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Friction and wear response of vegetable oils and their blends with mineral engine oil in a reciprocating sliding contact at severe contact conditions

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ABSTRACT

Although many studies investigating the tribological performance of pure vegetable oils have been conducted, a better understanding of vegetable oil tribological performance at extreme conditions is still needed. Similarly, little work has been carried out to study the influence of the vegetable oils on the performance of a lubricant formed from a blend of vegetable oil and conventional mineral engine oil. This work presents the tribological performance of vegetable oils, and their blends with mineral oil, in a high temperature and contact pressure reciprocating contact. Palm and soybean based vegetable oils were mixed with a commercial mineral engine oil at a 1:1 ratio by volume. The conventional mineral oil was also tested to provide a benchmark. The pure palm oil exhibited lower friction than soybean oil, but for wear performance, this was reversed. The friction performance of the palm oil was competitive to that of the mineral engine oil. The mineral engine oil was far superior in wear resistance over both vegetable oils. When blended with mineral engine oil both vegetable oils demonstrated a reduction in coefficient of friction when compared to their pure oil states. An improvement in wear performance was observed for both a blend of palm oil and mineral engine oil (25% improvement) and that of soybean and mineral engine oil (27% improvement). This work shows that for palm oil and soybean oil, the performance of a blended oil is influenced by its vegetable oil component and that tribological characteristics of vegetable oils are dominant. That said, the significant limitation of these vegetable oils is their ability to provide a satisfactory level of wear resistance. It is suggested that any future work in this area should have a greater emphasis on the enhancement of wear resistance.

Keywords: Palm oil**,** Soybean oil**,** Mineral Oil, Blend, Friction, Wear

1. Introduction

Commercial engine lubricants are either synthetic or based on mineral oil. Synthetic lubricants are derived from synthetic base oils like polyalphaolefins and they are increasingly popular as they have favourable properties like; good performance over a wide range of temperatures, good oxidative stability, low corrosivity and manufacturing flexibility that allows the compositions to be customised according to the end-users' needs [1]. The market price for synthetic lubricants is relatively expensive compared to mineral lubricants, however. Mineral engine oil (MO) has been used for a long time in engine lubrication systems. MO is made from crude petroleum oil through distillation processes. Commercial engine lubricants are MOs formulated from its base oil and additives [2] which are synthetic chemicals used to modify the base oil properties. Due to increase concern of MO effects on the environment [3, 4] and the anxiety over oil depletion [5, 6], interest in developing alternative lubricants (biolubricants) has received increasing attention. Vegetable oil, besides being used in cooking, is also an important subject of research in the field of biolubricants. Vegetable oil could be preferable as a base oil in alternative lubricants due to the fact it is renewable and its environmental friendliness (less toxicity and biodegradable) [7, 8].

Tribological performance of vegetable oils as biolubricants has been reported in many experimental studies. Vegetable oils were tested in various forms typically comprising pure oil [9-19]; blended with other oil [20-22]; formulated with additives [12, 16, 23-27] and with modification through chemical synthesis [18, 27-32]. It is important to evaluate the performance of vegetable oil in the form of pure oil before any modification of base oil can be developed because basestocks have a strong influence on the lubricant chemical and tribological properties [33]. The vegetable oils that have been evaluated tribologically include coconut oil [12], safflower oil [10], corn oil, rapeseed oil [34], jojoba oil [35], olive oil [14], castor oil [14], palm oil [15] and soybean oil [31].

Palm oil (PO) and soybean oil (SBO) are the two types of vegetable oil that have the highest consumption globally from 1995 to 2015, when more than 100 million metric tons were produced [36]. Chemically, these two oils differ by virtue of different fatty acid makeup (both type of and percentages of) [37]. PO has a higher level of saturated fatty acids compared to soybean oil. Saturated fatty acids that exist in palm oil, like palmitic acid and stearic acid, have no double bond in their carbon chains and are thus less reactive to oxidation. PO has exhibited outstanding oxidation stability when tested at 180°C [38]. SBO, on the other hand has higher level of unsaturated fatty acids which contain carbon double bonds in their chemical structure and thus is

vulnerable to oil oxidation [39, 40]. However, these unsaturated fatty acids (linoleic acid and alpha linolenic acid) could increase the melting point, thus SBO has higher liquidity at a lower temperature than PO.

The response of pure PO and SBO as lubricants has been reported in many friction and wear tests. Some researchers compared the performance of PO and SBO with other vegetable oils [9-11, 13, 14, 16], others have reported the performance compared with mineral oil [15, 19]. The performance comparison between PO and SBO has also been reported, but this was limited to a four-ball tribotester [9, 11], in which a steel ball is rotated on three clamped steel balls. It is reported by Jagadeesh [11], at 400N load and 75 °C, PO has lower coefficient of friction (COF) and produced less wear compared to SBO. However, at lower load, 147 N and 392 N (ASTM D4172) Syahrullail [9] found that although the PO has a lower COF than SBO, in terms of wear resistance, SBO performed better than PO. Contrary to this, it was seen that the SBO produced a lower COF and less wear than PO at a higher load (1236 N) [9]. It is important, however, to study the tribological performance of vegetable oils at higher temperature (100 °C) as this is a typical temperature of oil in the sump of an internal combustion engine running at steady state [41, 42].

In replicating the lubrication system of an internal combustion engine, a reciprocating test rig is more applicable than a four ball test rig. Masjuki [15] tested a piston ring on a plate made from grey cast iron (GCI) and compared the PO with a MO based lubricant by a reciprocating test. It was found that although the PO produced a higher COF than the MO based lubricant, the wear resistance of PO was found to be better [15]. However, the test was run at room temperature with a low load, 10 N (3.0 MPa contact pressure) [15] and the lubrication regime was not classified. Gerbig [14] tested a steel ball on a steel plate with several vegetable oils including SBO and compared them with MO without any additives at higher load (300 N) at a temperature of 50 °C with a reciprocating test rig. Gerbig reported that MO without additive was far superior than any vegetable oils in friction and wear resistance [14].

Although many tribological tests have been performed on pure vegetable oils, a better understanding of vegetable oil tribological performance at extreme conditions is still needed. This is important as changes on the surface layer due to excessive wear may occur and consequently lead to failure of machine parts. Investigating the PO and SBO lubrication behaviour at extreme conditions (a combination of high temperature and high pressure) would be an interesting, prior to modification of their base oil. In this context, “extreme conditions” are defined as higher contact pressures and a higher lubricant temperatures than the typical values used in previous studies [9-11, 13-16.]

In this work, the performance assessment of pure PO and SBO was carried out using a linear reciprocating test at 100 °C lubricant temperature and an initial contact pressure of >1 GPa. GCI was used as the flat specimen. Hardness characterisation was conducted on the intended wear scar region prior to the test. Tests were also performed using a commercial MO suitable for both diesel and petrol car engines for comparison with the tests using PO and SBO. This MO is classified by the American Petroleum Institute (API) as API SN/CF and the European Automobile Manufacturers Association (ACEA) as ACEA A3/B3.

In addition to this, the PO and SBO were blended individually with commercial mineral engine oil at 1:1 ratio by volume (50% of each oil). This ratio was chosen so that any domination of one of the oils over another can be clearly seen. This additional work aimed to build understanding into the wear and friction response of a mineral engine oil-vegetable oil blend. By blending both of these oils, the cost of lubricant could be reduced and furthermore the total dependency on petroleum base stock could also be decreased.

2. Experimental Details

2.1 Specimens and Lubricants

A chrome steel ball and GCI flat specimen were used in this work. The hardness of the GCI flat specimens was characterised within the region of the intended wear scar region prior to the wear test. Only GCI specimens with an average hardness ranging between 200.0 ~ 210.0 HV were used for this study. The flat GCI specimen was EN1561-GJL-250 with average surface roughness of R_a = 0.15 µm, which is similar to those typically found in contacts in a four-stroke gasoline engine (R_a = 0.10 µm) [43]. The ball specimen was AISI 52100 (6 mm diameter) with average surface roughness of Ra = 0.03 µm.

The lubricants used in this experiment consisted of PO, SBO and MO. The PO used was an ordinary cooking oil (Vesawit, Malaysia) which had undergone manufacturing processes like refining, bleaching and deodorising. The SBO used was a commercial organic type (Clearspring, Italy) that had undergone a cold pressing process and is also suitable for use as culinary oil. The MO sample was a commercially available mineral engine oil with SAE viscosity grade 15W40. The vegetable oils were also mixed at 50% by volume with the commercial mineral engine oil, which is equal to a 1:1 blend ratio. To ensure a uniform blend, an agitator stirred the mixed oil for 10 minutes just before the wear test began. The uniformity of each blend was judged by the visual appearance of the oil in which no significant layer or different colour seem in the oil blends. The details of the lubricants and their blends are listed in Table 1.

Table1: Properties of lubricants used in this study

	Lubricants	Abbreviation	Dynamic Viscosity (cP)		Total Acid Number (mgKOH/g)
			40°C	100°C	
1	Palm Oil	PO	38.08	7.78	0.24
2	50% MO + 50%PO	MO:PO	54.97	9.26	0.97
3	Mineral Engine Oil	MO	92.45	12.32	2.24
4	50% MO + 50% SBO	MO:SBO	46.44	8.77	1.13
5	Soybean Oil	SBO	30.72	7.10	0.98

2.2 Friction and Wear Testing

Selected specimens of ball and flat were tested on a Phoenix Tribology/Plint TE77 test rig for COF measurement. A point contact was chosen in order to minimise misalignment problems. The GCI flat specimen was mounted in the 'lubricant bath' and a steel ball then slid linearly in a reciprocating motion (Figure 1) while loaded against it. All test parameters applied in this study are described in Table 2 which were chosen in order to produce measurable and comparable wear scar between vegetable oils and MO lubricated specimen. Thus, the 40 N load was chosen based on trial and error testing.

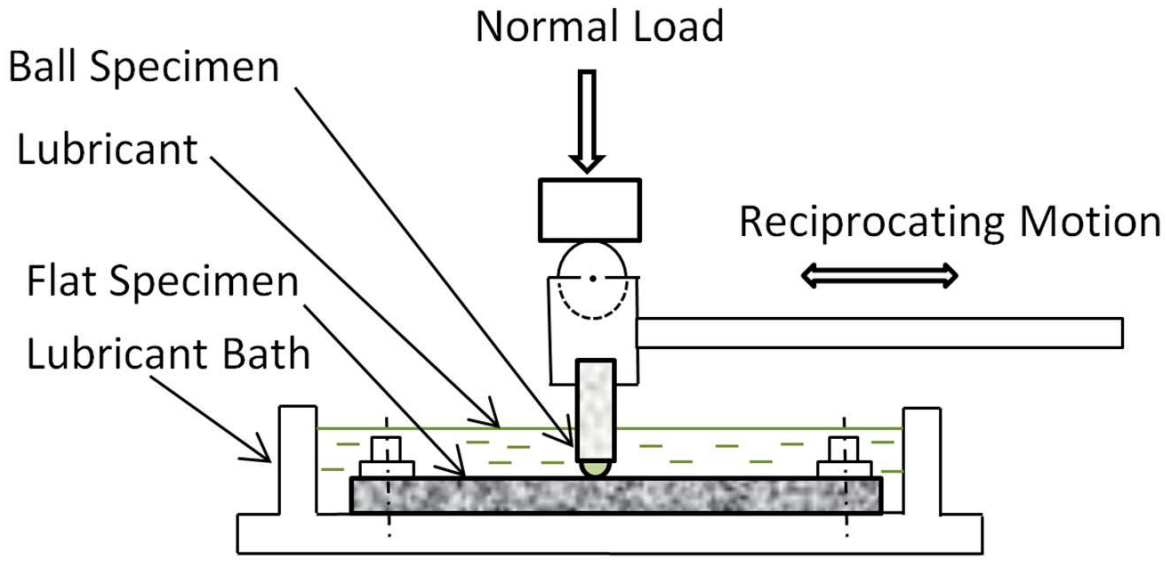

Figure 1

During the trial and error process of finding a suitable load, it was found that the vegetable oil specimens produced a much higher mass loss compared to MO specimens. For MO specimens, with a normal load lower than 40 N, the mass loss could not be measured. Higher load (more than 40 N) increased the contact pressure and thus, increased the depth of wear scar for vegetable oils specimens. It was not possible to measure the surface profile (waviness measurement, Section 3.3) if the wear scar depth was too high due to the limitation of the profilometer's stylus. The Hertzian contact pressure was calculated as 1.7 GPa. The scope of this paper is to run the test at only one condition so that the study can be focused on the response of the lubricants on friction and wear.

The wear of the specimen was characterised by the difference of mass before and after the test. The tests were run for three repetitions for each lubricant and the average mass loss and friction coefficient were then calculated. The standard deviation was plotted in the graph as an error bar. To determine the lubrication regime, the lambda factor (λ) was calculated [44] based on minimum film thickness (h_{min}) as stated by Hamrock et al. [45] in their non-dimensional formula:

$$H_{min} = 3.63U^{0.68}G^{0.49}W^{-0.073}(1-\mathrm{e}^{-0.68k}) \quad (1)$$

The non-dimensional parameters in Equation (1) (U, G, W) are related to material properties, specimens' geometries, normal load, sliding speed, lubricants viscosities and pressure-viscosity coefficient. The pressure-viscosity coefficient was calculated based on the formula in Equation (2) [46]:

$$\alpha_{EHL} = Z[5.1 \times 10^{-9}(\ln \mu_0 + 9.67)] \quad (2)$$

which involves the viscosity at atmospheric pressure and the pressure viscosity index. The root mean square roughness (σ^*) of contact bodies was also measured for the lambda factor (λ) calculation [44].

To assess the significance of the friction and wear data, a single variable ANOVA model was used with a significance criterion based on the 95% of a confidence level, known as the P value. If the P value < 0.05, then the data is statistically significant.

Table 2: Test parameters

Test parameters	Value
Normal load	40 ± 1 N
Lubricant temperature	100 ± 2 °C
Lubricant volume	25 ± 1 ml
Sliding stroke	15 ± 0.1 mm
Mean sliding speed	0.13 ± 0.01 m/s
Experiment time	60 min
Hertzian contact pressure	1.7 GPa

2.3 Surface Topography, Morphology and Elemental Analysis

Prior to inspection of wear scars using an optical microscope, scanning electron microscopy (SEM) and electron dispersive analysis of X-rays (EDX), the flat specimens were cleaned in acetone and rinsed in isopropanol in an ultrasonic cleaner for 5 minutes each. The wear scars of flat specimens were also characterised by surface roughness and waviness measurements by a profilometer.

2.4 Viscosity, Oxidation Stability and Elemental Test

The dynamic viscosity of the lubricants was measured by a rotary viscometer. The measurement was performed at 40 °C and 100 °C in a small sample adapter with an oil volume capacity of 6.7 ml. The viscosities of the fresh oil, the used oil taken from the oil bath the of test rig after 60 min, and the oil after the oxidation test were measured to study the influence of oil oxidation on oil viscosity. A rotary bomb oxidation test (RBOT) was conducted on the PO, SBO, MO and blended lubricants according to ASTM D2272-14a. This test was to determine how fast the oils were oxidised in the presence of oxygen gas in a closed chamber at 90 psi pressure and 150 °C temperature. The time taken for a drop of pressure at more than 25.4 psi below the peak pressure was considered as the oxidation time. The viscosity and TAN of oil samples after RBOT also were measured. The spectrochemical analysis was performed on the commercial MO and blended lubricants in order to identify the elements that existed in the oil which comes from the additive.

3. Results and Discussion

3.1 Friction Analysis

The average COF for specimens lubricated with PO, SBO, MO and the vegetable oil-mineral engine oil blends are shown in Figure 2a. The final COF value at 60 min is also depicted in Figure 2b. As a general trend, the COF for all specimens started with a low value and increased gradually until it reached steady state.

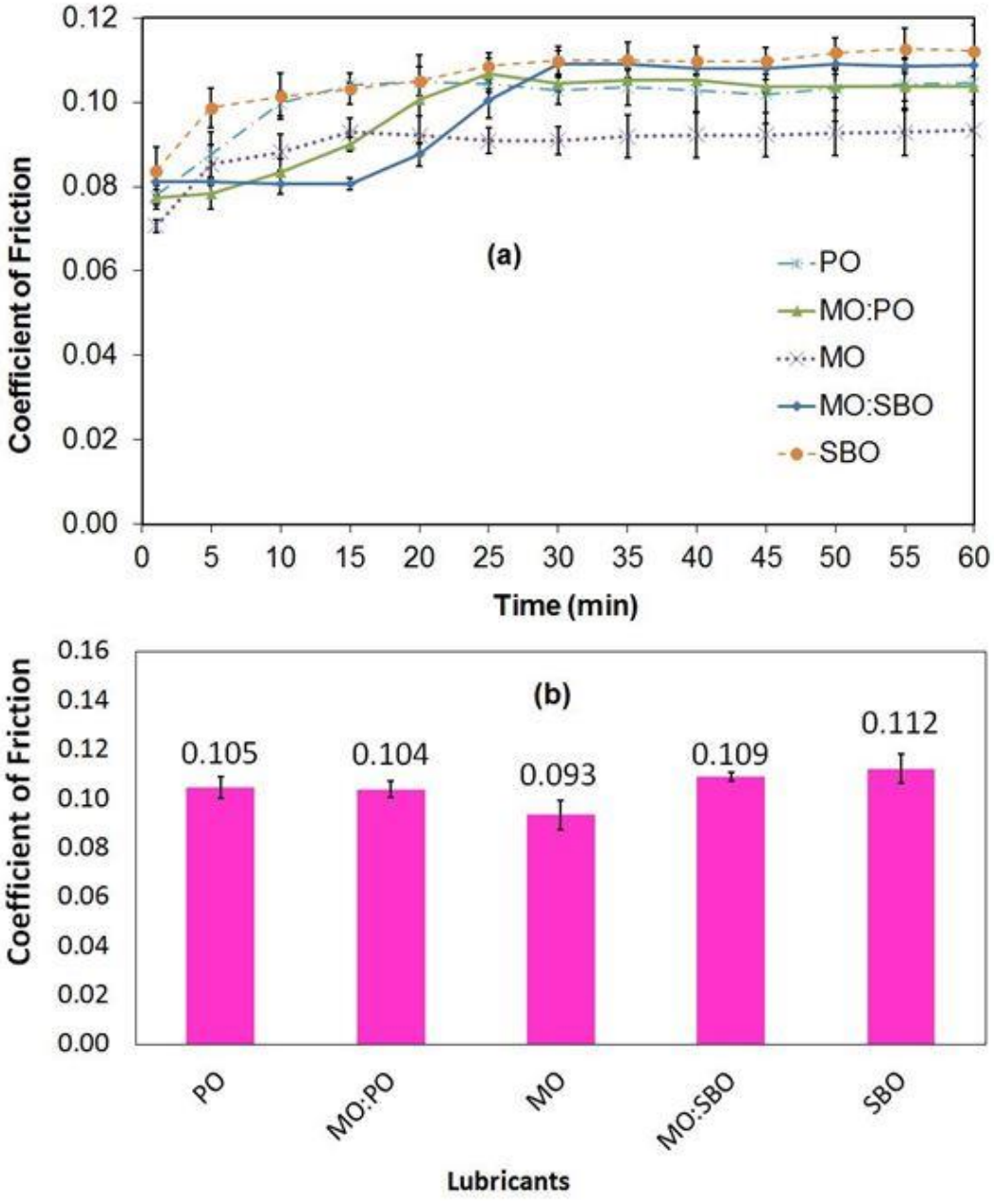

Figure 2

The palm oil lubricated specimen depicted lower COF (0.105) than the soybean oil counterpart (COF= 0.112) while the mineral engine oil demonstrated the lowest COF (0.093). The difference between the COF of PO and MO lubricated specimens is about 11%. The COFs for a blend of MO and vegetable oil generated a value in between their pure oil state with only a small reduction is noted compared to their pure state. For example, a blend of MO and PO (MO:PO) gave a COF of 0.104, 1% lesser than pure PO (COF = 0.105). A slight improvement of COF was also found in a blend of MO and SBO (MO:SBO), in which the COF (0.109) only reduced 3% from pure SBO (COF = 0.112). The result from single variable ANOVA analysis also showed that there is a significant difference (P value < 0.05) between the COF for all lubricants.

The effectiveness of fatty acids as a lubricant is well known [47]. The strong polarity of fatty acids that exist in vegetable oils contributes to the formation of a mono-molecular layer through the attraction of carboxyl group (COOH) to the metallic surfaces[48]. The difference between COF for PO and SBO could be influenced by the composition of saturated and unsaturated fatty acids that exist in vegetable oil. The COF increases with increasing in unsaturation of fatty acids in which the stearic acid (saturated acid) exhibited lower friction coefficient than the oleic and linoleic acid (unsaturated acids) [49]. Saturated fatty acids contain no double bond thus the molecules can easily align themselves in a straight chain and are closely packed on the surface to form a protective layer. Unsaturated fatty acids on the other hand have double bonds and produce a bend in their chain and are thus not closely packed on the surface. SBO contains more unsaturated fatty acids (oleic and linoleic acids) than PO [37], and thus produces higher friction than PO. The lowest friction response by the commercial MO lubricated specimen was due to the fact that its base oil has been treated by an additive package that may function as a friction modifier. The existence of molybdenum in a spectrochemical analysis for the MO (Table 3) suggests that the additive could be from molybdenum dithiophosphate (MoDTP) as this additive can reduce the friction in motor oil [50]. In addition to this, the value of COF for MO (0.093) in this study is close to the COF of MoDTP additive in hydrocarbon base oil (COF=0.08) [51]. The existence of friction modifier in the commercial lubricant is significant in reducing the friction as untreated MO (paraffinic MO) produced higher friction than PO at different normal load [52].

The analysis shown in Table 3 demonstrates that the composition of the elements that was detected in MO (calcium, zinc, phosphorus, molybdenum, boron and magnesium) was diluted into about 50% for vegetable oils-mineral engine oil blend (MO:PO and MO:SBO). This shows that the influence of the friction modifier

(from molybdenum [50]) in the vegetable oil-mineral engine oil blends also deteriorated. Thus, the COF for MO:PO and MO:SBO oils were recorded to be in between their pure oil states. It is also suggested that the base oil of vegetable oil influences the performance of the blend, for example the MO:PO blend produced a lower COF than MO:SBO as the pure PO produced a lower COF than pure SBO.

Table 3: Elements detected in lubricants in part per million (ppm) from spectrochemical analysis

Elements	PO	MO:PO	MO	MO:SBO	SBO
Calcium	0	1341	2825	1356	25
Zinc	1	389	781	393	3
Phosphorus	0	327	695	359	59
Molybdenum	0	80	167	80	0
Boron	2	20	43	20	1
Magnesium	0	6	32	13	17
Silicon	3	20	3	5	2
Aluminium	0	2	3	2	0
Iron	0	2	1	1	0
Sodium	2	7	0	7	3
Lead	0	1	0	1	0
Barium	0	1	0	0	0

3.2 Wear Analysis

Figure 3 shows the average wear data of the specimens lubricated with PO, SBO, MO and the vegetable oil-mineral engine oil blends. The PO lubricated specimens produced the highest wear with 45.76 mg in mass loss. The SBO lubricated specimen has a slightly lower mass loss (42.73 mg) than the PO lubricated specimens, a difference of about 7%. However, the MO showed superior wear resistance compared to vegetable oils in which the mass loss was 0.65 mg, about a 98% difference than the SBO lubricated specimen.

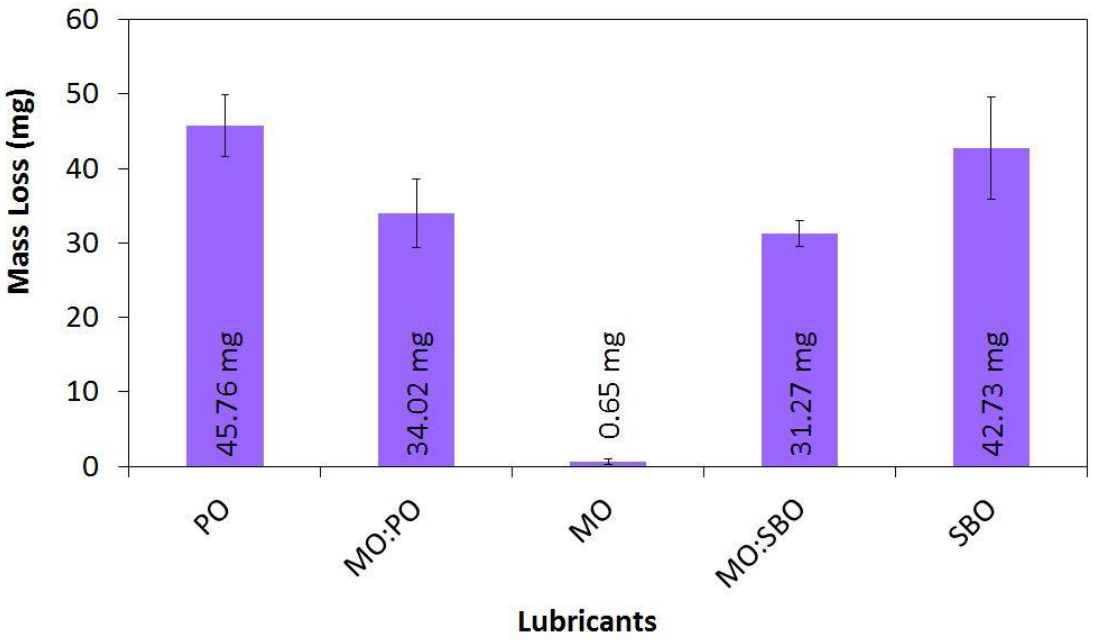

Figure 3

The specimens lubricated with MO and PO (MO:PO) generated a wear scar of a size in between their pure oil states (mass loss = 34.02 mg). A similar result was also observed for specimens lubricated with a blend of MO and SBO (MO:SBO) in which the mass loss (31.27 mg) was again in between the values for pure SBO and MO. However, it was observed that although the MO had a superior performance in preventing wear compared to the pure vegetable oils, the addition of 50% MO in both vegetable oils did not greatly influence the wear resistance result of the blended oils. For both cases of blended oil (MO:PO and MO:SBO), the mass loss of specimens differs by about fifty orders of magnitude compared solely to MO. It should also be noted that the type of vegetable oil influenced to the wear result of its blended oil with MO. For example, the MO:PO blend produced higher wear than the MO:SBO blend and this aligns with the fact that the PO generated higher wear than the SBO in their pure forms. The statistical analysis of single variable ANOVA also revealed that there is a significant difference (P value <0.05) between the mass loss of vegetable oils and their blends with MO studied here.

Table 4: Minimum film thickness, h_{min} and lambda ratio, λ for all lubricants

Lubricant	h_{min} (nm)		λ	
	Initial	Final	Initial	Final
Palm Oil (PO)	2.42	2.45	0.01	0.01
MO:PO	2.86	2.82	0.01	0.01
Mineral Engine Oil (MO)	3.62	3.71	0.02	0.04
MO:SBO	2.67	2.65	0.01	0.01
Soybean Oil (SBO)	2.19	2.25	0.01	0.01

The calculated lambda ratio (λ) for all lubricants (Table 4) showed that the lubrication regime was boundary (λ<1). The film thickness at the end of the test was also calculated based on the values of oil viscosity and surface roughness of specimens at 60 min. Slight increments of film thickness for all oils were noticed at the end of the test due to an increase in viscosity of the oil. From the results of COF (Section 3.1) and wear between PO and SBO, it can be seen that the wear and friction have no relation in vegetable oil lubrication. The lower wear result of specimen lubricated with SBO compared to PO is similar to the four ball test results reported by Syahrullail [9]. Further investigation of surface morphology (Table 5) revealed that the PO lubricated specimen has a lower oxygen element than the SBO counterpart. This suggests the possibility that less of an oxide layer is retained with PO to prevent wear. However, the statistical analysis of single variable ANOVA revealed that there is no significant different (P value > 0.05) between the wear of the specimen lubricated with PO and SBO.

Table 5: Elemental analysis of wear scar for all lubricants specimen by EDX

Element	Weight % (wt%)					Atomic % (at%)				
	Lubricants									
	PO	MO: PO	MO	MO: SBO	SBO	PO	MO: PO	MO	MO: SBO	SBO
C	3.79	4.41	3.38	4.27	3.77	14.67	16.44	10.96	15.93	14.56
O	**1.17**	**2.21**	**10.43**	**2.38**	**1.43**	**3.39**	**6.2**	**25.58**	**6.66**	**4.15**
Si	3.29	3.02	2.70	2.99	2.91	5.44	4.82	3.77	4.78	4.80
P	0.10	0.04	0.72	0.06	0.15	0.15	0.06	0.91	0.09	0.22
S	0.04	0.12	1.36	0.00	0.00	0.06	0.16	1.66	0.00	0.00
Mn	0.66	0.76	0.73	0.87	0.84	0.55	0.62	0.52	0.71	0.71
Fe	90.95	89.24	79.80	89.43	90.91	75.73	71.57	56.06	71.83	75.56
Zn	**-**	**0.19**	**0.90**	**0.01**	**-**	**-**	**0.13**	**0.54**	**0.01**	**-**

At this stage, it is interesting to discuss the role of the fatty acids' molecular chain structure in influencing both friction and wear as proposed in Figure 4. Figure 4a illustrates the linear structure of a saturated fatty acid chain that enriches in the PO composition. This linear chain makes it easier it to be aligned in a parallel form after a polar group of carboxyl acid (-OH) is adsorbed to the metal surfaces (ball and flat). The straight and parallel arrangement of these carbon chains could promote a smoother interaction during motion, particularly in the same direction. However, due to its linearity, it might be possible for the chain to fill the gaps in between and increase metal-to-metal contact. SBO, on the other hand, has a higher degree of unsaturated acid which aligns themselves in a bent chain. Although the bent chain structure promotes higher motion resistance (due to 'unsmooth' interaction during motion), it provides better protection in minimising the metal-to-metal contact (Figure 4b).

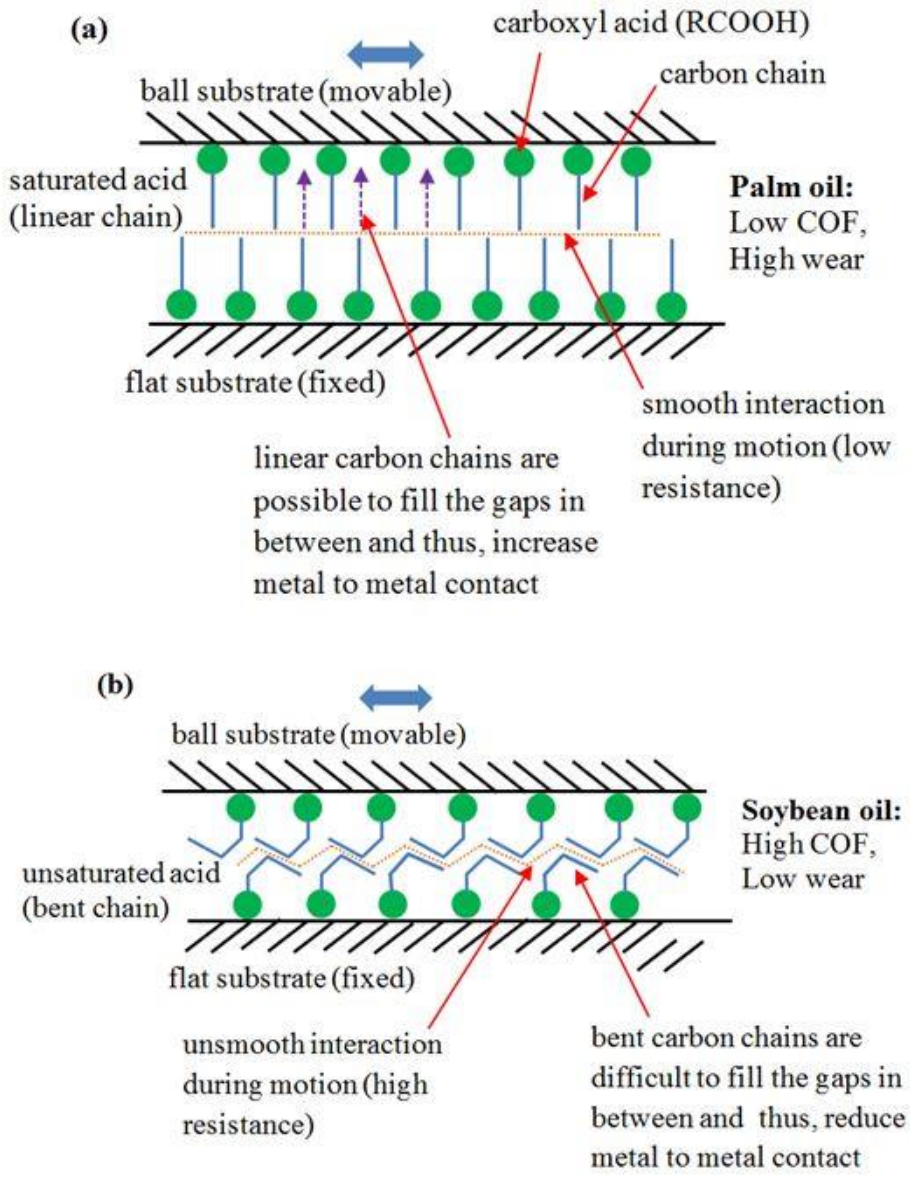

Figure 4

It was reported that the untreated MO (paraffinic oil) produced lower wear than PO, however the difference is just about 20% [52]. The superior wear resistance performance exhibited by the commercial MO over vegetable oils (98% difference) in this study could be attributed by the existent of the additive package which included an antiwear agent, zink dialkyl dithiophosphate (ZDDP). This is shown by the detection of Zinc element in spectrochemical analysis (Table 3) and elemental analysis (Table 5). It was reported that at mild contact conditions (room temperature and 3.0 MPa contact pressure) the wear of palm oil lubricant was better than mineral oil [15]. However, at severe contact conditions (this study) the wear of the palm oil lubricant gave a much higher value than the mineral engine oil lubricant. This is due to the adsorption mechanism of the polar group of fatty acid (-OH) molecules in the vegetable oil in reducing metal to metal contact only being effective

at low temperature and low load [53]. Further inspection of the worn surfaces of the PO and SBO lubricated specimens suggests that the breakdown of lubrication occurred which led to severe wear. These ideas are supported by the presence of a burn mark (visible under the optical microscope) (Figure 5) which is could be caused by frictional heat due to metal to metal contact on the PO and SBO specimens. However, this appearance was not reported in normal contact conditions [15].

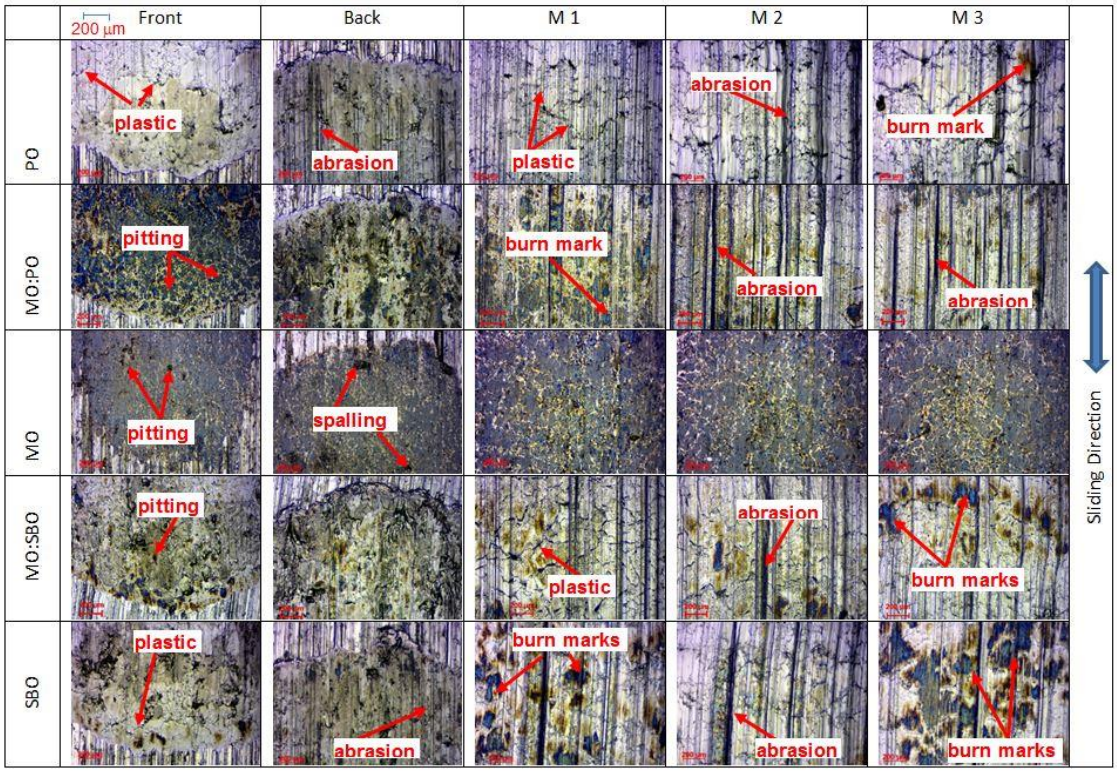

Figure 5

3.3 Surface Topography and Waviness Analysis

The wear scar appearance for all specimens at 60 min is compared in Figure 6a. The primary profile along the wear scar is plotted with the waviness measurement value in Figure 6b. The wear scar appearance of MO (Figure 6a) has narrow width and a smoother profile than the others. Compared to normal contact conditions [15], the vegetable oil lubricated specimens and vegetable oil-mineral engine oil blends (MO:PO and MO:SBO) lubricated specimens in this study produced similar unsmooth appearance (wavy-shaped scar). The PO specimen produced the deepest wear scar depth. In terms of surface waviness, the PO lubricated specimen produced the highest value (Wa = 41.43 µm) compared to SBO and vegetable oil-mineral engine oil blends

(MO:PO and MO:SBO) counterparts. The MO lubricated specimen produced the lowest surface waviness (Wa = 1.40 μm).

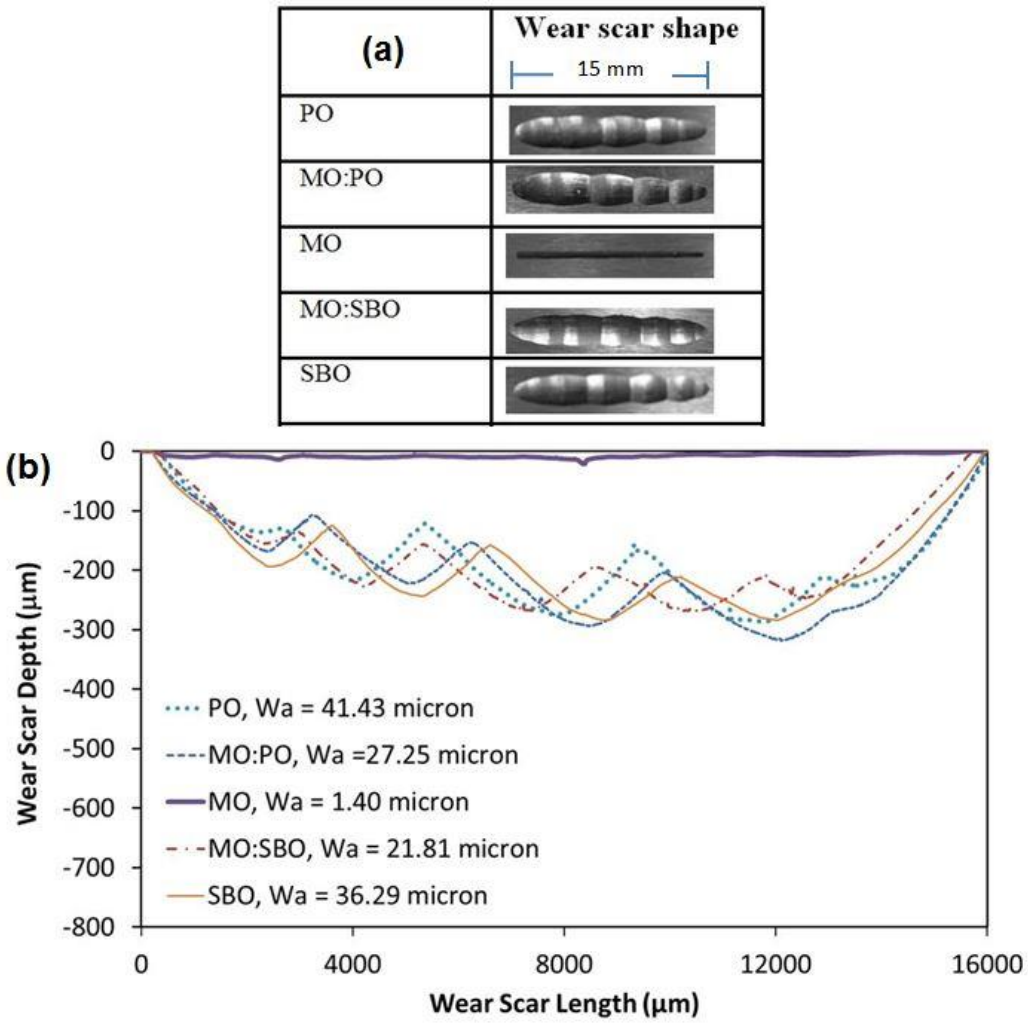

Figure 6

The formation of a wavy-shaped scar on specimens lubricated with vegetable oils suggests that plastic ratcheting and shakedown occurred during the sliding process. This is due to the higher contact pressure applied. The contact condition entered the plastic ratcheting region [54]. However, the relatively smaller and smoother wear scar produced by the MO lubricated specimen suggests that the anti-wear additive (ZDDP) that exist in the commercial MO performed very well in reducing the wear and preventing deeper penetration of the ball specimen into the flat specimen. Although the PO lubricated specimen produced lower COF than the SBO counterpart, its surface waviness value showed the highest value (Wa = 41.43 μm). This shows that the COF was not influenced by the surface waviness value in the vegetable oil lubricated surface.

Although the amount of zinc (possibly from ZDDP in the MO) in the blended oil of MO and vegetable oils (MO:PO and MO:SBO) is reduced into almost half (Table 3), the wear resistance of both lubricants were not similarly reduced by this amount. This indicates that the vegetable oil was dominant in the wear performance of the oil blends with MO. The high wear produced by the blended oils showed that the role of antiwear additive that exists in the MO is diminished in the blended oil. The existence of only about 50% of zinc (Table 3) in the blended oil (from the MO) had failed in preventing the metal to metal contact between the ball and flat specimen, thus, promoting severe wear and the plastic flow observed.

3.4 Surface Roughness Analysis

The average surface roughness, R_a, of specimens across the wear scar was measured at different points (Figure 7b) and depicted in Figure 7a. The MO lubricated specimen showed the lowest and most consistent surface roughness along the wear scar compared to vegetable oils counterparts. The PO lubricated specimen produced lower roughness than the SBO counterpart. Point Middle 2 and Middle 3 were found to contribute rougher surfaces than other area for PO and SBO lubricated specimen. This suggests that both points (Middle 2 and Middle 3) experienced higher abrasive wear due to the debris that accumulated in the groove in point Middle 2. The surface roughness result across the wear scar supported its relation to COF value for all specimens as higher surface roughness may contributed to higher COF [55].

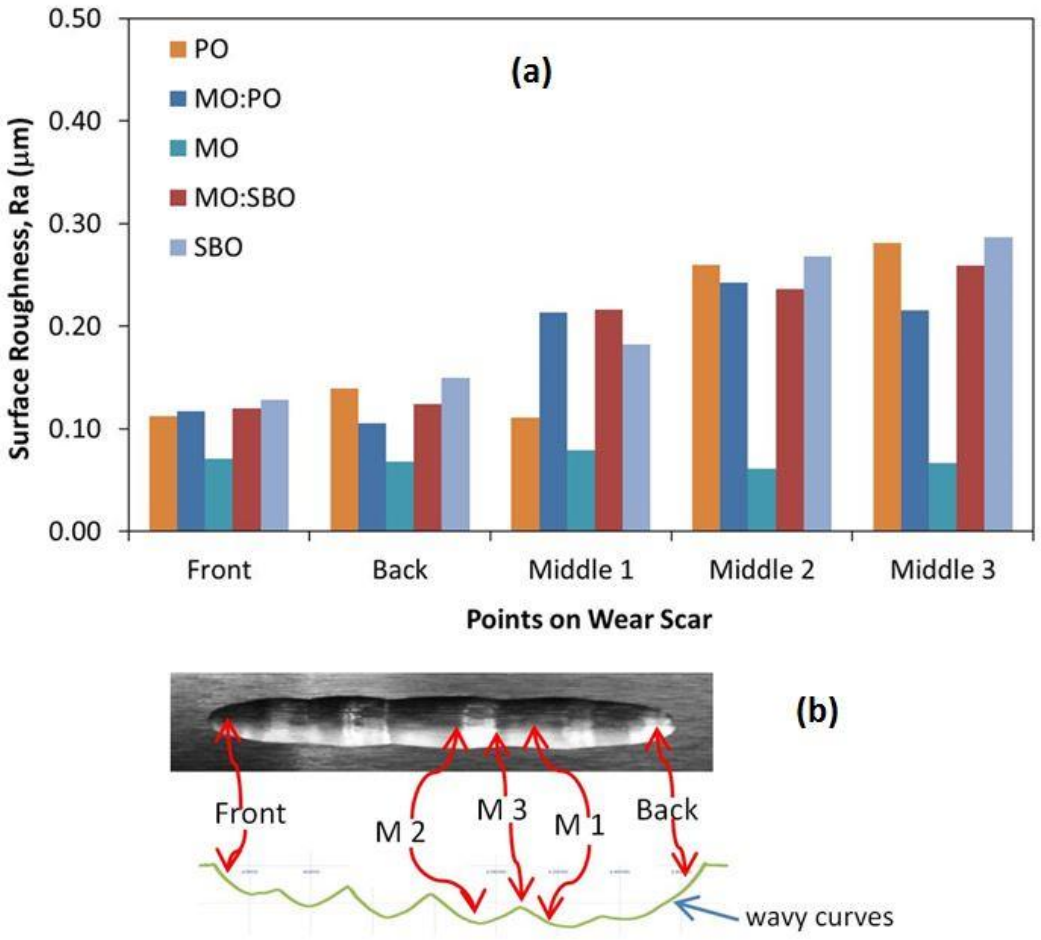

Figure 7

The blend of MO and vegetable oils (MO:PO and MO:SBO) produced higher surface roughness compared to the MO specimen especially at the middle point. It is therefore suggested that the addition of 50% MO in vegetable oils did not greatly influence to the reduction of surface roughness. Higher surface roughness measured on the specimens lubricated with a blend of PO and SBO (PO:SBO) reflects its highest of the recorded COF (Figure 2b).

3.5 Surface Morphology and Elemental Analysis

The surface morphology of wear scars under an optical microscope (Figure 5) at 60 min are depicted at different points (Front, Back, M1, M2 and M3) according to Figure 7b. The specimen lubricated with MO exhibited almost similar appearance at each point with some pitting and spalling especially at point Front and

Back which indicate more damage at stroke ends. The same tendency has also been seen before where more severe scuffing damage occurred at the stroke ends in reciprocating pin-on-pin for fuel lubricated test [56]. In reciprocating sliding test, the speed turns to minimum at stroke ends before changing the direction. The lower velocity at stroke ends cause a lower film thickness and thus promotes scuffing. Further investigation of the MO lubricated surface by SEM (Figure 8c) was confirmed the existence of spalling (delamination) and cracks suggesting that the wear mechanism involved is fatigue wear.

For the specimen lubricated with PO and SBO, the main wear mechanism was found to be abrasion with some evidence of plastic deformation on the surface (Figure 5), especially at stroke ends (Front and Back). The abrasive marks are found to be reduced at point Front and Back for PO and SBO specimens compared to the middle points. This suggests that the wear particles accumulated at the middle point of PO and SBO specimens probably due to the wavy-shape of the wear scars, and thus contributed to three-body abrasive wear. Some burn marks were also found on specimens lubricated with PO and SBO which suggests that high frictional heating occurred probably due to breakdown of lubrication (Figure 5).

Further investigation of specimens lubricated with vegetable oils and their blends through SEM (Figure 8a, 8b, 8d and 8e) revealed some surface fatigue and evidence of delamination. This indicates that the wear mechanism for these lubricants is a combination of abrasion and surface fatigue. However, the abrasive marks for vegetable oil–MO blends (Figure 8b and 8d) were found to be smaller compared to PO and SBO counterparts.

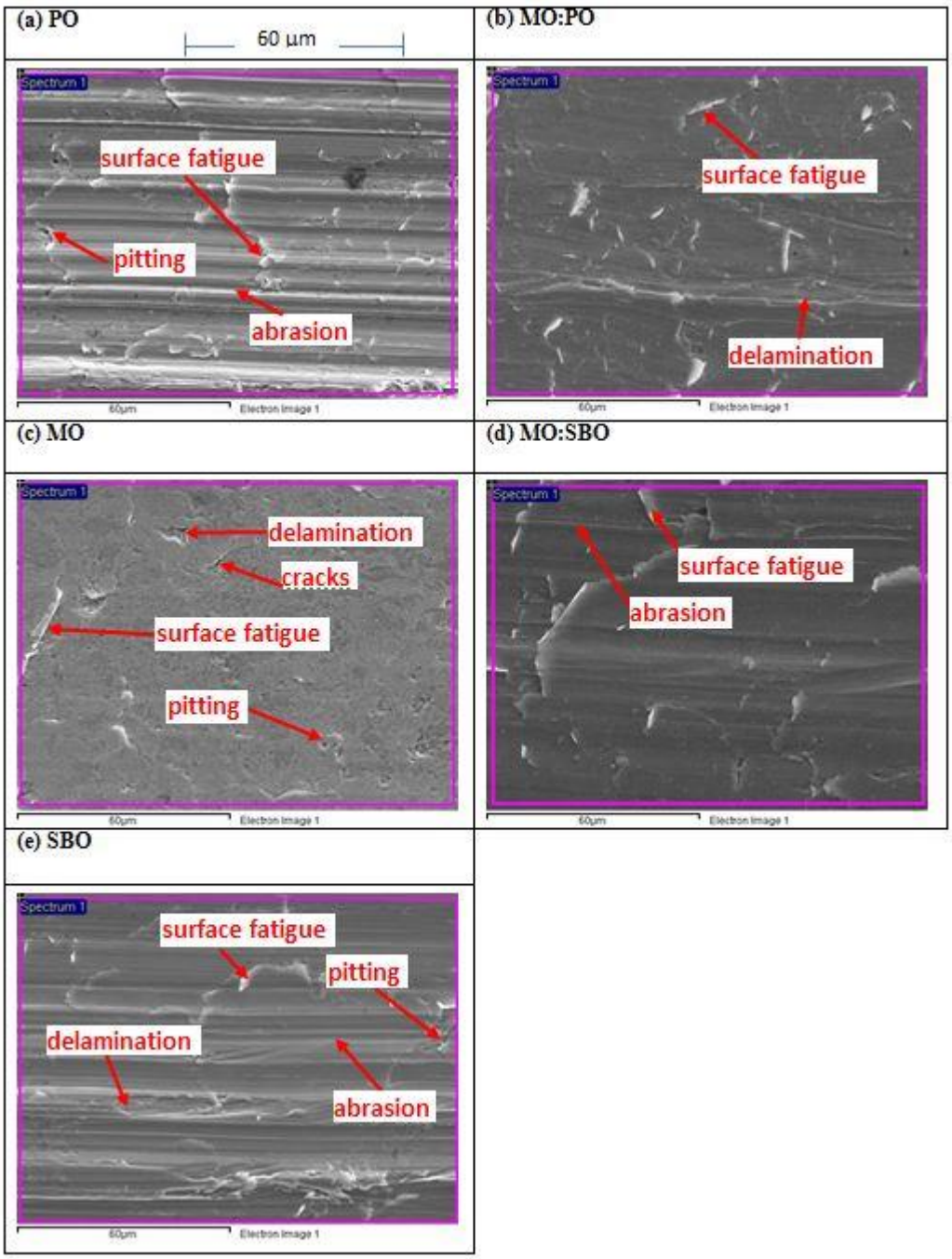

Figure 8

The elemental analysis of lubricated specimens by EDX is presented in Table 5. It was found that the oxygen element in the PO specimen was slightly lower than the SBO counterpart. The specimen lubricated with MO has a higher content of sulphur (1.36 wt%) and phosphorus (0.72 wt%) compared to the other specimens. A higher percentage of oxygen and a small amount of zinc (0.90 wt%) were also detected at the MO specimen's surface.

The higher percentage of oxygen in the SBO specimen than the PO counterpart suggests that more oxide layer is retained on the surface in reducing the metal to metal contact thus lower mass loss is produced in the SBO specimen. A similar reason could be applied to the specimen lubricated with MO in which a higher oxygen element is detected, suggesting that more oxide layer exists in preventing the metal to metal contact [57]. However, the lower amount of oxygen found in specimens lubricated with PO and SBO compared to the other specimens could be due to absorption of oxygen in the oil as vegetable oil is susceptible to oil oxidation [37]. The higher content of phosphorus in the MO specimen compared to others suggests that this element came from the MO (Table 3). The existence of zinc in the MO specimen suggests that the additive package contains this element. The most probable additive related to zinc is the antiwear additive, ZDDP.

For specimens lubricated with MO-vegetable oils blended in 1:1 ratio (MO:PO and PO:SBO), the oxygen appeared not to be greatly retained (Table 5). For the blended oils, MO:PO produced 2.21 wt% while PO:SBO gave 2.38 wt%. These oxygen amounts are about one-fifth from the amount of oxygen retained on MO lubricated surface. Furthermore, the amount of zinc detected on the blended oil surfaces were relatively small compared to the MO specimens and this could have caused the low wear resistance.

The domination of vegetable oil in influencing the wear for vegetable oil-mineral engine oil blend is proposed in the mechanisms in Figure 9 (comparison between PO, MO and MO:PO). The polarity of vegetable oil (carboxyl group in fatty acids molecules) has made it possible for them to adhere to metal surfaces (Figure 9a), but during sliding at severe contact conditions, some of these fatty acids molecules are removed and thus, produce severe wear (Figure 9b). In the case of MO, the anti-wear additives are effectively present on the surface to provide a protective layer in reducing metal-to-metal contact (Figure 9c), and this layer is retained even after sliding at severe contact conditions (Figure 9d). However, in the vegetable oil-mineral engine oil blend, the additives are unable to form a fully protective layer due to most of the surface is already covered by the carboxyl group of vegetable oil (Figure 9e). This has caused to higher wear of MO:PO lubricated specimens compared to MO lubricated specimens since only a small amount of anti-wear additives are formed on the surface (Figure 9f).

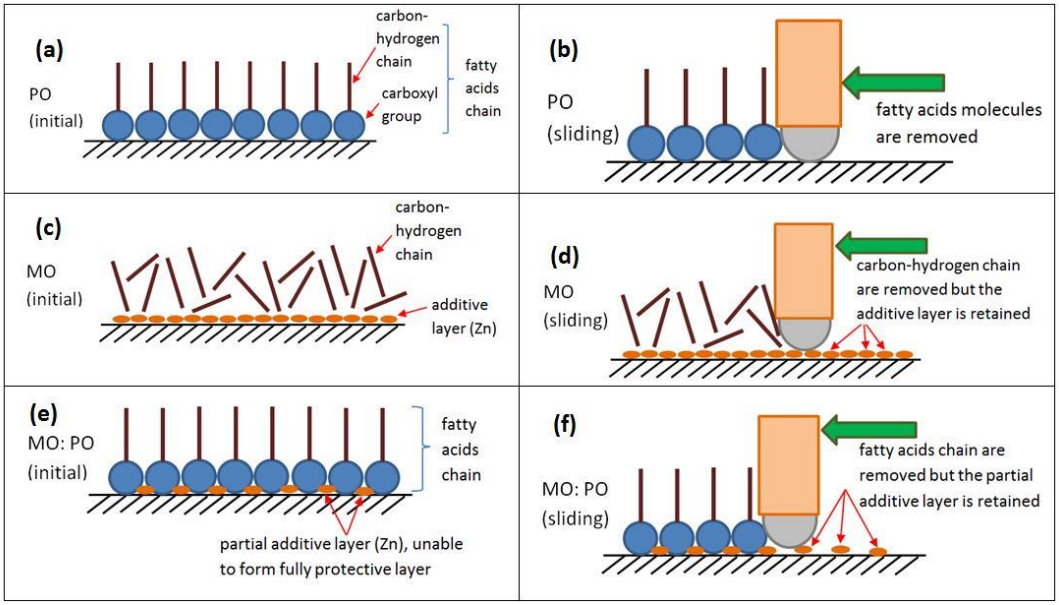

Figure 9

3.6 Total Acid Number Analysis

Figure 10 shows the total acid number (TAN) measurement result which dictated the lubricant degradation for MO, PO, SBO and vegetable oil-mineral engine oil blends before and after the test. For fresh oil, the PO has a lower TAN value than SBO while MO has the highest TAN. It is clearly seen that all used oil after the test produced higher TAN than new oil. The difference of TAN for new and used oil (after wear test) is lowest for MO (0.16 mgKOH/g) than PO (0.21 mgKOH/g) and SBO (0.30 mgKOH/g). The TAN values for all oil samples after RBOT were greatly increased.

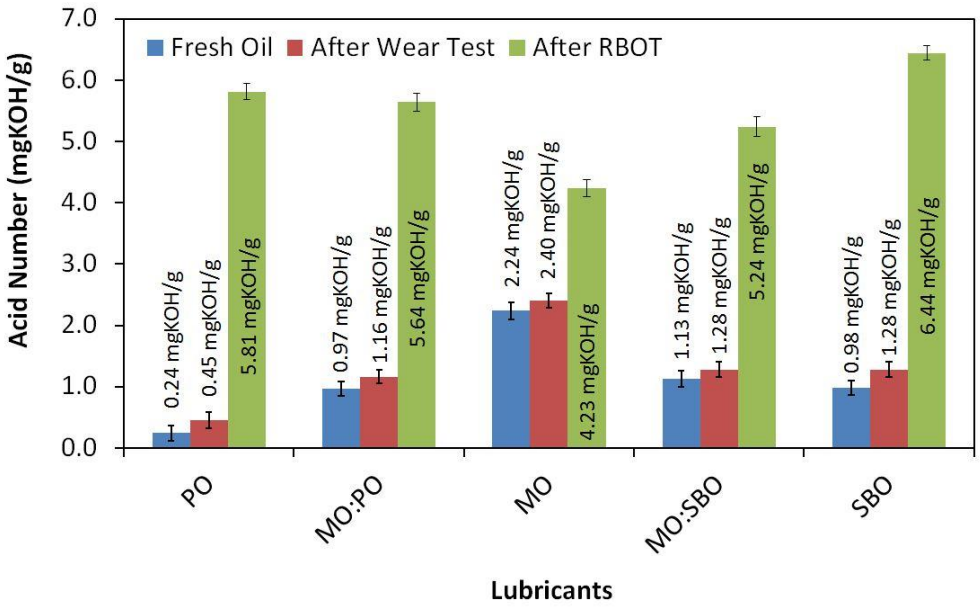

Figure 10

The higher TAN value exhibited by SBO than PO suggests that the SBO sample used in this study is more acidic than the PO sample. Higher TAN in MO compared to vegetable oil could be attributed to the existence of ZDDP additive as the ZDDP was found to increase the TAN for base oil [58]. An increase in TAN for the used oils (both from wear test and RBOT) in Figure 10 indicate that the oils have been undergoing a process of oxidation during the wear test as acids are formed during the oil oxidation process. The highest difference of TAN before and after test for SBO (0.30 mgKOH/g) compared to other oil showed that the SBO is more vulnerable to oxidation due to the higher unsaturation fatty acids (oleic, linoleic and linolenic acids) that exist in SBO. The lower oxidation stability of SBO could lead to higher COF as oil oxidation could increase the friction force [59].

For blended oils (MO:PO and MO:SBO), the TAN are generated in between the values of their pure oils and were influenced by the type of the vegetable oil in the blend (either PO or SBO). However, the difference of TAN before and after the wear test for blended oils (MO:PO and MO:SBO) are smaller than their pure PO and SBO. This is probably due to the existence of antioxidant additive from the MO in the oil blend that assists in prolonging the oxidation process.

3.7 Oil Viscosity Analysis

The dynamic viscosity for fresh oil, used lubricants (from wear test rig) and oil samples after RBOT test were measured at 40 °C and 100 °C (Figure 11). For fresh oil at 100 °C, the MO showed highest viscosity (12.56 cP) followed by PO and SBO. A similar trend of viscosity is found for all fresh oils at 40 °C. All lubricants demonstrated decreasing viscosity at higher temperature, 100 °C compared to 40 °C. However, the vegetable oils showed more resilience to viscosity changes due to temperature than MO. This is due to the vegetable oils having a higher viscosity index than MO. It was exhibited by RBOT samples that increases of oil oxidation could increase the viscosity. Although the TAN for used oils (from wear test rig) in this study have increased which suggests they underwent an oxidation process, the viscosity difference for fresh and used oil is not clearly significant. This shows that the oil oxidation process occurring during the test was not very severe.

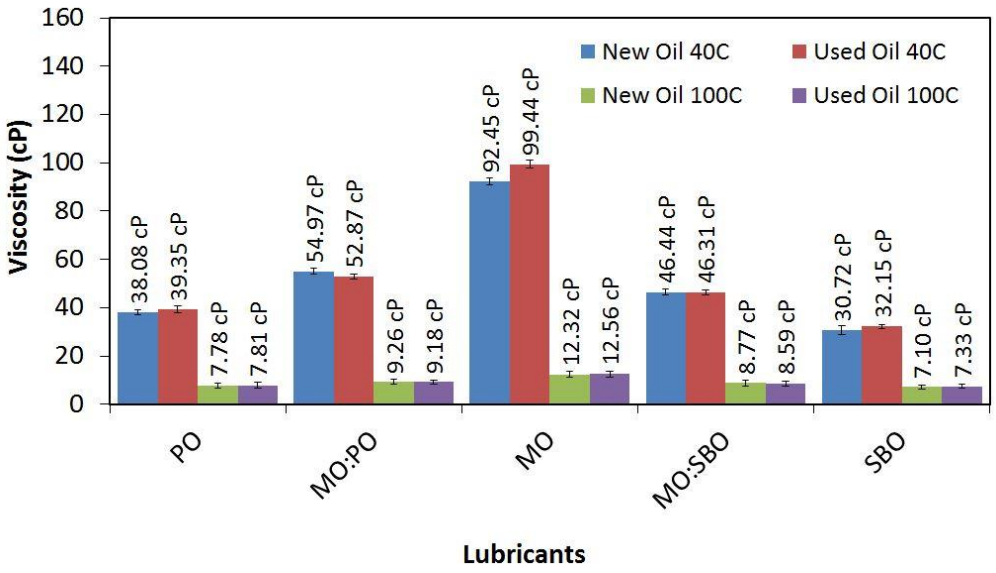

Figure 11

It is also noted that the viscosities for fresh blended oils (MO:PO and MO:SBO) were reduced to a level where their viscosities are nearer to the values of the pure vegetable oils (PO and SBO) rather than MO. For example at 40°C, the fresh MO:PO oil produced a viscosity of 54.97 cP. This value is closer to the PO viscosity (38.08 cP) rather than MO viscosity (92.45cP). The lower viscosity that exists in the pure vegetable oils greatly influenced the viscosity of their blends with MO. It was reported that the oil viscosity increases with oxidation which amount of the increase depends on the amount of oxygen reacted [60]. The values of viscosity for

the used oils in this study were not greatly changed compared to fresh oils. This suggests that although the oxidation process was occurred in the wear test rig (from TAN result in Figure 10), the level of oxygen reacted with the oils is considerably low.

3.8 Oxidative Stability Analysis

Figure 12 depicted the oxidation stability result which shows how fast the MO, PO, SBO and blended oils oxidised in pressurised oxygen in a pressure vessel. The peak pressure shows the maximum pressure that the oil can achieve before the pressure drop. The peak pressure was found to be proportional to the oxidation time. Higher oxidation time indicated higher peak pressure in the pressure vessel that can be achieved.

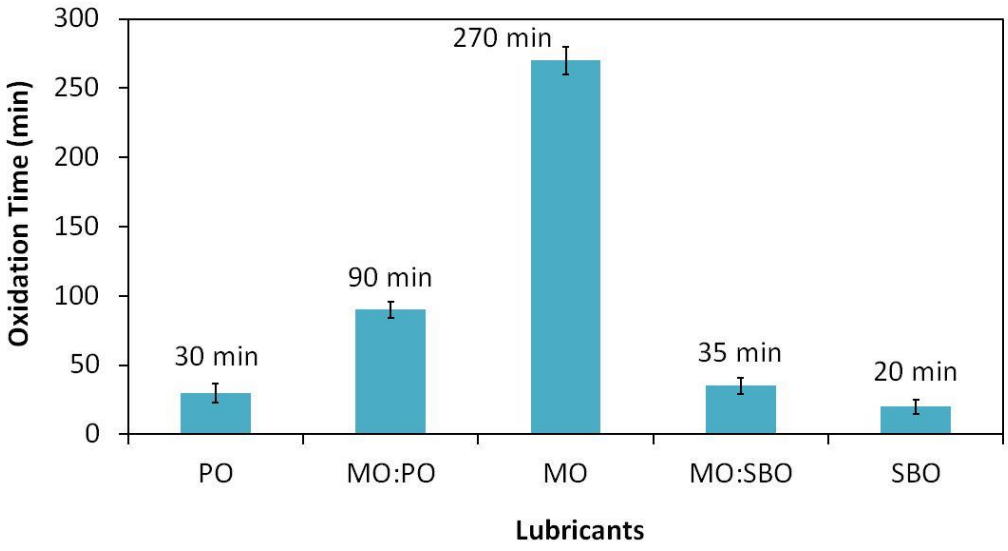

Figure 12

Based on the oxidation time and the peak pressure value, the MO has far greater stability than both vegetable oils. This could be due to the existence of antioxidant additive packages in the MO that include ZDDP, thus, prevent the rapid oxidation. The PO was more stable in oxidation than SBO. The lower oxidation time of SBO compared to PO is due to the existence of higher unsaturated fatty acids which may promote oxidation. The inferior performance of PO and SBO in the oxidative stability test compared to commercial MO validates the vegetable oils downside that may influence their tribological performances as oxidised oil could increase the wear [11].

The PO blended with MO recorded 90 minutes of oxidation time while SBO-MO blend oil recorded about 35 min. The PO-MO blend oil demonstrated a significant improvement compared to other oils. The higher oxidation time in PO-MO blends when compared to SBO-MO blend could be attributed to the higher saturated fatty acids that exist in PO which helps to delay the oxidation process.

4. Conclusions

From the results of experiments for vegetable oils and vegetable oil-mineral engine oil blended lubricants (1:1) conducted at extreme conditions, the following conclusions can be drawn:

- Pure palm oil exhibited a lower friction coefficient than soybean oil, while soybean oil showed better wear protection than palm oil. This shows that friction and wear are not related in vegetable oil lubrication and that the selection of vegetable base oil type for use as an engine oil is important (towards either friction or wear). The tribological performance of the mineral oil-vegetable oil blends is influenced by the tribological performance of the vegetable oil in its pure state.

- The molecular structure of fatty acids on the vegetable oils influences the oxidation performance of palm oil and soybean oil. It could also explain the relation between the friction and wear results of vegetable oils lubrication. A linear chain structure (as in palm oil) tends to provide a smoother interaction of molecules during a relative motion thus, minimising friction but it is susceptible to metal-to-metal contact. A bent chain structure (in soybean oil) however, provides a better surface protection, minimising wear, but promotes a higher resistance to motion on the contacting surfaces.

- The vegetable oil was dominant in influencing the wear performance of the mineral oil-vegetable oil blends. The high wear produced by the blended oils showed that the role of antiwear additive that exists in the mineral oil is lessened on the contacting surfaces. This is likely influenced by the polarity of carboxyl group in fatty acids molecules of vegetable oils, which makes it possible for them to adhere to the surfaces. The adherence of these polarity molecules on the metal surfaces furthermore, may prevent the anti-wear additive from the mineral oil to form a fully coverage layer as a protective film.

- Vegetable oils in their pure oil state are potential base fluids for lubricant formulation, particularly when friction performance is a key requirement. However, there are still some significant drawbacks, particularly in terms of wear resistance and oxidation stability that need to be improved and emphasised before they are capable as a competitive alternative to the hydrocarbon-based lubricant.

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