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Wear and friction behavior of semi synthetic engine oil blended with palm oil/TMP ester and nano glass powder additive

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KEYWORDS

Trimethylolpropane (TMP) Ester
Palm oil
Engine oil
Tribology

ABSTRACT

Mineral oil has been dominated the market as the base oil for engine oil due to its availability, low cost and good performance. However, due to the decomposition issues and emission of toxic gases during its use, it becomes a source of pollution to the environment. This paper evaluates the effects of blending semi synthetic engine oil (SSEO) with palm oil (PO) and palm oil-based trimethylolpropane (TMP) ester on its tribological properties. The aim is to assess the potential of alternative base oil for engine oil which is more environmentally friendly and effective in reducing wear and friction. Consequently, experimental investigations were conducted to analyse the coefficient of friction (COF) and wear scar diameter (WSD) by using four ball tribotester. The blend of palm oil with 2 wt% TMP ester exhibited the lowest COF and WSD of 0.075 and 485.7 μm. Adding 0.5 wt% of nanoglass powder (NG) to the mixture oil consisting of 30 wt% (2 wt% TMP ester and 98 wt% PO) with 70wt% of SSEO, reduce the COF from 0.0609 to 0.057 and WSD from 318.9 to 295.53 μm. Indeed, tribological properties of SSEO improved with the incorporation of palm oil and TMP ester.

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1.0 INTRODUCTION

Automotive engines or also known as internal combustion engines are one of the most important mechanical equipment and oil is used to reduce friction and corrosion in engines (Lockwood; Ali et al., 2015). When the engine is in service, one of the most indicating friction result is an increase in temperature that affects the efficiency of the engine as well as the operating life time (Yadav et al., 2018). Therefore, the oil must be used in the lubrication process continuously to avoid friction and wear which adversely affects the performance of the engine and consumes more (Norrby, 2003; Zulikifli et al 2013; Rudnick, 2020) The lubrication or engine oil creates a very thin layer that separates the metal parts from each other to diminish friction or reduce it, thus reduces the heat transformation resulting from friction and wear of metal parts (Zulkifli et al 2013; Rudnick, 2020). Engine oils also reduce engine heat through convection currents and transfer to air through cooling (Sidik et al 2017). Reduction in friction losses and wear in an inward combustion engine is essentially a feature of progressed lubrication. Consequently, advanced lubricants are actually being formulated to reduce the damage and friction of the tribological component of the engine. The improvement of cutting-edge lubricants and their correct usage are of remarkable importance for the national economy, individual and environment. Lubricants, optimally adjusted to a given duty, can reduce expenditure within the case of an industrialized country, lessen wear, reduce upkeep necessities and consequently the hassle of air pollution (Masjuki et al., 1999; Baba et al., 2019).

Palm oil-based lubricants have shown better rendering in terms of wear and tear, and the mineral oil-based lubricants display better overall performance in terms of friction (Masjuki et al., 1999). The oil formulated with palm oil-based trimethylolpropane (TMP) ester lubricant improves the wear preventive lubrication properties in terms of coefficient of friction (COF) and wear scar diameter (WSD) (Zulkifli et al 2013). Syahrullail et al., (2013) reported that by blending palm fatty acid distillate (PFAD) into commercial metal forming oil (CMFO), the coefficient of friction (COF) decrease from 0.08 to 0.054 (20% PFAD). The PFAD oil has more lubricant competencies in regards to friction and wear than the mineral-based engine oil and hydraulic oils at various weight percentages compared to pure mineral oil formulations (Golshokouh. 2014). The use of other non-edible feedstock blending also reported (Masjuki et al., 1999) and suggest the long fatty acid molecules in the modified jatropha oils (MJOs) found to be able to reduce the friction at the contact surfaces (Talib et a., 2017). Modified jatropha oil MJO also show good results in friction and wear behaviour by reducing 75% and 20% respectively, especially when compared to SE. Even thought, the properties of lubricating oil mixed with vegetables are less toxic, easier to handle, and less harmful to the environmental in case of accidental spillage. In spite of this, vegetable oil-based lubricating oils lack oxidative and thermal stability, therefore causes a small disadvantage in comparison to the mineral oil (Chhibber et al., 2015).

Noted, the addition of nanoparticles to oil may result in greater change of viscosity of oil (Wu et al., 2007) or a change in thermal stability or thermal properties of the oil. Depending on its shape and size, it can act as a Nano-ball bearing that rolls between the surfaces to reduce friction (Lahouji et al., 2011). Nanoparticles have the ability to prevent worn surfaces by sticking to them and protecting the surfaces by forming a triple protective film (Wu et al., 2007; Liu et al., 2004). Evidently, COF between two moving surfaces decreases remarkably after the addition of nanostructures to the lubricant oil. Former study reported that an addition of 0.05 wt% of hBN nanoparticles in MJO remarkably reduced the friction and wear up to 76% and 24% respectively (Talib et al., 2017). Similarly with Gulzar et al., (2015) study, whose found that the addition of CuO and MoS_2 nanoparticles into the chemically modified palm oil (CMPO) rendered greater reduction of anti-wear (AW) and extreme pressure (EP) and successfully enhanced the AW/EP by 1.5 times (Gulzar et al. 2015). Likewise, Safiyah et al. (2016) showed that when graphene nanoplatelets (GNP) were added into polyalphaolefins (PAO), blended with 5 % palm -TMP ester volume, viscosity, density, VI, and Total acid number (TAN) of oils increased, while total base number (TBN) values decreased. The results also showed a good reduction in COF and WSD at 0.05 wt% of GNP (Azman et al., 2016).

TMP esters synthesized from methyl esters of palm and palm kernel oils, showed excellent potential as base oil in biodegradable lubricant system (Yadav et al., 2018). TMP esters (TMPE) are utilized mostly in synthetic lubricant formulations and used in crank case lubricant, 2-cycle oils, high temperature greases, compressor oil, hydraulic fluid etc. (Ali et al., 2015). TMP ester has also been probed as a lubrication booster as it provides quality improvement for properties like: higher viscosity, stable flash point, proper density, and freezing point for engine oil (Norrby, 2003). TMP esters have comparable load carrying potential and tribological properties as that of mineral fully formulated lubricant (Azman et al., 2016). Therefore, this study focuses on using TMPE to improve the lubricating performance of palm oil (PO) and later the TMPE and PO blend will be blended with mineral oil (semi synthetic engine oil). The lubricating properties of all blends are evaluated in terms of its wear and friction and the relationship with other physical properties are also assessed.

2.0 MATERIALS AND METHODS

2.1 Materials

Palm oil (PO) (refined, bleached, and deodorized) and semi synthetic engine oil (10W-40) were purchased from the domestic market. TMP ester was synthesized from the transesterification reaction of palm oil methyl ester with trimethylolpropane alcohol based on the method described by Abd Hamid et al. (2016). Nanoglass powder (NG) was prepared in the laboratory.

2.2 Lubricant Sample Preparation

The experimental section is divided into three steps (steps A, B, and C) to obtain the best formulation. Step A involved blending palm oil with TMP ester at different percentages, that is, 2%, 4%, 5%, 6%, and 7%, with continuous stirring using a magnetic stirrer for 30 min at 100 °C. The compositions of each blend are shown in Table 1. The best blend with lowest COF and WSD from step A was blended further with SSEO at 0%, 10%, 30%, and 50% in step B. The mixing method was similar to that in step A, and the composition of each sample is summarized in Table 2 and 3. All blends in three steps were subjected to viscosity at 40-100 ^{o}C and density analyses at 15 ^{o}C before and after a four-ball tribotester, and according (ISO VG68) and ASTM D445 method by using SVM 3000 Stabinger viscometer. In addition the Pour point test (PP) conducted according to the method described in ASTM D97-05.

Table 1: Composition of palm oil-TMP ester blends.

Sample	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
Palm oil (wt%)	100	98	96	95	94	93
TMP ester (wt%)	0	2	4	5	6	7

Table 2: Composition of mineral oil (best sample from step A).

Mineral oil (wt%)	**100**	**90**	**70**	**50**
Best of step A (wt%)	0	10	30	50

Table 3: Composition of different samples for step B.

Sample	**2% PO.TMP (2% TMP + 98% palm oil)**	**4% PO.TMP (4% TMP + 96% palm oil)**	**Semi 800 Mineral oil**
B1	100	0	0
B2	10	0	90
B3	30	0	70
B4	50	0	50
B5	0	100	0
B6	0	10	90
B7	0	30	70
B8	0	50	50
B9	0	0	100

In step C, the best sample formulation with lowest COF and WSD of step B was blended with various nanoglass powder (NG) concentrations (i.e., 0.25, 0.50, and 0.75 wt%) using the ultrasonic bath for 8 h to disperse it in the lubricant base oils as shown in Table 4.

Table 4: Step C-samples wt% of nanomaterial additive to best formulation.

Constituents	**Formulation ratio (wt%)**		
	C1	**C2**	**C3**
Best of step B	99.75	99.50	99.25
Nanomaterial	0.25	0.50	0.75

2.3 Four-Ball Configurations

The configuration of the four-ball tribotester device was set up according to ASTM D4172. This device consisted of a ball bearing (up), which can be rotated and is in touch with three constant balls bearing (down) immersed in the oil, as shown in Figure 1. The rotating ball was held in a special chuck at the lower end of the vertical spindle of a consistent pace electric motor. The balls fixed downward were placed in a counter position from each other in a cup using a clamping ring and a locking nut. The test was run with steel balls with standard properties of 12.7 mm diameter, 0.1 μm surface finish, and hardness in the range of 64–66 RC. Prior to the test, the balls were cleaned carefully with toluene and dried. Approximately 10 mL of the sample volume was required for each test, which was performed at 40 kg load, 75°C operating temperature, 1200 rpm rotational speed, and 1 h duration.

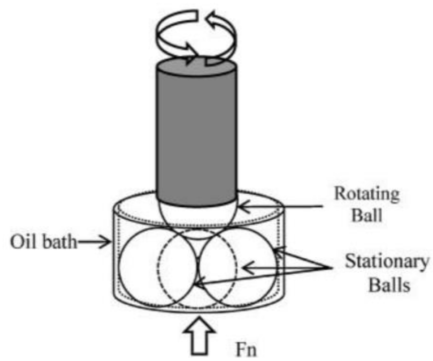

Figure 1. Scheme of four-ball tribotester.

2.4 Thermogravimetric Analysis (TGA)

The thermal stability of the oil formulation was measured with the thermal degradation analysis of oils using a TGA, that is, Mettler Toledo model 851E using high-temperature furnace controlled by an IBM compatible PC at the University Putra Malaysia (UPM). The weight changes of the material as a function of time and temperature were measured by the TGA. The TGA was also used to estimate the oil content. The TGA result analysis uses the following equation (Broido et al., 1969) (Broido, 1969):

$$ln\left(ln\left(\frac{1}{y}\right)\right) = -\frac{Ea}{RT} + constant, \quad (1)$$

Where, y represents the normalized weight obtained by dividing wt with wi, where wt refers to the weight of the sample at any time t, while wi refers to the initial weight of the sample; T refers to the temperature (in K), and R represents the gas constant (8.32 J/mol K). The line graph of ln (ln(1/y) versus 1/T is a straight line, the slope of which gives activation energy (Ea) using multiple heating rate method.

First, 15 mg formulated oil was heated at temperatures ranging from 25 °C to 600 °C, at a heating rate of 10 K/min and flow rate of 50 mL/min into the air and N_2 environment.

2.5 Differential Scanning Calorimetry (DSC)

In the DSC analysis, a sample and reference were heated at the same temperatures in a closed system and isolated from the surrounding environment. DSC is used to determine the thermal transformations in the sample (endothermic and exothermic) that can be used to analyse the properties and composition of the materials and the purity of the sample. DSC is also used to illustrate the behaviour of the materials as a function of temperature or time. DSC analysis can be achieved at the same time with TGA because it is complementary to the TGA results.

In this study, DSC analysis was conducted at the Institute of Advanced Technology, UPM, Serdang using the equipment with the following specification: Mettler Toledo Model 851E, at the temperature ranging from 25 °C to 600 °C in a controlled furnace by an IBM compatible PC. The heating rate was set at 10 k/min in two environments, that is, air and N2 with the flow rate at 50 mL/min. The mass of the sample for each analysis was approximately 15 mg.

3.0 RESULTS AND DISCUSSION

3.1 Physical Properties of Lubricants

Table 5 lists the properties of the lubricants. Viscosity is one of the important functional properties that should be considered for the oil to lubricate the engine. Inadequate lubrication occurs when the viscosity is not within the specified range, thereby increasing friction, wear, and heat. During engine operation, a number of chemical and physical changes may take place in the oil that can influence oil pumpability. Table 5 shows that the viscosity of the TMP ester (42.5 cSt) was slightly higher than that of palm oil (40.1 cSt), while the semi synthetic engine oil has a high viscosity (90.4 cSt). Oil with high viscosity can provide the thickness necessary to keep metal components in contact and separated in the engine under high load at high temperatures [6]. Consequently, the best formulated samples B3 with the lowest COF and WSD and a viscosity of 64.14 cSt is suitable for lubricants grade ISO (VG68).

Table 5: Properties of palm oil, TMP ester, and mineral oil lubricants.

Properties	**Viscosity**	**Density**	**Pour point**	**VI**
TMP ester	42.5	0.911	-29	221
Palm oil	40.1	0.918	2	191
Mineral oil	90.4	0.866	-30	155

Table 1: Pour point for all samples of step A.

Sample	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**	**A7**
Pour point (°C)	2	2	2	1.8	1.8	1.5	−29

Table 2: Pour point for all samples of step B.

Sample	**B1**	**B2**	**B3**	**B4**	**B5**	**B6**	**B7**	**B8**	**B9**
Pour point °C	6	-20	-8	-1	7	-16	-9	0	-27

Viscosity is an important indicator for selecting lubricants. Viscosity can be used to calculate the thickness and strength of the film layer in the machines and assess its effects on other important factors, such as wear rate, lubricant temperature, life expectancy of oil, and energy consumption. Viscosity index (VI) assesses the viscosity stability of the oil at different temperatures (Nagendramma & Kaul, 2012; Bart et al., 2013). In this study, samples B1 and B5 showed the highest VI as shown in Figure 2. These samples contain 100% of palm oil and TMP ester blends with no semi synthetic engine oil. The presence of fatty acid esters in palm oil and TMP ester enhance its viscosity-temperature behaviour as indicated by higher VI as shown in Figure 3. The higher the VI, the lesser the viscosity is affected by changes in temperature. Figures 2 and 4 show that the changes in VI and density for all samples before and after the tribotester are not significant, which indicate the stability of the formulations.

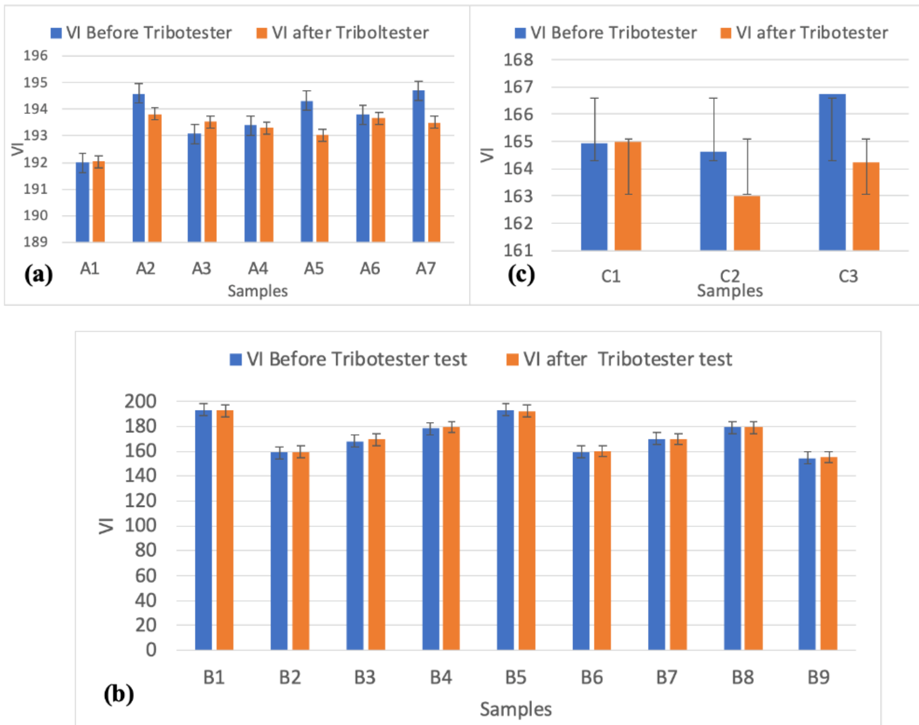

Figure 2: Viscosity index for all formulation before and after four-ball Tribotester (a) for step A (b) for step B (c) for step C.

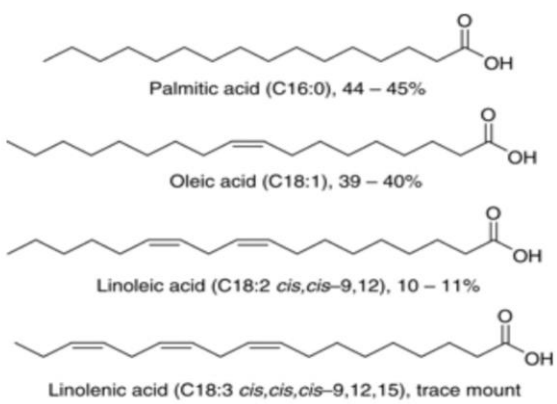

Figure 3: Fatty acid composition in palm oil (Armylisas et al., 2017).

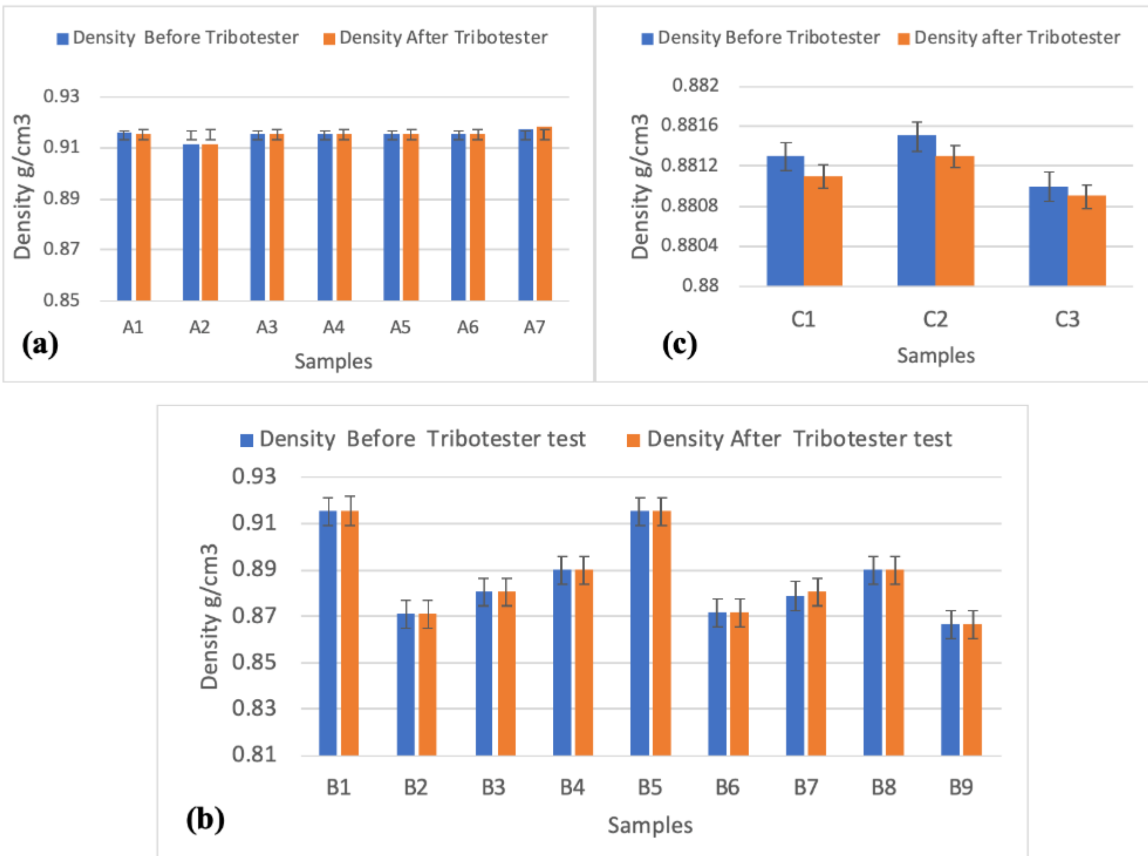

Figure 4: Density at 15 °C for all samples before and after four-ball Tribotester (a) for step A (b) for step B (c) for step C.

To avoid the potential engine failure modes associated with a cold start, the oil should be kept flowing even under extremely low-temperature environments. Thus, a low pour point is necessary for a smooth operation. Table 6 & 7 lists the pour point of step A & B. The pour point of TMP ester is almost identical with SSEO at −29 °C and −30 °C, respectively, while the pour point for PO is approximately 2 °C. The pour point of PO is high because of the palmitic acid content as shown in Table 6.

Table 8 shows the results for the samples in step C. The best formulation from step B was B3, with the PP of -8. The addition of the nanomaterial affected the pour point because it has a better thermal conductivity than pure oil, which gave the thermal conductivity ranging from 0.21–0.10 $W{\cdot}m^{-1}{\cdot}K^{-1}$. When nanoglass was added to the oil, the blend showed a slight decrease in PP. When NG was added, the PP was least affected because of its similarity to thermal conductivity (1.05–0.94 $W{\cdot}m^{-1}{\cdot}K^{-1}$), which is close to the thermal conductivity of the sample B3 (Zhang et al., 2014). Its thermal conductivity is in the range of 0.136 – 0.172 W·m-1·K-1 which are the thermal conductivity of SSEO and PO resistivity. Hence, the nanomaterials are a good additive in terms of pour point improvement because it can increase the PP for the engine oil slightly. The nanomaterial also had good thermal conductivity, that is, higher than those of oils, and thus, it can dissipate heat easier than the samples without nanomaterial addition.

Table 8: Pour point for all samples of step C.

Samples	C1	C2	C3
Pour point (°C)	-9	-9	-9

3.2. Coefficient of Friction (COF)

The COF results for samples with different percentages of palm oil and TMP ester in step A are illustrated in Figure 5 (a). In general, many studies showed that vegetable oils have good friction coefficient and excellent performance against wear because of its chemical composition. In the present study, the two samples A2 & A3, which consist of 98%, 96% PO and 2%, 4% TMP ester, have the lowest COF among the other samples. Any increase in the added ratio of TMP ester affected the friction coefficient adversely. The result also showed that the COF increased significantly when the TMP ester concentration was increased to 2%. Esters that are polar in nature are attracted to the metal surface and placed a film of oil between the mating surfaces (Rudnick., 2020). At 2% TMP ester concentration, the oil exhibited good resistance to shear strength. However, at high TMP ester concentration, the COF increased slightly because of the inability of TMP ester to form a continuous protective film over metal surfaces (Baba et al., 2019; Nik et al., 2005) In addition, the presence of fatty soap component in TMP ester may have affected the friction behaviour of the ester (Gnanasekaran et al., 2018; Naghshineh et al., 2010; Li & Li, 2016). The best sample from step A was A2 with the lowest COF at 0.075. A2 contains 98% PO and 2% TMP ester.

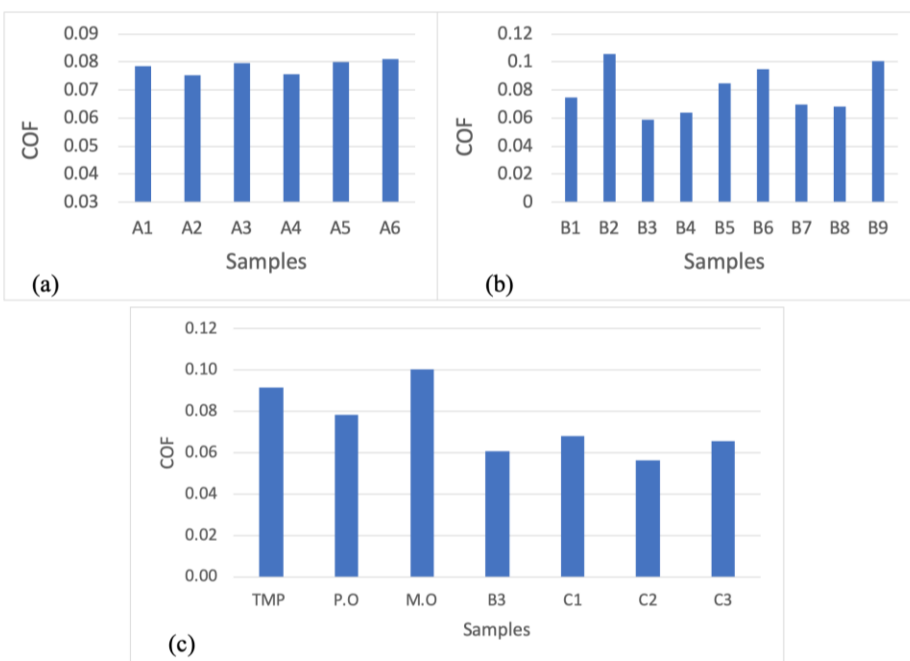

Figure 5: Coefficient of friction for three steps and different samples of (a) Step A (b) step B (c) step C.

Figure 5 (b) shows the COF results for step B. In step B, the B3 sample had the lowest COF values of 0.0609. Sample B3 contains 30% of (2% TMP + 98% PO) blend. Chemical interaction may be present between the molecules that changed the physical characteristics of the new mixture as result of mixing the different oils (Zulkifli et al., 2014). The van der Waals forces, hydrocarbon bonds, and ionic bonds all had a positive effect on the new compound and reduced the coefficient of the friction and wear scar diameter (WSD) (Zulkifli et al., 2013). These results showed that samples with PO/TMP ester recorded a significantly lower COF than SSEO at COF more than 0.1. The percentage reduction of approximately 40% was observed for these samples.

The COF for the B3 sample was the lowest at 0.0609. The nanoparticles were then added to B3 in different concentrations (0.25, 0.50, and 0.75 wt%). The effects of adding nanomaterials are shown in Figure 5 (c). The lowest COF at 0.057 was obtained after adding NG, which was slightly less than the COF before adding NG. The increase in the COF of the other samples was significant. The high COF may be due to the size of the nanoparticles, which were larger than the holes on the surface of the metal, thereby not allowing these particles to enter these holes and reducing the roughness of the surface. The nanoparticle accumulation and aggregation to form a large body may contribute to the increase in the COF (Wu et al. 2007; Thakur et al 2016). The nanofluids showed good stability, it have been stored for 50 days and the blends form homogenous mixture and do not separate out

3.3 Wear Scar Diameter (WSD)

The WSDs of all samples are presented in Figure 6. The average WSDs for B3 and B4 samples were 318.9 and 336.1 μm, respectively, compared with that of pure SSEO (S800), at 478.5 μm. This phenomenon also showed the effect of adding palm oil and TMP ester on SSEO (Zulkifli et al., 2013), which reduced the extent of wear significantly. In the B4 sample, the deformation of the ball's surface was in contrast to that in the B3 sample, as shown in Figure 7. This result may be because of the low percentage of PO/TMP ester in the sample, which led to the inability of the lubricant oil to form the necessary insulating film (Zulkifli et al., 2016; Rajendiran et a.., 2016).

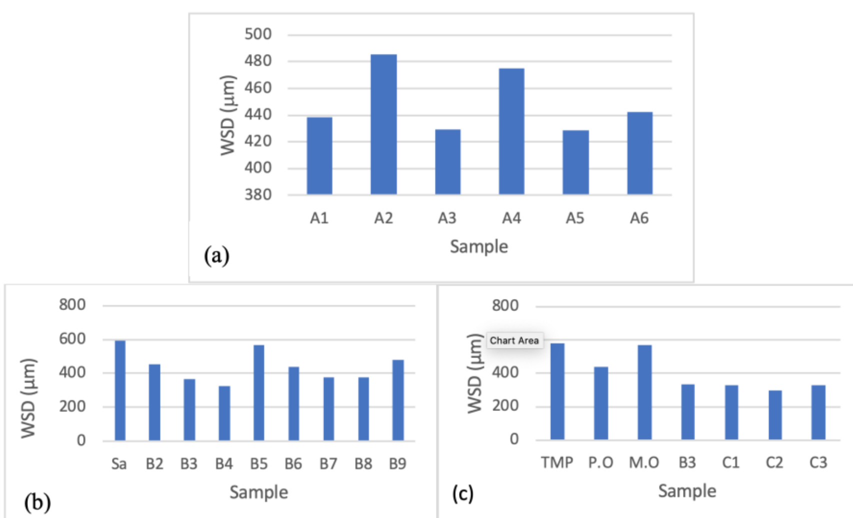

Figure 6: Wear scar diameter measurement from SEM for samples from step A (a) step B (b) and step C (c).

The addition of nanomaterials into the engine oil was reported to reduce the WSD values. The physical properties of the nanomaterials, such as size, shape, hardness, and solidity, and the nanomaterial concentration in engine oil and nanoparticle aggregation and agglomeration to create large-size particle affect the erosion of the surface and WSD (Battez et al., 2007). The analysis results of the WSD are shown in Figures 6 and 7.

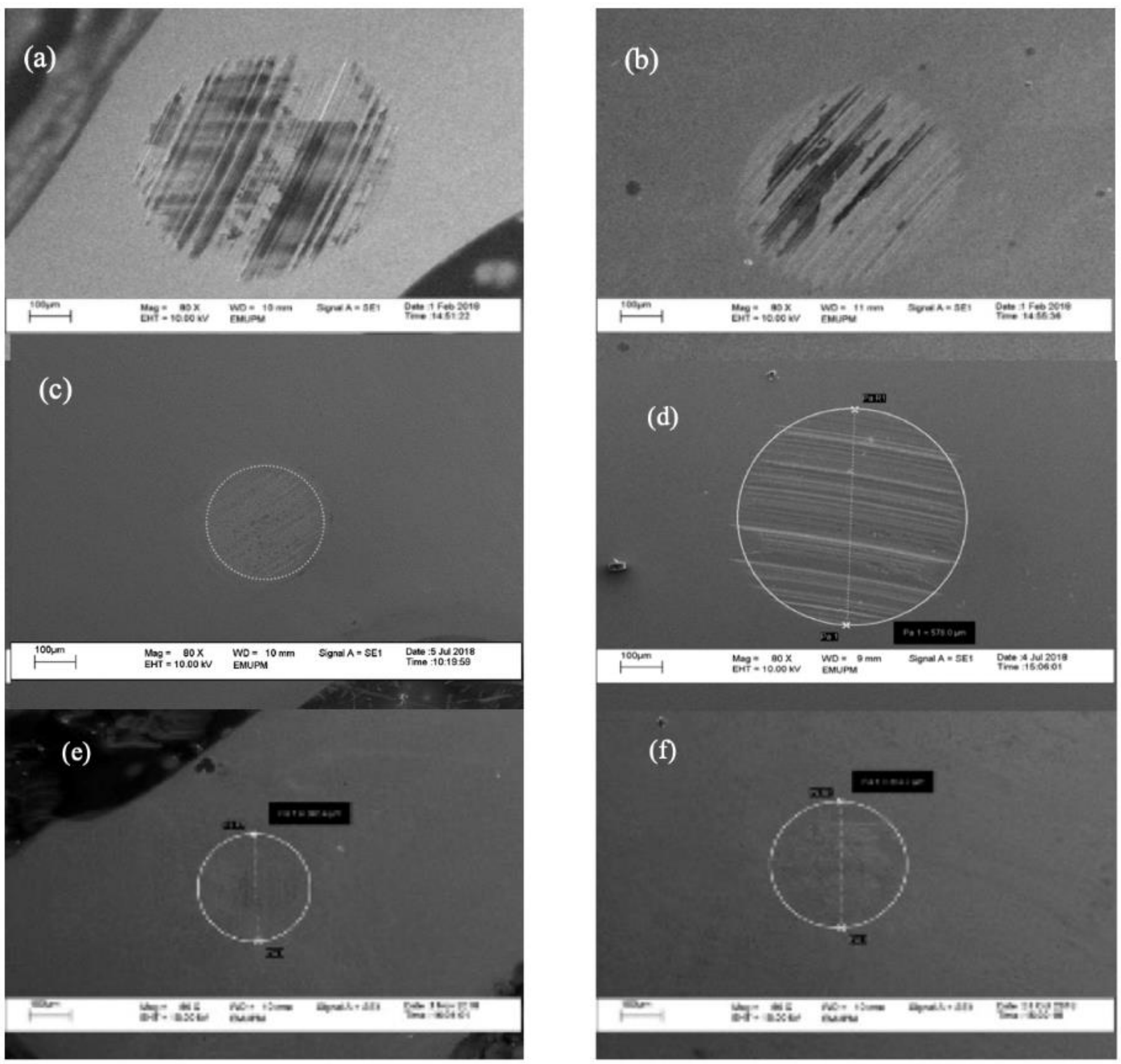

Figure 7: SEM photomicrographs for surface ball for (a) 100% mineral oil, (b) 10% A2 sample (98% P.O. + 2% TMP) + 90% mineral oil, (c) 30% B3 sample (98% P.O. + 2% TMP) + 70% mineral oil B, (d) pure TMP ester, (e) C2 sample (B3 + 0.5 wt% nanoglass), and (f) C3 sample (B3 + 0.75 wt% nanoglass).

The WSD for the B3 sample prior to the addition of nanomaterials (318.9) µm had the lowest value as compared with the other samples. Nanoglass exhibited good results compared with other materials. The average WSD for oil with NG was 295.53 µm, which was lower than all the WSD values of other nanomaterials. The glass particles were not attracted to each other to agglomerate, which caused scratches in the contact metal surface. The oily layer was formed between the two minerals and reduced the film thickness. The low hardness of the glass caused it to break into small parts, which entered the gaps instead of settling on the surface, increased its roughness, and increased the WSD value.

3.4. Effect of Palm Oil/ TMP Ester Under Fluid Film Lubrication

TMP ester oil exhibits better lubrication characteristics than semi synthetic engine oil. TMP ester oil has a higher density and high VI, than that of SSEO because of its chemical structure. This results indicated that the thick film of TMP ester oil is strong enough to separate the metal parts in the machine and reduce the COF and WSD values. The existence of long methyl ester chains in palm oil provides high strength lubricant films that interact strongly with metal surfaces, thereby reducing both frictions and wear (Havet et al., 2001).

According to the study results presented in Figure 8, the B3-NG sample showed the lowest friction torque at approximately 0.09 Nm compared to the other samples. Meanwhile, the SSEO showed the highest friction torque because the viscosity was extremely high and created a thick film, which will cause additional friction. The addition of PO/ TMP ester in the SSEO reduced the viscosity of the lubricant, thereby providing a good thin film at the surface and reducing the friction. According to the experimental results, the addition of PO/TMP ester and NG to the SSEO based lubricant improved the frictional torque of the lubricants.

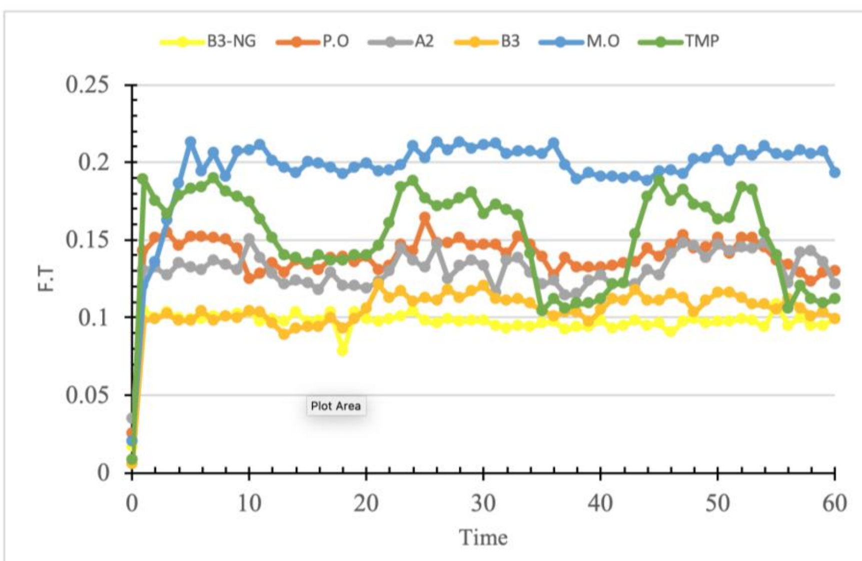

Figure 8. Relationship of friction torque with time under hydrodynamic lubrication.

4.0 THERMAL AND OXIDATIVE DEGRADATION

The thermal decomposition of an engine oil depends on several factors, such as the chemical structure of the compound, molecular weight, length of the chain and branches, number of molecules, and type of double bonds. To investigate the thermal decomposition in this study, we performed TGA on five samples, namely, semisynthetic 10W-40 (SSEO), palm oil, TMP ester, sample B3 and formulation addition of nanoglass to B3 (B3-NG).

4.1 Degradation in Air Environment

The results in Figure 9 showed evidences of the differences in the decomposition of the samples in the air environment. The decomposition test was performed in three steps, as follows. The first step was the loss of water or moisture content (Sichina, 2011). In the second step, the test was performed to determine the loss of the light compounds, breakage of bonds, and restructuring of the chemical composition of the compound and several complex reactions. Meanwhile, in the third step, the compound was oxidized completely and the loss of the maximum amount of material with the remaining ash was determined.

SSEO was the first sample that started to decompose at 208°C because of its simple chemical composition, which is mostly dominated by paraffin (Karacan et al., 1999). Subsequently, palm oil started to decompose at 271 °C, followed by the TMP ester, which began to decompose at 259 °C because of the activation energy required to initiate the reaction in palm oil is greater than the TMP ester (Gamlin et al 2002). However, palm oil became fully degraded faster than the TMP ester, which ended at 491°C, while TMP degradation ended at 499°C because the chemical compositions of palm oil and TMP ester were almost similar. Palm oil has β-hydrogen, while TMP ester replaces the unstable β-hydrogen with ethyl group by transesterification process because of the presence of O2 that is involved in several reactions to form the peroxides formation. Additional reactions from ketones, aldehydes, acids, alcohols, and several hydroxyl compounds, as well as the chemical composition of C16:0, C18:0, C18:1, and C18:2 (Gamlin et al 2002; Rattana-amron & Chotsuwan 2019). Given that all-natural base oil possesses naturally occurring antioxidants, it is more resistant to oxidation than the semisynthetic and fully synthetic (Gamlin et al 2002).

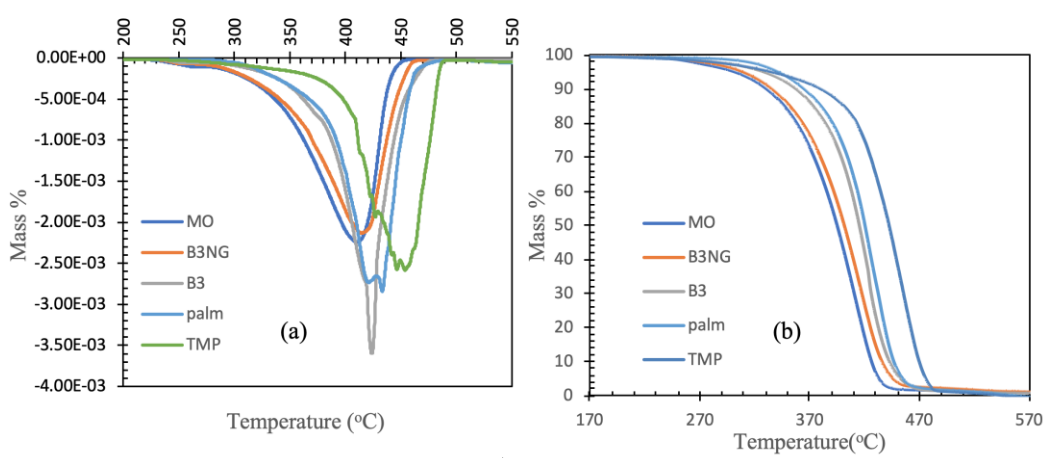

Figure 9: (a) TGA and (b) integral in the air environment.

The degradations of the B3 and B3-NG samples are in the middle, as shown in Figure 10. B3 sample consist of 70% SSEO, while the structure of the B3-NG sample is similar to that of the B3 sample with a 0.05% addition of NG. The addition of NG decreased the initial decomposition temperature at 219°C from 227 °C of the B3 sample. The characteristics of the B3 and B3-NG samples in decomposition are closer to those of semi synthetic engine oil. Therefore, adding NG is detrimental to the thermal stability of the blends.

Figure 10 further illustrate the thermal stability of TMP in the air environment compared with those of PO and SSEO. Upon blending with SSEO, the B3 sample acquired the thermal stability of palm oil and TMP ester. However, NG addition had a detrimental effect on the thermal stability of the B3 sample. The melting temperature of NG was approximately 150 °C, thereby decreasing the stability of the B3 sample.

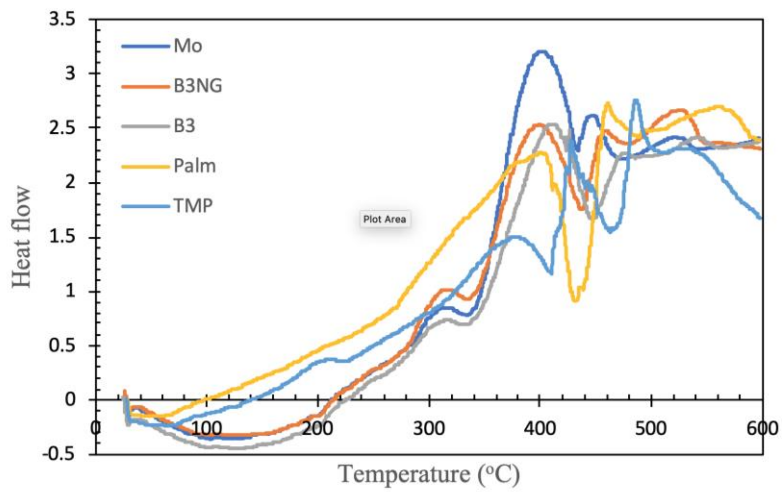

Figure 10: DSC analysis in air environment for all oil samples.

4.2 Degradation in N_2 Environment

The results from TGA analysis under nitrogen environment showed the relative amount of moisture present in the samples, as well as showing the effect of chemical structure of the compounds, double bonds, impurities and inorganic compounds on thermal degradation in inert environment. The self-ignition of oil can also be identified by using an inert nitrogen environment where oxygen is absent to ignite and the calculation of the amount of heat required to fully oxidize the oil (Gamlin et al 2002).

The results in Figure 11 present the differences in the sample degradation in the N2 environment as compared to in air environment. The first step showed the loss of moisture (Sichina, 2011), while in the second and third steps, the process of degradation of oils took place due solely to thermal degradation and not to the oxidation reaction. This is because of inadequate amount of O2 to stimulate the oxidation process and break the unsaturated bonds. Free radicals are also present to form compounds that are easy to thermally degrade and decompose (Rattana-amron & Chotsuwan 2019).

The results illustrated that the B3 sample began to degrade at a temperature of 197 °C, followed by the B3-NG sample at 217 °C and SSEO at 220 °C. Given the absence of O2, the process turned into thermal degradation instead of chemical reactions. Due to the presence of moisture in B3 sample, the onset temperature for thermal degradation was lower than the onset temperature for oxidation. The degradation temperatures for palm oil and TMP ester were at 334 °C and 352 °C, respectively. Given the presence of long fatty acid chains and double bonds, high energy is needed to overcome and degrade it (Gamlin et al 2002). The thermal stability effect of adding TMP ester and palm oil will be clearly shown in the analysis of activation energy and subsequent study using DSC.

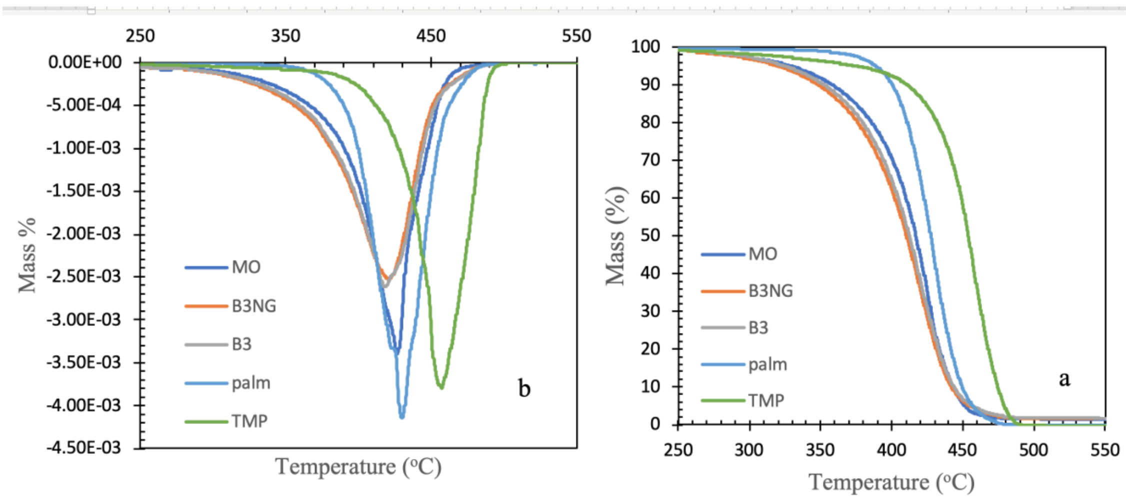

Figure 11: (a) TGA and (b) integral in N2 environment for all oil samples.

4.3. Activation Energy (Ea)

Activation energy, Ea is the minimum energy required to start reacting or breaking bonds or to cause any chemical change to the compound. The E_a of the engine oil should be determined to avoid oil degradation during engine use, which can lead to changes in its properties (Rattana-amron & Chotsuwan 2019).

The TGA results in Table 9 show that the required E_a to initiate the degradation are almost similar for pure palm oil and TMP ester (Tripathi et al., 2019). This is because palm oil and ester contain similar long chains fatty acid and double bonds. Palm oil required 100.8 KJ/mol of energy to degrade initially in an air environment, which is less than the results reported by Nik et al. (2005). Meanwhile, TMP ester requires 106.5 KJ/mol for initial degradation due to the variation in palmitic, oleic, and linoleic contents (Nik et al. 2005).

Meanwhile, SSEO required only 84.8 KJ/mol to initiate the degradation. When palm oil and TMP ester were added to SSEO in B3 formulation, the E_a increased slightly to 88.8 KJ/mol due to the presence of the fatty acid chain. Adding nanoglass has a detrimental effect, decreasing Ea to 86.90 KJ/mol; while the Ea for pure nanoglass is 11.9 KJ/mol. This is because the glass is inorganic compound and contains oxygen atoms and does not contain any long chain or fatty acid.

The value of E_a required in an N_2 environment to degrade the same sample of oils is greater than that in the air environment due to the absence of O2. The sequence of the degradation was the same in both environments. The difference was significant in the TMP ester and palm oil because of the presence of the β-hydrogen in palm oil. In the N_2 environment, the E_a increased by

29.6%, while that of TMP ester increased by 21.3% compared with the air environment. Table 10 shows the degradation test results in an N_2 environment.

Table 9: Activation energy in the air environment.

Sample	Temperature (°C)		Equation	Slope	Ea (kJ/mol)
	From	To			
MO	208	471	y = -10192x + 15.027	-10185	84.73
NG 0.5	220	485	y = -10443x + 15.204	-10445	86.90
PT2M70	227	491	y = -10674x + 15.238	-10675	88.82
NG	34	389	y = -1428.5x - 1.1169	-1428.5	11.88
Palm	262	493	y = -12102x + 16.984	-12111	100.76
TMP	275	549	y = -12799x + 17.112	12799	106.49

Table 3: Activation energy in N_2 environment.

Sample	Temperature (°C)		Equation	Slope	Ea (kJ/mol)
	From	To			
MO	222	489	y = -10212x + 15.812	−10212	84.96
NG 0.5	217	504	y = -10492x + 15.056	-10492	87.29
PT2M70	198	509	y = -12152x + 17.41	-12152	101.10
NG	38	598	y = -1210.9x - 1.8647	-1210.9	10.075
Palm	332	480	y = -21127x + 33.945	-211	175.78
TMP	351	492	y = -21323x + 23.576	-21323	177.41

4.4 DSC analysis

The results of DSC analysis, which was conducted in air and N_2 environments, are shown in Figure 12. Table 11 shows the results that manifest the improvement of adding palm oil and TMP ester to SSEO. The largest increase in onset temperature was observed at 41 °C. SSEO had the lowest onset temperature at 334 °C, while the TMP ester and PO exhibited the highest onset temperatures of 399 °C and 401 °C, respectively. When PO with the TMP ester was added to SSEO, the onset temperature increased to 375 °C. When the NG were added to SSEO, the difference in the onset temperature was minimal, that is, the onset temperature was 343 °C compared with that of SSEO itself. The addition of PO and TMP ester improved the thermal stability of the formulated oil in the air environment, which exceeded those of commercial lubricants. The blend of PO-TMP ester with SSEO without NG also showed better performance than that of the oil blended with NG.

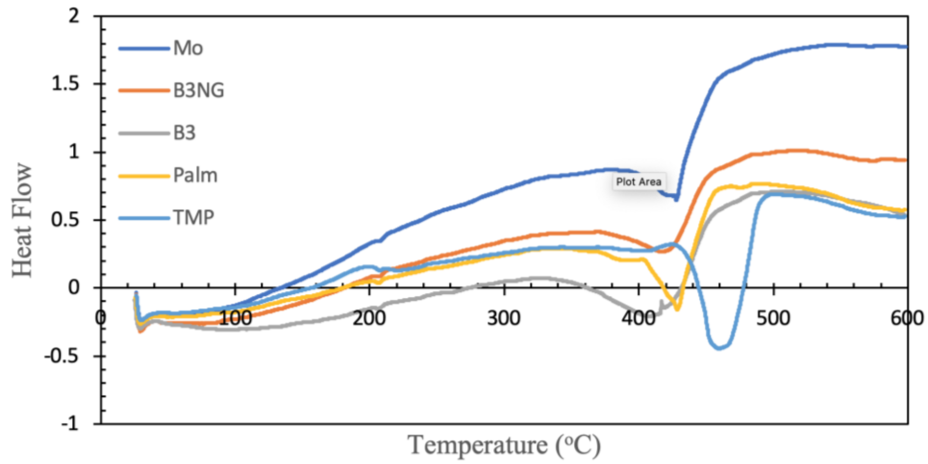

Figure 12: DSC analysis in N_2 environment.

Table 11: Onset temperature for DSC analysis in air.

Samples	**Mineral oil**	**Palm oil**	**TMP ester**	**PT2M70**	**NG 0.5**
Onset temperature (°C)	334.12	401.24	399.33	375.28	343.02

5.0 DISCUSSIONS

The findings of this study suggest that the blend of palm oil and TMP ester has the potential to improve the wear and friction behaviour of SSEO. The addition of 2% TMP to palm oil has improved the COF and WSD diameter to 0.075 and 485.7 μm respectively. This represents 5% improvement to COF and 1% to WSD of palm oil. This blend was later added to the semi-synthetic engine oil (SSEO) and the COF of SSEO was improved by as much as 40% by adding 30% of PO-TMP ester blend into SSEO. The finding is consistent with those of Masjuki HH et al. (2014), which also found a reduction in COF when jatropha oil-based TMP ester is blended with mineral oil (Zulkifli et al., 2016). Yunus et al. (2004) found a lower WSD when using palm oil-based TMP ester than when using commercial hydraulic fluids. Masjuki et al. (1999), Rico et al. (2002) found that palm-based lubricating oil has better wear performance than that of mineral oil.

The base oils used in this research are different in the chemical structure, distribution of carbon atoms and length of the carbon chains. The base oils also contain other elements, such as O_2, with bilateral and triangular bonds between these atoms. Thus, the difference affects the physicochemical characteristics of these oils significantly, especially when they are combined with each other (Abd Hamied et al., 2016). In blending, the strength of several properties from a base oil can complement properties from other base oils. The presence of fatty acid ester chain in PO /TMP ester blend tend to increase the adsorbed (formed) film thickness, thereby increasing the length of protected surfaces. Thus, the thickness of the lubrication film is maintained because of the reduction in COF and WSD, thereby improving oil performance (Abd Hamied et al., 2016). An increase in the number of ester groups also leads to remarkable binding of the molecules and resistance to shear forces. Most of the properties (i.e., density, viscosity, VI, etc.) of the samples did not change after a four-ball tribotester.

Adding NG enhances the oil's ability to reduce COF and WSD to 0.057 and 295 μm, respectively. The non-reactivity of NG with oil and non-agglomeration of the nanoparticles helped the particles to diffuse in oil and improve the properties of oil compared to other nanomaterials, which increased COF and WSD of the blends.

A summary of the key results obtained from the experiments on the effect of adding TMP ester to palm oil (Step A), effect of adding a blend of Palm oil and TMP ester to the semi-synthetic engine oil, SSEO (Step B) and effect of adding nanoglass to the final best blend from Step B (Step C) is given in Figure 13.

4.0 CONCLUSIONS

Palm oil/TMP ester has excellent potential as an anti-wear component for engine oil. The blend of up to 70% SSEO and 30% palm oil/TMP ester improves the overall friction and wear properties of the original semi synthetic engine oil (SSEO). In addition, the thermal stability and oxidative stability are also markedly improved. This is important as it could extend the engine life span and reduce the operational cost. The following individual conclusions can be drawn from the results of this study:

(a) The blends of SSEO with palm oil/ TMP ester fulfil the requirements of the ISO viscosity grade (ISO VG 68) for engine oil.
(b) Palm oil blended with 2% TMP ester showed the lowest friction at a COF of 0.075.
(c) Compared with SSEO, the blend of SSEO with 30% PO/TMP ester reduced COF by 40%.
(d) The 30% blend improved the WSD to 318.9 μm from 478.5 μm of pure SSEO. This value indicates a 33% improvement in wear reduction.
(e) The use of NG additive at 0.5 wt% to the blend containing 70% SSEO and 30% (PO/TMP ester) improved the COF and WSD to 0.057 and 295 μm, respectively.

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