Effect of surfactants on thermal conductivity of graphene based hybrid nanofluid

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Abstract. Various hybrid nanofluids have been researched in this decade. The quality of this said-to-be alternate heat transfer medium depends on two major features – long term stability and high thermal conductivity. In recent years, graphene-based nanofluid was reported to exhibit distinguished heat transfer performance compared to most materials investigated in past studies. This study aims to compare the effect of different surfactants on thermal conductivity of graphene-based nanofluid. Sodium dodecylbenzenesulfonate (SDBS) and hexadecyltrimethylammonium bromide (CTAB) were mixed separately in advance with the mixture of water and ethylene glycol. After mixing surfactants and base fluid, total 0.025 to 0.1 wt% of nanoparticles were added into the mixture and followed by ultrasonication. Mono nanofluid was produced by adding graphene nanoplatelets (GnP) only whereas a novel hybrid combination was composed of graphene nanoplatelets and titanium dioxide. Stability of each sample was inspected using zeta potential analysis and Uv-vis spectroscopy. Thermal conductivity of samples from 30 °C to 60 °C was measured using Decagon KD2 Pro. Both surfactants contributed to high zeta potential value and minimal sedimentation for all nanofluids. CTAB improved the thermal conductivity of hybrid nanofluid more compared to SDBS, with 11.72% difference at 0.1 wt% nanoparticles concentration when compared to base fluid at 60 °C. The highest enhancement (23.74%) on base fluid was spotted at 60 °C, where 0.1 wt% of GnP was mixed with CTAB. These findings could strengthen literature on suitable surfactant to be used on graphene based nanofluid since limited comparison work has been done. High thermal conductivity of the hybrid nanofluid at high temperature could be used as coolant in cooling system.

1. Introduction
Miniaturization of devices and materials is the most dominant trend nowadays, which is proved to achieve less-power consumption and higher system efficiency. In the last few decades, many researchers have been examining the performance of nanoscale technology in diverse applications including biomedical, energy storage, photovoltaic, electronics, molecular science and others. One of the biggest concerns in industry today is waste heat conversion, in which the efficiency of power plants affects the amount of unused heat rejected. Thus, number of researches to enhance heat transfer efficiency in various systems is escalating. One of the most popular approach involves the use of efficient coolant with high thermal conductivity. Highly thermal conductive fluid can be produced by
mixing solid particles with base fluid. The mechanism for the improved thermal properties is due to the intrinsic high thermal conductivity of solid materials [1]. Aforementioned solid particles are being engineered in nano size (< 100 nm) and dispersed in base fluid through chemical and physical processes. Eventually, the mixture obtained is phrased as ‘nanofluid’. Nanofluid is widely researched due to their distinct behavior as a possible alternative as heat transfer fluid in different systems. Various materials including metals, metal oxides and non-metals such as Al₂O₃ [2], TiO₂ [3], Cu [4], and graphene [5] were reported to show outstanding enhancement when added to base fluid. Based on literature, low quantity of nanoparticles could enhance thermophysical properties of base fluid significantly.

After a decade, the concept of hybridizing different materials in nanofluid was initiated by Jana et al. [6]. Since then, various combinations were studied and eventually both enhancement and deterioration were observed. There were theories or hypothesis proposed on these anomalous behaviors, which is mainly due to the presence of synergistic effect [7]. A recent study [8] reported 19.2% of thermal conductivity enhancement by adding 3 vol% hybrid of Al₂O₃-TiO₂ in water. They also found that same concentration of Al₂O₃-water and TiO₂-water nanofluid showed 17.7% and 14.1% of enhancement only. Sulgani et al. [9] reported 4 wt% of Al₂O₃-Fe₂O₃ improved thermal conductivity of 10w40 engine oil by 33% at 65 °C. On the other side, MWCNT-based nanofluid was found to exhibit higher thermal conductivity than its hybrid with TiO₂ [10]. These studies suggested that the importance of synergistic effect in the enhancement of hybrid nanofluid.

In the present study, authors focused on measuring thermal conductivity of hybrid nanofluid mixed with different surfactant. Based on authors’ best knowledge, there were several studies reported on properties of mono-nanofluids with various surfactants but none of them compared using hybrid nanofluid. Only a past study compared hybrid nanofluid (Cu-TiO₂) with the same approach [11], where they found out that thermal conductivity of TiO₂ nanofluid was higher than its hybrid when gum Arabic was added. This study aims to find out the effect of surfactant on thermophysical properties of mono and novel hybrid nanofluid which comprises of graphene nanoplatelets and titanium dioxide nanoparticles. Range of study covered suspension stability due to ultrasonication duration and thermal conductivity results from nanoparticles concentration and working temperature.

2. Methodology

2.1 Preparation of nanofluid

Both mono and hybrid graphene-based nanofluids were prepared in this study. Base fluid used was made up of 60% distilled water and 40% ethylene glycol. Surfactant was added into base fluid and stirred for 10 minutes. COOH-functionalized graphene nanoplatelets (COOH-GnP) was added in base fluid as mono nanofluid. For hybrid nanofluid, titanium dioxide powder was mixed directly with COOH-GnP in the ratio of 1:1 and stirred for 30 minutes. The mixture was then vigorously agitated using probe sonicator (FS-1200N, 20 kHz, 1.2 kW). Ice bath was used to maintain sample temperature during sonication process to avoid degradation of surfactant.

2.2 Stability inspection

Surfactant was used to enhance stability of nanofluid. Impact of two different surfactants on nanofluid stability were compared, namely hexadecyltrimethylammonium bromide (CTAB) and sodium dodecylbenzenesulfonate (SDBS). Stability of all samples was evaluated at 0.1 wt% concentration and four ultrasonication durations were considered. Visual sedimentation method was first used to observe formation of supernatant and sediment in suspension after two months. Then, quantitative analysis on stability was performed using Uv-vis spectrophotometer (Perkin Elmer Lambda 750). Long term stability analysis of nanofluid was reported in term of absorbance change.

2.3 Measurement of thermal conductivity

Thermal conductivity of all samples was measured using Decagon KD2 Pro (KS-1 sensor). Samples were initially immersed in water bath for at least 15 min to achieve temperature equilibrium. This device comes with ±5% of error. Thus, average of 10 readings with 5 min interval time was reported.
3. Result and Discussion

3.1 Stability
Visual sedimentation method is the easiest method to determine stability of nanofluid. It is used to observe the formation of sediment and supernatant formed in suspension using naked eye. Figure 1 shows 0.1 wt% nanofluids (with different surfactant) which had been sonicated for 60 minutes. The drawback of this method is the difficulty to differentiate similar samples. In this study, it was inaccurate to judge respective stability of these samples, nevertheless all four samples showed minimal sedimentation after 60 days. Thus, a quantitative analysis namely UV-vis spectroscopy was used to evaluate degree of stability.

Perkin Elmer Lambda 750 spectrophotometer was used to measure absorbance of samples. Absorbance value at supernatant portion drops when nanoparticles sediment at the bottom of suspension. Absorbance indicates concentration and this relationship is known as Beer-Lambert law, indicated as equation (1).

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A = \epsilon c l = \log \frac{I_0}{I}
\]

where \(\epsilon\), \(c\), \(l\), \(I_0\) and \(I\) indicate molar absorption coefficient, concentration of suspension, length of light path passing through suspension, initial light source intensity, and intensity of light source after passing through the suspension, respectively. Relative absorbance (\(A/A_0\)) was used to describe the concentration change over time, which is equal to sedimentation behavior of nanoparticles. Figure 2 shows stability of nanofluids up to 35 days. As expected, longer sonication duration led to better stability and 90 minutes was found to be sufficient for producing stable suspension. At 35th day, hybrid nanofluid with CTAB showed 5.12% of absorbance drop whereas SDBS hybrid suspension showed 2.46% more sedimentation. This suggested that CTAB could disperse both mono and hybrid nanoparticles slightly better than SDBS in base fluid.
3.2 Thermal Conductivity

Experimental data was validated based on ASHRAE [12], where maximum and average deviations shown in Figure 3 were 3.12% and 2.57% respectively. Figure 4 shows that thermal conductivity of all samples was increasing with temperature and nanoparticles concentration. It was observed that CTAB improved thermal conductivity of both mono and hybrid nanofluids more than SDBS samples at high temperature. At low temperature (30 and 40°C), both surfactants caused deterioration of thermal conductivity. This is believed due to the lacking of Brownian motion, where GnPs were moving slowly in suspension and hence less collision and heat transfer rate. The gradual increment of thermal conductivity for all samples was dominantly due to the effect of temperature. At 60°C, 23.74% and 21.59% of increment was observed for CTAB-based mono and hybrid nanofluids, respectively, which was 3.05% and 11.722% higher than SDBS-based nanofluids. These results suggested that CTAB is more suitable for this novel hybrid nanofluid at high working temperature.
4. Conclusion
Stability and thermal conductivity of graphene-based nanofluids were investigated. Ultrasonication up to 90 minutes was enough to produce nanofluids with good stability. Visual sedimentation method was
not suitable to evaluate the degree of suspension stability in this study. Thus, UV-vis spectroscopy was performed to obtained concentration change of suspension over time. Both surfactants contributed to high stability up to 35 days. Thermal conductivity of both mono and hybrid nanofluids was enhanced by the use of CTAB and SDBS. The highest enhancement (23.74%) was observed at 0.1 wt% nanoparticles concentration and 60 °C.

Density and viscosity of these samples were not reported as both properties were mainly affected by the addition of nanoparticles. Relatively low increment was observed for viscosity (2.78%) and density (0.05%) when 1 wt% of surfactant was added. Thus, the most significant impact of surfactant was observed on thermal conductivity compared to other properties. A good choice of surfactant should at least stabilize suspension and has less impact on main property (thermal conductivity in this study). Results obtained in this study provide various information on nanofluids with different surfactant as these properties directly affect the efficiency of a heat transfer system. High thermal conductivity enhances heat transfer and low viscosity reduces pumping power. In future work, authors will be employing nanofluids with the best surfactant (CTAB) as coolant in vehicle cooling system.

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