Colloidal stability measurements of graphene nanoplatelets covalently functionalized with tetrahydrofurfuryl polyethylene glycol in different organic solvents


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1. Introduction

In recent years, carbon-based nanomaterials have drawn great interest among scientists in the field of advanced materials. Graphene nanoplatelets (GNPs) refer to a new generation of carbon-based nanomaterials [1]. GNPs are promising materials for a wide range of applications including nanocomposite structures, phase change systems, supercapacitors, and thermal management [2–6], which is due to the extraordinary properties of these material. For instance, the mechanical strength of GNPs is higher than that of steel by two orders of magnitude, with a theoretical modulus of ~1 TPa. In addition, GNPs have high electron mobility and thermal conductivity, with a value of ~2.5 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} and ~3000 \text{ W m}^{-1} \text{ K}^{-1}, respectively. More importantly, GNPs have a large surface to volume ratio, which provides large contact surface area with polymer [7–10]. Despite the excellent intrinsic mechanical and electrical properties as well as high thermal conductivity of GNPs on a weight basis, these nanomaterials are more cost-effective for industrial applications compared with carbon nanotubes [11,12].

The remarkable properties of GNPs render these materials favorable to be incorporated with other materials in order to create multi-functional material systems [13,14]. It has been proven that GNP suspensions significantly enhance the thermal conductivity of conventional working fluids, which in turn, boosts the thermal performance of heat transfer systems [15,16]. A number of studies have shown that GNP nanofluids have remarkable thermal properties [17–19]. However, preparing homogeneous and stable organic solvent-based GNP nanofluids in order to enhance the
thermal performance of heat transfer systems is one of the main challenges to realize their applications [20, 21]. This is due to their strong Van der Waals forces between the benzene-ring like structures of GNPs and therefore, these nanomaterials tend to form irreversible coagulations [22, 23]. There are two types of chemical functionalization methods commonly used by researchers in order to address this issue, which involve modifying the surface of the GNPs either by covalent functionalization or non-covalent functionalization procedures [24].

Using the appropriate non-covalent functionalization method will significantly enhance the dispersibility of GNPs in the base fluid, where the GNPs are wrapped with long-chain stabilizers such as surfactants or polymers [25, 26]. The main mechanism underlying this method is π–π stacking interactions between the functional groups and surface of the graphene sheets, which minimize impact on the surface of GNPs and prevent disruption of electron conjugation [27, 28]. However, the main disadvantage of the non-covalent modification method is the large amount of surfactant molecules present, which limits the enhancement of mechanical, electrical and thermal properties of GNPs [29–31].

Unlike non-covalent functionalization, covalent functionalization involves chemical reactions between carbon in the main structures and other functional groups, producing new functionalized materials with different properties [32]. Acid treatment is one of the ways to covalently functionalize GNPs and this method is commonly used by researchers to improve the dispersibility of GNPs in different solvents [3]. Despite altering the original structure of the material, acid treatment is known to be an effective method to prepare stable dispersions of carbon-based nanostructures [33]. However, a high degree of functionalization is necessary with this method in order to achieve GNPs with a high level of dispersibility [34]. A high degree of functionalization results in a high rate of production of sp3-hybridized carbons in the main backbone, which produces many favorable properties [34]. Hence, selecting functional groups with long-chain branches and great hydrophilicity is indeed an ingenious idea to minimize the production of sp3-hybridized carbons in the main backbone.

Polyethylene glycol (PEG) is one of the common polymers used to functionalize nanomaterials [35]. PEG can easily disperse in organic solvents and therefore, it is an ideal candidate to increase the solubility of GNPs. With covalent functionalization, PEG can improve the solubility of GNPs in water or other common solvents [36]. However, since PEG is a straight chain polymer, PEG may lead to aggregation of GNPs due to cross-linking between the GNPs [37]. Interestingly, monofunctional oligomers such as monofunctional, tetrahydrofurfuryl-terminated polyethylene glycol (TFPEG) can prevent cross-linking of the adjacent GNPs sheets. Functionalization with monofunctional groups can enhance the colloidal stability of GNPs in distilled water and common organic solvents such as ethylene glycol [38].

In order to prepare organic solvent-based GNP nanofluids, the GNPs need to fulfill the following criteria: (1) long-term colloidal stability, (2) ability to disperse well in a variety of organic solvents, and (3) reversible particle aggregation [39, 40]. A number of studies have been carried out to enhance the dispersibility of GNPs with TFPEG. Arzani et al. [41] synthesized TFPEG-functionalized GNPs for use in heat transfer applications. However, they used a high amount of aluminum chloride (AlCl3), which is rather costly and impractical to functionalize GNPs with TFPEG in bulk quantities. In addition, it is undesirable to use high amounts of AlCl3 to functionalize GNPs because AlCl3 is toxic to humans and therefore, one needs to adhere to a stringent safety procedure when handling this chemical [42].

In this study, a strategy was proposed to significantly enhance the dispersibility of GNPs in organic solvents by covalent functionalization of GNPs with TFPEG using a facile and cost-effective approach. Carboxylated GNPs were directly grafted with TFPEG molecules in the presence of zirconium(IV) oxychloride octahydrate that served as an effective catalyst for direct esterification. In addition, this catalyst is non-toxic and inexpensive [43]. The catalyst forms a cationic cluster structure in which ester condensation takes place through a series of protonation of –COOH ligands in the GNPs, forming carbocations. This process facilitates the TFPEG molecules to complete the reaction, where water is formed as a by-product [44].

Upon confirming that the covalent functionalization process was successful, TFPEG-treated GNP nanofluids were prepared by dispersing TFPEG-treated GNPs into different solvents namely distilled water, methanol, ethanol, ethylene glycol, and 1-hexanol. Lastly, the thermophysical properties of water-based TFPEG-treated GNP nanofluids were measured to determine the potential of these nanofluids as working fluids for heat transfer applications.

2. Experimental section

2.1. Materials

The GNPs (specific surface area: 750 m2/g) was purchased from XG Sciences, Inc., USA. TFPEG (molecular formula: C12H26O(C2H4O)n–OH (n = 1–5), molecular weight: ~200 g mol–1 atoms) and zirconium(IV) oxychloride octahydrate (ZrOCl2·8H2O) were obtained from Sigma-Aldrich (M) Sdn. Bhd., Malaysia. Sulfuric acid (H2SO4, purity: 95–97%), nitric acid (HNO3 purity: 65%), and tetrahydrofuran (THF) were sourced from Friendemann Schmidt Pty. Ltd., Australia. Methanol, 1-hexanol, and ethylene glycol were obtained from Merck, Germany and ethanol was purchased from J. Kollin Chemicals, John Kollin Corporation.

2.2. Preparation of carboxylated graphene (GNP-COOH)

In the first stage of preparation, as-received GNPs (12 g) without any purification was poured into H2SO4 (300 mL) and was stirred for 30 s. Next, the container was transferred into an ice bath and nitric acid (100 mL) was subsequently added dropwise into the solution mixture. A sulfuric acid to nitric acid ratio of 3:1 was used due to the superior potential for carboxylation of carbon allotropes [45, 46], which results in the formation of carboxylic groups on the surface of GNPs (Fig. 1). The solution mixture was stirred at a temperature of −55 °C for 5 h and was subsequently cooled to 25 °C. The resultant black solution was further diluted with distilled water (6 L) and HCl (3 wt%) and was finally centrifuged at 4000 rpm to remove the excess acid.

2.3. Functionalization of GNP-COOH with TFPEG

In order to synthesize the TFPEG-treated GNPs (Fig. 2), zirconium(IV) oxychloride octahydrate (0.6 g, molecular formula: ZrOCl2·8H2O) was mixed with TFPEG (12 g) through continuous stirring for 30 min. Next, THF (500 mL) was added into the solution mixture. Following this, the GNP-COOH was poured into the solution mixture and the solution mixture was stirred for 24 h at 80 °C. Once the reaction was completed, the solution mixture was centrifuged at 7500 rpm for 15 min. Lastly, the resultant solution was washed with distilled water and ethanol a few times and then dried in an oven set at 60 °C for 48 h.

2.4. Characterization of TFPEG-treated GNPs

The main structure of the TFPEG-treated GNPs and pristine GNPs was analyzed using Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, high-resolution transmission
electron microscopy (HRTEM), and thermogravimetric analysis (TGA). The samples were prepared for HRTEM by sonicating the TFPEG-treated GNPs and pristine GNPs in deionized water for 15 min. Then a drop of each sample was placed onto a lacey carbon grid. For FTIR spectroscopy, potassium bromide (KBr) pellets comprising of the TFPEG-treated GNPs and pristine GNPs were prepared and the FTIR spectra was evaluated within a wavenumber range of 400–4000 cm⁻¹. The Raman spectra of the TFPEG-treated GNPs and pristine GNPs was recorded within a wavenumber range of 500–3200 cm⁻¹ at 25 °C. For TGA, the weight loss of the samples was measured within a temperature range of 20–600 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

2.5. Colloidal stability of water-based and organic solvent-based TFPEG-treated GNP nano fluids

The samples of water-based, methanol-based, ethanol-based, ethylene glycol-based, and 1-hexanol-based TFPEG-treated GNP nanofluids with the concentration of 0.01 wt% were prepared through sonication process for 15 min. Next, the colloidal stability of the water-based and organic solvent-based TFPEG-treated GNP nanofluids was analyzed using ultraviolet–visible (UV–Vis) spectrophotometry and zeta potential measurements. By UV–Vis spectrophotometry, the colloidal stability of the samples was able to be determined based on the light absorbance of the suspensions. The Shimadzu UV-spectrophotometer (Model: UV-1800, Shimadzu Corporation, Japan) was used and the spectrophotometric analysis was conducted within a wavelength range of 200–800 nm. A dilution ratio of 1:20 with respect to the solvent was used to ensure that UV–Vis radiation passes through the samples and the degree of absorption is detected within the range of wavelengths investigated in this study. Special quartz glass cuvettes were used which are suitable for use in the UV–Vis wavelength region. The samples were measured at different time intervals over a period of 15 days. The zeta potentials and particle size distributions were measured using a two-angle particle and molecular size analyzer based on dynamic light scattering (Model: Zetasizer Nano ZS, Malvern Instruments Ltd., UK) to evaluate the colloidal stability of the samples [45].

2.6. Thermophysical properties of water-based TFPEG-treated GNP nanofluids

The thermophysical properties of interest in this study are viscosity and thermal conductivity. For the measurement, the samples of water-based TFPEG-treated GNP nanofluids at different particle concentrations (0.100, 0.075, 0.05 and 0.025 wt%) were prepared through sonication process for 15 min. The measurement steady-shear viscosity of the water-based TFPEG-treated GNP nanofluids was measured using a rotational rheometer (Model: Physica MCR 301, Anton Paar GmbH, Austria). The viscosity measurements were carried out within a fluid temperature range of 20–50 °C and shear rate of 20–200 s⁻¹. The thermal conductivity of the water-based TFPEG-treated GNP nanofluids was measured using a fully portable field and laboratory thermal property analyzer (Model: KD2 Pro, Decagon Devices, Inc., USA) and the measurements were conducted within a fluid temperature range of 20–60 °C. The hot wire method using the KS-1 probe was used, which consists of a single needle sensor with a length and diameter of 60 and 1.3 mm, respectively. The WiseCirc® WCR digital precision refrigerated bath circulator (Model: WCR-P6, DAIHAN Scientific Co., Ltd., South Korea) with a total power consumption of 1.4 kW and an accuracy of 0.1 °C was used to ensure that the sample temperature remained constant during the measurements. The measurements were taken
for 15 min in between successive readings in order to allow the sample temperature to reach steady-state condition.

3. Results and discussion

3.1. Characterization of TFPEG-treated GNPs

The results obtained from characterization of the carboxylated GNPs covalently functionalized with TFPEG were presented in this section. As mentioned previously, TFPEG is a monofunctional oligomer which prevents cross-linking between the adjacent GNP sheets [37,38]. In order to evaluate the degree of functionalization of GNPs with TFPEG, both qualitative (FTIR spectroscopy) and quantitative (Raman spectroscopy and TGA) methods were used to characterize both pristine GNPs and TFPEG-treated GNPs.

3.1.1. Fourier transform infrared spectroscopy

Fig. 3 shows the FTIR spectra of pristine GNPs and TFPEG-treated GNPs. The main IR peaks and the assigned bonds interpreted from the FTIR spectrum of the TFPEG-treated GNPs are summarized in Table 1. It can be observed from Fig. 3 that the TFPEG-treated GNPs show absorbance peaks at 2922, 1635, and 1380 cm\(^{-1}\), which represent C–H, C–O, and C–O bonds, respectively. These bonds are present due to the attachment of TFPEG molecules on the edge and surface of the GNP sheets. The existence of C–O and C–O bonds indicates that the direct esterification reaction is successful. In addition, the TFPEG–treated GNPs show a broad absorbance peak within a wavenumber range of 3000–3500 cm\(^{-1}\), which is ascribed to the –OH chains of the TFPEG [37,38]. The appearance of these peaks in the FTIR spectrum for the TFPEG–treated GNPs qualitatively proves the success of the covalent functionalization procedure.

3.1.2. Raman spectroscopy

As mentioned previously, Raman analysis was used to provide more evidence on the success of the covalent functionalization procedure. In a Raman spectrum, the presence of a G-band is due to the presence of sp\(^2\) carbon network whereas the presence of a D-band is due to the defects that occur on the chemical structure [20]. Fig. 4 shows the Raman spectra of pristine GNPs and TFPEG-treated GNPs. The ID/IG ratios of the pristine GNPs and TFPEG-treated GNPs are 0.508 and 0.757, respectively, as shown in Table 2. The ID/IG ratio is higher for the TFPEG-treated GNPs compared with the pristine GNPs due to the formation of covalent bonds on the graphene sheets resulting from covalent functionalization.

3.1.3. Thermogravimetric analysis

TGA provides quantitative information regarding the amounts of functional groups decorating the edge and surface of the GNP sheets. Fig. 5 shows the TGA curves of pristine GNPs and TFPEG-treated GNPs. It is found that the initial weight losses of the pristine GNPs and TFPEG-treated GNPs are 12 and 8.80%, respectively, within a temperature range of 20–60 °C, which was attributed to the adsorbed moisture. It can be seen that there is a minor weight loss within a temperature range of 60–600 °C for the pristine GNPs, which was attributed to pyrolysis of the main carbon-based structures [46]. In contrast, a noticeable weight loss (14.21%) was observed within a temperature range of 100–300 °C for the TFPEG-treated GNPs, which was due to the decomposition in the functionality of TFPEG as well as carboxyl and hydroxyl groups produced during the oxidation procedure as unstable organic moieties.

<table>
<thead>
<tr>
<th>Wavenumber at which peak occurs (cm(^{-1}))</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>3448</td>
<td>–OH stretching vibration</td>
</tr>
<tr>
<td>2922</td>
<td>C–H stretching vibration</td>
</tr>
<tr>
<td>1635</td>
<td>C–O stretching vibration</td>
</tr>
<tr>
<td>1380</td>
<td>C–O stretching vibration</td>
</tr>
</tbody>
</table>

**Table 1**

Interpretation of the IR peaks for TFPEG-treated GNPs.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>D-band (cm(^{-1}))</th>
<th>G-band (cm(^{-1}))</th>
<th>ID/IG ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine GNPs</td>
<td>1592</td>
<td>1599</td>
<td>0.757</td>
</tr>
<tr>
<td>TFPEG-treated GNPs</td>
<td>1599</td>
<td>1599</td>
<td>0.757</td>
</tr>
</tbody>
</table>

**Table 2**

Displacement and intensity ratios for pristine GNPs and TFPEG-treated GNPs obtained from Raman spectroscopy.
The degree of functionalization (DF) was calculated using the following equation:

$$DF = \frac{WL_{AF}\ (g) \times 1000 \ mmol}{MW_{AF} \ WL_{GNP}\ (g)}$$

(1)

where $DF$ represents the degree of functionalization in millimoles per gram (mmol g$^{-1}$), $MW_{AF}$ is the molecular weight of the attached functional group, and $WL_{AF}$ and $WL_{GNP}$ represent the weight loss of the attached functional group and weight loss of the GNPs, respectively, in grams (g).

The degree of functionalization of the TFPEG-treated GNPs was obtained at 0.8279 mmol g$^{-1}$, which is excellent. In general, it can be summarized that there is a good agreement between the results obtained from FTIR spectroscopy, Raman spectroscopy, and TGA to verify the covalent functionalization of GNPs with TEPEG molecules.

![Thermogravimetric curves of the pristine and TFPEG-treated GNPs.](image)

**Fig. 5.** Thermogravimetric curves of the pristine and TFPEG-treated GNPs.

![TEM images](image)

**Fig. 6.** (a) HRTEM image of pristine GNPs; (b) Closeup HRTEM image of pristine GNPs; HRTEM images of TFPEG-treated GNPs at different magnifications (c), 0.5 µm, (d) 0.5 µm, and (e) 200 nm.
3.1.4. High-resolution transmission electron microscopy

The morphologies of the pristine GNPs and TFPEG-treated GNPs were observed using HRTEM and the results are shown in Fig. 6. It can be seen from Fig. 6(a) and (b) that the pristine GNPs consist of two sheets with fairly transparent structures, smooth surfaces, and the edges are clearly intact. After functionalization, the addition of TFPEG and carboxyl groups onto the surfaces and edges of the GNPs makes the sheets appear slightly blurry with loads of crumples and wrinkles, as shown in Fig. 6(c). The changes in the morphology along with analysis of the functional groups indicate that the reaction between the GNP-COOH and TFPEG is indeed successful. The presence of folded flakes with defects and roughness at the edges (Fig. 6(d) and (e)) also indicates that the covalent functionalization procedure is successful.

3.2. Colloidal stability

3.2.1. Pristine GNPs and TFPEG-treated GNPs

The visual inspection of the pristine GNPs and TFPEG-treated GNPs were conducted and the images were presented in Fig. 7. From the observation, the pristine GNPs were unable to stabilize in distilled water after 24 h, and sediment forms at the bottom of the sample vial, as shown in Fig. 7(a). This is due to the Van der Waals forces of the GNPs, which leads to agglomeration of the GNPs in distilled water [23]. In contrast, the TFPEG-treated GNPs show remarkable colloidal stability in distilled water after 24 h, as shown in Fig. 7(b).

3.2.2. Water-based TFPEG-treated GNP nano fluids

Fig. 8 shows the UV–Vis spectra of the water-based TFPEG-treated GNP nanofluids which were prepared at different particle concentrations (0.0025, 0.0050, 0.0075, and 0.0100 wt%). It can be observed that there is a single peak within a wavelength range of 260–270 nm. The sharp absorption peak at ~265 nm is likely due to the π→π* transition of C=C bond of the GNPs [47]. It is evident that the peak intensity increases with an increase in particle concentration, in accordance with the Beer-Lambert law [40].

Fig. 9 shows the colloidal stability of the water-based TFPEG-treated GNP nanofluids at different concentrations over a 15-day period. The results are indeed encouraging because the water-based TFPEG-treated GNP nanofluid shows excellent colloidal stability within the period of investigation, judging from the high relative particle concentrations. Thus, it can be deduced that TFPEG is a superior candidate to achieve highly stable water-based GNP nanofluid. In addition, the percentage of sediment formed in the nanofluid is not significant, where the relative particle concentrations after 15 days remained at 89, 85, 79, and 78% for nanofluids containing 0.0100, 0.0075, 0.0050, and 0.0025 wt% of TFPEG-treated GNPs, respectively. The relative particle concentration was determined based on the percentage ratio of the current concentration to the concentration of a fresh sample. It was found that the highest and the lowest percentage of sediment formed for the water-based TFPEG-treated GNPs were ~22 and 11%, respectively. It is apparent from the results that all of the water-based TFPEG-treated GNP nanofluids show remarkable colloidal stability with an average percentage of sediment of less than 25% after 15 days.

The particle size distributions and zeta potentials of pristine GNPs and TFPEG-treated GNPs dispersed in distilled water were
Fig. 10. Particle size distributions of pristine GNPs on (a) Day 1 and (b) Day 15; Particle size distributions of TFPEG-treated GNPs on (c) Day 1 and (d) Day 15; Zeta potential of pristine GNPs on (e) Day 1 and (f) Day 15; Zeta potential of TFPEG-treated GNPs on (g) Day 1 and (h) Day 15. Note that the particle concentration is 0.01 wt% and distilled water is used as the base fluid.
analyzed after 15 days and the results were plotted, as shown in Fig. 10. It shall be noted that the particle concentration of each sample was set at 0.01 wt%. The excellent stability of TFPEG-treated GNPs obtained in (Fig. 9) was further confirmed by the particles size and zeta potential results which show much narrow size distribution coupled with sustained particle count (Fig. 10(c), (d) and (g),(h)).

The average particle size, polydispersity index, zeta potential, and mobility values of the water-based pristine GNP nano fluid and water-based TFPEG-treated GNP nano fluid on Day 1 and Day 15 after sample preparation are summarized as shown in Table 3. It is evident that average particle size is very large (more than 1000 nm) for pristine GNPs after 15 days. In contrast, the average particle size is significantly smaller for the TFPEG-treated GNPs (less than 250 nm). This indicates that the TFPEG-treated GNPs are stable colloids in water, and this property can be exploited to boost the thermal performance of heat transfer systems [48].

The colloidal stability of the water-based TFPEG-treated GNP nanofluid was also verified based on the magnitude of electrostatic interactions between the colloidal particles, as indicated by the zeta-potential and polydispersity index values. The zeta potential must be a high positive or negative value in order to create repulsive forces between the particles [40]. It was found that the zeta potential was at \(-24.7\) mV for the water-based pristine GNP nanofluid on Day 1, which indicates that the dispersion is less stable. The pristine GNPs dispersion becomes more unstable after 15 days, which is evident from the increase in zeta potential (\(-14.2\) mV). This indicates that the pristine GNPs are not stable in water. Meanwhile, the TFPEG-treated GNPs show high colloidal stability in water, where the zeta potential was at \(-40.3\) mV on Day 1 and there is only a slight increased in the zeta potential after 15 days (\(-32.5\) mV). This proves that the TFPEG-treated GNPs are stable in water after 15 days of preparation [49].

### Table 3
Average particle size, polydispersity index, zeta potential, and mobility values of pristine GNPs and TFPEG-treated GNPs in water after 1 day and 15 days of preparation. Note that the particle concentration is 0.01 wt%.

<table>
<thead>
<tr>
<th>Day (s)</th>
<th>Average particle size (nm)</th>
<th>Polydispersity index</th>
<th>Zeta potential (mV)</th>
<th>Mobility (µm cm V(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pristine GNPs</td>
<td>TFPEG-treated GNPs</td>
<td>Pristine GNPs</td>
<td>TFPEG-treated GNPs</td>
</tr>
<tr>
<td>1</td>
<td>1060.0</td>
<td>239.8</td>
<td>0.508</td>
<td>0.270</td>
</tr>
<tr>
<td>15</td>
<td>1133.0</td>
<td>247.1</td>
<td>0.404</td>
<td>0.332</td>
</tr>
</tbody>
</table>

Fig. 11. Dispersibility of TFPEG-treated GNPs in ethanol, methanol, 1-hexanol, and ethylene glycol within a 24-h period.

Fig. 12. UV–Vis spectra of the methanol-based, ethanol-based, 1-hexanol-based, and ethylene glycol-based TFPEG-treated GNP nanofluids. Note that the particle concentration of the TFPEG-treated GNPs in the base fluid is 0.01 wt%.

Fig. 13. Relative particle concentration versus the number of days after preparation for methanol-based, ethanol-based, 1-hexanol-based, and ethylene glycol-based TFPEG-treated GNP nanofluids. Note that the particle concentration of the TFPEG-treated GNPs in the base fluid is 0.01 wt%.
0.01 wt% of TFPEG-treated GNP s [47].

In addition, the relative particle concentrations of the samples over a 15-day period were determined and the results are shown in Fig. 13. It was found that the percentage of sediment values are 18, 25, 36, and 47% for the ethylene glycol-based, methanol-based, ethanol-based, and 1-hexanol-based TFPEG-treated GNP nano-fluids, respectively. Interestingly, the TFPEG-treated GNPs was found to have superior stability in ethylene glycol and methanol, judging from the low percentage of sediment values. The high dispersibility of the functionalized GNPs may be due to the miscible TFPEG functional groups. Based on the results, it is believed that direct decoration of GNP-COOH with TFPEG will be a useful procedure to prepare working fluids with excellent colloidal stability for use in industrial heat transfer systems.

3.3. Thermophysical properties

In order to validate the reliability of the viscosity measurements made using the rotational rheometer, the viscosities of distilled water were measured at different temperatures and the results were compared with the standard data published by the National Institute of Standards and Technology (NIST). The results are shown in Fig. 14(a). It was found that the average error in the viscosity for distilled water is ±2.47% at different temperatures. This indicates that the difference in the viscosity values measured using the instrument in the present and those given in the NIST standard data is pretty small. Hence, it can be deduced that rotational rheometer is reliable to measure the viscosities of the nanofluids and the results can be taken with confidence.

The viscosity of the water-based TFPEG-treated GNP nanofluids (at different particle concentrations) and distilled water as a function of temperature were plotted, as shown in Fig. 14(b). The viscosity measurements were performed within a fluid temperature range of 20–50 °C. It can be seen from Fig. 14(b) that the viscosity decreases with an increase in temperature for both water-based TFPEG-treated GNP nanofluids and distilled water. It is believed that this is due to the weakened intermolecular forces of the nanofluids as the fluid temperature is increased [50]. In addition, the viscosity is higher as the concentration of TFPEG-treated GNPs in distilled water is increased, as shown in Fig. 14(b). However, it is apparent that there is no significant difference in the viscosities between the water-based TFPEG-treated GNP nanofluids and distilled water, and there is only a slight increment in the viscosities for the nanofluids. This slight increment is certainly an advantage of the water-based TFPEG-treated GNP nanofluids because this will reduce the pumping power required if these nanofluids are used as working fluids in heat transfer systems [45, 51].

The thermal conductivity of the water-based TFPEG-treated GNP nanofluids was measured using the KD2-Pro thermal property analyzer within a fluid temperature range of 20–60 °C. In similar manner, the thermal conductivity measurements were validated by comparing the thermal conductivities of distilled water measured using the instrument with those of the NIST standard data [52] and the results were plotted in Fig. 15(a). It can be observed that the thermal conductivity of distilled water

![Fig. 14. Viscosity versus temperature for (a) distilled water (experiments and NIST standard) and (b) water-based TFPEG-treated GNP nanofluids at different particle concentrations and distilled water.](image)

![Fig. 15. (a) Comparison of thermal conductivity values of distilled water between NIST standard [52] and KD2 Pro thermal property analyzer measurements. The error bars indicate an average error of ±5%. (b) Thermal conductivity versus temperature for water-based TFPEG-treated GNP nanofluids at different particle concentrations and distilled water.](image)
increases with an increase in temperature. It was found that the average error in the thermal conductivity is only ±0.9%, indicating that the KD2 Pro thermal property analyzer is reliable to measure the thermal conductivity of the samples. The thermal conductivity of the water-based TFPEG-treated GNP nanofluids and distilled water as a function of temperature were plotted, as shown in Fig. 15(b). It can be observed that the thermal conductivity increases with an increase in temperature from 20 to 60 °C for all samples, and the thermal conductivity values are higher for the water-based TFPEG-treated GNP nanofluids compared with those for distilled water. In addition, it is apparent that the thermal conductivity increases when the concentration of TFPEG-treated GNP's in distilled water is increased. Indeed, the results indicate that the TFPEG-treated GNP's have the potential to enhance the thermal conductivity of the base fluid. Previous studies have also shown that nanofluids with high thermal conductivities improved the convective heat transfer coefficient of thermal systems [53–58].

4. Conclusions

In this paper, a facile, efficient, and cost-effective approach to synthesize TFPEG-treated GNP's was presented, by which the zirconium(IV) oxychloride octahydrate as the catalyst was used, representing a non-toxic and inexpensive catalyst. The method involved acid treatment process, where the carboxylic acid groups are attached onto the surface of pristine GNP's and the GNP's are then grafted by TFPEG in order to enhance the dispersibility of GNP's in different organic solvents. Direct esterification of carboxylic acid on the GNP's with the hydroxyl chains of TFPEG was achieved due to the use of zirconium(IV) oxychloride octahydrate in the covalent functionalization procedure. The success of the covalent functionalization was verified by FTIR spectroscopy, Raman spectroscopy, and TGA. Meanwhile, the morphology of the TFPEG-treated GNP's was examined by using HRTEM.

The colloidal stability of nanofluids prepared by dispersing 0.01 wt% of TFPEG-treated GNP's into different aqueous media: (1) distilled water, (2) methanol, (3) ethanol, (4) ethylene glycol, and (5) 1-hexanol was examined by UV–Vis spectroscopy over a 15-day period. The percentage of sediment values after 15 days were found to be 11, 18, 25, 36, and 47% for the water-based, ethylene glycol-based, methanol-based, ethanol-based, and 1-hexanol-based TFPEG-treated GNP nanofluids, respectively. Hence, the water-based, ethylene glycol-based, and methanol-based TFPEG-treated GNP nanofluids showed superior colloidal stability in this study. Due to the superior colloidal stability of the TFPEG-treated GNP's in water and different organic solvents (particularly, ethylene glycol and methanol) as well as simplicity and cost-effectiveness of the proposed covalent functionalization procedure, it is believed that this method will be very useful to mass-produce TFPEG-treated GNP's on a large scale. More importantly, this method is an environmentally friendly alternative to common surfactant methods. Finally, the viscosity and thermal conductivity of water-based TFPEG-treated GNP nanofluids were measured at different particle concentrations (0.100, 0.075, 0.050, and 0.025 wt%). The water-based TFPEG-treated GNP nanofluids was found to have low viscosities (close to those for distilled water) and high thermal conductivities, indicating that the TFPEG-treated GNP's are potential additives that can be used to enhance the thermophysical properties of working fluids in industrial heat exchangers.

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References


