PREPARATION OF STABLE NANOFLUIDS WITH SURFACE FUNCTIONALIZED NANOPARTICLES AND DETERMINATION OF THE CHANGE IN THERMAL CONDUCTIVITY OF NANOFLUIDS

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REFERENCE NO	ABSTRACT
NANO-01	Aqueous dispersions of non-covalently functionalized graphene nanoplatelets (GNP) were successfully prepared through ultrasound technology in the presence of polyethylene glycol-polyhedral oligomeric silsesquioxane (PEG-POSS) as a stabilizer. The pH values of dispersions containing 0.05, 0.1, and 0.5 wt% GNP, with two different amounts of (0.1 and 0.2 wt%) PEG-POSS, were all adjusted via ammonium hydroxide (NH_4OH) solution before sonication to the value where the dispersions would be expected to be stable. Stability evaluations were carried out by Ultraviolet-Visible (UV-Vis) spectrophotometry and zeta potential measuring device (Zetasizer Nano). Aqueous dispersion of 0.5 wt% GNP with no PEG-POSS showed the best stability with a zeta potential of -42 mV. Whereas, the dispersions containing PEG-POSS provided higher thermal conductivity values.
Keywords: Graphene, POSS, nanofluid, thermal conductivity	

1. INTRODUCTION

The term "nanofluids" was first used by Choi in 1995, stating that nanofluids have substantially higher thermal conductivities than those of the base heat-transfer fluids, such as water, oil, ethylene glycol (radiator fluid) or a refrigerant [1]. Further experimental and theoretical studies have been carried out by many researchers, with different nanofluids. Nanoparticles have been dispersed in base fluids and remain suspended in the fluid to a much greater extent than was previously achieved with microparticles. This is mainly thought to be due to Brownian motion preventing gravity settling and agglomeration of particles, resulting in a much more stable, suspended fluid. A significant part of experimental results indicates that nanofluids have the potential to be used as new generation heat-transfer fluids [2].

Attempts to improve the heat transfer properties by adding solid particles to the liquids have been a much more advanced method, but large sized solid particles provide a very low recovery in thermal properties at high volumetric additive ratios, resulting in precipitation of particles, erosion of parts in the system, and pressure drop. Moreover, the ever-shrinking heat exchanger elements and plugging of the microchannels with these micro-fluidized fluids render the use of micro-sized particles impossible. As a result of previous experimental studies on thermal conductivity of nanofluids [3], it is stated that the increase in thermal conductivity of nanofluids cannot be explained by the traditional effective thermal conductivity models. Although there are various interpretations as to which factors this increase depends on, with every new theoretical study, possible reasons previously defended by a few research groups are rejected by some other researchers and disparate reasons are defended. The situation has become such that more theoretical model studies have been included in the literature than almost systematic experimental work [4]. Besides, the increasing number of researches in recent years indicate that the experimental results obtained by different research groups show very important differences even in the same type of nanofluids [5, 6].

Meeting the refrigeration needs of the systems is a major problem in various industries. Especially in the last two decades as a result of rapid developments in electronics, communications, and computer technologies, while systems have shrunk in size, increasing processing speeds and storage capacities have led to very severe thermal management problems. Of course, this is not just a problem specific to small systems. For example, the cooling systems of the vehicles used for transport are very large and significant reductions in fuel consumption can be achieved by reducing them. In many large or small size systems, the need for increased cooling capacity is achieved, which takes up less space. One of the methods is to expand the wings or microchannels however the use of surfaces has now reached its limits. Another method is to increase the heat transfer ability of the fluid used.

In the scope of the study, the method based on the principle of detection of the third harmonic (3ω method) using AC hot-wire and lock-in amplifier together, was developed to measure the thermal conductivity of fluids and an experimental system was established [7]. Since it uses a radial heat flow from a single element acting as a heater and thermometer, the 3ω method is quite similar to the transient hot wire method. However, the main difference is that electricity is used by the transient hot wire method instead of the time-dependent response used by the current frequency dependence response. When a sinusoidal current at the frequency ω passes through the metal wire, a heat wave can be generated at a frequency of 2ω, which is generated by the voltage component at the frequency of 3ω.

Many organic and inorganic stabilizers have been used to stabilize the graphene, and stabilizer usage has increased over the years [8]. However, besides these chemicals, the use of derivatives of POSS (poly(hedral oligomeric silsesquioxane)), an effective stabilizer source that researchers have recently shown and strongly encouraged. The POSS with cage-like structure has a unique chemical physicochemical properties due to its organic and inorganic hybrid components. And it is soluble in many organic-inorganic solvents [9]. The POSS structure is a hybrid structure consisting of silicon and oxygen. Monofunctional and multifunctional monomers such as styryl-POSS, methacrylate-POSS, norbornyl-POSS, vinyl-POSS, epoxy-POSS and siloxane-POSS have been synthesized by adding to the structure. Unlike other organic compounds, POSS derivatives are odorless, non-volatile, and environmentally friendly chemicals. In this study, a hybrid nanoparticle was prepared using PEG(polyethylene glycol)-POSS for stabilization of GNP.

2. MATERIALS AND METHODS

Graphene nanoplatelets (GNP) with a specific surface area of 750 m^2/g was supplied from XG Sciences, Inc. PEG-POSS (PG1190) was purchased from Hybrid Plastics. All specifications of GNP and PEG-POSS are shown in Table 1. Ammonia (NH_3) anhydrous, ≥99.98% was purchased from Sigma-Aldrich.

Table 1. Material specifications of GNP and PEG-POSS.

GNP		PEG-POSS	
Appearance	Black powder	**Appearance**	Clear, colorless liquid
Carbon Content	> 99.5	**Molecular Weight**	~5576 g/mol
Bulk Density	0.2-0.4 g/cm^3	**Viscosity (at 25 °C)**	280 cP
Relative Gravity	2.0-2.25 g/cm^3	**Thermal Stability**	5 wt% loss at 250 °C
Specific Surface Area	750 m^2/g	**Solvent Stability**	Water, alcohols
Particle Diameter	< 2μm		
Thickness	2 nm		

2.1 Preparation of Nanofluids

For preparation of GNP nanofluids, distilled water was used as a base fluid. Ultrasonicator (UP400S, Hielscher Ultrasonics GmbH, Teltow, Germany) at a setting of cycle 0.5 and amplitude 50%, was used for aqueous GNP dispersions. Nanofluids having 0.05, 0.1, and 0.5 wt% GNP concentration were sonicated for 10 min. before pH adjustment. The

nanofluids including PEG-POSS were prepared by first sonicating distilled water and PEG-POSS together for 5 minutes, then GNPs were added into the solution and later, sonication was performed for extra 10 minutes.

Due to electrokinetic properties, high stability is related with pH control [10]. 0.1 M and 1 M NH$_4$OH solutions were prepared and added into 10-min-sonicated dispersions. During addition of NH$_4$OH solutions, Innolab Multi 9310 pHmeter was used for pH measurements of all samples at around 25 °C. Initial and final pH values and added drops of NH$_4$OH solutions are given in Table 2, Table 3, and Table 4, for the dispersions without PEG-POSS, with 0.1wt% PEG-POSS, and 0.2 wt% PEG-POSS, respectively. After pH adjustment, dispersions were sonicated for 50 minutes. To prevent overheating, ice bath was used during sonication.

Table 2. The pH adjustments of PEG-POSS free dispersions with 0.1 M NH$_4$OH and 1M NH$_4$OH solutions.

GNP [wt%]	Initial pH	NH$_4$OH Conc. [M]	Added Drops	Final pH
0.05	6.94	0.1	15	8.10
0.10	6.56	0.1	22	8.14
0.50	4.65	0.1	68	8.17
0.05	6.57	1.0	3	8.48
0.10	6.36	1.0	2	7.95
0.50	5.30	1.0	12	8.07

Table 3. The pH adjustments of 0.1 wt% PEG-POSS dispersions with 0.1 M NH$_4$OH solution.

GNP [wt%]	Initial pH	NH$_4$OH Conc. [M]	Added Drops	Final pH
0.05	5.88	0.1	30	8.50
0.10	5.59	0.1	39	8.13
0.50	4.67	0.1	220	8.05

Table 4. The pH adjustments of 0.2 wt% PEG-POSS dispersions with 0.1 M NH$_4$OH solution.

GNP [wt%]	Initial pH	NH$_4$OH Conc. [M]	Added Drops	Final pH
0.05	5.91	0.1	25	8.04
0.10	5.44	0.1	40	8.16
0.50	4.68	0.1	170	8.15

3. RESULTS AND DISCUSSION
3.1 Stability of Nanofluids

Stability of nanofluids was evaluated by UV-Vis Spectrophotometry and Zeta Potential measuring device (Zetasizer Nano). UV-Vis Spectrophotometry is the measurement of the transmittance or absorbance of a sample in a cuvette b beam path of light of a certain wavelength. The Beer-Lambert Law is given in Equation 1, showing that absorbance is proportional to the dispersed concentration.

$$A = -\log\left(\frac{I}{I_0}\right) = \varepsilon bc \qquad (1)$$

Thus, higher absorbance value refers to a well dispersed nanofluid. For this purpose, UV-Vis Spectrophotometer (Thermo Scientific, Evalution Array) was used in the wavelength region between 200 and 800 nm. First, samples were diluted with distilled water at 1:20 ratio [11, 12], then absorbance values of samples were measured for three consecutive weeks. The UV-Vis spectra of 0.05 and 0.1 wt% GNP dispersions are shown in Figures 1 and 2, respectively. However, no reliable data were obtained for 0.5 wt% GNP dispersions.

The highest absorbance value was observed in the region between 280 and 290 nm. As time passes, a decrease in absorbance is expected to be recorded due to the sedimentation.
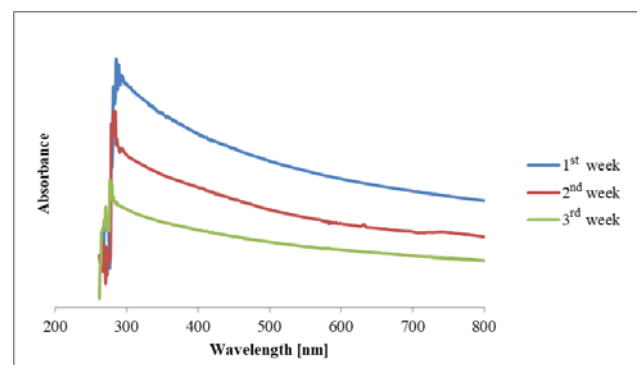

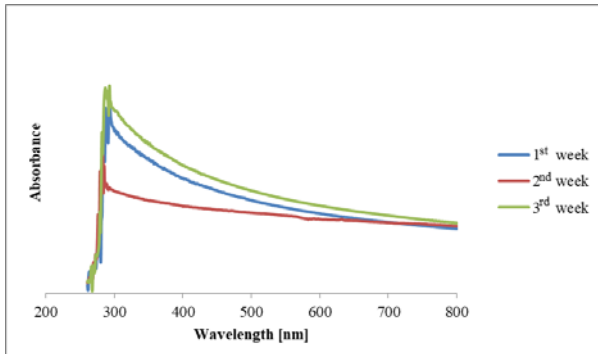Figure 1. Weekly UV-Vis Spectra of 0.05 wt% GNP dispersion.

Figure 2. Weekly UV-Vis Spectra of 0.1 wt% GNP dispersion.

In suspensions or dispersions, the charge at interface occurs due to contact with liquid and particle, causing location change of free ions in liquid. Then the particle is surrounded by counter-ions. This area is called Electrical Double Layer (EDL) [13]. When a charged particle is dispersed, it develops on the surface of a double layer of adsorbed, often referred to as EDL [14]. The inner layer is mostly composed of the opposite charged ion/molecules of the particle Stern layer. Beyond the stern layer, electrostatic effects resulting from the surface load on the particles are reduced according to the discharge law, indicating that the distance of each flow decreases by 1/e factor of the field [15]. Although mathematically this electrostatic effect extends to infinity, it is experimentally only available from particle surface to a few nm.

A dispersed layer of the same and counter-loaded ion/molecules grows beyond the Stern Layer and the Stern Layer forms EDL. The composition of this dispersed layer is dynamic, depending on various factors such as pH, ionic strength, concentration, etc. When an electric field is applied to such a distribution, charged particles move towards the opposite electrode (electrophoresis). In this common layer, there is a hypothetical plane that acts as an interface between moving particles and the dispersed layer around during electrophoresis. This plane is slipping plane, and the particle behaves like a unique object from Stern Layer to Slipping Plane in the dispersion.

The potential at the slipping plane is called as Zeta Potential. Figure 3 shows a negatively charged particle and its electrical double layer redrawn from reference [5].
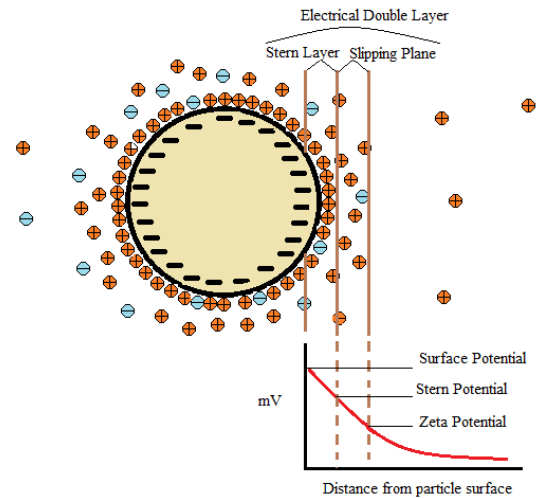

Figure 3. A negatively charged particle and its electrical double layer (Redrawn from ref. [5]).
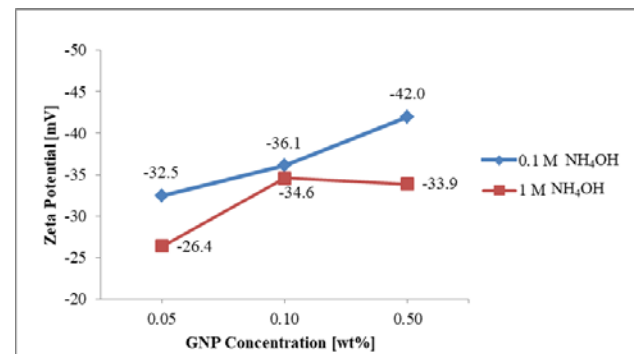

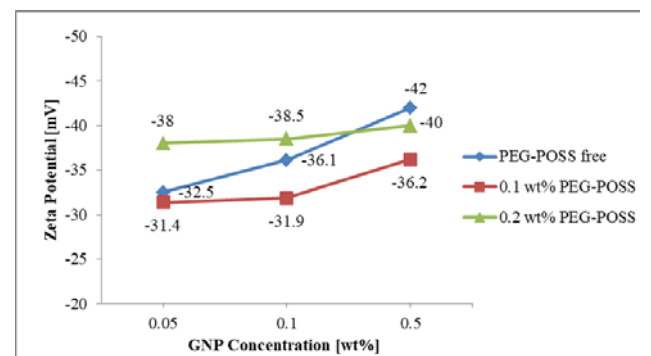Figure 4. Zeta potential versus GNP concentration for PEG-POSS free dispersions.

Figure 5. Comparison of all nanofluids in their zeta potential value enhancement (pH values were adjusted with 0.1 M NH$_4$OH solution).

Zeta potential values of PEG-POSS free aqueous dispersions with respect to GNP concentration (wt%) are given in Figure 4, showing that pH adjustment with NH$_4$OH solution of low molarity (0.1 M), provided

better stabilization. Figure 5 compares zeta potential values against GNP concentration for all dispersions with 0.1 and 0.2 wt% PEG-POSS and also without PEG-POSS. The zeta potential increased with GNP concentration, reaching the highest value of -42 mV for 0.5 wt% GNP dispersion. Mehrali et al. reported that graphene nanoplatelets with a specific surface area of 750 m^2/g had the highest stability in nanofluids, compared to GNPs having lower surface areas [16].

3.2 Thermal Conductivity of Nanofluids

The 3ω method has proven to be reliable method for measuring the thermal conductivity of different type of materials [7]. In this research, a lab made setup was utilized for determining the thermal conductivity of the nanofluid based on an AC excited hot-wire with a 3ω lock-in detection technique. Turgut et al. [17] provided in details a full description of the theoretical background and the measurement procedures of the used setup. Nevertheless, a brief overview of this technique will be presented here. Briefly, a linear heater (very thin-wire) is excited by a sinusoidal current at an angular frequency ω. This, according to Ohms law, generates heat at 2ω which consequently resulting in both a temperature fluctuation in the wire also at the same frequency. The phase and the amplitude of the temperature oscillation are mainly related to the properties of the heater and thermal characteristics of its surroundings. Thus, the thermal conductivity k of the surrounding medium (including nanofluid) can be determined by a developed model based on the resulted temperature oscillation. Sensing the temperature oscillation is very challenging and can be performed through sensing the resistance oscillation of the wire since these two parameters are related directly by β (temperature coefficient of the wire material resistance). The resistance fluctuation can be measured by measuring the induced voltage signal at 3ω, based on which the method obtained its name.

The schematic diagram of the used measurement setup, as shown in Figure 6, illustrates its main part. The employed thermal probe (ThP), which is made of a metallic wire (Nickel) of length $2l$=19.0 mm and diameter of $d=50$ µm, is totally immersed in the nanofluid sample. The wire of the ThP is acting simultaneously as a heater and a thermometer, as discussed above. The selection of the 3rd harmonic (3ω) form the differential voltage signal across the bridge is performed by a Stanford SR-850 lock-in amplifier. It is important to mention here that to achieve a good signal-to-noise ratio, the first harmonic 1ω must be cancelled by a Wheatstone bridge arrangement (Figure 6).
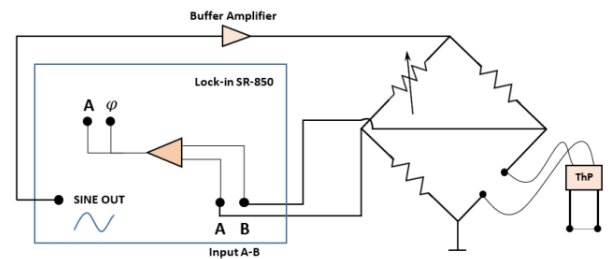

Figure 6. Schematic diagram of the experimental setup for 3ω hot-wire measurements (Thermal probe (ThP), Wheatstone bridge, lock-in amplifier, and buffer amplifier (ref. [18]).

Table 5 presents the thermal conductivity measurements of nanofluids with respect to GNP and PEG-POSS concentrations (wt%). The thermal conductivity value of nanofluids increases with the increment of GNP concentration. Moreover, PEG-POSS used as a stabilizer has a positive effect on the acquired enhancements since it improved stability of the GNP within the dispersion. Furthermore, the increment of the thermal conductivity ratios with the stabilizer concentration also supports this claim.

Table 5. Thermal conductivity enhancement (%) with different GNP and PEG-POSS concentrations.

GNP [wt%]	PEG-POSS [wt%]	Thermal Conductivity Enhancement %
0.1	-	-
0.1	0.1	-
0.1	0.2	0.15
0.5	-	0.45
0.5	0.1	0.54
0.5	0.2	0.86

However, the obtained enhancements did not meet the expectation when they are compared with the one reported in literature [16]. This can be attributed to the difference in the utilized measurement setups. Most of the related researches employed commercial devices of the THW technique (KD2 thermal conductivity meter) [19]. Nevertheless, a recent paper of Antoniadis et al. [20] discussed the chaos and the exaggeration in the previously reported experimental results; hence, they proposed several necessary conditions that should be applied in order to increase the reliability and the accuracy of the thermal conductivity measurements performed by the THW method. Consequently, although the thermal conductivity enhancements obtained by 3ω method are much less than expected, they are more realistic.

4. CONCLUSION AND FUTURE WORK
In this study, GNP/distilled water and GNP/PEG-POSS/distilled water nanofluids were successfully prepared, using ultrasound technology. For stability enhancement, pH was adjusted to the value (around 8), where the nanofluids would be expected to be stable. Thermal conductivity measurements and stability evaluations were performed using 3ω method, UV-Vis spectrophotometry, and zeta potential measuring device (Zetasizer Nano). Zeta potential analysis showed the highest value as -42 mV for 0.5 wt% GNP aqueous nanofluids. Increase in nanoparticle concentration provided better stability and thermal conductivity increment in nanofluids. Besides, the usage of PEG-POSS as a stabilizer improved both thermal conductivity and stability. The highest thermal conductivity enhancement was measured as 0.86%. Since the study has not yet been completed, further experimental work will be performed with ethylene glycol and mineral oil as base fluids, different GNP and PEG-POSS concentrations, higher pH values (around 9), and longer sonication time (up to 100 min). In addition, various imaging techniques like scanning electron microscope and atomic force microscope will be used for nanofluid characterization, along with some rheological measurements of nanofluids.

Nomenclature
A	Absorbance
I	Intensity
c	Concentration
b	Beam path
k	Thermal conductivity
l	Length of the probe
d	Diameter of the probe

Greek Letters
ε	Molar absorptivity
β	Temperature coefficient of resistance
ω	Angular frequency

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