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Nanofluids containing carbon nanotubes treated by mechanochemical reaction

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ABSTRACT

Multi-walled carbon nanotubes (CNTs) were treated by using mechanochemical reaction method to enhance their dispersibility for producing CNT nanofluids. The thermal conductivity was measured by a short hot wire technique and the viscosity was measured by a rotary viscometer. The thermal conductivity enhancement reaches up to 17.5% at volume fraction of 0.01 for an ethylene glycol based nanofluid. Temperature has no obvious effects on thermal conductivity enhancement for the as prepared nanofluids. With an increase in thermal conductivity of the base fluid, the thermal conductivity enhancement of a nanofluid decreases. At low volume fractions (<0.4 vol%), nanofluids have lower viscosity than corresponding base fluid due to lubricative effect of nanoparticles. When the volume fraction is higher than 0.4 vol%, the viscosity increases with nanoparticle loadings. The prepared nanofluids, with no contamination to medium, good fluidity, stability, and high thermal conductivity, would have potential applications as coolants in advanced thermal systems.

1. Introduction

Adding particles into heating and cooling fluids has long been regarded as a promising approach to enhance heat transfer. However, the applications of the particle–fluid mixtures are held back due to the poor stability of those suspensions containing milli-/micro-sized particles. In the past decade, a novel kind of particle suspensions, nanofluids [1], have been developed and have attracted increasingly attention because of their intriguing properties such as high thermal conductivity, stability, and prevention of clogging in micro-channels. Researchers have demonstrated that nanofluids, containing a small amount of metal (e.g., Cu) or nonmetal (e.g., SiC, Al_2O_3, and CuO) nanoparticles, exhibit substantially enhanced thermal conductivities compared to those of the base fluids [2–5]. The enhanced thermal conductivities have been found to be much higher, even up to an order of magnitude greater, than those values predicted by the traditional models, e.g. Maxwell model [6], Hamilton and Crosser model [7], and Davis model [8], that are satisfied for computing the effective thermal conductivity of mixture consisting of fluid and micro- or larger-sized solid particles.

Nanofluids in nature are nanoparticle–fluid mixtures. According to the theories of the effective thermal conductivity of mixtures, high thermal conductivity and larger aspect ratio are very helpful to enhance the effective thermal conductivity. Theoretical and experimental studies demonstrated that carbon nanotubes (CNTs) have very high thermal conductivity [9–11]. And their aspect ratios are very large. Therefore, CNTs are excellent candidates as dispersions for preparing thermal conductivity enhanced nanofluids. However, severe aggregation always takes place in the as prepared CNTs due to its non-reactive surfaces, the intrinsic Van der Walls forces, and the very large specific surface areas and aspect ratios [12]. Surfactant addition is an effective way to enhance the dispersibility of CNTs [13–15]. However, in nanofluid applications, surfactants might cause several problems. Firstly, the addition of surfactants may contaminate the heat transfer media. Secondly, surfactants may produce foams when heating, while heating and cooling are routinely 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, 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. On the other hand, when dispersed in a base fluid, very long CNTs are prone to form entanglements and aggregations. The entanglements and aggregations may enlarge the viscosity of nanofluids and may cause clogging in micro-channel flows. It is essential to cut CNTs to shorter ones with optimal aspect ratios.

The objective of this study is to provide a technical route for preparing CNT contained nanofluids. The nanofluids have the

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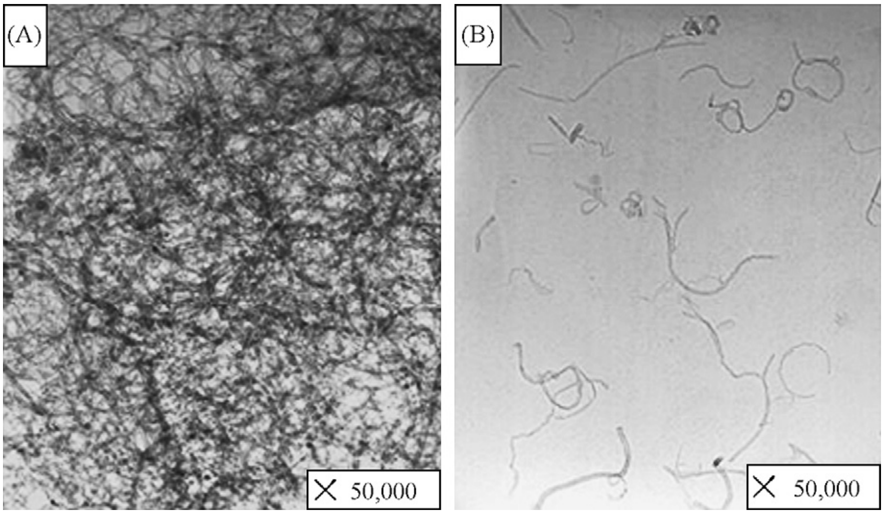

Fig. 1. TEM images of PCNTs (A) and TCNTs (B).

features of high thermal conductivity, long term stability, and surfactant-free.

2. Experimental

Multi-walled CNTs were purchased from Chengdu Organic Chemicals Company Ltd. of Chinese Academy of Sciences. The CNTs were produced by chemical vapor deposition method. The average diameter and length of these CNTs are about 15 nm and 30 μm, respectively. Transmission electron microscope (TEM) observation reveals that the as received pristine CNTs (PCNTs) were not only aggregated, but also entangled (Fig. 1A). It is evident that these PCNTs are not ready to form stable suspensions. Surface treatment is desired to prepare surfactant-free nanofluids. The treatment process has been described previously [16]. Briefly the present steps involved in the preparation of CNT nanofluids include: (1) disentangle the nanotube aggregates and introduce hydrophilic functional groups on the surface of the nanotubes by mechanochemical reaction and (2) disperse the chemically treated CNTs into a base fluid. Potassium hydroxide has been used to modify the surfaces of CNTs. Distilled water (DW), ethylene glycol (EG), and glycerol (Gly) were used as base fluids. TEM micrograph for treated CNTs (TCNTs) (Fig. 1B) shows that the aggregates and entanglements of PCNTs have been broken after chemical treatment. CNTs were cut short by the intensive mechanical forces during the ball milling process.

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 oleylamine, PCNTs cannot be dispersed into nonpolar liquid like decene. Fig. 2 shows the comparison of the stability of nanofluids containing PCNTs and TCNTs. For the suspension with 0.1 vol% PCNTs dispersed in DW, almost all the nanotubes were sedimented after 5 min, leaving upper fluid transparent. In sharp contrast to PCNTs, TCNTs were dispersed in many kinds of polar fluids, like DW, alcohol, and EG without using surfactant. The TCNTs/fluid suspensions remain stable for many months with no visible precipitation at the bottom.

Thermal conductivities of the base fluids and the CNT nanofluids were measured by a transient short hot wire method. The detailed principle and the apparatus setup were described elsewhere [17]. A copper wire with a diameter of 50.0 μm was used for the hot wire, and it served as both a heating unit and as an electrical resistance thermometer. The wire has a layer of insulation coating with a thickness of 7.0 μm for insulation. Initially the copper wire immersed in media is kept at equilibrium with the surroundings. When a regulated voltage is supplied to initiate a measurement, the electrical resistance of the wire changes proportionally with the rise of the temperature. The thermal conductivity can be calculated from the slope of the rise in the wire's temperature against a logarithmic time interval. The uncertainty of this measurement is estimated to be less than 1.0%.

3. Results and discussion

Fig. 3 depicts the thermal conductivity enhancements of the CNT nanofluids as a function of the volume fraction of nanotubes. In this article, k and k_0 represent the thermal conductivities of the nanofluid and the base fluid, respectively, and $\Delta k = k - k_0$ is the thermal conductivity enhancement. ϕ is the volume fraction of TCNTs. Substantial increases in thermal conductivity are seen for all measured nanofluids, with thermal conductivity enhancement up to 17.5% observed for nanotube loading at 1.0 vol% in EG. The experimental data clearly indicate that the ratios of the enhancements increase monotonously with the volume fraction of TCNTs. For all the measured volume fractions, the thermal conductivity enhancement ratios of DW based nanofluids are smaller than the corresponding values of EG based nanofluids.

For alumina nanoparticle contained nanofluids, it was reported that thermal conductivity augmentation ratios decrease with the increase in thermal conductivity of the base fluid [4,18]. TCNT sus-

Fig. 2. Stability comparison of nanofluids containing PCNTs or TCNTs.

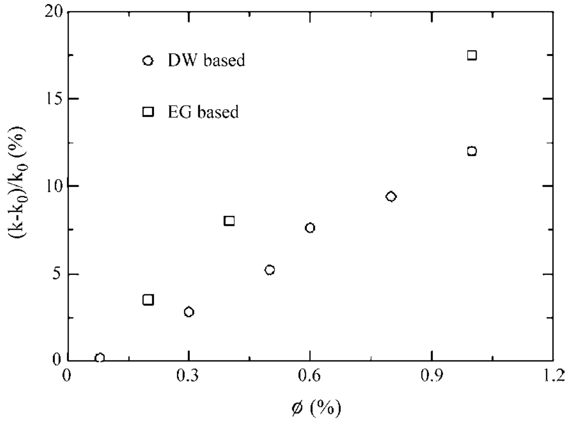

Fig. 3. Thermal conductivities of nanofluids as a function of nanotube loadings.

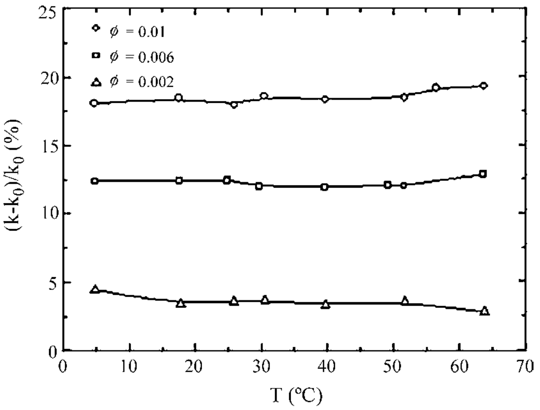

Fig. 5. CNT nanofluids have weakly temperature-dependent thermal conductivity.

pensions present a similar behavior. As shown in Fig. 4, much more dramatic improvement in thermal conductivity of nanotube suspension is seen for a base fluid with lower thermal conductivity. At 1.0 vol%, the thermal conductivity enhancements are 17.5%, 16.0%, and 12.0% for CNT nanofluids in EG, Gly, and DW, respectively. No matter what kind of base fluid is used, the thermal conductivity enhancement of CNT nanofluids is much higher than that reported for alumina nanoparticle suspensions [4] at the same volume fraction. The reason would lie in the substantial difference in thermal conductivity and morphology between alumina nanoparticle and carbon nanotube.

Choi et al. [19] firstly reported that the thermal conductivity enhancement for suspension with 1.0 vol% nanotubes in olefin oil ($k_0 = 0.1448\,\mathrm{W\,m^{-1}\,K^{-1}}$) was 160%, much higher than the present experimental value, 17.5% for nanofluid with 1.0 vol% TCNT in EG ($k_0 = 0.259\,\mathrm{W\,m^{-1}\,K^{-1}}$). This discrepancy would not be attributed to the difference in the thermal conductivity of the base fluid. Preparation method and CNT specification may account for the difference. Since detailed information about how CNTs were dispersed in the oil and formed a stable nanofluid as well as crystallinity of the CNTs was not described in Ref. [20], direct comparison could not be made. Assael et al. [20] measured the thermal conductivity of multi-walled and double-walled carbon nanotube suspensions and obtained a maximum thermal conductivity enhancement of 34% for a water based nanofluid containing 0.6 vol% multi-walled carbon nanotubes. They used CTAB as surfactant. Liu et al. [21] reported a thermal conductivity enhancement of 12.4% for CNT–EG suspensions at a volume fraction of 0.01. This result is close to the value presented in Ref. [22]. Xie et al. [22] firstly made effort to produce CNT nanofluids without surfactant. They tailored the surfaces of MWNTs through oxidation with concentrated acids and successfully obtained surfactant-free CNT nanofluids. However, severe weight loss may happen during the oxidation procedure. In the present work, the authors used mechanochemical reaction technique to treat the CNTs and also obtained surfactant-free CNT nanofluids. Another advantage is that the length of the CNTs may be controlled through adjusting the ball milling time. The thermal conductivity enhancement ratios of the present nanofluids are larger than those corresponding values reported in Ref. [22] (see Fig. 4).

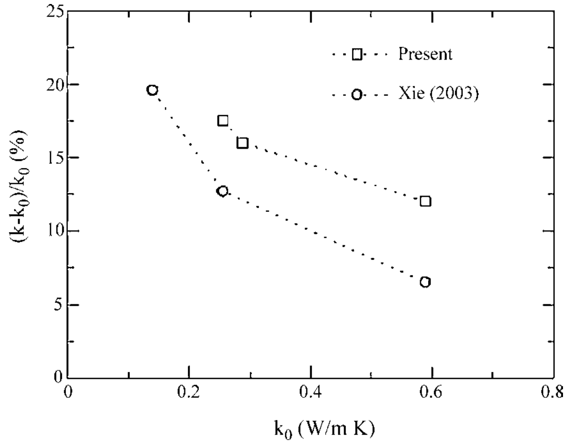

Fig. 4. Thermal conductivity enhancement ratios as a function of thermal conductivities of the base fluids. The volume fractions of all these nanofluids are 0.01.

Fig. 5 shows the thermal conductivity enhancement ratios of CNT nanofluids at different temperatures. The base fluids for all the measured CNT nanofluids in Fig. 5 are EG. It is observed that the thermal conductivities of CNT nanofluids are higher than those of the base fluids at all the tested temperatures. Patel et al. reported that the thermal conductivity enhancement ratios of Cu nanofluids are enlarged considerably when the temperature increases [23]. However, our CNT nanofluids show different thermal conductivity enhancement behaviors. It is seen from Fig. 5 that for all the nanofluids at different volume fractions of 0.01, 0.006, and 0.002, the thermal conductivity enhancement ratios almost keep constant when the tested temperatures vary. Brownian motion differences in these two nanofluid systems may contribute to the observed differences. In the experiments of Ref. [23], water and toluene were used as base fluids and spherical copper nanoparticles were used as additions. The viscosities of these two base fluids are small.

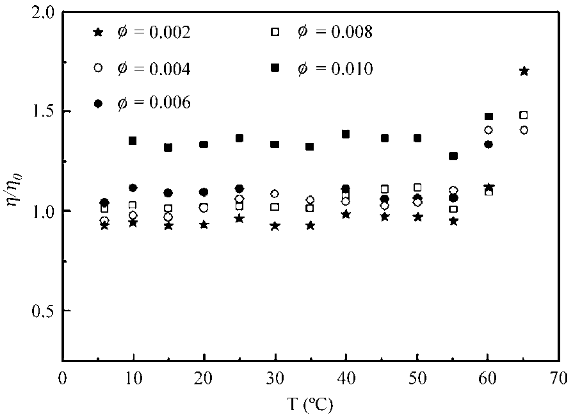

Fig. 6. Relative viscosities vary with the tested temperature.

Therefore, Brownian motions of the suspended Cu nanoparticles are prone to take place and will become more intensive when the temperature is ascended. The micro convection caused by the Brownian motions would help to enhance the thermal conductivity of the suspensions. Here in our experiments, EG was used as base fluids and cylindrical nanotubes with large aspect ratios were used as additions. The effect of Brownian motion is not so obvious.

The ratios of the viscosity of the CNT nanofluid (η) to the corresponding value of the base fluid (η_0) are shown in Fig. 6. The base fluids of all the nanofluids in Fig. 6 are DW. At low volume fractions ($\phi < 0.004$), nanofluids have lower viscosity than the corresponding base fluids due to lubricative effect of nanoparticles. When the volume fraction is higher than 0.004, the viscosity increases with nanoparticle loadings. When the temperature is higher than 55 °C, η/η_0 appears to increase substantially with the temperature. Further investigation is needed to clarify the phenomena.

4. Conclusions

In summary, a novel two-step technique for preparing surfactant-free carbon nanotubes (CNTs) nanofluids has been developed. The surfaces of the CNTs were tailored to be hydrophilic through mechanochemical reactions and the dispersibility of the CNTs was dramatically enhanced. Thermal conductivity measurements revealed that the thermal conductivity enhancement reaches up to 17.5% at a volume fraction of 0.01 for an ethylene glycol based nanofluid and the temperature variation has no obvious effects on the thermal conductivity enhancement for the as prepared nanofluids. The thermal conductivity enhancement is reduced with an increase in the thermal conductivity of the base fluid. Because of lubricative effect of nanoparticles, nanofluids may have lower viscosity than the corresponding base fluids if the volume fraction is low. The promising features of without surfactant, good fluidity, long-term stability, and high thermal conductivity would enable the CNT nanofluids to be used as advanced coolants in thermal energy engineering.

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