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Investigation of thermal conductivity and viscosity of ethylene glycol based ZnO nanofluid

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ABSTRACT

Ethylene glycol (EG) based nanofluids containing ZnO nanoparticles were prepared, and the thermal transport properties including thermal conductivity and viscosity were measured. The results show that the thermal conductivity of ZnO-EG nanofluids is independent of setting time from 20 to 360 min. The absolute thermal conductivity increases with temperature for different temperatures ranging from 10 to 60 °C, while the enhanced ratios are almost constant. The thermal conductivity of ZnO-EG nanofluids depends strongly on particle concentration, and it increases nonlinearly with the volume fraction of nanoparticles. The enhanced value of 5.0 vol.% ZnO-EG nanofluid is 26.5%, consistent with the prediction values by the combination of the aggregation mechanism with the Maxwell and Bruggeman models. The facts indicate that there is no magic physics behind nanofluids and the classical theories predict the measurements well. The rheological behaviors of the nanofluids show that ZnO-EG nanofluids with low volume concentrations demonstrate Newtonian behaviors, and for higher volume concentrations nanofluids, the shear-shinning behavior will be observed, because the effective volume fraction of aggregates is much higher than the actual solid volume fraction.

1. Introduction

Nanofluids, which are suspensions of nanoparticles in conventional fluids such as water, ethylene glycol (EG) and engine oil, are proposed as the next generation heat transfer fluids due to the fact that their thermal transport capacities are significantly higher than those of the base liquids [1]. Nanofluids have attracted great interest due to their potential benefits for numerous applications such as microelectronics, energy supply, transportation and HVAC [2]. To now, more than twenty laboratories worldwide have published experimental data on the thermal conductivity of nanofluids, and the results show that nanofluids exhibit substantially higher thermal properties particularly thermal conductivity even when the concentration of suspended nanoparticles is lower than 5% in volume fraction [3]. At present the thermal conductivity data measured by different groups are scattered. A literature [4] divided the experimental thermal conductivity values into "low group" and "high group". The dispersion is believed to be due to various factors such as the measuring techniques, the particle size and shape, the particle clustering and sedimentation. Many papers neglect some important factors including the stabilities of nanofluids, the measured temperature, and the setting time after nanofluid preparation. Although the significant dependence of nanofluid thermal conductivity on temperature has clearly been shown, the amount of data remains very limited [5–7]. Many thermal conductivity data were measured at so-called "room temperature". The setting time is another vital factor. The measured data demonstrate that the apparent thermal conductivity is highest right after nanofluid preparation and decreases considerably with elapsed time, showing a time-dependent characteristic. However, most of the papers have not stated the setting time clearly [8–10]. All the above-mentioned factors may account for the discrepancy of the results to some extend. The lack of reliable experimental data is certainly one of the main reasons for no universal theoretical or empirical model for the thermal conductivity of nanofluids.

The viscosity of nanofluids is another important transport property for applications of nanofluids as a new class of heat transfer fluids in thermal devices or systems such as heat exchangers or cooling systems. For example, Ko et al. studied the viscosities of CNT nanofluids prepared by using surfactant or acid treatment methods [11]. However, experimental data for the viscosity of nanofluids are scarce compared with their thermal conductivity [12,13]. Many kinds of metallic nanoparticles and oxide nanopartices are used as the additives of nanofluids. Among the additives, Cu, CuO, Al_2O_3, TiO_2, Fe_3O_4, SiC and CNT are most commonly studied [3], while the thermophysical properties of ZnO nanofluids has not well been investigated.

In the present paper, we prepared nanofluids containing ZnO nanoparticles. The thermal transport properties including thermal

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conductivity and viscosity were measured. The effects of the particle volume fraction, measured temperature, setting time on the thermal conductivity were further investigated.

2. Experimental

ZnO nanoparticles (Hangzhou WanJing New Material Company, China) with an average diameter of 10–20 nm (Fig. 1) and the density 5.6 g/cm^3 were used. Ethylene glycol was of analytical reagent (AR) grade, and it was obtained from Shanghai Chemical Reagents Company. The fixed quality of ZnO nanoparticles with different volume concentrations (ϕ: 0.002–0.05) was dispersed in ethylene glycol. Sample preparation was carried out by using a sensitive mass balance with an accuracy of 0.1 mg. The volume fraction of the powder was calculated from the weight of dry powder using the true density provided by the supplier and the total volume of the suspension. The nanofluid mixture was stirred and sonicated (40 kHz, 150 W) continuously for 3 h. This ensured uniform dispersion of nanoparticles in the base fluid.

The size and morphology of the dry ZnO nanoparticles were examined by using field-emission scanning electron microscopy (Hitachi S4800). Particle size distribution and average particle size of ZnO nanoparticles dispersed in EG were measured by a Malvern Nanosizer (Malvern Instrument, UK). A transient short hot-wire (SHW) technique was applied to measure the thermal conductivities of the nanofluids from 10 to 60 °C [14]. In addition to hot-wire system, a temperature-controlled bath was used to maintain different temperatures of nanofluids during the measurement process. The experimental apparatus was calibrated by measuring the thermal conductivity of deionized water, and the accuracy of these measurements was estimated to be within ±1%. In the thermal conductivity measurements, the vessel containing the tested sample was placed in a temperature-controlled bath and a thermocouple inside the vessel was used to monitor the sample temperature. After the sample temperature reached the bath temperature, the sample was kept at the temperature for further 30 min to ensure temperature equilibrium before a measurement. The rheological property of nanofluids was measured by a viscometer (LV DV-II+ Brookfield programmable viscometer, America) with a temperature-controlled bath [15]. Viscosity measurements were started at 60 °C, and temperature was gradually reduced to 20 °C in 10 °C interval. Spindle SC-18 was used in this viscometer and was calibrated by using Brookfield viscosity standard fluids. All the viscosity measurements were recorded at steady state conditions, and the time of nanofluids sample in the sample chamber was 10 min. Due to the restriction of measurement range of the instrument, this work will not cover a wide range of shear rate.

3. Results and discussion

Fig. 2 shows the influence of ultrasonification processing time on the particle size distribution and average particle size, and it indicates that the average size decreases rapidly in the first 3 h. After 3 h the average size is about 210 nm, and the nanoparticles in nanofluid have a narrow particle size distribution. The ultrasonification processing time was therefore set for 3 h for preparing all the nanofluids. The measured average particle size in the formulated nanofluids is much larger than the size of primary particles. This indicates that ultrasonification was not able to break the agglomerates into primary particles.

In our process, a transient short hot-wire technique was applied to measure the thermal conductivities of the nanofluids. To ensure consistency of the measurement, the setting time (the placed time after the sample temperature reached the bath temperature) of nanofluids should be determined firstly. Fig. 3 shows the enhanced ratio of thermal conductivity, $(k-k_0)/k_0$, as a function of the setting time, k and k_0 represent the thermal conductivities of the nanofluid and base fluid, respectively. The result shows that the thermal conductivity of ethylene glycol based ZnO (ZnO-EG) nanofluids is independent of setting time from 20 to 360 min. To ensure the reliability of measurement of thermal conductivity, the setting time of nanofluids should be more than 30 min. Several researchers observed the "time-dependent characteristic" of thermal conductivity [8–10], that is to say, thermal conductivity was highest right after nanofluid preparation, and then it decreased considerably with elapsed time. In our opinion, the "time-dependent characteristic" cannot illustrate the essence of the enhancement of

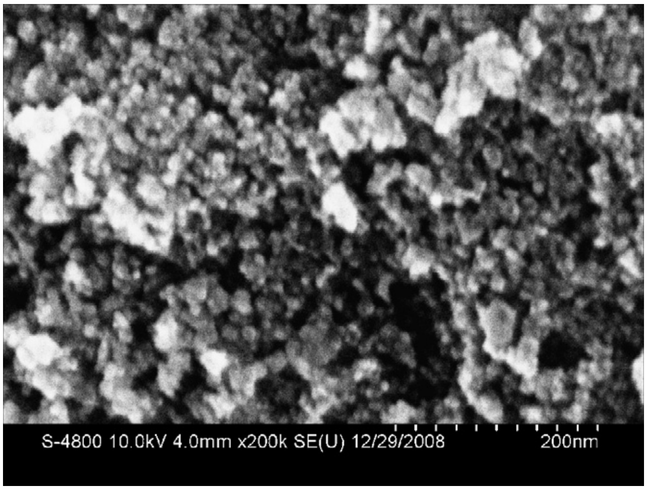

Fig. 1. SEM micrograph of ZnO nanoparticles as received.

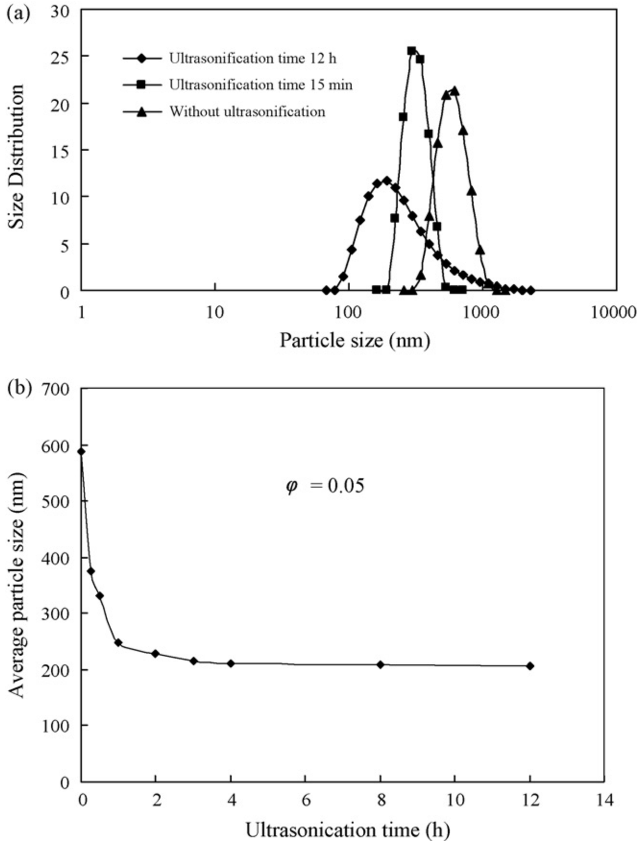

Fig. 2. Particle size distribution (a) and average particle size (b) as a function of ultrasonification processing time for 5.0 vol.% ZnO-EG nanofluid.

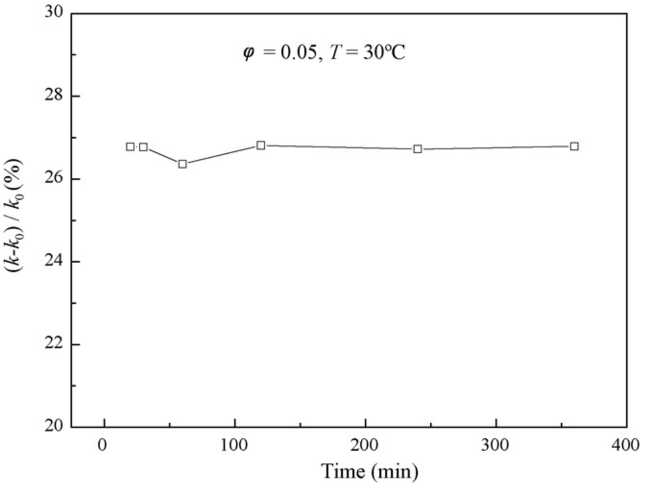

Fig. 3. Thermal conductivity enhancement with setting time for ZnO-EG nanofluid.

thermal conductivity. The temperature of nanofluids as a function of time after preparation shows that the temperature of nanofluid is gradually decreasing. The obtained thermal conductivity measured right after preparation does not reflect the true value at the set temperature. Some literatures reported that the sedimentation of nanoparticles in the nanofluids caused the decrease of the effective volume concentrations when the nanofluids were not stable. This indicates that the unstability is another factor accounting for the “time-dependent characteristic”, so the stability of nanofluids should be paid more attentions [16,17].

Although some groups have reported studies of the thermal conductivity enhancement at elevated temperatures, there are relative fewer effective data to reach a unanimous conclusion about the influence of temperature on thermal conductivity. In this paper, the effect of temperature on the enhancement of effective thermal conductivity of nanofluids was investigated by measuring the thermal conductivity of nanofluids for different temperatures ranging from 10 to 60 °C. As shown in Fig. 4, the absolute thermal conductivities increase with the increasing temperature, while the enhanced ratios are almost constant, and the thermal conductivities of the nanofluids track the thermal conductivities of the base liquid, which is similar to the conclusion of Timofeeva and co-workers [18,19]. The temperature has a very small effect on the effective thermal conductivity enhanced ratios of the nanofluids, because of the high viscosity of the base liquid and relatively large aggregates of the nanoparticles, and the contribution of other factors such as the Brownian motion are small, which is consistent with the prediction by Chen’s model [20].

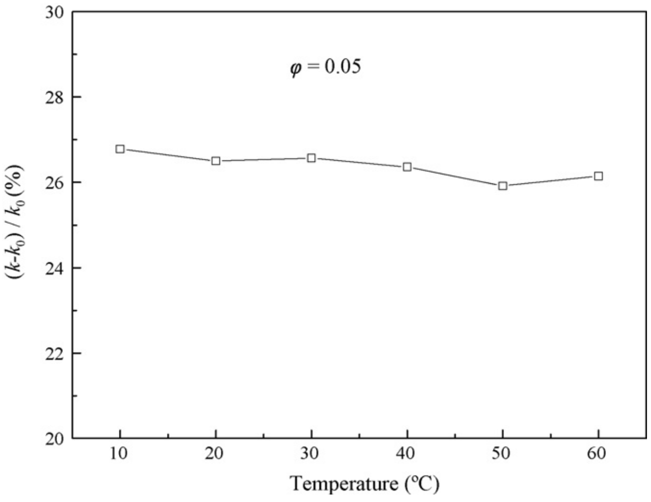

Fig. 4. Thermal conductivity enhancement with temperature for ZnO-EG nanofluid.

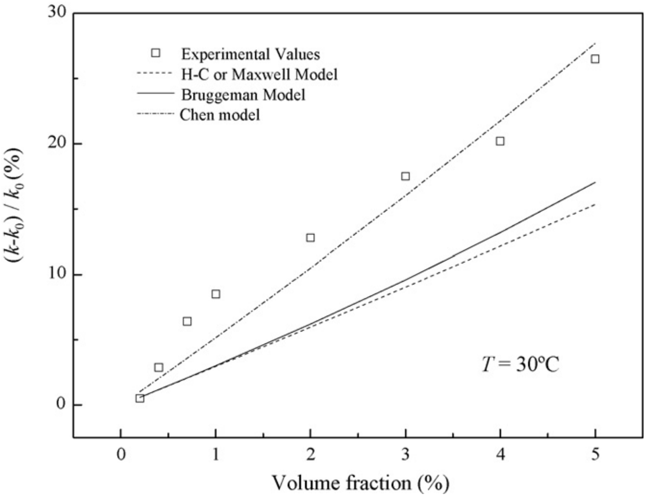

Fig. 5. Thermal conductivity enhancement as a function of volume fraction for ZnO-EG nanofluid.

Fig. 5 shows the enhanced thermal conductivity as a function of volume fraction in ZnO-EG nanofluids. It is apparent that the thermal conductivity of ZnO-EG nanofluids increases nonlinearly with increase in volume fraction of the nanoparticles, as the reported results [21,22]. At the lower volume fraction range from 0.2 to 0.7% and higher volume fraction range from 1 to 5%, there are two approximate lines given by the enhanced thermal conductivity versus volume fraction, and the slope at lower volume fraction is larger than that at higher volume fraction. The reason of lower enhancement at high volume fraction may be that the increase in the nanofluid viscosity is much higher than the enhancement in the thermal conductivity for high volume fraction ZnO-EG nanofluids [23]. In our experiments, the average diameter of ZnO nanoparticles is 10–20 nm, and the enhanced ratio at 3 vol.% is 17.5%, which is larger than that of 30 and 60 nm ZnO-EG, and similar to that of 10 nm ZnO-EG nanofluid [24]. The results exhibit that the thermal conductivity of the nanofluid is strongly dependent on the size of suspended particles.

Maxwell model is known as following equation,

$$\frac{k}{k_0} = \frac{k_\mathrm{p} + 2k_0 - 2\phi(k_0 - k_\mathrm{p})}{k_\mathrm{p} + 2k_0 + \phi(k_0 - k_\mathrm{p})} \tag{1}$$

where k_p and φ are the thermal conductivity of nanoparticles and the volume fraction of nanoparticles. For solid–liquid mixtures in which the ratio of conductivity of two phases is larger than 100, Hamilton and Crosser (H–C) developed the following model,

$$\frac{k}{k_0} = \frac{k_\mathrm{p} + (n-1)k_0 - (n-1)\phi(k_0 - k_\mathrm{p})}{k_\mathrm{p} + (n-1)k_0 + \phi(k_0 - k_\mathrm{p})} \tag{2}$$

For spherical particles, the H–C model is the same as the Maxwell model. The above two models cannot give a good prediction for the thermal conductivity of nanofluids, and these models usually underestimate the enhancement of thermal conductivity. Chen et al. proposed the aggregation mechanism to interpret the facts [20]. They introduced the concepts k_a and φ_a in the Maxwell equation

$$\frac{k}{k_0} = \frac{k_\mathrm{a} + 2k_0 - 2\phi_\mathrm{a}(k_0 - k_\mathrm{a})}{k_\mathrm{a} + 2k_0 + \phi_\mathrm{a}(k_0 - k_\mathrm{a})} \tag{3}$$

where k_a and φ_a are the thermal conductivity of aggregates and the effective volume fraction of aggregates given by $\varphi_\mathrm{a} = \varphi/\varphi_\mathrm{ma}$ with φ_ma the maximum packing fraction of aggregates. As aggregates do

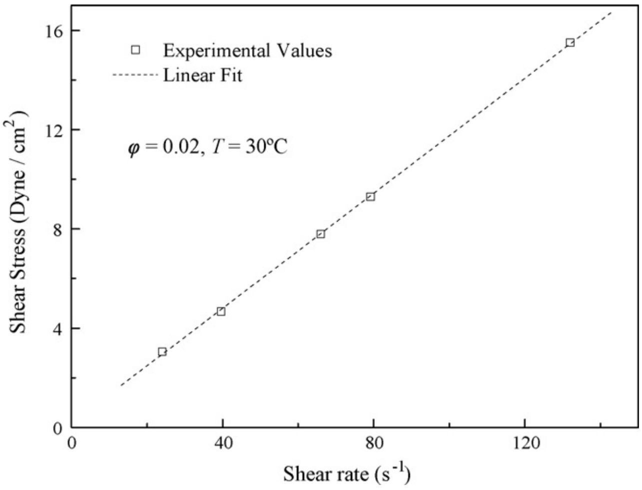

Fig. 6. Shear stress versus shear rate for 2 vol.% ZnO at 30 °C.

not have constant packing throughout the structure, the packing density is assumed to change with radial position according to the power law with a constant index (D). So, $\varphi_a = \varphi(\alpha_a/\alpha)^{3-D}$, where α_a and α are the radii of aggregates and primary nanoparticles, respectively. The term D has a typical value of 1.8 for nanofluids according to the diffusion limited aggregation (DLA) [25–27].

Bruggeman model can be applied to calculate the thermal conductivity of aggregates, which can be regarded as concentrated liquid–solid mixtures [20,28],

$$\frac{k_a}{k_0} = \frac{1}{4}\left\{(3\phi_{in}-1)\frac{k_p}{k_0} + (3(1-\phi_{in})-1) + \left[\left((3\phi_{in}-1)\frac{k_p}{k_0} + (3(1-\phi_{in})-1)\right)^{1/2} + 8\frac{k_p}{k_0}\right]\right. \tag{4}$$

where φ_{in} is the solid volume fraction of aggregates given by $\varphi_{in} = (\alpha_a/\alpha)^{D-3}$. Taking $\alpha_a = 3.34\alpha$ and $D = 1.8$, one can obtain k_a, and the effective thermal conductivity of the nanofluids can be estimated by Eq. (3). Fig. 5 shows the experiment and predicted increment of thermal conductivity as a function of nanoparticle volume fraction. The results indicate that the classic H–C model and Maxwell model without taking the aggregates into account greatly underpredict the measured thermal conductivity, while the combination of the aggregation mechanism with the Maxwell and Bruggeman models gives a good prediction of the effective thermal conductivity of the nanofluids.

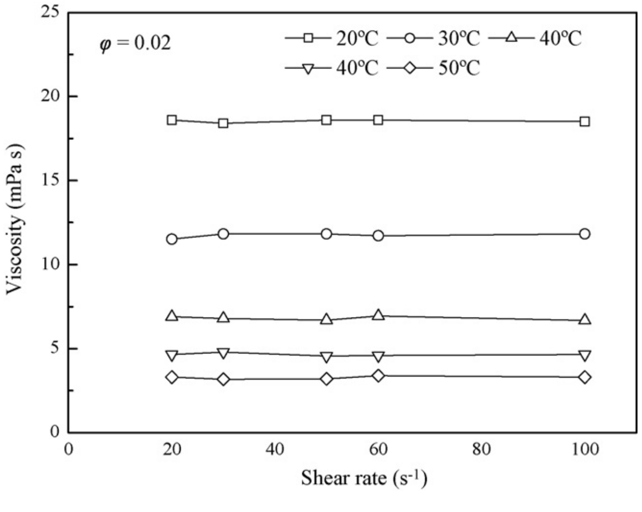

Fig. 7. Viscosity as a function of shear rate for 2 vol.% ZnO-EG nanofluid at different temperature.

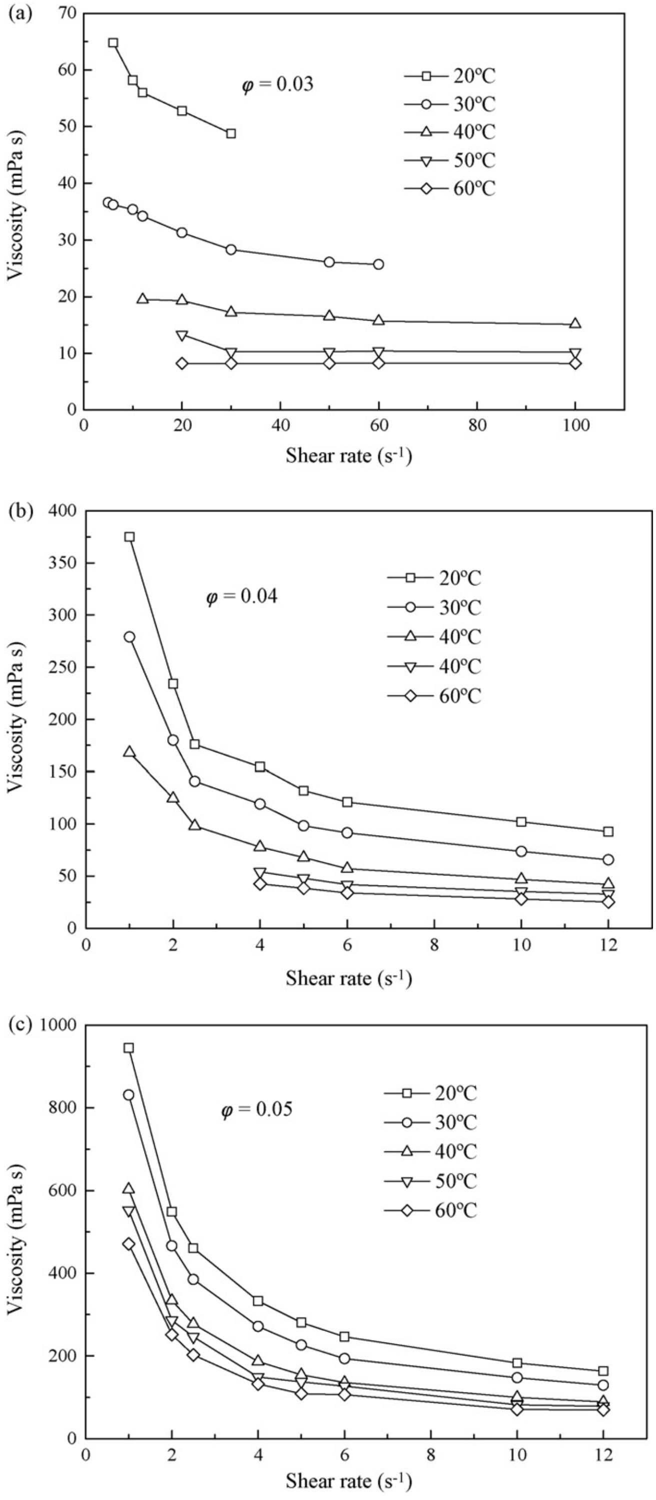

Fig. 8. Viscosity as a function of shear rate for 3, 4 and 5 vol.% ZnO-EG nanofluid at different temperature.

Viscosity is related to molecular momentum transport. In general, the viscosities of nanofluids are abnormally increased, well beyond the prediction of classical models for viscosity. There are some debates about whether the nanofluids are Newtonian or non-Newtonian fluids [4]. The analysis of Kabelac and Kuhnke

[4] shows that the viscosities of Al_2O_3 nanoparticle suspensions decrease with the shear rates. On the contrary, Prasher's results demonstrate that the viscosities of nanofluids of Al_2O_3-propylene glycol are independent of shear rates, indicating that nanofluids are Newtonian fluids in nature [29]. In order to investigate the rheological behaviour, whether ZnO-EG nanofluid is Newtonian or non-Newtonian fluid should be verified firstly. The equation governing Newtonian behavior of a fluid is given by

$$\tau = \mu \gamma \tag{5}$$

where τ is the shear stress, μ is the coefficient of viscosity, and γ is the shear strain rate. The shear stress versus shear rate for 2 vol.% ZnO-EG nanofluid at 30 °C is shown in Fig. 6. The linear relation between shear stress and shear rate shows that 2 vol.% ZnO-EG nanofluids demonstrate Newtonian behavior under the conditions of this work. Chen et al. studied the rheological behaviors of 0.5–1.8 vol.% TiO_2-EG nanofluids [30], and the results show that the TiO_2-EG nanofluids are Newtonian from 20 to 60 °C covering a wide range of shear rate ($0.056–1000\,s^{-1}$). The conclusion is similar to that of ZnO-EG nanofluids.

Viscosity as a function of shear rate for 2 vol.% ZnO-EG nanofluid at different temperature (Fig. 7) also demonstrates that the viscosity of 2 vol.% ZnO-EG nanofluid is independent of shear rate from 20 to $100\,s^{-1}$ in the range of 20–60 °C. The results for other concentrations ($\varphi \le 0.02$) are similar. While for the ZnO-EG nanofluid with $\varphi \ge 0.03$, the shear-shinning behaviour will be observed (Fig. 8). For higher volume concentrations and lower temperatures, the shear-shinning behaviours are more obvious. These facts show that ZnO-EG nanofluids with $\varphi \ge 0.03$ demonstrate non-Newtonian behaviors. According to Chen's aggregation mechanism [30], $\varphi_a = \varphi(\alpha_a/\alpha)^{3-D}$, taking $\alpha_a = 3.34\alpha$ and $D = 1.8$, the effective volume fraction of the aggregates for ZnO-EG nanofluid with $\varphi = 0.03$, 0.04 and 0.05 will up to 0.13, 0.17 and 0.21, respectively. ZnO-EG nanofluids with the higher effective volume fraction show the different rheological behaviors from those with low effective volume fraction [30].

4. Conclusions

Well dispersed ethylene glycol based ZnO nanofluids were obtained by dispersing ZnO nanoparticles into the base liquid under sonication. The transient short hot-wire technique was applied to measure the thermal conductivities of the nanofluids. The result shows that the thermal conductivity of ZnO-EG nanofluids is independent of setting time from 20 to 360 min. The absolute thermal conductivity increases with the increasing temperature for different temperatures ranging from 10 to 60 °C, while the enhanced ratios are almost constant, and the thermal conductivities of the nanofluids track the thermal conductivities of the base liquid. The thermal conductivity of the nanofluid is strongly dependent on the size of suspended particles. The thermal conductivity of ZnO-EG nanofluids increases nonlinearly with an increase in volume fraction of the nanoparticles, and the enhanced value of 5.0 vol.% ZnO-EG nanofluid is 26.5%, well beyond the values given by the existing classical models for the solid–liquid mixture, and is consistent with the prediction values by the combination of the aggregation mechanism with the Maxwell and Bruggeman models. The facts indicate that there is no magic physics behind nanofluids and the classical theories predict the measurements well. The rheological behaviors of the nanofluids were studied. The results show that ZnO-EG nanofluids with low volume concentrations ($\varphi \le 0.02$) demonstrate Newtonian behaviors under the condition of this work, and the viscosity significantly decreases with increasing temperature. While for higher volume concentrations ($\varphi \ge 0.03$) ZnO-EG nanofluids, the shear-shinning behavior will be observed, showing the non-Newtonian behaviors, because the effective volume fraction of aggregates is much higher the actual solid volume fraction.

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