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Thermal Conductivity of Reduced Graphene Oxide by Pulse Laser in Ethylene Glycol

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Graphene oxide was prepared using modified Hummers method. Stable ethylene-glycol nanofluids containing graphene oxide nanosheets were provided. Nd: YAG pulsed laser was applied to prepare reduced nanofluids. Experimental results revealed that thermal conductivity of the nanofluids is increased with increasing the concentration of graphene oxide (GO) in ethylene glycol. The enhancement ratio of 0.05% mass fraction of GO was 16.32%. Thermal conductivity improved with increasing the temperature about 14.28%. The dynamic light scattering and results of zeta potential analyses, after one week and eight months, showed the same results which demonstrated the stability of nanofluids.

Keywords: Graphene oxide, Ethylene-glycol, Thermal conductivity, Reduce, Concentration

INTRODUCTION

The most important technical challenge in many industries is cooling method. One solution for this problem is to increase the existing heat exchange surface area. Heat transfer fluids such as water, ethylene glycol or oil significantly have poor properties for cooling performance. Therefore, it is needed to improve the abilities of conventional heat transfer fluids [1]. Nanofluids have attracted much attention due to their strange thermal conductivity improvement [2]. Dispersing nanometer-sized solid particles in the base fluids fabricate suspensions of nanofluids. Quick slowdown is decreased in the stable nanofluids and clogging in the walls of heat transfer devices reduces. The high thermal conductivity of nanofluid causes more energy efficiency and lower costs [3-5]. Nanofluids with metal or nonmetal particles have high thermal conductivity. Carbon materials are popular because of their large thermal conductivity and low density compared with metals. Research results exhibit that nanofluids with carbon-based nanoparticles, such as carbon nanotubes [6-11], graphite nanoparticles [12,13], exfoliated graphite, nanofibers [14] and diamond nanoparticles [15,16], are appropriate to make suspensions.

Graphene is a monolayer of sp^2-bonded carbon atoms with a honeycomb lattice. Due to the two-dimensional structure, exceptional physical and chemical properties [17], it has attracted researchers' attention. Graphene has displayed some strange electrical, mechanical and thermal behaviors, such as very high carrier mobility [18], long-range ballistic transport at room temperature [19], quantum confinement in nanoscale ribbons [20] and single-molecule gas detection sensitivity [21]. Moreover, Graphene based nanofluids are expected to exhibit high thermal conductivity, because graphene is inherently a great thermal conductor. The number of graphene layers and interlayer spacing are known to have a significant influence on thermal conductivity. By increasing the number of layers and the spacing between them the thermal conductivity can be significantly reduced. Therefore, reduction of graphene

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oxide (GO) is important to increase the thermal conductivity. GO is generally reduced by chemical and thermal treatments to remove the oxygen-containing functional groups [22,23]. Effective low temperature methods and environment friendly methods for reduction of GO is highly demanded. Recently reduction of GO by laser has attracted the researches' attention [24].

In this study, homogeneous and stable ethylene glycol (EG) based nanofluids containing GO nanosheets were prepared and reduced by pulse laser irradiation. The effects of temperature, particle size and reduced graphene oxide concentration on the thermal conductivity were investigated.

EXPERIMENTAL

Graphite flakes (Sigma-Aldrich, cat #332461, 150 µm lateral dimensions) were used as the raw materials for synthesis of graphene oxide (GO) using modified Hummers method [25]. Then, GO nanosheets were dispersed in ethylene glycol resulted homogeneous and stable nanofluids. The mass fraction of GO in ethylene glycol (GO-EG) was maintained 0.01, 0.03 and 0.05 [26]. Then Nd: YAG pulsed laser (Quantel, Briliant b class4 with 532 nm wavelength, 5 ns pulse duration, 10 Hz repetition rate, 0.3 W power, and 300 mJ maximum pulse energy in 7 mm beam diameter) was applied for reduction of GO at room temperature condition. The laser beam was directed towards a quartz tube containing nanofluids. GO-EG suspension was stirred using a magnetic stirrer without using focusing lens to obtain a large irradiation area. The total time of laser irradiation was considered 5, 7, 10 and 12 min to find the highest reduction. These nanofluids were named RGO-EG.

The stability of the nanofluids was confirmed by the measurement of zeta potential. Reduction of GO nanosheets was achieved using Fourier transform infrared spectroscopy (FTIR, model 410). Morphological and structural features of the nanofluids were investigated by TEM (Philips, model CM120). Dynamic light scattering (DLS, model Malvern Instruments-MAL1008078) was used to determine the size distribution profile of small particles in suspension. Optical absorption spectra were recorded using a Perkin Elmer UV-Vis spectrometer. Transient short hot wire (SHW, KD2, DECAGON) technique was applied to determine the thermal conductivity of nanofluids for different temperatures and concentrations.

RESULTS AND DISCUSSION

The measured stability was -40.8 and -47.3 mV for GO-EG and RGO-EG nanofluids, respectively. Reducing the oxygen-containing groups of RGO-EG due to the pulsed laser irradiation was investigated using FTIR spectroscopy (Fig. 1). The absorption bands appeared in the IR spectrum of GO nanosheets were found to be located at 3340 cm^{-1} (O-H stretching band), 1730 cm^{-1} (C=O stretching band), 1630 cm^{-1} (skeletal vibrations of aromatic domains), 1401 cm^{-1} (bending absorption of carboxyl group O=C-O), 1226 cm^{-1} (O-H bending vibrations), and 1044 cm^{-1} (C-O stretching vibrations), consistent with the previous reports [28]. Figure 1 shows that after 10 min laser irradiation, the intensity of all the main absorption peaks relating to the oxygen-containing functional groups (including O-H, C=O and C-O bonds) significantly is reduced.

Figure 2 shows the typical TEM images of GO and GO-EG. GO nanosheets incline to congregate together to form multilayer agglomerates graphene (Fig. 2a). After dispersing GO in EG, the sheet-like morphology of the prepared graphene appears, while most of the graphene nanosheets are in style of the thin few-layer graphene and some are in the format of tiny agglomerates, as shown in Fig. 2b.

DLS is a valuable tool for determining and measuring the agglomeration and characterizing the size of nanosheets in suspensions. Size and distribution of particles in the nanofluid have important role in determining the thermal conductivity. As seen in Fig. 3, maximum number of the size of particles for GO-EG is 317 nm (Fig. 3a) and 292 nm for RGO-EG (Fig. 3b). Due to reduction of GO nanosheets, nanoparticle size is decreased and less agglomeration in GO-EG nanofluids occurs.

The UV-Vis spectra of the GO suspension before and after different laser irradiation time from 5 to 12 min are shown in Fig. 4. The degree of deoxygenation is calculated based on the position of the absorption peak of the spectra. The GO-EG suspension displays an absorption peak at ~235 nm due to the $\pi \rightarrow \pi^*$ transition of aromatic C═C bonds [29, 30]. Furthermore, a shoulder at ~300 nm is observable which can be attributed to the $n \rightarrow \pi^*$ transitions of the carbonyl groups. The intensity of GO-EG absorbance peak is stronger than that of RGO-EG sample, indicating

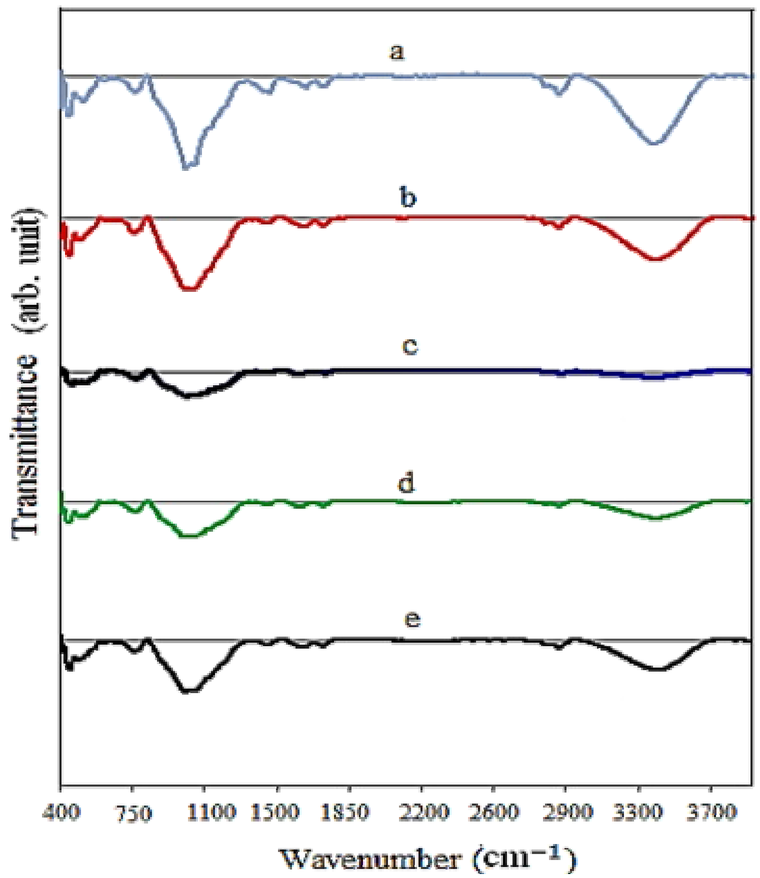

Fig. 1. FTIR spectra of a) GO-EG and RGO-EG at b) 12, c) 10, d) 7 and e) 5 min.

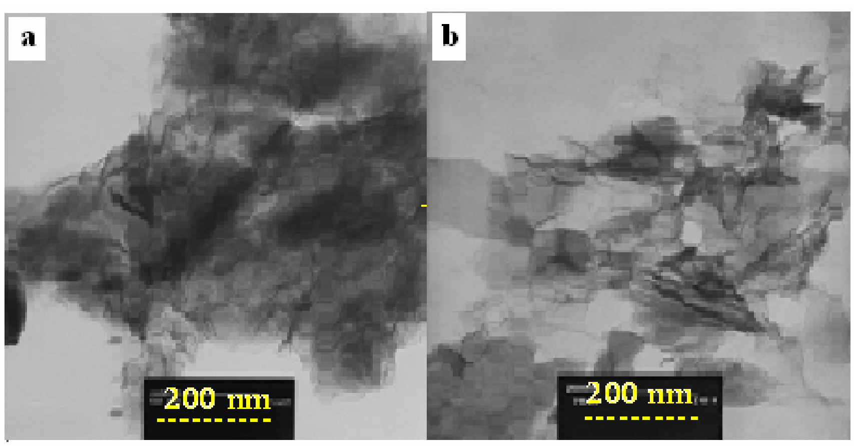

Fig. 2. TEM image of a) GO powder and b) GO-EG.

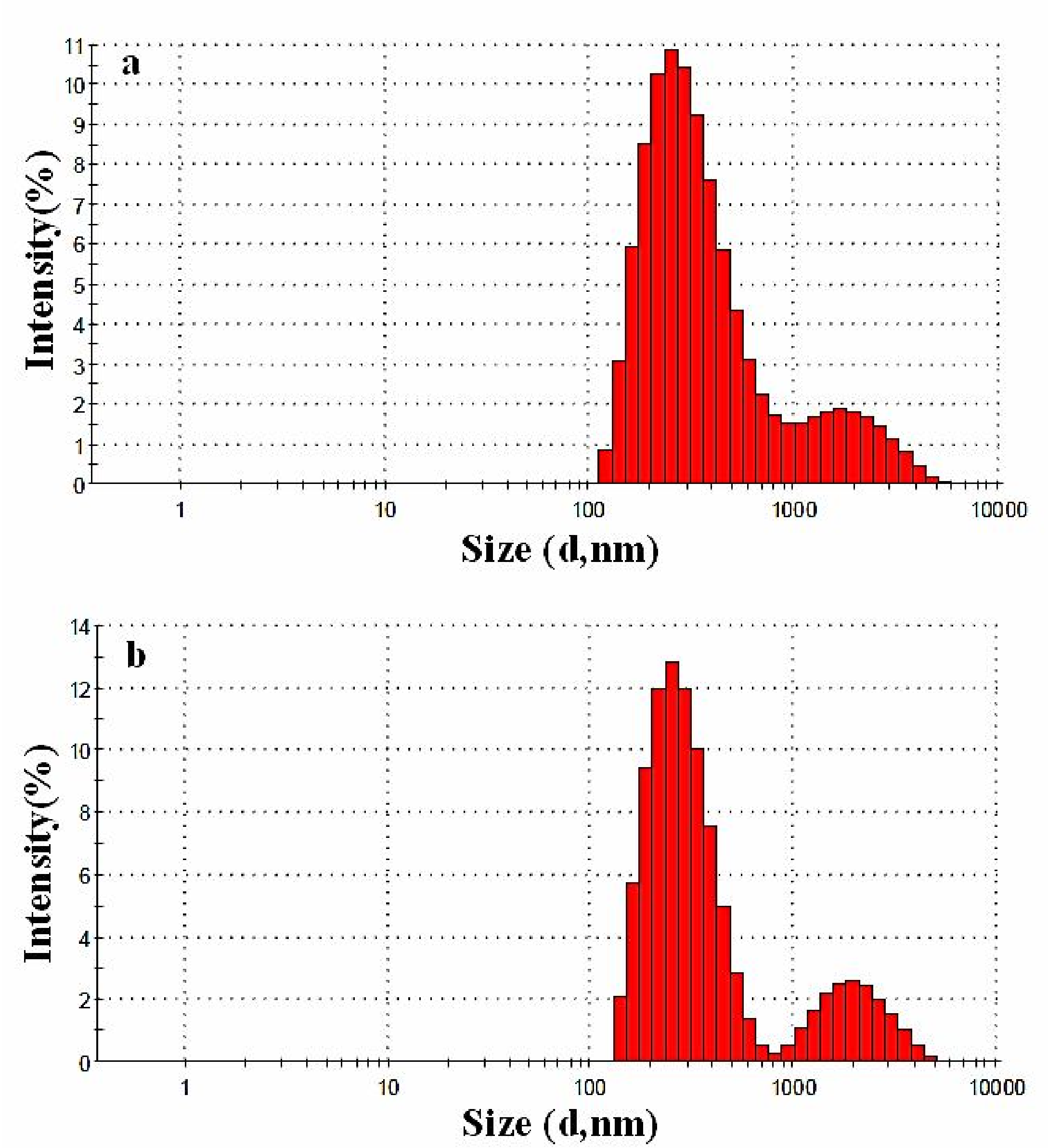

Fig. 3. Particles size distribution of a) GO-EG and b) RGO-EG nanofluids.

progressive restoration of the electronic conjugation within the reduced graphene oxide sheets [31] under the laser irradiation. The UVVis spectra of RGO-EG show a monotonic decrease in absorbance with increasing wavelength. The red shift of the stronger adsorption peak from 235 to ~255 nm is due to more $\pi \rightarrow \pi^*$ transitions in the aromatic bands with lower energy for the electronic transition. The shoulder on the peak (~300 nm) also disappeared after pulsed laser deposition, which means removing of the carbocyclic and carbonyl groups. The best reduction time for RGO-EG was found 10 min.

Thermal conductivity of GO-EG and RGO-EG (with 10 min laser irradiation) nanofluids was measured by KD2 at different temperatures. GO-EG and RGO-EG nanofluids

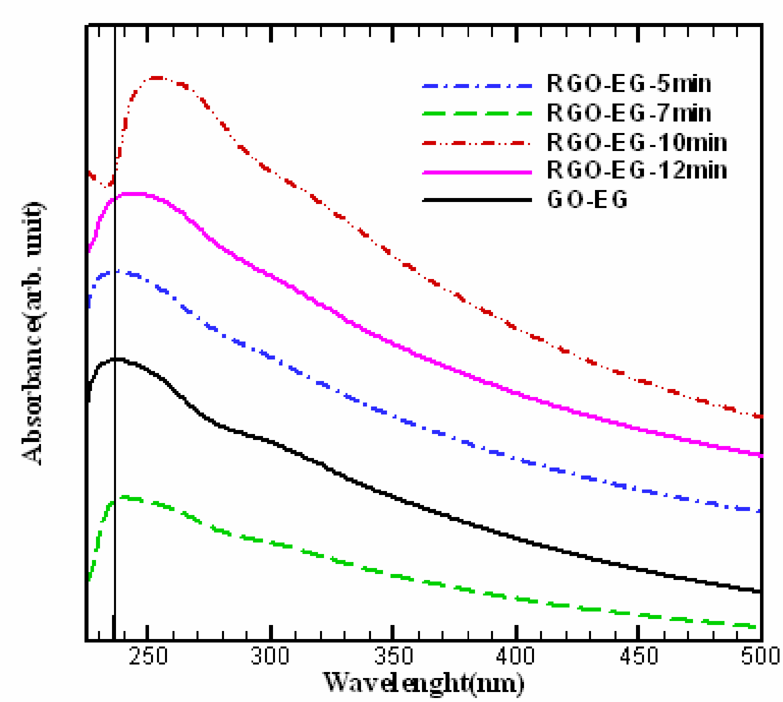

Fig. 4. The UV-Vis spectra of GO-EG and RGO-EG suspensions reduced by pulsed laser irradiation at the different irradiation periods of b 5, 7, 10 and 12 min.

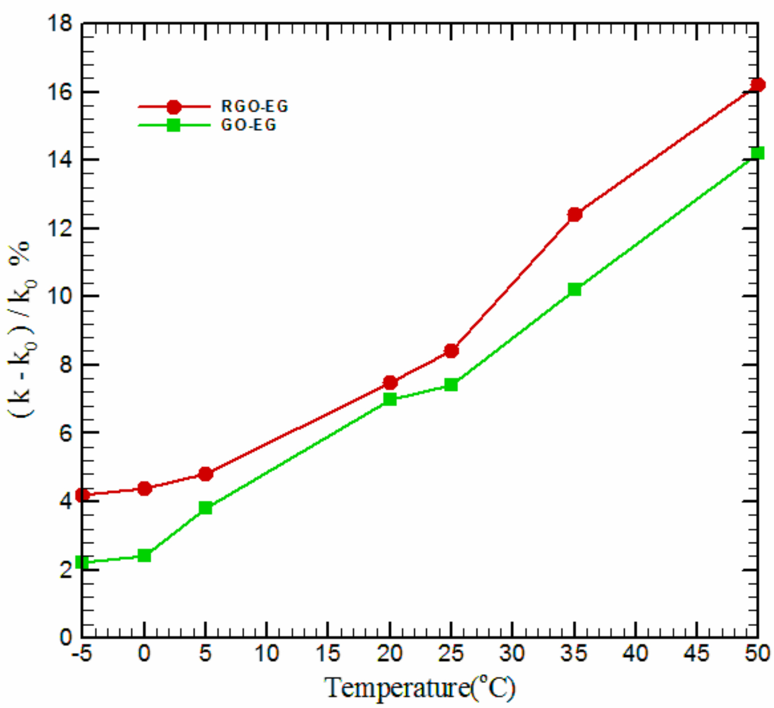

Fig. 5. Thermal conductivity of GO-EG and RGO-EG nanofluids at different temperatures.

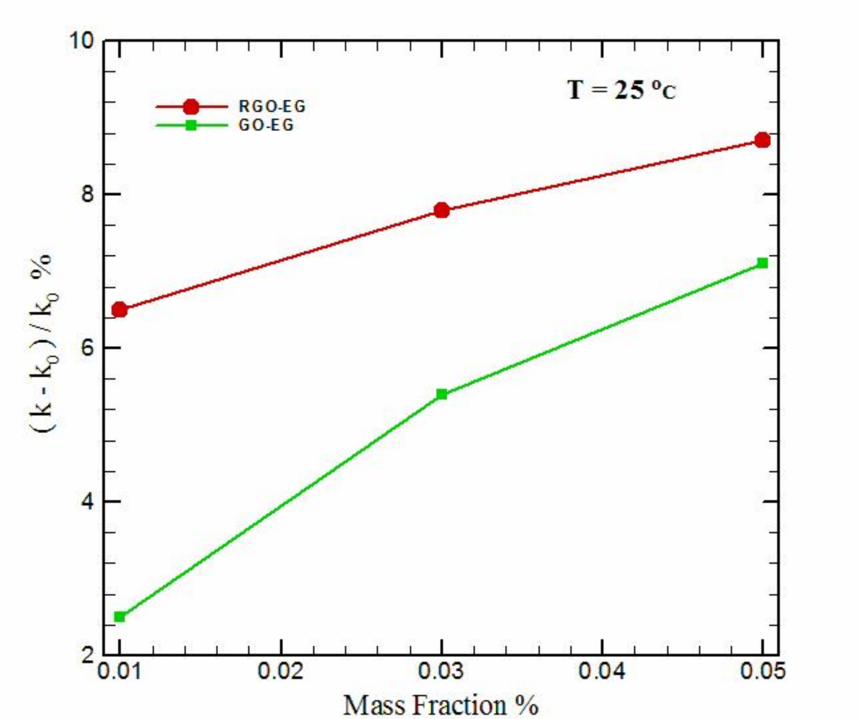

Fig. 6. Thermal conductivity of GO-EG and RGO-EG nanofluids with different concentrations (T = 25 °C).

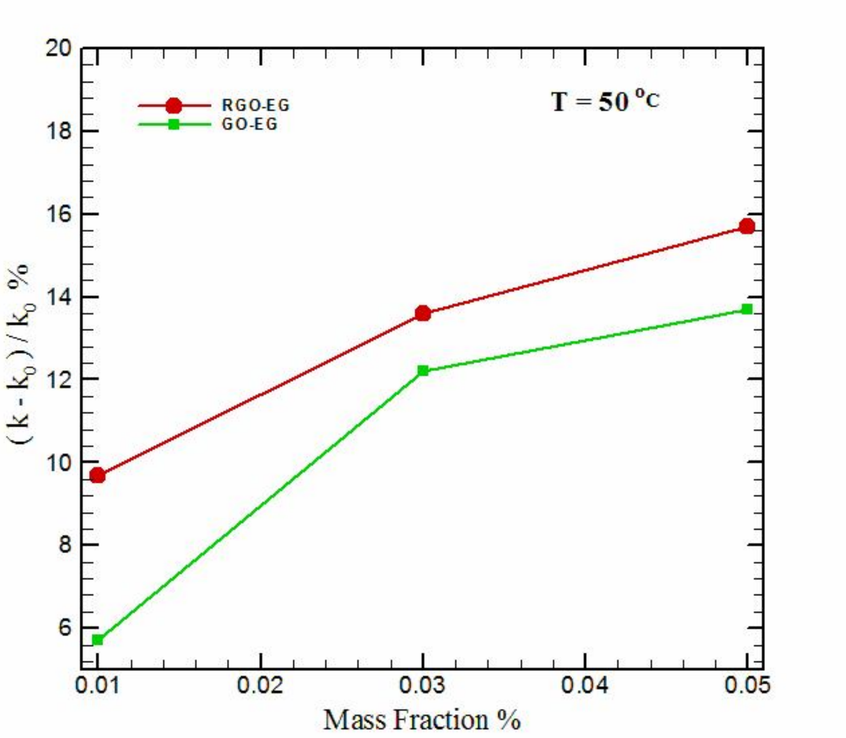

Fig. 7. Thermal conductivity of GO-EG and RGO-EG nanofluids with different concentrations (T = 50 °C).

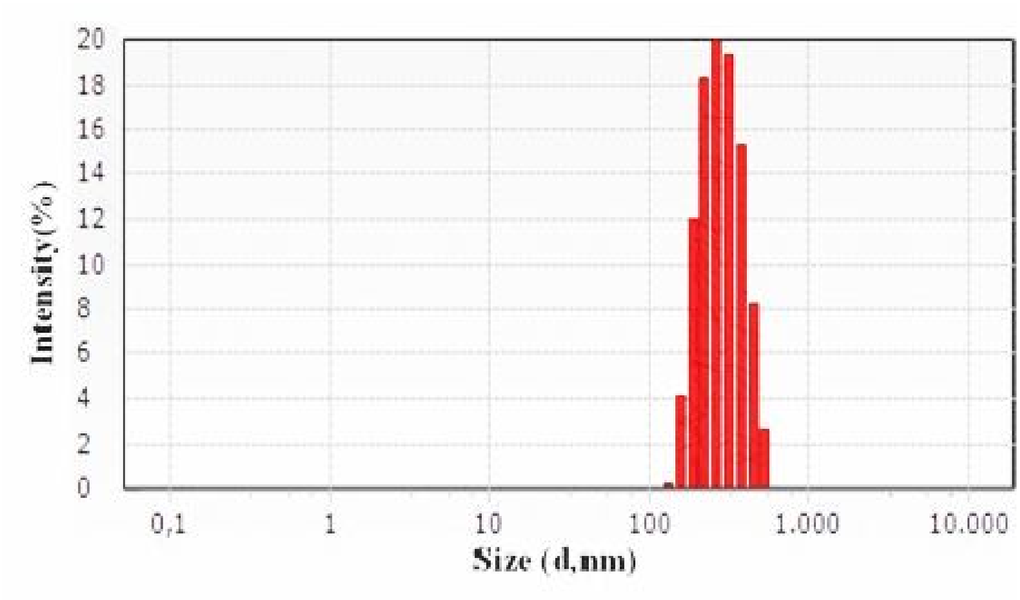

Fig. 8. Particles size distribution of RGO-EG nanofluids after eight months.

with 0.05% mass fractions were prepared. The percentage of enhancement in thermal conductivity is calculated using $(k - k_0) \times 100/k_0$, where "k_0" is the thermal conductivity of base fluid and "k" is that of nanofluids. Different temperatures from -5 to 50 ° C were used for measuring thermal conductivity of the nanofluids which improved from 2.2% to 14.28% for GO-EG and from 4.38% to 16.32% for RGO-EG nanofluids (Fig. 5).

The thermal conductivity for different concentrations of 0.01, 0.03, 0.05 mass fraction at 25 °C (Fig. 6) and 50 °C (Fig. 7) also was measured. With increasing mass fraction the thermal conductivity increased from 2.46% to 14.28% for GO-EG and from 6.55% to 16.32% for RGO-EG nanofluids in a nonlinear manner. The nonlinearity in thermal conductivity of carbon-based nanofluids has been reported [6]. The enhancement of thermal conductivity for EG based nanofluids at 50 °C compared to 25 °C illustrates better results for the reduced nanofliuds. In the present study, very low concentration, *i.e.*, ~10^{-4} g cm^{-3} was selected, so that the viscosity of the nanofluids was not increased which is not desirable in application. These results are comparable with reported thermal conductivity data [32 ,33]. In order to study the stability of nanofluieds, the zeta potential and DLS (Fig. 8) analyses were repeated after eight months from preparation of RGO-EG. The measured stability was -47.1 mv for RGO-EG nanofluids.

CONCLUSIONS

Stability and thermal conductivity of ethylene-glycol nanofluids containing graphene oxide nanosheets have been studied. Temperature range from -5 to 50 °C was used and different concentrations of 0.01, 0.03, 0.05 mass fraction at °C and 50 °C were considered. The nanofluids were stable after eight months. GO-EG showed higher thermal conductivity than ethylene-glycol and the highest thermal conductivity was for RGO-EG. The thermal conductivity was improved from 2.2% to 14.28% for GO-EG and from 4.38% to 16.32% for RGO-EG nanofluids. This improvement was remarkable with respect to the amount of GO nanosheets which was about 10^{-4} mass fraction. There are some reports about higher increase in thermal conductivity of nanofluids, however their corresponding mass fraction is much more than that in our samples [34]. The method used to reduce GO-EG in our experiments has an important effect on enhancement of thermal conductivity. Therefore, we can conclude that RGO-EG nanofluids could be useful and low cost materials for heat transfer applications along with a straight forward method to develop to large-scale production of RGO-EG nanofluids without any surfactant stabilizers.

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