motion of the nanoparticles, and the aggregation of the nanopaticles, have been proposed to play roles on the heat transfer characteristics of nanofluids. Extensive efforts have been made to improve the thermal conductivity of nanofluids and to elucidate the thermal transport mechanism in nanofluids. Several comprehensive review articles have addressed the features of nanofluids.[13−19]

Nanofluids can be taken as composites containing nanoparticles. Obviously, CNTs would be excellent candidates as dispersions for preparing thermal conductivity enhanced nanofluids. In the past decade, several groups have been carrying out the studies on CNT nanofluids. The results on the thermal performances suggested a strong potential of CNT nanofluids as a promising kind of enhanced heat transfer media. The purpose of this article is to address the recent progresses in the study of heat transfer

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using CNT nanofluids. The preparation methods are discussed first, with the experimental and theoretical investigations on the heat transfer performances as followings.

2. PREPARATION OF CNT NANOFLUIDS

Two techniques have been routinely applied to prepare nanofluids, that is, a two-step technique and a one-step technique. Most of the studied nanofluids were prepared by the two-step technique. During the procedure of two-step technique, the dispersed nanoparticles were prepared by chemical or physical methods first, and then the nanoparticles were added into a specified base fluid, with or without pretreatment and surfactant based on the need. In the preparation of nanofluids containing metallic nanoparticles, one-step technique was often employed.[20] Till now the one-step technique is not applicable for preparing CNT nanofluids and the two-step technique has been used by all researchers. It is of utmost importance to prepare homogeneous and long-term stable suspensions to fully utilize the superior heat transfer performances of CNT nanofluids. As known severe aggregation always takes place in the as prepared CNTs (pristine CNTs: PCNTs) because of the nonreactive surfaces, intrinsic Von der Waals forces, and very large specific surface areas and aspect ratios.[21] For PCNTs, they are prone to aggregate and precipitate to the bottom when dispersed in most of the fluids even after long-time intensive sonication if surfactant is not added. Even with surfactant like olelamine, PCNTs cannot be dispersed into nonpolar liquid like decene. Xie et al.[22] showed that almost all of the nanotubes in a suspension with ϕ_m of 0.175 % PCNTs dispersed in distilled water precipitated in only 5 min after preparation, leaving the upper fluid transparent. Therefore, in the preparation of CNT nanofluids, surfactant addition or pretreatment is needed to improve the dispersibility of the loaded CNTs.

Jiang et al.[23] produced stable water-based CNT suspensions using sodium dodecyl sulfate (SDS) as dispersing agent. SDS is a cationic surfactant containing a sulfate hydrophilic segment and a hydrocarbon hydrophobic segment. They derived from FTIR and AES analysis that the strong adsorption existed between the CNT surface and SDS. The experiments revealed that the magnitude of zeta potential for the SDS-adsorbed CNTs was higher than that for the bare CNTs. They proposed that the electrostatic repulsion between the negatively charged cluster surfaces played an essential role in the stabilization of the CNT clusters in water with SDS. Long alkane groups also provided external steric repulsion to help the particles overcome the attractive van der Waals force at contact. They concluded that the surfactant containing a single straight-chain hydrophobic segment and a terminal hydrophilic segment would modify the CNTs−suspending medium interface and prevent aggregation over long periods. Assael et al.[24] also used SDS as dispersant to prepare a series of nanofluids containing multiwalled CNTs (MWNTs). They investigated the effects of the dispersion procedure and the loading of SDS on the stability of the suspension. In their following studies, Assael et al. used double-walled CNTs (DWNTs) as well as MWNTs as additives.[25] Two kind of surfactants, that is, hexadecyltrimethyl ammonium bromide (CTAB) and Nanosperse AQ, were tested. Various factors including surfactant type, surfactant concentration, sonication time, CNT type, and CNT fraction were evaluated. They concluded that CTAB was probably a suitable dispersant, since there was a strong indication that it interacted with both MWNTs and DWNTs, modifying the surface of the outermost nanotubes.

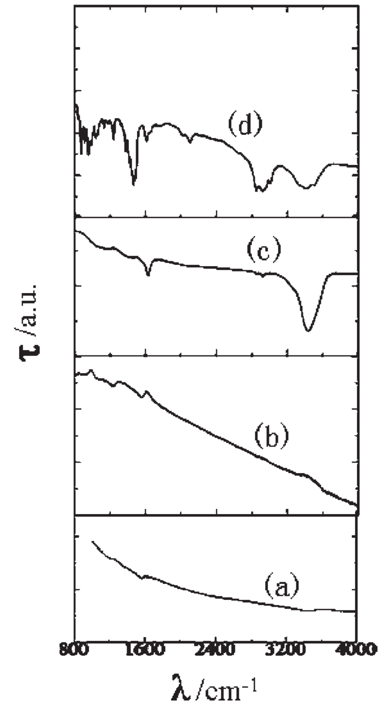

Figure 1. FTIR spectra of the CNTs: τ, transmittance; λ, wavenumber. (a) PCNT, (b) acid treatment, (c) mechanochemical reaction, and (d) surfactant attachment.

In order to decrease the loading of the surfactant, we employed a new type of surfactant, cationic gemini surfactant (12-3(4,6)-12,2Br^{-1}), for preparing CNT nanofluids.[26,27] The surfactant was synthesized by a single-step reaction, in which two dodecyl trimethyl ammonium bromide molecules reacted with one 1,3(4,6)-dibromopropane molecule to generate one 12-3(4,6)-12,2Br^{-1} molecule. The detailed description about the reactions was presented in ref 28. It has been reported that the critical micelle concentration of 12-3-12,2Br^{-1} is $9.6 \pm 0.3 \cdot 10^{-4}$ mol·kg^{-1} at room temperature.[29] Ten times critical micelle concentration of 12-3-12,2Br^{-1} is at ϕ_m of 0.6 %. Solutions of 12-3-12,2Br^{-1} with different concentrations (ϕ_m = 0.6 %, 1.8 %, and 3.6 % at room temperature) were selected to prepare CNT nanofluids. It was observed from FTIR spectra for pure 12-3(4,6)-12,2Br^{-1} (not shown in this article) that the strong bands at 2925 cm^{-1} and 2850 cm^{-1} were due to asymmetrical and symmetrical stretching of $-CH_2-$, respectively. The band at 2960 cm^{-1} was assigned to the asymmetrical stretching of $-CH_3$. The symmetrical and asymmetrical bending vibrations of $-CH_3$ were represented at 1380 cm^{-1} and 1470 cm^{-1}.[30] The peak at 950 cm^{-1} was associated with C−N vibrations. For the FTIR spectra of CNTs with 12-3(4,6)-12,2Br^{-1} attaching (see Figure 1d), the asymmetrical and symmetrical stretching vibrations and bending vibrations of $-CH_2-$ remained a constant. The intensity of the asymmetrical stretching of $-CH_3$ at 2960 cm^{-1} shows significant decrease. It was different from the bending vibration of $-CH_3$, which also decreased seriously but was not eliminated. The still existent intensity of the bending vibration of $-CH_3$ should be attributed to the existence of $-CH_3$ in the head groups. All of these changes indicated that the hydrophobic chains of the 12-3(4,6)-12,2Br^{-1} molecules absorbed on

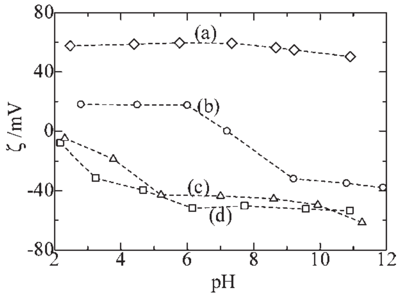

Figure 2. Zeta potentials of CNT suspensions as a function of pH: (a) surfactant attachment, (b) PCNT, (c) mechanochemical reaction, and (d) acid treatment.

the CNT surfaces. Zeta potential measurements revealed that CNTs were positively charged after attached with cationic gemini surfactant. All of the zeta potentials were higher than 40 mV in the tested pH ranges (see in Figure 2). The electrostatic repulsive force was shown to be high enough to overcome the attractive force between CNTs, which lead to more separate CNTs by increasing the tube−tube distance. The distance would exceed the hydrogen bonding range between CNTs and further reduce the probability of CNT coagulation and settling.[31] Stable CNT nanofluids were made after the cationic gemini surfactants were used in their preparation.

Surfactant addition is an effective way to enhance the dispersibility of CNTs.[24−27,32] However, in nanofluid applications, surfactants might cause several problems. First, the addition of surfactants may contaminate the heat transfer media. Second, surfactants may produce foams when heating, while heating and cooling are routine processes in heat exchange systems. Furthermore surfactant molecules attaching on the surfaces of CNTs may enlarge the thermal resistance between the CNTs and the base fluid,[33] which limits the enhancement of the effective thermal conductivity. To fully utilize the superior thermal performance of CNTs and to extend the application fields of CNT contained nanofluids, it is important to prepare nanofluids without surfactants. To this consideration, Xie et al.[22] first employed concentrated acid treatment to functionalize CNT surfaces and directly dispersed the treated CNTs into several polar base fluids to form surfactant-free nanofluids. In the procedure of the acid oxidation, 1 g of PCNTs and 40 mL of acid mixture were boiled and refluxed at 120 °C for 30 min. The acid mixture consisted of concentrated nitric and sulphuric acids in a ratio of 1:3, respectively. The sample after reaction was diluted by distilled water, filtered, and washed repeatedly until the washings show no acidity. The cleaned CNTs were collected and dried at 100 °C for 24 h to remove the attached water. FTIR analysis revealed that no detectable transmission band presented on the spectra for the PCNTs in the wavenumber range covered in the study. For the acid-treated CNTs (ACNTs), the FTIR spectrum (see Figure 1b) had a transmission band centered at 1717 cm^{-1}, which was characteristic of the stretching vibration of C═O. The band at 1213 cm^{-1} was corresponding to the stretching band of C−O.[34] Zeta potential (ζ) results (see in Figure 2) showed that PCNTs had an isoelectric point (IEP) of about 7.1. After acid oxidation, the IEP shifted to a much more acidic value lower than 2.5. The absolute value of the zeta potential at pH 7.0 was larger than 40 mV. The negative zeta potential tendency was usually observed on ceramic suspensions mixed with anionic dispersants.[35] These changes in zeta potential values would be attributed to the surface chemical modification of CNTs, which introduced carbonyl groups onto the surfaces of CNTs. The results were consistent with the above-mentioned FTIR analysis. The very large absolute zeta potential helped to keep the CNTs suspended in nanofluids from aggregation due to the formation of electrical double layer with ionic accumulation of a few angstrom thicknesses. The CNT surface attached with carbonyl functional groups could also increase the affinity between TCNTs and polar base fluids. Therefore the stability of the CNT nanofluids was substantially improved.

Acid treatment is effective to tailor the surface chemistry and break the aggregates and thus to enhance the dispersibility of CNTs. However, self-entanglement and even ring-formation[22,36] have been observed for CNTs in suspensions since the treated CNTs were slender and still very long. Recent analytical study revealed that the finite aspect ratios and nonstraight geometries of the CNTs as well as the tube-end thermal resistance had the dominant influence on the effective thermal conductivity properties of CNT composites, rather than the lateral interfacial thermal resistance.[37] Compared with the vertically aligned CNT array embedded in composites, curvature and self-entanglement of CNTs are primary obstacles to the thermal conductivity enhancement of nanofluids.[38] Moreover, the entanglement and further aggregation may enlarge the viscosity of nanofluids and may cause clogging in microchannel flows. Cutting treated CNTs into the proper length and tailoring the tube-ends are effective ways to optimize dimensional parameters (aspect ratio and straightness) and to reduce interfacial thermal resistance, thus improving the heat transfer characteristics of CNT nanofluids. Xie et al.[39] further utilized ball-milling to cut ACNTs into different lengths by adjusting the milling time. Transmission electron microscope (TEM) observation revealed that the PCNTs were not only aggregated but also entangled (Figure 3A). It was evident that these PCNTs were not ready to form stable suspensions. The TEM image showed that the aggregates of PCNTs were broken after acid treatment (Figure 3B). However, most of the ACNTs without milling were in curled and self-entangled states (Figure 1B) because they were still very long. When the ACNTs were milled for 10 h, the average tube length was decreased to about 600 nm (Figure 3C), and the relatively short and straight tubes with excellent monodispersion were obtained. The average length of ACNTs decreased with increase of ball milling time. With further ball milling treatment, aggregations form along with decrease of tube average length. As shown in Figure 1F, almost no monodispersions appeared when the ball milling time was increased to 38 h.

The mechanochemical reaction method was also used by the authors to modify the surfaces and morphologies of PCNTs.[40−43] In the procedure of mechanochemical reaction treatment, 1 g of PCNTs was mixed with 20 of potassium hydroxide (KOH), and the mixture was ball-milled for 12 h in a planetary milling machine. The sample after reaction was diluted by distilled water, filtered, and washed repeatedly until the washings showed no alkalescence. For the FTIR spectrum of CNTs treated by mechanochemical reaction (MCNTs; see Figure 1c), the band at 1095 cm^{-1} corresponded to the stretching band of C−O, whereas the band at 782 cm^{-1} could be interpreted to the bending stretching band of hydroxyl groups. The strong transmission band at about 1629 cm^{-1} could be attributed to the stretching mode of −C═C− in an enol form.[44] The zeta potential behavior of MCNTs was similar to that of ACNTs. Hydroxyl functional groups attached on the MCNT

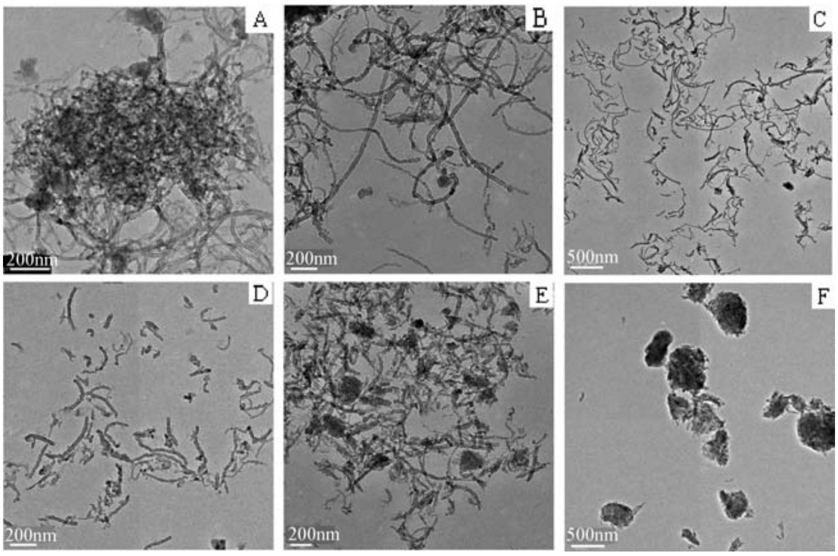

Figure 3. TEM photographs of PCNTs (A) and ACNTs with different milling times (B, 0 h; C, 10 h; D, 18 h; E, 28 h; F, 38 h).

surfaces could increase the affinity between MCNTs and polar base fluids, leading to stable CNT nanofluids.

3. EXPERIMENTAL INVESTIGATIONS OF THE THERMAL PERFORMANCE OF CNT NANOFLUIDS

3.1. Thermal Conductivity Enhancement. In the studies of thermal characteristics of nanofluids, thermal conductivity is the first referred one and has been paid the most attention because it is believed to be the most important parameter responsible for heat transfer enhancement. Several techniques including steady state methods like parallel plate method,[45] semisteady method like the 3ω method,[46,47] and transient methods like the transient hot wire (THW) method.[48−51] Of the techniques developed for thermal conductivity measurements of fluids, THW method has been regarded by many as a technique producing generally excellent results and it has been used widely for measurements of the thermal conductivities, and in some cases, the thermal diffusivities of fluids with a high degree of accuracy.[48−51] The most attractive advantage of this method for application to fluids is its capacity of experimentally eliminating convective error and the data obtained are more reliable than those obtained using the steady state method. The authors of this article employed a transient short hot wire (SHW) to measure the thermal conductivity of nanofluids. SHW[52−55] was developed from THW and the measurement procedure is similar to that of THW. The feature of SHW is that a metal wire as short as about 10 mm is used as a hot wire, and a relative smaller sample cell is needed. It is easier to keep initial equilibrium during measurements. In the author's studies, a platinum wire with a diameter of 50 μm was used for the hot wire, and it served as both a heating unit and as an electrical resistance thermometer. Initially the platinum wire immersed in media was kept at equilibrium with the surroundings. When a regulation voltage was supplied to initiate the measurement, the electrical resistance of the wire changed proportionally with the rise in temperature. The thermal conductivity was calculated from the slope of the rise in the wire's temperature against the logarithmic time interval.

Choi et al. investigated the thermal conductivity of poly(α-olefin) oil based SWNT nanofluids. The experimental results showed that the thermal conductivity of nanotube suspensions was nonlinear with nanotube loadings. An anomalously high thermal conductivity enhancement of 160 % was observed when the mass fraction of the added CNTs was only 1.75 %.[56] However, later researchers could not obtain the same magnitude of the thermal conductivity enhancement of CNT nanofluids. Liu et al.[32] reported that the thermal conductivity of carbon nanotube-synthetic engine oil suspensions was higher compared with that of same suspensions without the addition of surfactant. The presence of surfactant as stabilizer had a positive effect on the carbon nanotube-synthetic engine oil suspensions.

Choi et al.[47] employed a modified 3ω method applied to a suspended platinum microwire to measure the thermal conductivity of a water-based SWNT suspension (metallic SWNTs with a diameter of 1.33 nm and mass fraction of 0.89 %). The thermal conductivity measured in the nanofluid was enhanced by 19.4 %, which was attributed to the contribution of suspended SWNTs. Assael et al.[24] measured the thermal conductivities of the aqueous suspension of CNTs by using a THW method and the influences of various factors including surfactant type, surfactant concentration, sonication time, CNT type and CNT fraction were examined. With SDS as the dispersant, the largest thermal conductivity enhancement obtained was 38.0 % for a nanofluid with CNT mass fraction of 1.05 %. When the surfactant was substituted with CTAB, the largest thermal conductivity enhancement obtained was 34.0 % at a same mass fraction of CNTs.[25] Ding et al.[57] prepared water-based CNT nanofluids by using gum Arabic as surfactant. A mass fraction of 0.25 % with respect to water was sufficient for producing stable CNT nanofluids. Thermal conductivity measurements revealed that the effective thermal conductivity increased with increasing temperature and CNT concentration, with the dependence of the conductivity on temperature much more significant. The enhancement of the thermal conductivity was slightly higher than that reported by Assael et al.,[24] Xie et al.,[22] and Wen and Ding.[58] They suggested that this discrepancy be associated with the thermal properties of CNTs used, liquid-CNT interfacial resistance, and the aspect ratio of CNTs used. Furthermore the base liquid used also played a role.

Meibodi et al.[59] investigated the stability and thermal conductivity of CNT/water nanofluids. They examined the affecting parameters including size, shape, and source of nanoparticles, surfactants, power of ultrasonic, time of ultrasonication, elapsed time after ultrasonication, pH, temperature, particle concentration, and surfactant concentration. An accepted way for obtaining the optimized condition was proposed based on the design of experiments and statistical analysis. Amrollahi et al.[60] found strong dependence of the effective thermal conductivity on temperature and volume fraction of CNT nanofluids. Brownian motion and the inter-particle potential, which influences the particle motion, were proposed to account for the phenomenon. The experiments showed that using a 4.35 % mass fraction of CNTs resulted in a 20 % increase in the thermal conductivity of the base fluid (ethylene glycol).

Han et al.[46] used a new type of complex nanoparticle, a hybrid sphere/carbon nanotube (CNT) particle consisting of numerous CNTs attached to an alumina/iron oxide sphere for applications in nanofluids. The hybrid sphere/CNT particles were synthesized by spray pyrolysis followed by catalytic growth of CNTs. The spheres were about 70 nm in diameter on average, and the attached CNTs had a length up to 2 μm. These hybrid nanoparticles were dispersed to poly alpha-olefin with sonication and a small amount of surfactants to form stable nanofluids. A 3ω-wire method was employed to measure the thermal conductivity over a temperature range (10 to 90) °C. It was emphasized that mass fraction of CNTs in the hybrid sphere/CNT particles was very small, approximately 3.0 % in mass fraction, whereas the center spheres occupied about 97 % in mass fraction. However, comparison studies demonstrated that the hybrid sphere/CNT particles could provide a conductivity enhancement much higher than those for simple spheres and even slightly higher than those for simple CNTs. They proposed that in such hybrid nanoparticles heat might transport rapidly from one CNT to another through the center sphere and thus lead to less thermal contact resistance between CNTs when compared to simple CNTs dispersed in fluids. CNTs had an extremely high thermal conductivity, but thermal resistance between the CNTs and the fluid had limited their performance in nanofluids. They obtained a thermal conductivity enhancement of about 21 % at room temperature for particle mass fractions of about 0.45 %.

Wensel et al.[61] investigated the thermal conductivity of nanofluid systems containing small amount of additives of 0.02 % in mass fraction of CNTs and metal oxides (MgO/Fe_2O_3) in water. They obtained very interesting result of 10 % increase in the thermal conductivity. While the measured viscosity was the same as water. This low waterlike viscosity was critical for a heat transfer coolant application. Normally at least 0.5 % in mass fraction of nanotube loading in the fluid was required in order to get a 10 % thermal conductivity increase. However, nanofluids with 0.5 % in mass fraction of nanotubes are very viscous and the fluid is very difficult to be used for coolant applications. Wensel et al. proposed that the interesting thermal conductivity enhancement in the very dilute suspension was attributed to the local aggregation of the metal oxide nanoparticles on the surface of the nanotubes by electrostatic attraction and possibly forming chains along the nanotube. Their further experimental results utilizing pH adjustment, magnetic field, and surfactant type strongly supported this mechanism.

Hong et al. introduced a new concept of incorporating magnetically sensitive metal or metal oxide nanoparticles in a CNT contained nanofluid. They invesigated systematically the effect of the external magnetic field on the thermal conductivity of these magnetically sensitive CNT nanofluids. For a nanofluid system containing a small amount of additives of 0.01 % in mass fraction of nanotubes and 0.02 % in mass fraction of Fe_2O_3 nanoparticles in water,[62] the thermal conductivity enhancement was around 13 % without external magnetic field. When an external magnetic field was applied, the thermal conductivity showed very interesting behavior. Initially it increased with the time but eventually it reached a peak. On longer time holding in a magnetic field, the thermal conductivity decreased and it finally decresed to be around (0.63 to 0.64) $W \cdot m^{-1} \cdot K^{-1}$, even lower than that of the fluid with CNTs but without magnetic particles. The maximum thermal conductivity was about 50 % higher than distilled water value and 35 % higher than the nanofluid without magnetic field. Hong et al. attributed this interesting phenomenon to the Fe_2O_3 nanoparticles forming contacting networks and chains, which also induced the CNTs to physically contact more, thus resulting in improved thermal conductivity values. On longer holding in magnetic field, the particles gradually moved and formed a clump of particles and a clump of CNTs, thus decreasing the thermal conductivity. For nanofluid systems containing 0.01 % and 0.02 % in mass fraction of Ni coated CNTs in water,[63] similar results were obtained. It indicated that under a relatively strong magnetic field, small magnetic particles formed connected networks and also tended to get somewhat oriented toward the field direction, no matter whether these magnetic particles attached to the CNTs or not. They moved the CNTs nearby and induced more physical contacts, thus improving the thermal conductivity. Further microstructure observations by high speed microscopy strongly supported the explanation that the alignment process dominated the thermal conductivity enhancement rather than microconvection.[64]

In the past few years, the authors carried out a series of studies on the heat transfer performance of nanofluids. A variety of nanofluids have been produced by the one step method or two step method. The base fluids used include deionized water (DW), ethylene glycol (EG), glycerol, silicone oil, and the binary mixture of DW and EG (DW—EG). Al_2O_3 nanoparticles (NPs) with different sizes, SiC NPs with different shapes, and MgO NPs, ZnO NPs, SiO_2 NPs, Fe_3O_4 NPs, TiO_2 NPs, diamond NPs (DNPs), and CNTs with different pretreatments have been used as additives. The thermal conductivities of these nanofluids have been measured by THW method or SHW technique.[20] The authors have employed four different methods, namely, acid oxidation method,[22] mechanochemical reaction method,[40−43] surfactant addition,[26,27] and the method of ball milling following acid oxidation,[39] to make homogeneous and long-term stable CNT nanofluids. Some important findings are addressed in the following.

Most of the studies of the thermal conductivity of nanofluids have demonstrated that the thermal conductivity enhancement increased with nanoparticle loading. Same tendency has been obtained in the author's studies. Substantial enhancements in the thermal conductivity were observed for nanofluids with CNT addition, and the enhancement ratio increases with the volume fraction of CNTs. Four typical kinds of the tested nanofluids were selected and their mass fraction dependent thermal conductivity enhancement ratios are presented in Figure 4. These four nanofluids include: (1) EG based nanofluid containing MWNTs treated by ball milling for 10 h after acid oxidation, (2) EG based nanofluid containing MWNTs treated by mechanochemical reaction, (3) DW based nanofluid containing MWNTs with gemini surfactant, and (4) EG based nanofluid

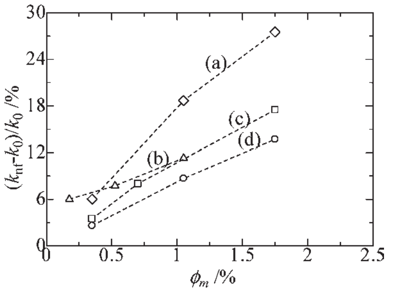

Figure 4. Mass fraction dependent thermal conductivity enhancement ratio of CNT nanofluids: (a) MWNT-EG (milled for 10 h after acid treatment), (b) MWNT-DW (gemini addition), (c) MWNT-EG (mechanochemical reaction), and (d) MWNT-EG (acid treatment).

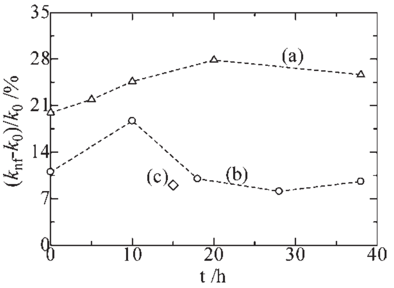

Figure 5. Thermal conductivity ratio varying with the ball milling time: (a) MWNT-EG, ϕ_m = 1.05 %, (b) MWNT-SO, ϕ_m = 0.945 %, and (c) MWNT-Gly, ϕ_m = 0.875 %.

containing MWNTs treated by acid oxidation without further milling. k_{nf}, k_0, $(k_{nf} - k_0)/k_0$, and ϕ_m refer to the thermal conductivity of nanofluid, thermal conductivity of base fluid, thermal conductivity enhancement ratio of nanofluids, and the mass fraction of CNTs, respectively. Although PCNTs were the same, $(k_{nf} - k_0)/k_0$ was very different in these four nanofluids, highly depended on the pretreatment method and the suspending technique.

Besides mass fractions, the morphologies of CNTs play dominant roles on the thermal transport in the nanofluids. Figure 5 represents the thermal conductivity enhancement ratios of the nanofluids with close CNT loadings in EG as a function of ball milling times (t). Theoretical research into the thermal conductivity of composites containing cylindrical inclusions has demonstrated that the aspect ratio is a positive factor.[65−67] Intuition suggests that increasing the milling time should therefore decrease $(k_{nf} - k_0)/k_0$ because of the reduced aspect ratio. Figure 5, however, shows clear peak value in the thermal conductivity enhancement with respect to the milling time for MWNT-EG nanofluid and silicone oil (SO) based nanofluid containing MWNTs (MWNT-SO nanofluid). For MWNT-EG nanofluid at a mass fraction of 1.05 %, the thermal conductivity enhancements present a peak value of 19.0 % when the milling time is 10 h, whereas for MWNT-SO nanofluid at a mass fraction of 0.945 %, the thermal conductivity enhancements present a peak value of 28.0 % when the milling time is 20 h. It is indicated that the ball milling time is not same for different nanofluid system.

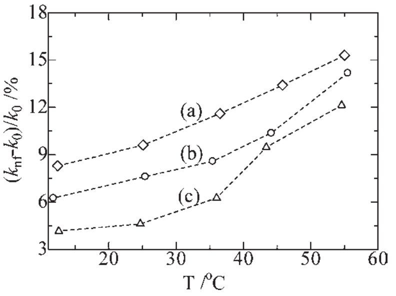

Figure 6. Temperature dependent thermal conductivity enhancement ratio of CNT nanofluids: (a) SWNT-DW, (b) DWNT-DW, and (c) MWNT-DW.

Table 1. Thermal Conductivity Enhancement Ratios of CNT Nanofluids with 12-3-12,2Br^{-1} as Surfactant

ϕ_m of surfactant	$(k_{nf} - k_0)/k_0$				
	%				
%	T = 5.5 °C	T = 19 °C	T = 34 °C	T = 49 °C	T = 64 °C
0.6	5.35	6.02	8.19	11.92	18.22
1.8	3.88	4.18	5.39	6.42	7.43
3.6	1.05	1.82	2.24	3.59	4.45

SWNTs, DWNTs, and MWNTs were used to prepare nanofluids to investigate the nanotube size effect on the thermal conductivity of CNT nanofluids. Mechanochemical reaction technique was employed as a pretreatment method for these three kinds of CNTs. Figure 6 shows the thermal conductivity enhancement ratios of SWNT-DW, DWNT-DW, and MWNT-DW nanofluids. The mass fractions of the CNTs for all of these three nanofluids are 0.35 %. It is seen that the thermal conductivity enhancements present differences among the nanofluids containing CNTs with different diameters, with highest $(k_{nf} - k_0)/k_0$ for SWNT-DW nanofluid and lowest $(k_{nf} - k_0)/k_0$ for MWNT-DW nanofluid, respectively. Two factors may account for the experimental results. The first one is the difference in the intrinsic thermal conductive capability of these three kinds of CNTs. Theoretical and experimental studies have demonstrated that the thermal conductivity would decrease when the number of the nanotube wall layer increases.[5,7] SWNTs have the highest thermal conductivity among the three kinds of CNTs, whereas the thermal conductivity of the MWNTs is the lowest one. Second the three CNTs show considerable difference in the aspect ratio. It is well-known that larger aspect ratio of cylindrical inclusions in filler−matrix mixture would lead to higher thermal conductivity. In the study, the average diameter of the MWNTs was about 30 nm, much larger than those of ∼ 3 nm for DWNTs and ∼ 1 nm for SWNTs. Jiang et al.[68] reported the CNTs could build up high thermal conductivity percolation paths to enhance the thermal conductivity of nanofluids. The longer the percolation path is, the greater the enhancement of thermal conductivity is. Higher aspect ratio of the CNTs would results in longer percolation path and the greater thermal conductivity enhancement.[68]

Table 1 presents the thermal conductivity enhancement ratios of CNT nanofluids with 12-3-12,2Br^{-1} as surfactant. The mass fraction of the CNTs is 0.175 %. Solutions of 12-3-12,2Br^{-1} with different mass fraction (0.6 %, 1.8 %, and 3.6 %) were selected to prepare CNT nanofluids. It is seen from Table 1 that $(k_{nf}-k_0)/k_0$ decreases with the increase of the mass fraction of 12-3-12,2Br^{-1}

Table 2. Thermal Conductivity Enhancement Ratios of CNT Nanofluids with 12-3(4,6)-12,2Br^{-1} as Surfactant

	$(k_{\mathrm{nf}}-k_0)/k_0$				
	%				
surfactant	T = 5.5 °C	T = 19 °C	T = 34 °C	T = 49 °C	T = 64 °C
12-3-12,2Br^{-1}	5.35	6.02	8.19	11.92	18.22
12-4-12,2Br^{-1}	5.27	6.00	7.59	8.71	10.85
12-6-12,2Br^{-1}	4.85	5.27	6.40	7.44	8.82

at all the measured temperatures. When the mass fraction of 12-3-12,2Br^{-1} is 0.6 %, $(k_{\mathrm{nf}} - k_0)/k_0$ reaches up to 18.2 % at 65 °C with CNT loading of only 0.175 %. Because the surfactant of 12-3-12,2Br^{-1} acts as a stabilizer, more 12-3-12,2Br^{-1} addition would improve the stability of the CNT nanofluids. Liu et al.[32] reported that the thermal conductivity of CNT-synthetic engine oil suspensions was higher compared with that of same suspensions without the addition of surfactant. The presence of appropriate amount of surfactant as stabilizer has positive effect on the CNT nanofluids. However, excess addition of 12-3-12,2Br^{-1} may deteriorate the thermal conductivity enhancement of the CNT nanofluids. The nanotube-fluid interfacial thermal resistance arising from the coating of the excess surfactants on the CNT surfaces would strongly decrease the thermal conductivity enhancement of nanofluids.[33] Furthermore, the viscosity of the nanofluid increases with the amount of the excess surfactant.[25] The viscosity increment would significantly decrease the heat transfer capacity of nanofluids,[69] which also leads to the reduction of thermal conductivity enhancement of nanofluids. The authors' previous study also indicated that the viscosity of the nanofluid containing surfactants decreased with improvement of temperatures, and the less addition of surfactants accelerated the decrease of nanofluid viscosities. Therefore the thermal conductivity enhancement increases greatly with temperatures when the mass fraction of the surfactant is lower.

The thermal conductivity enhancement ratios of the CNT nanofluids with different gemini surfactant are presented in Table 2. The mass fractions of CNTs and surfactant are 0.175 % and 0.6 %, respectively. The spacer chain length of the cationic gemini surfactant increases from 3 methylenes to 6 methylenes. It is seen from Table 2 that $(k_{\mathrm{nf}} - k_0)/k_0$ increases with the decrease in the spacer chain length of cationic gemini surfactant. Zeta potential analysis revealed that the CNT nanofluids stabilized by gemini surfactant with shorter spacer chain length had better dispersion stabilities. Increase in the spacer chain length of surfactant might give rise to the possibility of the sediments of CNTs in the nanofluid, resulting in the decrease of the thermal conductivity enhancement of CNT nanofluid. This kind of effect is especially obvious at higher temperatures.

3.2. Convective Heat Transfer Coefficient. Convective heat transfer coefficient is a thermal properties related closer to applications. Extensive investigations have been conducted on the convective heat transfer of nanofluids in the past decades.[15,18,70] The most used additives were oxide nanoparticles, while very little literature referred to convective heat transfer of CNT nanofluids.

Ding et al.[71] investigated the heat transfer behavior of aqueous suspensions of CNT nanofluids flowing through a horizontal tube. The test section was a straight copper tube with 970 mm length, 4.5 mm inner diameter, and 6.35 mm outer diameter. In their study, significant enhancement was observed of the convective heat transfer in comparison with pure water as the working fluid. It was reported that the enhancement depended on the flow condition, CNT concentration and the pH level, and the effect of pH was observed to be small. They found that the enhancement was a function of the axial distance from the inlet of the test section. The enhancement increased first, reached a maximum, and then decreased with increasing axial distance, when other conditions were given. There appeared to exist a critical Reynolds number above which a big increase in the convective heat transfer coefficient occurred when the CNT concentration and pH level were specified. They proposed that the shear thinning behavior might be the cause. It was also observed that the position at which the maximum enhancement occurred increased with CNT concentration and the Reynolds number when other conditions were given. An intriguingly high heat transfer enhancement of 350 % at Re = 800 was obtained when the working medium was CNT nanofluid with a CNT mass fraction of 0.5 %. This maximum enhancement occurred at an axial distance of approximately 110 times of the tube diameter. Further they found that the observed enhancement of heat transfer coefficient was much higher than the increase in the effective thermal conductivity. They declared that the observed large enhancement of the convective heat transfer could not be attributed to the enhancement of thermal conduction under the static conditions. Other factors including particle rearrangement, shear induced thermal conduction enhancement, reduction of thermal boundary layer thickness due to the presence of nanoparticles, as well as the very high aspect ratio of CNTs might also account for the enhancement.

Choi et al.[47] first utilized a modified 3ω method to measure simultaneously the natural convective heat transfer coefficients and thermal conductivity of a water-based SWNT solution. They derived an equation for calculating the convective heat transfer coefficient by measuring 3ω signals. In their measurements, the sensor, a platinum wire, was fully submerged in the nanofluid during the entire experiment. They made the measurement at room temperature and observed an enhancement of 18.9 % in the convective heat transfer as compared to water. The suspended SWNTs would be the cause of this enhancement. They argued that they could measure the thermal conductivity of the nanofluid with reasonable accuracy. However, the investigation of the convective heat transfer could be challenging due to a lack of knowledge of the thermophysical properties of nanofluids.

Kamali et al.[72] numerically studied the heat transfer performance of non-Newtonian CNT nanofluids through a straight tube under laminar flow and constant heat flux conditions. For the simulation of nanofluid flow field, the incompressible Navier—Stokes equations coupled with energy equation were solved numerically using the finite volume method. The shear-thinning behavior of non-Newtonian CNT nanofluid was investigated using the non-Newtonian power law. They stated that the numerical method coupled with the non-Newtonian model was capable of modeling the action of CNT nanofluid passing the tube. The analytical results showed that the heat transfer coefficient was dominated by the wall region due to non-Newtonian behavior of CNT nanofluid.

3.3. Boiling Heat Transfer Characteristic. With the continuous advances in miniaturization and manufacturing of electronic devices, the power density has been increasing to an unacceptably high level. For example, at the upper limit of future applications, high-end military and aerospace band gap amplifier will produce waste heat flux on the order of 1000 $W \cdot cm^{-2}$.[13] It is critical for the safety and stability of the devices to remove the heat generated quickly and smoothly. Phase change (boiling) heat transfer might be an applicable solution for such high dissipation rates. Nanofluids have been investigated as heat transfer media, and substantial improvements in critical heat flux (CHF) were obtained. From these results we can see the high potential of boiling of nanofluids in cooling systems. However, oxide nanofluids were dominantly in the studies of boiling heat transfer. Only a few researchers considered CNT nanofluids.

Liu et al.[73] studied experimentally the pool boiling heat transfer of DW based CNT suspensions on a flat copper surface under atmospheric and subatmospheric pressures. The experiments indicated that both the heat transfer coefficient (HTC) and the critical heat flux (CHF) of CNT nanofluids were much higher than those of DW. Various factors including CNT loading, surrounding pressure, and surface characteristic were examined. They reported that the CNT loading had strong impacts on both the HTC and the CHF of CNT suspensions. When the CNT mass fraction was 2.0 %, the maximum heat transfer enhancements were obtained for all of the tested pressures. The HTC and CHF enhancements increased apparently with the decrease of the pressure. At atmospheric pressure, the HTC and the CHF were enhanced by about 60 % and 63 %, respectively, whereas at a subatmospheric pressure of 7.4 kPa, the enhancements were up to about 130 % and 200 % compared with those of DW. They further found that on the same coated surface at a subatmospheric pressure the solid/liquid contact angle or the surface characteristics of the heated surface was not sole influencing factor to enhance heat transfer of CNT nanofluids.

Park et al.[74] investigated the nucleate boiling heat transfer using CNT nanofluids. The objective of their study was to examine the effect of CNTs on overall heat transfer performance in nucleate boiling that occurs at the boilers and evaporators of power plants and refrigeration and air-conditioning equipment. In nucleate boiling, vapor was generated by nucleation of bubbles at the surface. The experimental results showed that the addition of CNTs led to enhancement in boiling heat transfer coefficients of these fluids. A large enhancement up to 28.7 % was observed at low heat fluxes less than 30 $kW \cdot m^{-2}$ when the mass fraction of CNTs was 1.0 %. However the enhancement was suppressed with increasing heat flux. At 80 $kW \cdot m^{-2}$, the heat transfer enhancement of water was only 6.3 %. They attributed this behavior to the bubble generation. At low heat flux, the bubble generation was not vigorous at the surface and CNTs with high thermal conductivity could penetrate into the bubble zone near the surface and touch the surface (or thermal boundary layer) to instantly generate more bubbles. As the heat flux increases, however, more bubbles are generated and the chance of penetration and touching the thermal boundary layer by CNTs becomes low. They further found that CNTs did not cause fouling on the heat transfer surface, which was different from conventional nanoparticles. The same measurements were carried out a few times to see the fouling effect over a period of 3 weeks, and the results varied little and little contamination was seen on the surface. They argued that conventional nanoparticles had the affinity to the metal surface but that CNTs did not show this kind of behavior.

4. THEORETICAL CONSIDERATIONS

The reported intriguing thermal performances of nanofluids stimulated the passion of the researches on the heat transfer mechanisms in this new kind of heat transfer media. Keblinski et al.[75] proposed first that Brownian motion of the nanoparticles, molecular-level layering of the liquid at the liquid/particle interface, the nature of heat transport in the nanoparticles, and the effects of nanoparticle clustering might play key roles on the heat transport in nanofluids. Considering a nanolayer with thickness of a few nanometers existing at the interface between particle and fluid, expressions for calculating the effective thermal conductivity of nanofluids have been derived based on effective medium theory and Maxwell model. These models' predictions have shown that measurable enhancement of the effective thermal conductivity could be expected when nanolayers were accounted for.[76−78] Some researchers emphasized the contribution of dynamic part related to particle Brownian motion.[79−81] Jang and Choi[82] reported a formula for calculating the effective thermal conductivity of nanofluids considering the contribution of microconvection caused by nanoparticle Brownian motion. A predicting expression was also derived by the authors by combining the contributions of microconvection and nanolayer.[78] However the results of analysis by Wang et al.[45] and numerical simulation by Keblinski et al.[75] showed that the contribution of Brownian motion to heat transport in nanofluids is negligible. Gao et al.[83] investigated the mechanisms experimentally by thermal conductivity measurements and structural analysis for the same materials in both liquid and solid states. These studies strongly suggested that clustering held the key to the thermal conductivity enhancement of nanofluids. Murshed et al.[15] evaluated the thermal conductivity models of nanofluids instructively in their review paper. It can be found from the literature that most of the theoretical models are established for calculating the effective thermal conductivity of nanofluids containing spherical nanoparticles. For nanofluids containing cylindrical inclusions like CNTs, it is far more complicated due to the complex morphologies and surface chemistry. More factors including aspect ratio, straightness, and percolation would have significant effects on the thermal transport in the CNT contained nanofluids.

Keblinski et al.[84] examined the effective medium theories for fiber composites and compared the available experimental data of the thermal conductivities of CNT nanofluids with the predicted values. They found that the experimental data were much smaller than the values predicted by the effective medium theories. They ascribed the discrepancy to the very large interfacial thermal resistance existing between the CNTs and the matrix. Huxtable at al.[33] made transient absorption measurements on individual SWNTs dispersed in D_2O by a modulated laser system to investigate the nanotube−matrix interface conductance. The nanotubes were encased in cylindrical micelles of SDS surfactant to produce a stable suspension. SDS molecules consist of a hydrophobic alkane tail which adsorbs to the nanotube surface and a hydrophilic polar headgroup. Therefore, the interface conductance measured was between the nanotube and the hydrophobic alkane side of the SDS micelle. An interfacial conductance of 12 $MW \cdot m^{-2} \cdot K$ was extracted, and similar results were obtained from their molecular dynamics simulations. The equivalent matrix thickness for the low-conductivity organic matrix ($\sim$ 0.1 $W \cdot m^{-1} \cdot K^{-1}$) for the above values of interfacial resistance was about 10 nm, indeed a large value. The very large value of the interfacial resistance associated with weak coupling between the rigid tube structure and the soft organic liquid was also obtained by Shenogin et al.[85] using classical molecular dynamics simulations. Atomistic-based simulations by

Thomas et al.[86] showed that several functionalization parameters involving the grafting density and chain length (short linear hydrocarbon chains covalently bonded to the CNT surface) had a strong influence on the effective thermal conductivity. Increasing chain length and grafting density would lower the interfacial thermal resistance. The presence of defects adjacent to grafting sites caused very little change in the predicted values of the interfacial thermal resistance. It was indicated that the dependence of thermal conductivity of CNT nanofluids on the interfacial thermal resistance was most pronounced at shorter CNT lengths. CNT length was a critical factor in the resulted thermal conductivity at finite values of the interfacial thermal resistance. CNT atoms that are chemically functionalized with intrusive atoms/molecules attaching have different bonding strength and geometry (sp^3) than the remaining tube carbon atoms (sp^2). They will therefore act as scattering centers for the heat carriers (phonons) and reduce intrinsic tube thermal conductivity. Shenogin et al.[87] found by using classical molecular dynamics simulations that chemical bonding significantly reduced tube-matrix thermal boundary resistance but, at the same time, decreased intrinsic tube conductivity. Estimates based on the effective medium theory predicted increase, by about a factor of 2, of the composite conductivity due to chemical functionalization of SWNTs with aspect ratios within 100−1000 range. Interestingly, at a high degree of chemical functionalization, intrinsic tube conductivity became independent of the bond density. Nonequilibrium molecular dynamics simulations by Pan et al.[88] also revealed that the thermal conductivity of a SWNT was reduced by about a factor of 1.5 when 5 % of the nanotube carbon atoms are hydrogenated. The degradation of thermal conductivity of functionalized CNTs was ascribed to the reduction of the phonon scattering length and the suppression of some thermal vibrational modes due to chemical attachment of hydrogen atoms.

Nan et al.[65] derived a simple formula for the thermal conductivity enhancement in carbon nanotube composites by incorporating the interface thermal resistance with an effective medium approach. This formula predicted that a large interface thermal resistance across the nanotube−matrix interface would cause a significant degradation in the thermal conductivity enhancement, even for the case with ultrahigh intrinsic thermal conductivity and aspect ratio of the CNTs embedded. Cherkasova and Shan[89] performed systematical investigations on the impact of both nanotube aspect ratio and dispersion state on the effective thermal conductivity of aqueous suspensions of surfactant-stabilized MWNTs. In addition to thermal-conductivity measurements, the nanofluid samples were characterized carefully. From the experiments of determination of aspect-ratio distribution, Cherkasova and Shan[89] calculated the volume-weighted average aspect ratio. They further compared the experimental results to the corresponding values calculated by Nan's model and good consistence was obtained.

Xue et al.[66] presented a theoretical model of the effective thermal conductivity for CNT composites by incorporating the interface thermal resistance with an average polarization theory. The effects of nanotube length, diameter, concentration, and interface thermal resistance on the effective thermal conductivity has been considered simultaneously in their treatment. Xue's model predicted that the large length of CNTs embedded had substantial effect on the thermal conductivity enhancement, while the nanotube diameter had a very small effect. The very large interface thermal resistance across the nanotube−matrix interface caused a significant degradation in the thermal conductivity enhancement. The thermal conductivity enhancement was shown to increase rapidly with decreasing the thermal conductivity of the base fluid and increases with increasing the thermal conductivity of the CNTs. Gao et al.[67] generalized Bruggeman effective medium theory for calculating the effective thermal conductivity of CNT composites. They adopted a symmetric microstructure in which CNTs and oil fluid are interdispersed and topologically equivalent. Their numerical results demonstrated satisfactory prediction of the nonlinear dependence of effective thermal conductivity on the nanotube volume fraction in nanofluids and very low percolation threshold for CNT/polyimide composites. It was stated that the nonlinear dependence originated from the symmetric microstructure together with the special properties of CNTs such as high aspect ratio and high conductivity. It was also showed that although SWNTs possessed a higher thermal conductivity than MWNTs, they induced less effective conductivity due to interfacial resistance. Moreover, the nonspherical shape of CNTs helped to achieve a large enhancement of the effective conductivity.

CNTs suspended in base fluids are long and slender and are usually crooked and self-entangled. Considering the fact that the vertically aligned CNT array embedded in composites could provide direct channels for transporting heat and more effectively increased the thermal conductivity of the composites,[38] Song et al.[90] proposed a factor, length efficiency, to analyze the thermal conductivity of nanocomposites with CNT loading. The theoretical analysis revealed that an appropriate length distribution of CNTs could improve their length efficiency and more effectively enhance the thermal conductivity of the composites. The measurements of the thermal conductivities of glycerin based nanofluids containing CNTs ball-milled to different length distribution proved the analysis. Song's results further indicated that, when length efficiency was taken into account, interfacial resistance effect would be less serious. Deng et al.[37] included the influences of volume fraction, anisotropic thermal conductivities, aspect ratio, nonstraightness, and interfacial thermal resistance of the CNTs into a simple model for the thermal conductivity enhancements in CNT nanofluids with low loadings of CNTs. The model predicted that using CNTs with higher aspect and straightness ratios was an efficient means to get much better thermal conductivity enhancements for CNT nanofluids. It was reported that using as straight as possible CNTs with aspect ratios not lower than 500 was a very efficient means to get much better thermal conductivity enhancements. In their analysis the previously observed nonlinear behavior on the enhancements versus low loadings of CNTs was attributed to an interaction effect among CNTs.

In pursuit of a comprehensive understanding to address the problem that an anomalously wide range of thermal conductivity enhancement values were reported in the experimental literatures, Sastry et al.[91] developed a theoretical model based on three-dimensional CNT chain formation (percolation) in the base liquid and the corresponding thermal resistance network. The model considered random CNT orientation and CNT−CNT interaction forming the percolating chain. They introduced a new dimensionless parameter that represented the ratio of thermal resistance of the liquid to that of the CNT chains. It was shown that various factors including the CNT geometry (length), volume fraction, thermal conductivity of the base liquid and the nanofluid (CNT−liquid suspension) preparation technique played significant role on the thermal conductivity enhancement.

They claimed that their predictions were in good agreement with almost all available experimental data, with a reasonable accuracy of ± 5 %. However their model could not predict the nonlinear variation of the effective thermal conductivities with the CNT volume fraction. To compensate the aforementioned limit, Koo et al.[92] improved the work by Sastry et al. by considering the "excluded volume" concept, which varied with particle volume fraction and CNT aspect ratio. A Monte Carlo simulation was performed in their study in order to elucidate the effects of length, diameter, volume fraction of CNT, and type of base fluid. They claimed that the revised and expanded model could explain the nonlinear increase of the thermal conductivity with CNT loading, as well as its dependence on the CNT diameter and aspect ratio. The nonlinear behavior of the effective thermal conductivity was ascribed to the nonlinear increase of the heat transfer distance in a CNT with the number of effective contact points and/or particle volume fraction. The thermal conductivity enhancement difference between DW-, EG-, and DE-based nanofluids could be explained as the result of the change in the excluded volume in different base fluids. The strong repulsive force in DW- and EG-based nanofluids would tend to align the particles, resulting in the decrease of the excluded volume. Koo et al.[92] further discussed that several other factors involving the interaction between CNTs in different base fluids, defects in CNTs, CNT configurations in base fluids, poly dispersive nature of CNT length and diameter, etc. should also be considered.

5. CONCLUSIONS

The preparation and thermal performances of CNT nanofluids were reviewed. Chemical and mechanical treatments have been shown to be effective to disentangle the aggregates and to enhance the dispersibility of CNTs for preparing homogeneous and stable nanofluids. Surface chemistry analysis revealed that functional groups (carbonyl group, hydroxyl group, or surfactant molecule) beneficial to the dispersibility could be attached onto the CNT surfaces after these treatments. The functional groups changed the surface characteristics of the CNTs and increased the repulsive forces between the CNTs, leading to the separation of one CNT from others and resulting in stable nanofluids. With the addition of CNTs, substantial enhancements were observed for nanofluids compared to the corresponding base fluids. The thermal conductivity enhancement ratios increased with the nanotube loading and the temperature but decreased with the average diameter of the included CNTs and the thermal conductivity of the base fluid. The thermal characteristics of nanofluids might be manipulated by means of controlling the morphology of the inclusions, which also provided a promising way to conduct investigation on the mechanism of heat transfer in nanofluids. CNT nanofluids as working fluid significantly enhanced the convective heat transfer in comparison with base fluid, with the enhancement depending on the flow condition, CNT concentration, and pH level. The large enhancement of the convective heat transfer could not be attributed to the enhancement of thermal conduction under the static conditions. Other factors including particle rearrangement, shear induced thermal conduction enhancement, reduction of thermal boundary layer thickness due to the presence of nanoparticles, as well as the very high aspect ratio of CNTs might also account for the enhancement. Using as working fluid in boiling heat transfer CNT nanofluids had the features of enhancing the critical heat flux and causing no fouling on the heat transfer surface. Theoretical investigations demonstrated that a variety of factors including aspect ratio, straightness and thermal conductivity of CNTs, interfacial thermal resistance between the CNT and the matrix, and dispersion status of the CNTs in the base fluid had significant effects on the thermal transport in the CNT nanofluids due to the complex morphologies and surface chemistry of the suspended CNTs.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hqxie@eed.sspu.cn. Tel & Fax: +86-21-50217331.

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