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TRIBOLOGICAL STUDIES ON GRAPHENE/TMP BASED NANOLUBRICANT

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Abstract

This paper presents studies on density, dynamic viscosity and tribological behaviour of nano graphene platelets (NGPs) dispersed in Palm Oil Trimethlolpropane (TMP) ester base lubricant. NGPs with concentrations ranging from 0.01 to 0.1 wt% are dispersed in the TMP ester via water bath sonication for 4 hours to form stable NGP nanolubricants. Physical properties such as density and viscosity was measured using Portable density meter and Brookfield viscosmeter (DV II+). No significant enhancement in density was observed, while a maximum enhancement on viscosity was 168% at 0.1 wt % NGPs concentration. The evaluation of frictional coefficient was performed using a four ball test at varying loads, from 40 kg to 80 kg, respectively. Results showed that the introduction of NGPs as an additive in the TMP lubricant reduced the coefficient of friction (COF) in NGP-Palm oil TMP Ester, achieving a maximum reduction of 7%, and 16.2% in the wear scar diameter at 0.05wt% NGP and 80 kg load. It was observed that addition of NGP has prevented oxidative attacks on the surface of the steel balls through the development of a sturdier lubricating film barrier between nanolubricant and the solid surfaces.

Keywords: Nanolubricant, Coefficient of friction, Four ball test, Graphene.

1. Introduction

Lubrication is important to overcome friction and wear that lead to energy and material losses in any moving mechanical assemblies. Under conditions of heavy loading, the chemical thin film generated from the lubricant may not be able to protect metallic surface completely. Studies have shown that the addition of nanoparticles to lubricant oil improves the tribological properties of lubricants and contact surfaces owing to the small nanoparticles size that are capable of accessing areas within extremely small surface asperities as well as enhance the supporting force during loading [1, 2].

The exponential growth in the field of nanotechnology has led to the development of carbon nanoparticles as lubricant additives. This could be attributed to their small size and extremely thin laminated structure, which offer low shear stress and prevent interaction between metal interfaces [3]. Graphene is a thin layer of carbon, where the carbon atoms are connected in hexagonal honey comb lattice, with one carbon atom covalently bonded to another three carbon atoms. Graphene platelets are two-dimensional graphene thin plates containing few layers of graphene sheets. Nano graphene platelets (NGPs) due to its nano-size and high thermal conductivity, are predicted to be able to cut down friction and can withstand enormous amounts of pressure [4]. Besides, graphene platelets in oil can easily enter the contact area and form protective film to prevent the direct contact between steel surfaces and improve the friction properties [3, 5-8].

Nanolubricant has been touted as the future of synthetic oil as conventional mineral oil based lubricant that contains large amounts of sulphur and phosphorous bearing additives as well as other heavy metals that is toxic and pose problem particulate emission problem [4]. The presence of these unwanted compounds in the lubricating oils also adversely affects the performance of after treatment devices, especially in diesel engines [4]. With enforcement of environment regulation to minimize release of heavy metals such as Sulphated Ash, Phosphorus and Sulphur (SAPS), plant based lubricant is gaining more and more attention [9]. Besides being a plant based source that is biodegradable, the fascination of TMP esters as lubricant base stocks is also contributed by its fast synthesis reaction and 98% of high conversion rate from palm oil [10]. Palm oil TMP ester has shown remarkable lubricant effects on metal surface, through the formation of a protective boundary film which results in increased wear resistance of the mating surfaces [11].

In view of this, it is anticipated that the combined properties of Palm Oil TMP ester and NGPs nanoparticles will form a major breakthrough in the field as a potential nanolubricant with enhanced friction and wear resistance, coupled with low sulphur and phosphorous content. This study focused on the tribological behavior (wear durability and friction reduction) of NGP TMP ester based nanolubricant by utilizing a four ball wear tester. The nanolubricant dynamic viscosity, coefficient of friction (COF) and wear characteristics in a boundary and hydrodynamic lubrication regime are studied with respect to contact loads from 40 kg to 80 kg and NGPs concentrations of 0.01% to 0.1%. In addition, the lubrication mechanism of the NGP nanoparticle systems in TMP ester oil will also be elucidated in this study.

2. Experimental Procedure

2.1. Materials

NGPs purchased from Graphene supermarket (USA) with an average diameter of 12 nm and purity > 95% was used. Palm Oil trimethylolpropane (TMP) ester was supplied by Oleon chemicals with viscosity grade of VG22, together with a recommended biodegradable lubricant additive, phosphate ester (PE). The TMP ester is derived from palm oil and has high lubricating properties, higher flash point and a higher viscosity index [12]. PE was used as a crankcase additive to increase the oxidative stability and viscosity index of the nanolubricant samples. For tribological studies, four carbon steel balls, AISI 52-100 with 12.7mm in diameter and 64-66 Rc hardness were used.

2.2. Preparation of NGP nanolubricant

Four different NGP nanolubricant were prepared and labelled with Sample 1 to 4, which consists of fixed amount of NGP, 5 wt. % phosphate ester (PE) and Palm oil TMP ester, giving a total weight of 60 g as shown in Table 1. The nanolubricant samples were first homogenized for 5 minutes by utilizing a high speed homogenizer (IKA-T18, ULTRA-TURRAXX, Germany) and then sonicated in an ultrasonic bath (Crest Ultrasonics, USA) for 4 hours at 50°C to ensure that the samples are well dispersed. The samples were kept at room temperature and found to be stable and no sign of NGP sedimentation was observed as shown in Fig. 1.

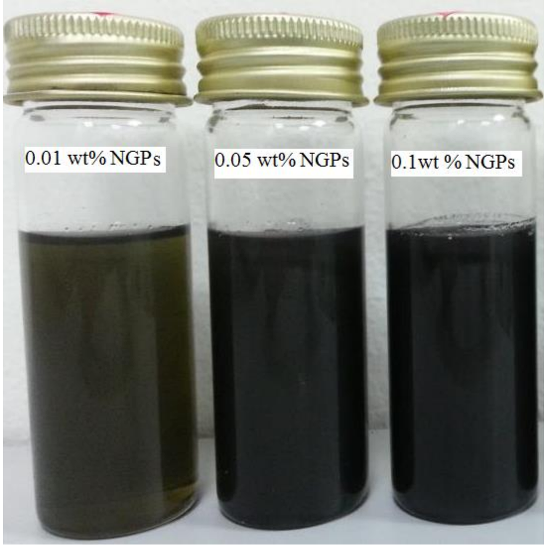


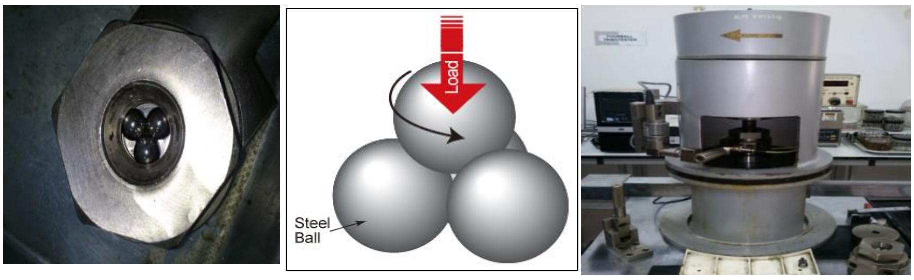
Fig. 1. Stable samples after 1week with NGP dispersed in palm oil TMP ester and PE additive.

Table 1. Composition of NGPs, phosphate ester and palm oil TMP ester used in preparation of nanolubricant.

Sample No.	NGPs (wt%)	**NGP (g)**	**PE (wt%)**	**PE (g)**	**TMP ester**
1	Blank	0	5	3	57
2	0.01	0.006	5	3	56.94
3	0.05	0.03	5	3	56.97
4	0.1	0.06	5	3	56.99

2.3. Test procedure

Figure 2 shows the four ball test assembly (Ducom TR-30H). Before each sample is tested, the new balls are wiped thoroughly with heptane to ensure a shiny polished surface is obtained. Besides that, the ball pot is also wiped with heptane in order to dissolve the residual oil that may affect the readings. The sample volume required for each test is approximately 10 ml.



(a) **(b)** **(c)**

Fig 2. For ball test assembly (a) ball pot, (b) ball rotation, and (c) complete assembly.

The test conditions were fixed at room temperature, with a rotational speed of 1200 rpm and repeated for varying loads of 40, 60 and 80 kg, respectively. Each test was run for 10 minutes after steady state conditions were achieved. In order to set up the experiment, the three balls were assembled as shown in Fig. 2, and tightened using a torque wrench. The fourth ball is then locked inside the collector using a spindle. The assembled components are loaded into the four ball tester. After each test, the wear produced on the bottom three balls are measured under an optical microscope, and the Scarview software is used to measure the wear scar diameter (WSD).

2.4. Tribology testing

A specific data acquisition system connected to the four ball machine records down the frictional torque at specific time intervals. The coefficient of friction is then calculated according to IP-239, as given in Eq. (1) [13];

$$\mu = \frac{T\sqrt{6}}{3Wr} \tag{1}$$

where μ is the friction coefficient, *T* is the frictional torque (kg mm), *W* is the load in kg, and *r*, the distance from the contact surface of the lower balls to the axis of rotation. The friction coefficient was calculated by the computer automatically.

2.5. Viscosity and density measurement

The viscosity tests were performed using a Brookfield viscometer DV-II+ (USA) equipped with the LV spindle. The enhanced Brookfield UL Adapter is used with the standard Brookfield Viscometer which allows measurements that require a smaller sample size (16ml). The UL Adapter consists of a precision cylindrical spindle rotating inside an accurately machined tube. The auto zero calibration was carried out before the samples were measured for viscosity by turning detaching any connected spindles, and then letting it auto calibrate itself by rotating freely. The UL adapter comes with the ULA-40Y water jacket that was attached to heat exchanger to heat and maintain the desired temperature of the sample. The viscosity was measured at 40, 75 and 100˚C, respectively. Each measurement was recorded only 10 minutes after the set temperature is achieved, and recorded only when the torque values were stable, allowing for a fluctuation of 0.1%. Density for the samples was measured using a DMA 35 portable density meter. The samples were tested at room temperature, around 25°C. Test for each sample was repeated three times to ensure the validity of the data.

3. Results and Discussion

3.1. Viscosity of nanolubricant

Viscosity of a lubricant must remain high enough in order to form a protective lubricating film thickness (Zulkifli et al. 2013), while at the same time low enough that it can be easily transported to areas where friction attacks prevail the most. For this study, the dynamic viscosity was measured at temperatures of 40° C, 75°C and 100°C. This temperature range is the usual operating temperature range for most industrial applications involving lubricants. From Fig. 3, it can be observed that the addition of NGP significantly affecting the viscosity of Palm Oil TMP esters. Sample 4 with the addition of 0.1 wt % NGPs produces a 122% increase in viscosity at room temperature, and the viscosity enhancement increases to 168% at 100°C. At lower concentrations of NGPs, the viscosity increments are still significant, bearing a 75% and an increment value of 11% for NGPs concentrations at 0.05wt % and 0.01 wt%.

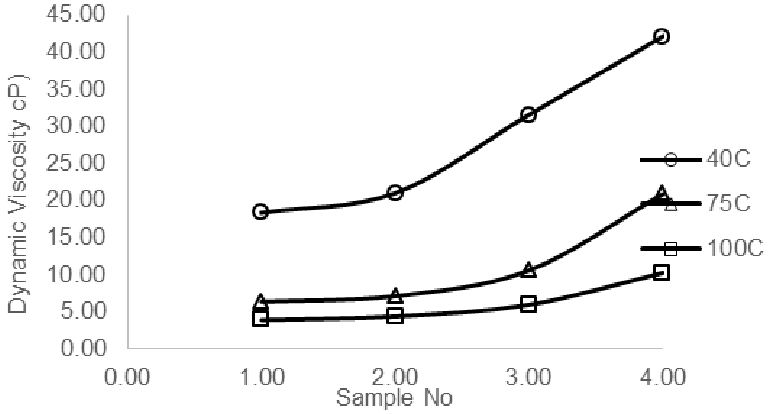


Fig. 3. Dynamic viscosity of nanolubricants as a function of temperature and NGP concentration.

3.2. Density of nanolubricant.

The density of a lubricant fluid can provide indications of its composition and nature. The density of lubricants, mainly hydrocarbons, varies between 0.860 and 0.980 g/cm^3 [1]. As observed from Table 2, the addition of NGPs did not have a drastic impact on the overall density of the TMP ester due to small volume fraction used and low density of NGP used in this study.

Table 2. Density of graphene nanolubricant.

Sample No.	**1**	**2**	**3**	**4**
Density (g/cm^3)	0.926	0.924	0.924	0.925

3.3. WSD and COF

Figures 4 and 5 show the effect of load on wear scar diameter (WSD) and coefficient of friction (COF). As seen in Figs. 4 and 5, nanolubricant samples, 2, 3 and 4, produces a lower WSD as well as COF compared to the biolubricant sample without NGP’s (sample 1). This agrees with the research shown that carbon nanoparticles tend to develop a thin film thickness that act as a separation from asperities which in turn produce lower COF [4]. Throughout the four varying loads used, the best results were produced by sample 3, which contained the highest amount of NGPs, 0.1%wt. It is interesting to note that while the COF of the nanolubricant samples do not have a very significant difference, the difference in WSD is strikingly evident when compared to pure TMP ester. This can be observed especially in Fig. 4 when a load of 40 kg is used, where the nanolubricant sample 4 with 0.1 wt% NGPs produces a very small WSD, a 16.2% reduction in WSD when compared to the WSD produced by sample 1, a pure TMP ester. It is important to note also that the reduction in WSD of sample 2 and sample 3 is negligible. This indicates that the differences in concentration of NGPs below 0.05 wt % are not as significant when added in larger quantities. This may be attributed to the fact that more than 0.05 wt % of NGPs is required to form a thick protective film, whereas at higher loads, the samples with lower NGPs fail in forming the protective lubricating film over the steel balls [4]. Besides this, the addition of NGPs also resulted in the decrease in COF. From Fig. 5, this is clearly evident. A maximum reduction of 6.9% in COF was achieved at a load of 80 kg when comparing nanolubricant sample 3 and pure TMP sample 1.

Relating the results back to the viscosities measured, it was noted that the addition of NGPs more than doubled the measured viscosity of TMP ester when added in a quantity of 0.1 wt %. This ensures that the thin film layer formed will not wear out at higher loads, coupled with fact that NGPs form an additional layer that binds to the solid surfaces. Hence justifying the performance of sample 3 throughout the test loads carried out. Although the tests were performed at room temperature, the friction produced from the rotating top ball increased the temperature of the lubricant up from room temperature up to 41°C. In theory, a higher load would show a greater failure of sample 1 (pure TMP) as temperature renders the lubricant a greater disadvantage due to the thinning of the lubricant film. As observed from Fig. 5, the change of COF vs load again emphasizes the superiority of the nanolubricants over the TMP ester; with samples 3 and 4 performing significantly better due to an increased concentration of NGPs.

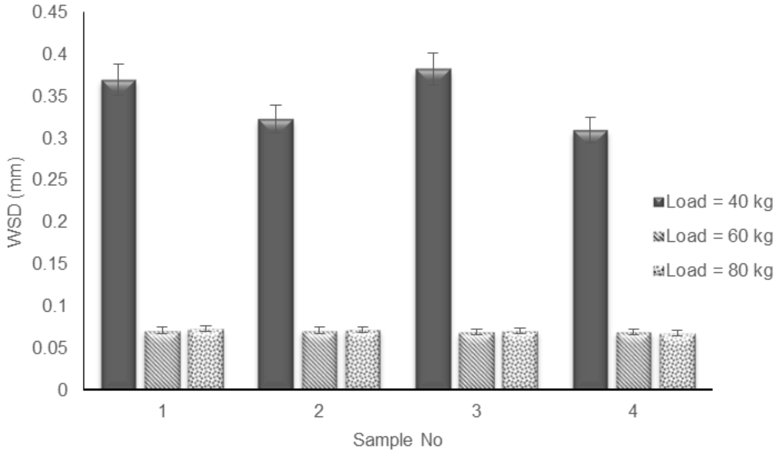


Fig. 4. Wear scar diameters (WSD) of nanolubricant at varying loads.

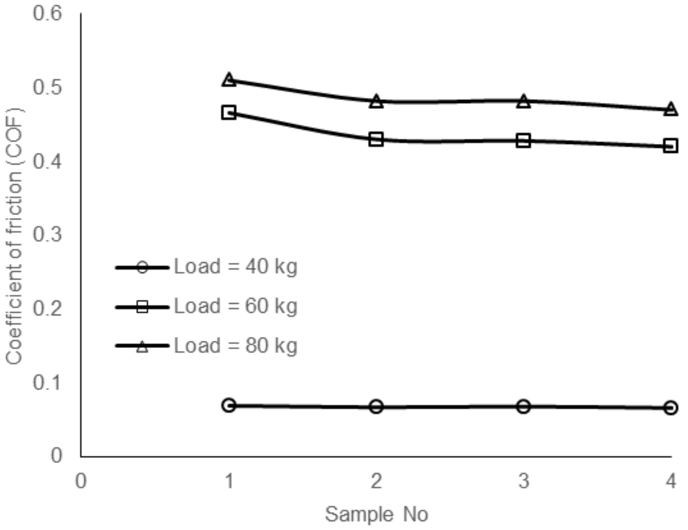


Fig. 5. Coefficient of friction (COF) of nanolubricant at varying loads.

3.4. Optical microscopy

Through the optical microscope, the images of the WSD on the balls were observed at 80 kg load as shown in Fig. 6. The wear scar produced for pure TMP ester reached a maximum of 5.08 mm, and there are signs of oxidation smears on the surface of the ball. This is similar to the finding that higher concentrations of TMP tend to present a corrosive black mark [14]. This is explained by the chemical composition of TMP ester that is susceptible to oxidation at higher temperatures hence producing corrosive acids that enhance the corrosive wear on the surface of the ball. This may indicate that NGPs somehow increase the oxidative stability of TMP esters, by providing a thicker protective film that is less susceptible to oxidative attacks.

Fig. 6. Wear scar image from the optical microscope;
Left: WS for sample 3 at 80 kg; Right: WS for sample 1 under 80 kg load.

4. Conclusion

In conclusion, it can be confirmed that the use of NGPs as an additive induces a positive response in terms of a tribological view point. The addition of 0.1 wt % produced the most significant reduction in terms of COF and WSD over the pure Palm Oil (TMP) ester sample. A significant reduction in COF up to a maximum of 6.9 %, as well as a reduction in WSD up to a maximum of 16.2% was achieved, while viscosity enhancements of up to 168% enabled the nanolubricant samples to endure higher loads than its pure TMP counterpart. Besides this, the NGPs that enhanced the viscosity also managed to prevent oxidation attacks on the TMP ester by forming a thicker and more stable thin film lubricant barrier on the hard surfaces of the steel balls.

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