Friction and wear phenomena of vegetable oil based lubricants with additives at severe sliding wear conditions

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Abstract

The tribological responses of palm oil and soybean oil, combined with two commercial antiwear additives (zinc dialkyl dithiophosphate and boron compound), were investigated at a lubricant temperature of 100 °C and under severe contact conditions in a reciprocating sliding contact. The friction coefficient of palm oil with zinc dialkyl dithiophosphate was closest to the commercial mineral engine oil, with a 2% difference. The soybean oil with zinc dialkyl dithiophosphate produced a 57% improvement in wear resistance compared to its pure oil state. The existence of boron nitride in vegetable oils was only responsive in reduction of wear rather than friction. The response of commercial antiwear additives with vegetable oils showed a potential for the future improvement in the performance of vegetable oils.

Keywords: vegetable oils, palm oil, soybean oil, zinc dialkyldithiophosphate, friction, wear, piston ring

1. Introduction

Commercial lubricants used in automotive engines are mainly manufactured from mineral oil (MO) due to its availability, satisfactory performance and cost competitiveness. However, the base stocks of MO are non-renewable, not readily biodegradable and not environmentally friendly. Biolubricants, which have vegetable oil as a base, are renewable resources and are a potential alternative internal combustion engine lubricant (1). Furthermore, the cost of vegetable oil is typically much lower than mineral oil.

An effective engine lubrication system is multifunctional and is required to reduce friction and wear in the engine, transfer heat, inhibit corrosion and oxidation, and remove wear debris and contamination. Base oils alone are not able to fulfil these requirements due to limited physicochemical properties and thus, they require modification. Many recent studies considering biolubricants have focused on the modification of vegetable oils in order to produce a better base oils. This can be performed through chemical synthesis (2, 3) or formulating the vegetable oils with additives (4). Additives typically represent about 1 to 25% of a lubricant (5) which may enhance some properties of the base oil or present a new property to the oil. Antiwear agents in lubricants are added to improve the wear resistance characteristics of contacting surfaces. They form a protective layer to prevent metal-to-metal contact by adsorption of their molecules on the substrate surface through physical adsorption or chemical adsorption processes (6). Among the most commonly used as antiwear agents in commercial engine oils are zinc dialkyl dithiophosphate (ZDDP) and Boron compounds.

There are three main mechanisms by which the ZDDP may act as an anti-wear agent in oil: by forming a protective film as a barrier to metal-to-metal contact; by removing corrosive oxidation products; and by absorbing the iron oxide particles thus limiting abrasion (7). Other than working as an antiwear agent, ZDDP is also very effective as an antioxidant. The antioxidant characteristic that exists in ZDDP has made it a potential substance to be mixed with vegetable oils since a limitation of vegetable oils is that they are very susceptible to oxidation (8). During the initiation process of vegetable oil oxidation, free radicals are produced by removing a hydrogen atom next to a carbon double bond of a fatty acid. A process is then propagated in which the free radicals react with oxygen to produce a peroxy radical. The fatty acid molecule is then attacked by the peroxy radical and the hydrogen atom is removed. A hydroperoxide is formed and another free radical. It has been reported that an

increase of the hydroperoxide level in oil may increase wear which is related to the degradation of oil and producing strongly corrosive element (9).

A number of researchers have reported the tribological performances of ZDDP mixed with various vegetable oils including with coconut oil (10), soybean oil (11), karanja oil (12), palm oil (13), corn oil (14), canola oil (14) as well as modified vegetable oil like palm oil based trimethylopropane ester (15). Many researchers found that the 2% of ZDDP in vegetable oils gave the best tribological results (10, 12, 14), particularly the friction and wear results from 2 % ZDDP in coconut oil were better compared to a commercial lubricant (SAE 20W50) when tested by in afour-ball-tester (10). Similar tribological performance was also achieved by a four-ball-tester when karanja oil mixed with 2% ZDDP was compared to mineral oil (SAE 20W40) (12). The ZDDP performance of palm kernel oil and palm stearin has been investigated using a pin-on-disc tribometer at room temperature (13). The friction and wear results showed that the palm kernel oil exhibited better performance with 3% of ZDDP while the palm stearin was superior at 5% ZDDP (13). Both corn oil and canola oil were also seen to give an improvement on friction coefficient at 2% ZDDP when tested by pin-on-disk tribometer (14). Evaluation of the addition of ZDDP in lubricating oil was also conducted using a four-ball-tribotester with 52100 steel balls. Chemically modified palm oil, palm oil-based trimethylopropane (TMP) and the base oil for synthetic lubricants, poly-alpha-olefin (PAO) (15) were tested. There was no improvement seen in friction behaviour for both TMP and PAO added with ZDDP at 1% although the wear resistance was better for a blend of TMP and PAO. It has also been reported that the addition of ZDDP to soybean oil gives improved wear resistance at higher sliding speeds when compared to tests with the pure oil (11). The results presented by a number of authors suggest that varying levels of a particular additive are required in different types of vegetable oil to achieve the same result.

Boron nitride is also is used as an antiwear additive in mineral engine oil and is a ceramic lubricant that works efficiently in improving wear resistance, especially at high temperature (16). Many improvements were found in the tribological performance of mineral oil mixed with hexagonal boron nitride (hBN) (17-19). Attempts have also been made to use the boron nitride as a vegetable oil additive such as in canola/rapeseed oil (20) and jatropha oil (21). It was found that 0.05% of boron nitride in modified jatropha oil reduced the friction coefficient and wear scar diameter when tested at 75 °C in a four-ball-tribotester, but any further increase in the concentration resulted in the friction and wear performance being

inferior to that of the base oil (21). The tribological performance of hBN in canola oil was affected by the surface roughness and the particles shape and size of hBN. Smaller particles (typically spherical) easily merge in the asperity valleys to produce a protective film on smooth surfaces whereas larger particles (typically plates) behave as a third body abrasive due to their size and geometry (20).

The work already highlighted is limited to unidirectional sliding test rigs. The work is also limited by being performed at a lubricant temperature of less than 100 °C which is below the typical operating temperatures of lubricants (e.g., a sump of an internal combustion engine) (22). Similarly, much higher contact pressures than those used in this previous work can be experienced by lubricants (e.g., pressures beyond the typical contact pressure of a piston ring (104~105 MPa)) (23).

Therefore, in this work, the tribological response of two commercial anti-wear additives; ZDDP and Boron compound in palm oil and soybean oil were evaluated at a lubricant temperature of 100 °C by a reciprocating tribometer. A point contact with an initial contact pressure > 1 GPa was applied, leading to a severe contact condition. Grey cast iron specimens with a narrow hardness range on intended wear scar were selected prior to testing. Surface morphology, elemental analysis and chemical analysis of oils were also conducted to support the main results. The tribological performance was then compared with a commercial mineral engine oil.

2. Experimental Methodology

2.1 Specimens, Lubricants and Additives

To investigate the tribological behaviour, a steel ball (AISI 52100) with 6 mm diameter and a rectangular flat specimen (66 mm x 25 mm x 4 mm) made of grey cast iron (EN1561-GJL-250) were chosen. The steel balls had an average surface roughness, Ra = 0.03 µm, a hardness in the range 60-67 HRC, and were held firmly by a brass tube. The flat specimen was machined and ground with an average surface roughness, R_a = 0.15 µm. The hardness of the flat specimen was measured close to the intended wear scar position due to the wide hardness range that is inherent in the grey cast iron (24). Flat specimens with a hardness range 200.0~210.0 HV were selected. The geometry of both specimens is depicted in Figure 1.

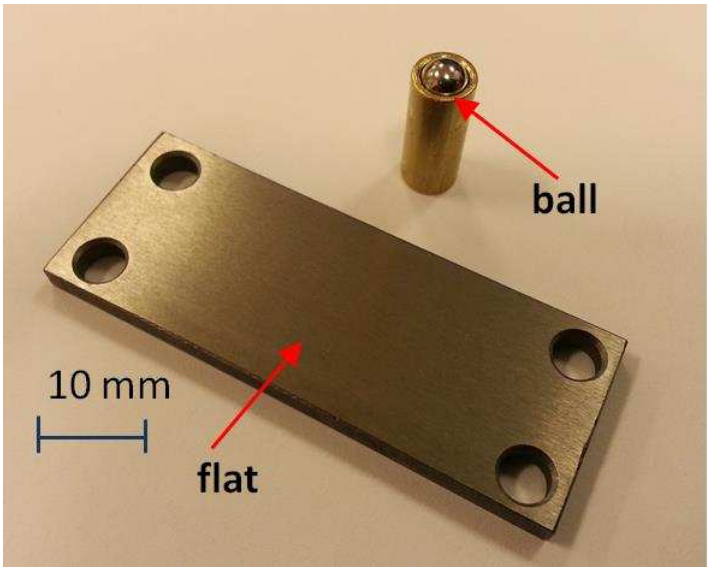

Figure 1 - Ball and Flat specimens.

The vegetable oils used in this study were those used for culinary purposes which consist of organic soybean oil (Clearspring, Italy) and refined palm oil (Veesawit, Malaysia). These two oils represent the highest volume of vegetable oil consumption globally (1995 to 2015) (25). Unrefined soybean oil was chosen because it is more oxidatively stable than the refined oil (26). The unrefined palm oil is a semi-solid at room temperature which makes it difficult to uniformly blend with an additive. Any type of palm oil is more oxidatively stable than soybean oil due to a different fatty acid composition. Thus, a refined palm oil was selected. The mineral oil used for comparison was a commercial automotive lubricant oil (SAE 15W40).

The commercial antiwear additives used were ZDDP (ZDDPlus, USA) and hexagonal boron nitride (hBN) with particle size 0.5 μm or less (Ceratec, Germany). The hBN particles were dispersed in a small volume of mineral oil as a carrier fluid by the manufacturer. An amount of 2% of ZDDP and 6% of hexagonal boron nitride in mineral oil was added in the vegetable oils as these are the ratio that was recommended by the manufacturer for optimum performance (based on their product sheet). The scope of this study is to investigate the influence of friction and wear of vegetable oil with commercial anti-wear additives which have been claimed by the manufacturer to perform well with mineral oil. It is not therefore possible to know the amount of ZDDP and boron nitride in this case (a limitation of this study).

In previous study of hBN in vegetable oils by Reeves et al. (20), a vortex mixer was used for blending so in this work the oil with the additive was stirred by an agitator for 10

minutes in order to ensure a uniform blend. The appearance of each oil mixture was observed at the end of the stirring process. In order to determine that a uniform blend was produced, the oil was checked for the formation of a noticeable layer of different density components, or a colour difference.

The lubricant oils were put into the test rig as soon as the stirring process was completed and it needed about 45 minutes for the temperature to rise to 100 °C. In internal combustion engine applications, lubricant oil has usually accumulated for a period of time in a different area (e.g. an oil sump) prior to engine starting before lubricating the system's contacts. Therefore, it is not necessary to wait and ensure the particles to settle down in the contact area in order to establish a colloidal suspension. The details of lubricants used in this study are shown in Table 1.

	Lubricants	Abbreviation	Dynamic Viscosity (cP)		Total Acid Number (mgKOH/g)
			40 °C	100 °C	
1	Mineral Oil	MO	92.45	12.35	2.24
2	Palm Oil	PO	38.08	39.35	0.24
3	Soybean Oil	SBO	30.72	7.10	0.98
4	ZDDP + Palm Oil	ZD:PO	38.31	7.98	1.98
5	ZDDP + Soybean Oil	ZD:SBO	30.60	7.36	2.53
6	hBN in mineral oil + Palm Oil	hBN:PO	38.59	7.85	0.44
7	hBN in mineral oil + Soybean Oil	hBN:SBO	30.43	7.08	1.21

Table 1 - Lubricants used in this study and their properties

2.2 Friction and Wear Test Method

A reciprocating sliding test rig (Phoenix Tribology/Plint TE77) with a calibrated load cell was used to evaluate the coefficient of friction (COF) for all lubricants. During the tests, the lubricant temperature was set at 100 ± 2 °C, as is typical in an engine oil sump (22). Each test ran for 1 hr with a mean sliding speed of 0.13 ± 0.01 m/s and a maximum stroke (15 ± 0.1 mm) was applied throughout the tests. A few trial tests were initially conducted with

different normal loads in order to obtain a measurable and comparable wear scar when lubricated with mineral oil. During this process, it was found that the vegetable oil specimens produced a much higher mass loss compared to MO specimens. For MO specimens, with normal load lower than 40 N, the mass loss was too small to be directly measured. Higher load (more than 40 N) increased the contact pressure and thus, increased the depth of wear scar for vegetable oils specimens. A normal load of 40 ± 0.1 N was then finalised leading to 1.7 GPa of Hertzian contact pressure. A schematic of the test rig is shown in Figure 2.

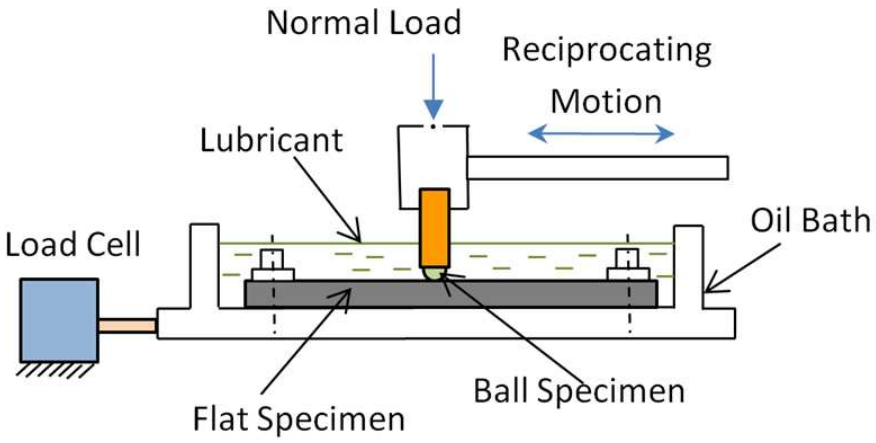

Figure 2 - A point contact of reciprocating sliding test rig.

The wear performance was established based on the mass loss of each specimen by measuring the mass before and after the test. All tests were repeated three times, an average value calculated and the standard deviation shown as an error bar in the graphs produced (Section 3.2). Single variable analysis of variance (ANOVA) was performed to recognise the significant of friction and wear data with level of confidence 95%. In this analysis, the null hypothesis is defined as: "all means of experimental data are equal". The probability of obtaining this null hypothesis is defined as P in which lower P value is an indication of strong evidence to reject the null hypothesis. Data points are statistically significant if the significance level, P value < 0.05.

In this study, boundary lubrication was targeted as it is usually resembles a more severe contact condition, and is often found in engine contacts (e.g. between the piston ring and cylinder liner) during the first half of the power stroke (27). In order to determine the lubrication regime, the minimum lubricant film thickness, h_{min} was estimated using a formula given by Hamrock et al.(28). Then, the lambda factor ($\lambda = h_{min}/ \sigma^*$) was calculated which is based on the ratio between the minimum film thickness, h_{min} and the root mean square

roughness of the two contacting surfaces, σ* (29). A lubrication regime is boundary if the λ value is less than 1. The values of λ factor for different lubricants are shown in Table 2.

Lubricant	h_{min} (nm)		λ	
	Initial	Final	Initial	Final
MO	3.62	3.71	0.02	0.04
PO	2.42	2.45	0.01	0.01
SBO	2.19	2.25	0.01	0.01
ZD:PO	2.45	2.42	0.01	0.01
ZD:SBO	2.21	2.16	0.01	0.01
hBN:PO	2.44	2.46	0.01	0.01
hBN:SBO	2.19	2.22	0.01	0.01

Table 2 - Minimum film thickness, hmin and lambda ratio, λ, for all lubricants

2.3 Surface Topography, Morphology and Elemental Analysis

After each test, the worn specimens were removed from the tribometers and then cleaned in acetone for 5 minutes by an ultrasonic cleaner followed by rinsing in isopropanol. An optical microscope, scanning electron microscope (SEM) and electron dispersive analysis of X-rays (EDX) were used for surface morphology analysis of worn specimens. The surface roughness measurements were performed by a two dimensional surface contact profilometer at several points across the sliding direction of wear scar. The surface waviness was also measured at the centre line, along the wear scar.

2.4 Viscosity, Acid Number, Oxidation Stability and Chemical Analysis of oils

The dynamic viscosity of the lubricants was measured by a rotary viscometer at 40 °C and 100°C. The acid number (AN) of oil samples was measured according to ASTM D664-11a. Both new oils and used oils from wear test rig were used for the viscosity and AN measurements. In order to determine the oxidative stability of each lubricant, a rotary pressure vessel oxidation test (RPVOT) was also conducted according to ASTM D2272-14a recording the time for a peak pressure to drop by 90 psi (0.62 MPa). The existence of elements in the oil were recorded in part per million (ppm) by a spectrochemical analyser. Gas chromatography tests were also carried out on selected oils to analyse the fatty acid compositions in vegetable oils and possible changes in their compositions after the additives were mixed.

3. Results and Discussion

3.1 Friction Analysis

The average coefficient of friction (COF) as a function of time (60 min) for all lubricants is plotted in Figure 3a. Figure 3b highlights the final average value of COF taken at the end of each test. The error bars show how much the value differ from the mean value of the data. All lubricants exhibited a similar running-in behaviour, starting with a lower COF which gradually increased before reaching steady state after about 30 minutes. The running-in behaviour in Figure 3a may be caused by the pressure drop due to increase in area of contact during the sliding process as the COF is inversely proportional with the mean pressure of contact (30). Another possible reason could be due to removal of lubricious contaminants from the contact surface gradually increasing the friction (31) or may be due to the disruption of an oxide layer on the counter-face thus increasing metallic contact (32).

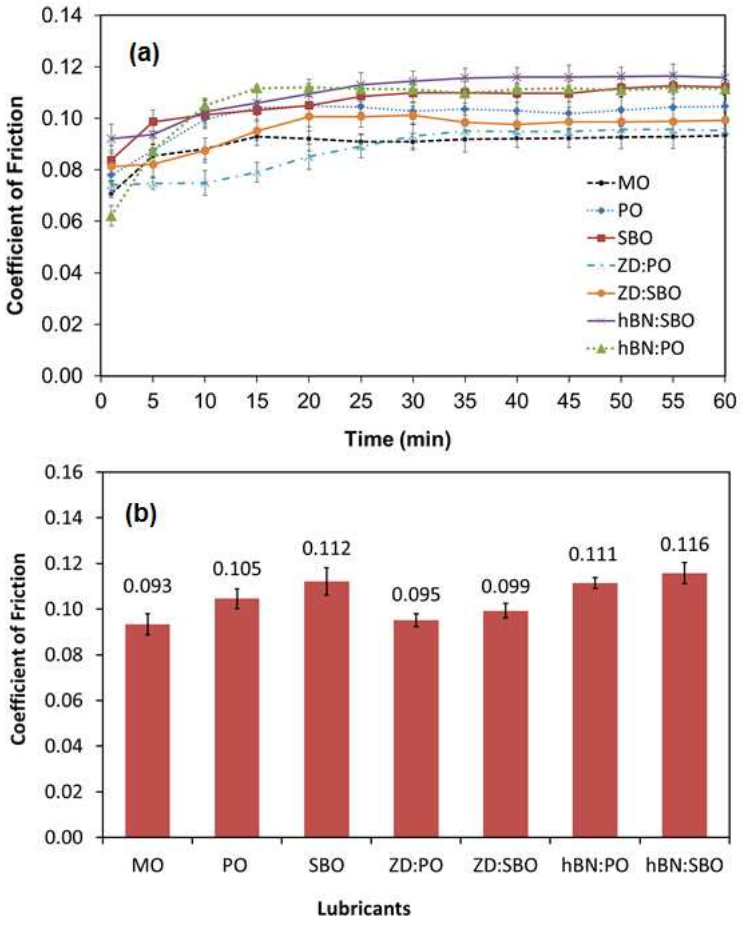

Figure 3 - (a) Average coefficient of friction profile versus experiment time and (b) Average coefficient of friction at 60 minutes.

The COF for the MO lubricated specimens (Figure 3b) showed the lowest value (0.093) while the highest COF was from specimens lubricated with hBN:SBO (0.116). Based on Figure 3b, the ZDDP blended with vegetable oils (ZD:PO and ZD:SBO) gave a reduction in their COF while the hBN in vegetable oils (hBN:PO and hBN:SBO) did not show any improvement compared to the pure oil state. In the pure oil state, the PO showed a lower COF (0.105) compared to SBO (0.112). This result seems to be similar for PO and SBO with additives. For example, the ZD:PO exhibited a lower COF (0.095) compared to the ZD:SBO lubricated surface (COF=0.099). An interesting COF result was noted on the ZD:PO lubricant in which it presented a very competitive value (0.095) compared to the MO (0.093). All COF data in Figure 3b shows a significant difference between the mean values when tested by ANOVA analysis of single variable (P value < 0.05).

The spectrochemical analysis of elements for all lubricants is shown in Table 3. Typically, the procedure of spectrochemical analysis (mass spectrometry) begins with the bombardment of the sample with electrons until it is ionised. These ions are then separated and detected by their mass in a magnetic field. The amount of elements in pure vegetable oils (PO and SBO) is relatively small compared to other lubricants. It is interesting to note that the pure SBO contained calcium (25 ppm), phosphorus (59 ppm) and magnesium (17 ppm). These metallic elements are those typically found in a natural soybean oil and are used to determine the quality of the vegetable oil before converting to a biodiesel (33).

Elements	MO	PO	SBO	ZD:PO	ZD:SBO	hBN:PO	hBN:SBO
Calcium	2825	0	25	25	49	120	147
Zinc	781	1	3	1153	1129	65	65
Phosphorus	695	0	59	879	917	51	106
Molybdenum	167	0	0	0	0	350	352
Boron	43	2	1	3	0	342	357
Magnesium	32	0	17	0	16	3	19
Silicon	3	3	2	8	65	5	3
Aluminium	3	0	0	0	0	5	6
Iron	1	0	0	0	0	0	0
Sodium	0	2	3	5	2	4	5
Lead	0	0	0	0	1	0	0
Barium	0	0	0	0	0	0	0

Table 3 - Elements detected in lubricants in part per million (ppm) from spectrochemical test

The existence of the additive package present in the commercial MO sample is indicated by the detection of calcium, zinc, phosphorus, molybdenum, boron and magnesium in the sample. Calcium (calcium hydroxide) is mostly used as lubricant detergent (to clean and neutralize oil impurities) due to its lower cost (34). The impurities in oil can cause deposits (oil sludge) on engine components. The molybdenum in the MO sample is from molybdenum-dithiophosphate (MoDDP) or molybdenum-dithiocarbamate (MoDTC) additives, as these additives have found an improvement result in reducing the COF in engine oil (35). These additives could also exist in the MO sample in this study and thus lead it to produce the lowest COF.

The addition of 2% commercial ZDDP in both PO and SBO has led to a significant difference in the amount of elements (calcium, zinc and phosphorus) compared to their pure oil state. The addition of ZDDP in PO and SBO has lowered the COF compared to their pure oil state which is typical for other vegetable oils (e.g., coconut, karanja, corn and canola oil) (10, 12, 14). Contrary to the lower friction result found in the ZDDP mixture with vegetable oils, the existence of ZDDP alone in base oil increases the friction compared to the oil without ZDDP (36). This work revealed (Figure 3b) that ZDDP, besides being known as an anti-wear agent and an antioxidant agent, also acts as a friction modifier for vegetable oils.

The existence of boron and molybdenum are abundantly observed in the vegetable oils (PO and SBO) blended with commercial boron based additive. The small amount of zinc and phosphorus that were found in the hbN:PO and hBN:SBO may come partly from the mineral oil used by the manufacturer as a carrier fluid for the hBN additive. Although the boron were detected in the spectrometer results from analysing the hBN:PO and hBN:SBO (Table 3), they did not appear on the worn specimens surfaces as analysed by EDX (Table 4). Detection of a light element (boron) by EDX is somewhat difficult due to low photon energy that it has which may leads to a high absorption in the specimen and in the EDX detector (37). Another possibility was that the boron elements have been removed from the counterface during the sliding process and thus, failed to perform their function as an effective lubricious film. The particles size of boron nitride used in this study (0.5 μm) are relatively larger than the average surface roughness of the flat specimens (R_a = 0.15 μm). This could be the reason why the boron was not merging in the asperity valleys of the contact surfaces. Larger particles act as a third body abrasive products and this may increase the friction (20) where the hBN were prevented from settling on the surface.

Element	Weight %							Atomic %						
	Lubricants													
	MO	PO	SBO	ZD:PO	ZD:SBO	hBN:PO	hBN:SBO	MO	PO	SBO	ZD:PO	ZD:SBO	hBN:PO	hBN:SBO
C	3.38	3.79	3.77	2.87	3.71	3.45	3.81	10.96	14.67	14.56	11.20	13.94	13.44	14.65
O	10.43	1.17	1.43	2.25	2.85	1.52	1.71	25.58	3.39	4.15	6.59	8.04	4.43	4.93
Si	2.70	3.29	2.91	2.99	2.90	3.05	2.64	3.77	5.44	4.80	4.99	4.67	5.07	4.34
P	0.72	0.10	0.15	0.16	0.13	0.00	0.14	0.91	0.15	0.22	0.25	0.20	0.00	0.21
S	1.36	0.04	0.00	0.00	0.09	0.12	0.10	1.66	0.06	0.00	0.00	0.13	0.18	0.14
Mn	0.73	0.66	0.84	0.81	0.73	0.63	0.75	0.52	0.55	0.71	0.69	0.60	0.53	0.63
Fe	79.80	90.95	90.91	90.88	89.50	91.23	90.85	56.06	75.73	75.56	76.26	72.37	76.34	75.10
Zn	0.90	-	-	0.03	0.09	-	-	0.54	-	-	0.02	0.06	-	-

Table 4 - Elemental analysis of wear scar for all lubricant specimens by EDX

3.2 Wear Analysis

Table 2 shows the calculated minimum film thickness (h_{min}) and lambda value (λ). It is found that the lubrication regime for all lubricated specimens was boundary ($\lambda<1$). The differences of minimum film thickness between initial and final (end of test) were calculated and mainly attributed to the differences in oil viscosity before and after the test (see Section 3.6). It was found that all lubricants experienced an increase in film thickness except for ZD:PO and ZD:SBO. However, the lambda values for most of lubricants did not change.

The average of mass loss for all specimens at the end of the test is show in Figure 4. It was observed that the MO specimens produced the lowest mass loss (0.65 mg) while the highest wear was from PO lubricated specimens (45.76 mg). In a pure oil state, the SBO produced a lower mass loss compared to the PO counterpart. This result is similar for the mixture of SBO and PO with additives, for example the hBN:SBO has a lower mass loss compared to hBN:PO. The influence of ZDDP on both vegetable oils has led to a significant difference in the wear resistance result.

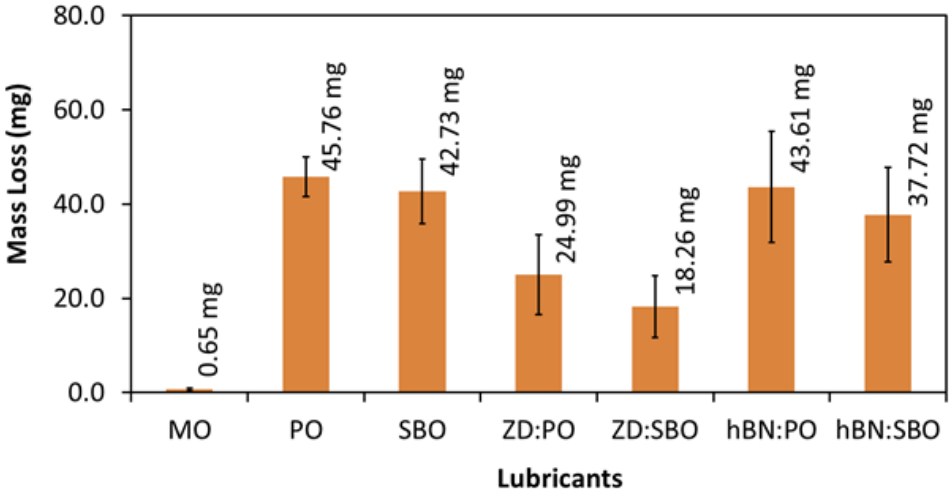

Figure 4 - Average Mass loss of lubricated specimens after 60 minutes.

Figure 4 shows that the mixture of ZD:SBO (mass loss=18.26 mg) improved the wear about 57% compared to pure SBO (mass loss=42.73 mg) while the ZD:PO (mass loss=24.99 mg) gave wear reduction about 45% compared to pure PO (mass loss=45.76 mg). However, only a small amount of mass loss was found in boron compound additives blended with vegetable oils. The hBN:SBO (mass loss=37.72 mg) recorded about a 12% improvement compared to the pure SBO state while hBN:PO (mass loss=43.61 mg) only improved about 5% compared to PO alone. The mass loss result for all biolubricant lubricated specimens showed a significant difference between the mean of data when tested by the single variable ANOVA analysis (P value <0.05).

The superior wear performance of the MO indicates that the anti-wear additives have successfully prevented severe damage to the sliding surface at the severe contact conditions applied in this study. This suggests that the antiwear additives (possibly ZDDP) that exist in the MO are capable of maintaining a protective layer in preventing metal-to metal contact throughout the test. The existence of ZDDP in the MO sample could be shown by a high amount of zinc and phosphorus detected by the spectrometer (Table 3). Although lower zinc concentrations (781 ppm) were found in the MO (spectrochemical analysis, Table 3) compared to ZD:PO (1153 ppm) and ZD:SBO (1129 ppm), the MO produced lower wear and friction than these two lubricants. This suggests that, the existence of another element in the MO like molybdenum (from MoDDP or MoDTC additive) could potentially acting together with the ZDDP in improving the wear and friction performance of MO. The molybdenum, however, was not significantly present in both ZD:PO and ZD:SBO.

Vegetable oils on the other hand, even though they presented competitiveness in friction coefficient; were still far behind in wear resistance performance compared to MO, especially in a severe test condition. In considering ZDDP as an additive in vegetable oils, both PO and SBO appear to have a capability to provide for the formation of a protective layer on the surface of grey cast iron. In a typical lubricant oil with the ZDDP additives, the phosphate layer is commonly found on the wear scar and serve as a wear reducing layer (38-40) which was also reflected by the highest phosphorus amount found on MO lubricated specimens (0.72 wt%, Table 4). Although the phosphorus amount on vegetable oils-ZDDP was higher (spectrochemical analysis, Table 3), it was discovered that the amount of this element (P) detected in worn specimens of ZD:PO and ZD:SBO were not significantly different when compared to their pure oil state (EDX analysis,Table 4). This suggests that, with vegetable oil, a different mechanism of formation of protective layer from ZDDP (other than phosphorus layer) could occur on the surface.

Zinc may also play this role on the counterface in order to minimise metal-to-metal contact. This is shown by the detection of zinc from the result of EDX analysis (Table 4) on worn specimens for ZD:PO and ZD:SBO lubricants. In order to determine that the wear improvement was solely due to the ZDDP additive, a test of fatty acids composition on PO, SBO, ZD:PO and ZD:SBO oils was performed by gas chromatography (Figure 5). It was noted that there was no significant difference found in the fatty acids composition of vegetable oil-ZDDP mixtures compared to their pure oil state. This indicates that the fatty acids compositions in the vegetable oil were not influenced by the existence of ZDDP.

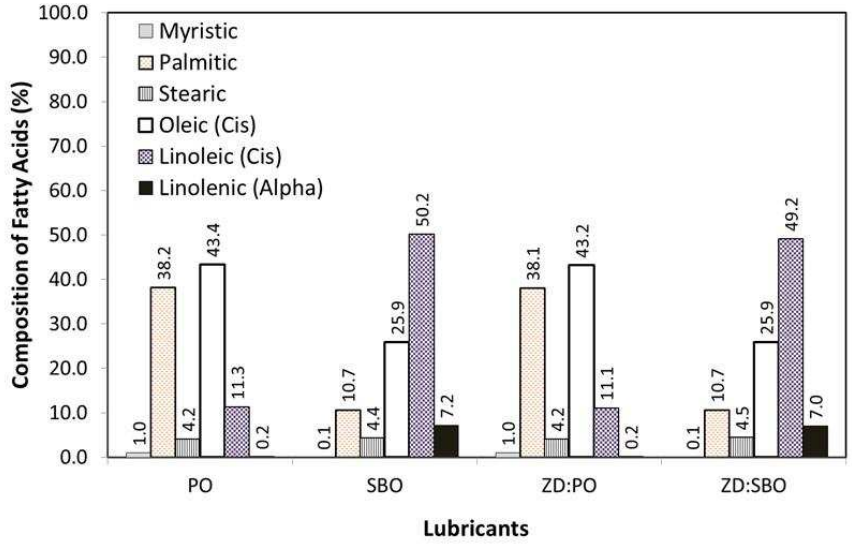

Figure 5 - Composition of fatty acids on selected oils extracted from gas chromatography test.

3.3 Surface Topography Analysis

The shape of wear scar after each test was examined visually (Figure 6a). The specimen lubricated with MO produced a straight narrow wear scar with a shallower depth compared to specimens lubricated with vegetable oils. The additive packages that exist in MO could possibly act as a barrier in preventing deeper indentation of ball into the specimen. However, specimens lubricated with vegetable oils and their mixtures with additives showed catastrophic damage with the formation of wavy-shape scars and a wider width. The formation of wavy-shaped scars also could suggest that there was plastic flow due to plastic ratchetting on the contact surface during sliding as a result of the high contact pressure. Due to the smoother wear profile produced by MO specimens, it is unlikely that the test apparatus made a significant contribution to the wavy-shaped wear scar profile.

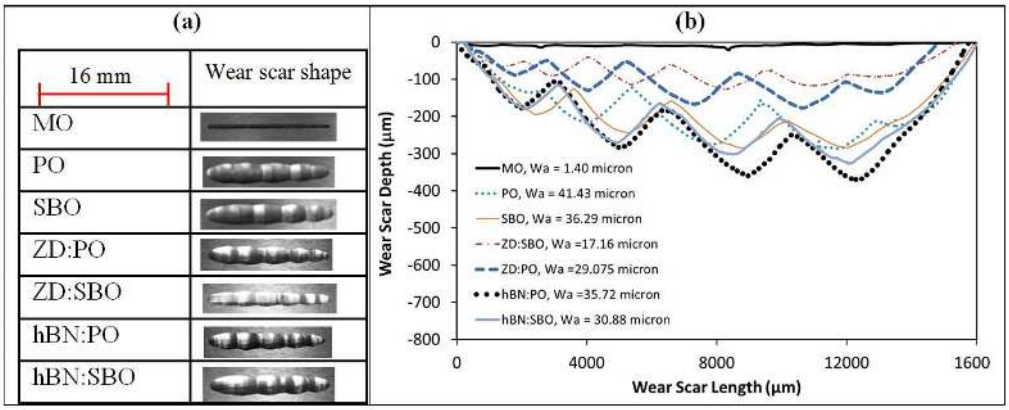

Figure 6 - (a) Wear scar shape for all lubricated specimens and (b) Primary profile and surface waviness, Wa of specimens measured along the wear scar.

Plastic ratcheting is likely to occur when the normal load applied is beyond the plastic shakedown limit (41). Ponter (41) described the relationship between Hertzian pressure to shear strength ratio and the COF (Figure 7). In this current study, the calculated Hertzian pressure was 1.7 GPa and the shear strength for GCI specimens was about 0.29 GPa (BS EN1561:2011). This yielded a Hertzian pressure-shear strength ratio of about 6. At COF = 0.112 (values taken from the COF of soybean oil) and Hertzian pressure to shear strength ratio of more than 6, Ponter suggests that the material deformation will enter the plastic ratcheting region. This is shown by the red dotted line in Figure 7. Plastic ratchetting occurs when the applied load exceeds the plastic shakedown limit, in which the progressive plastic deformation of surfaces occurs during repeated sliding (Figure 8) (42).

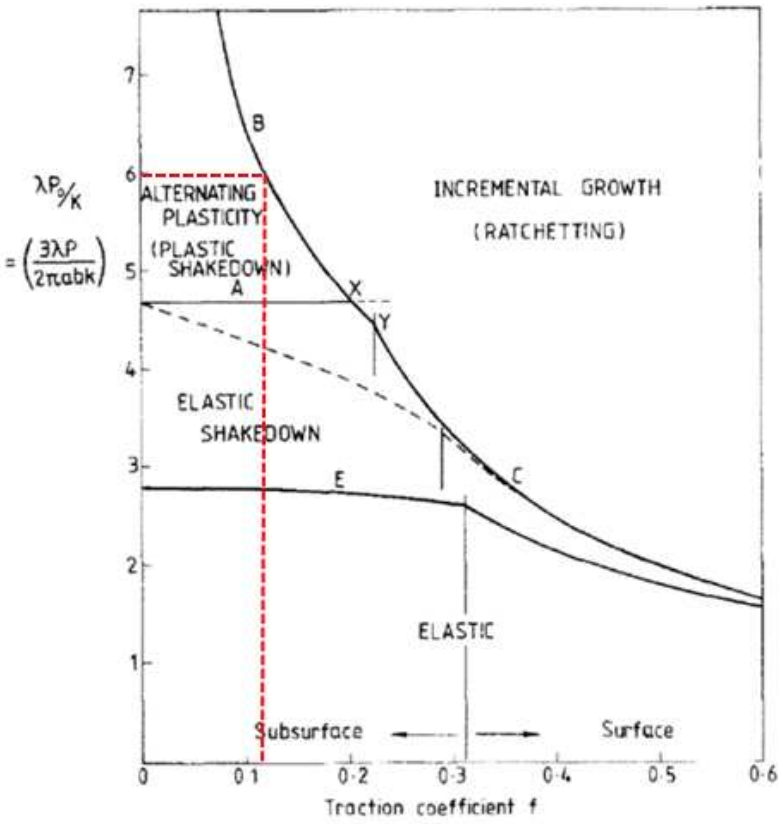

Figure 7 - The elastic, elastic shakedown, plastic shakedown and ratchetting region associated with Hertzian pressure, Po-shear strength ratio, K on coefficient of friction, f for sliding point contact (41).

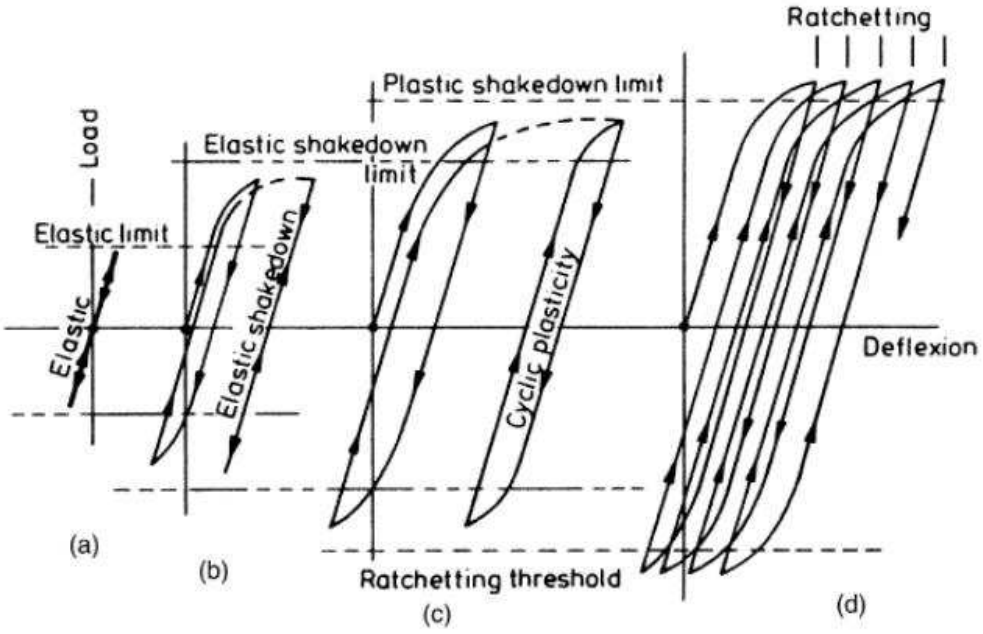

Figure 8 - The different forms of structural response to cyclic loading: (a) elastic, (b) elastic shakedown, (c) plastic shakedown and (d) ratchetting (42).

Although the vegetable oils exhibited poor performance in wear resistance at extreme contact condition, the addition of ZDDP additive in both PO and SBO has seen improvement in wear scar appearance in which narrower width of wear scars were produced. In order to further understand the characteristics of these wavy-shape wear scars, Figure 6b was plotted. This shows the primary profile of wear scars which represents the shape and depth of the worn surfaces measured by a two-dimensional profilometer along the wear scar. The surface waviness measurement was also recorded by altering the wavelength components of the primary profile (43). It can be seen that the shallowest profile and lowest surface waviness was from MO lubricated specimen (Wa = 1.40 μm). A closer examination of Figure 6(b) for MO specimens revealed that there was some small variation in wear scar depth along the wear scar length nearly at point 1000, 3000 and 9000 μm. This indicates that the wavy-shaped wear scar have started to form, but at a smaller magnitude due to plastic ratcheting as a result of high contact pressure. The highest surface waviness was from specimen lubricated with PO (Wa = 41.43 μm). It should also be noted that the addition of ZDDP in vegetable oils (ZD:PO and ZD:SBO lubricants) has caused the formation of shallower wear scar and lower surface waviness value. However, deeper penetration was found on specimens lubricated with hBN:PO and hBN:SBO and it was noted that the penetration of wear scar depth produced was dependent on the relative position of the waves. Where there is a higher penetration of the ball into the flat specimens (as shown by hBN:PO specimens compared to PO and ZD:PO in Figure 6b), the peaks of waviness shift within the length of the wear scar.

Figure 9a shows the surface roughness (R_a) measured across the wear scars of worn specimen (Figure 9b). It was noted that the MO lubricated specimen exhibited the lowest and more consistent surface roughness throughout the wear scar. However, for specimens lubricated with vegetable oils and vegetable oil-additive mixtures, the surface roughness varies along the wear scars. Higher roughness was recorded, especially at middle points (Middle 1(M1), Middle 2(M2) and Middle 3(M3)), compared to the MO specimen's roughness. The higher surface roughness commonly leads to higher COF and this was shown by the specimen lubricated with hBN:SBO which recorded the highest COF and roughness.

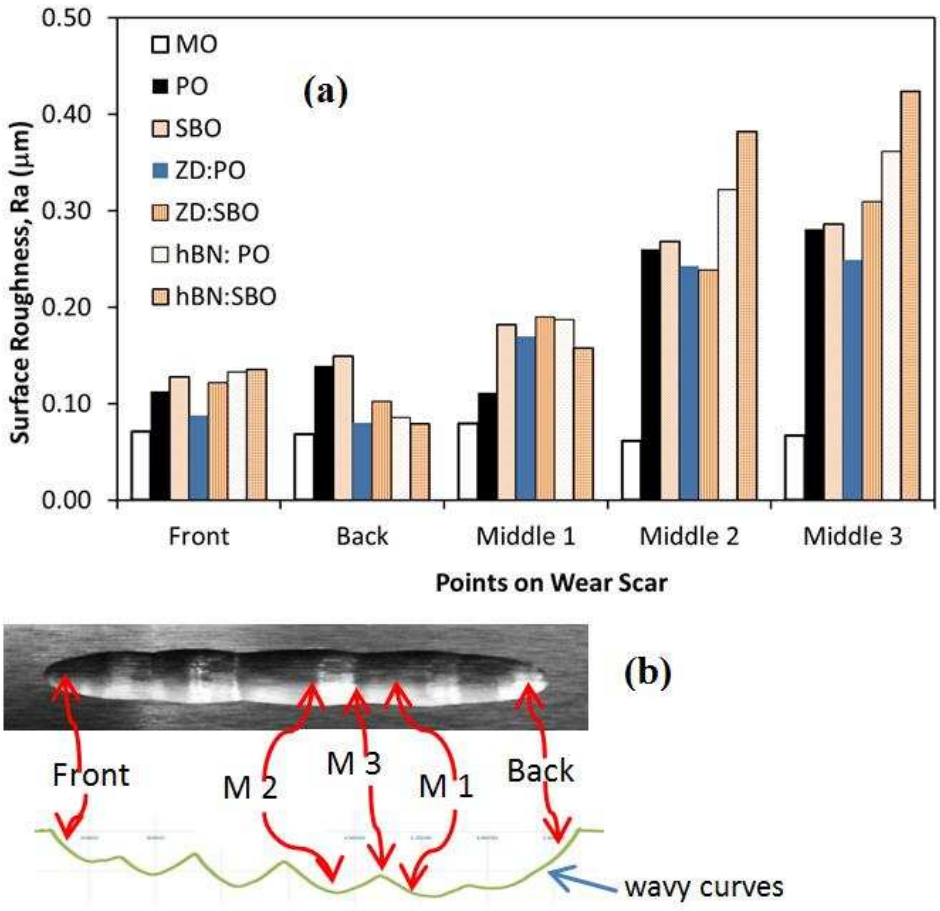

Figure 9 - (a) Surface roughness of specimens across the wear scar at a point according to diagram in (b).

3.4 Surface Morphology Analysis

The wear scar images of worn specimens taken at different points (Figure 9b) for all lubricants under optical microscope are shown in Figure 10. A more consistent appearance was seen for the MO worn specimen at each point compared to specimens lubricated with vegetable oils and vegetable oil-additive blends. Some pitting and spalling were found at end points (Front and Back) on the MO specimen indicating a different wear mechanism at the stroke ends (where velocity is zero, lowering the film thickness and promoting scuffing) of the reciprocating motion compared to the middle of the scar. These wear mechanisms at the stroke ends are similar to those from a reciprocating sliding test for pin on twin (a cylinder contact on a cylinder perpendicularly) with steel material and fuel lubricated in which severe scuffing was reported (44). Detailed examination of MO worn specimens under SEM (Figure 11) showed surface cracks and delamination suggesting fatigue wear.

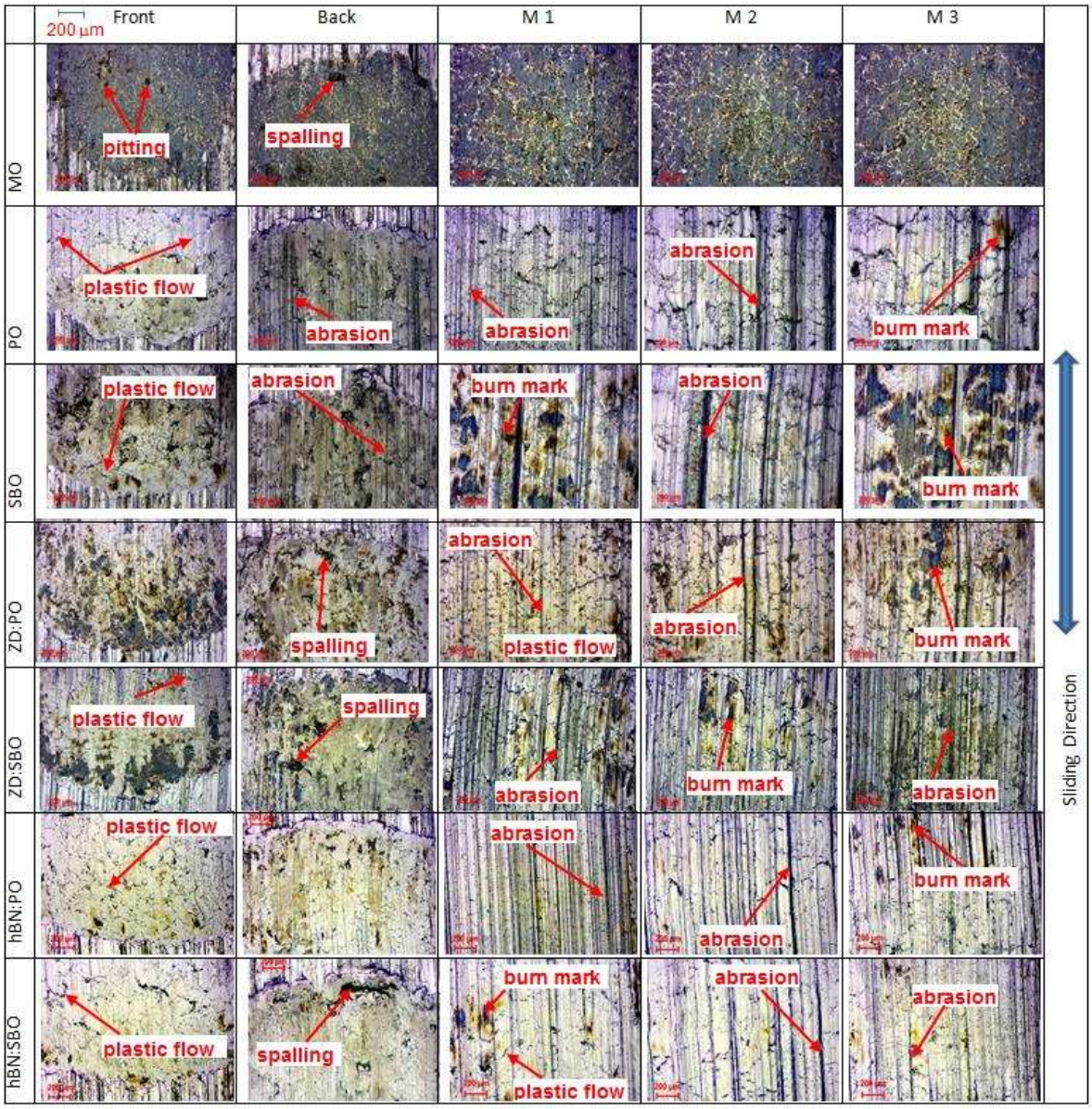

Figure 10 - Optical microscope images of wear scars for all lubricants (20X magnification).

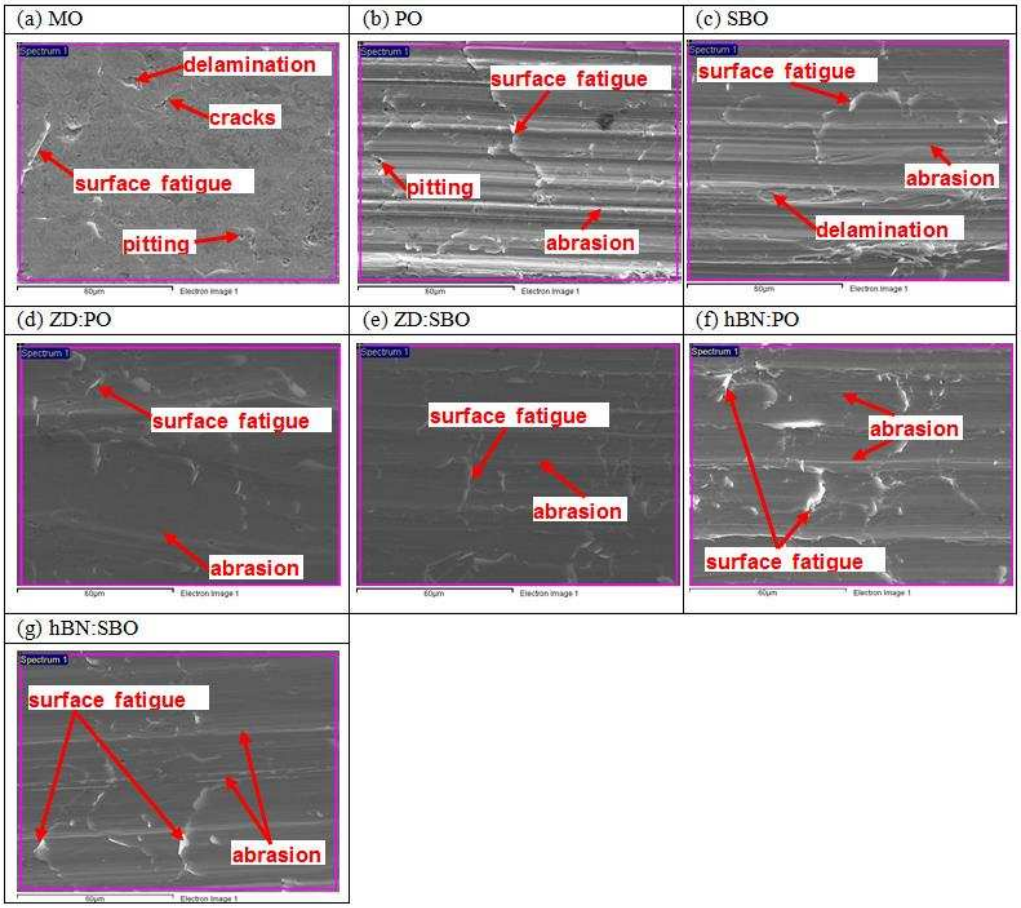

Figure 11 - Scanning electron microscopy (SEM) images (1000X magnification) and elemental analysis of wear scars for all lubricants.

The main wear mechanism for specimens lubricated with vegetable oils and vegetable oil-additive mixtures was observed to be abrasive. This can be clearly seen by the abrasive scratch marks on the worn surfaces especially at the middle points of the wear scar (Figure 10). It was also noted that at the stroke ends (Front and Back) more plastic flow can be seen on the surface which suggests that this occurred during the sliding process on the contacting surfaces. The addition of ZDDP in vegetable oils has seen a slight improvement on abrasive wear. Less abrasion with smoother surfaces was seen on ZD:PO (Figure 11d) and ZD:SBO (Figure 11e) specimens under detailed examination with SEM compared to their pure oil state (Figure 11b and 11c). Less abrasion was also seen in the specimen lubricated with hBN:PO and hBN:SBO (Figure 11f and 11g) with more surface fatigue likely to occur.

Some burn-like marks (brownish colour) could also be seen mainly at middle points on the worn surface for all specimens lubricated with vegetable oils and vegetable oil-additive mixtures (Figure 10). These marks possibly manifest as a result of the process of frictional heating caused by metal to metal contact which may raise the temperature at the

counterface. To support this idea, a calculation of surface temperature was performed based on the material properties and test parameters (45). The estimated surface temperature was then compared to the tempering colour of steel which indicates the brownish colour was likely to appear when the temperature was close to 200 °C (46). It was found that for the SBO lubricated specimen, the total contact temperature was around 182 °C. Based on this temperature, a good agreement was found between the colour of burn-like marks on worn specimens and the steel tempering colour. Thus, it is reasonable to suggest that the higher wear produced by vegetable oils and vegetable oil-additive mixtures compared to MO in this study were due to the breakdown of the lubricants. The burn-like marks were not observed with the mineral oil suggest that the antiwear additives were working efficiently with this oil to minimise metal to metal contact.

3.5 Elemental Analysis of Worn Specimens

EDX analysis was performed on worn specimens for all lubricants (Table 4). It is noted that the amount of oxygen and zinc that was detected on the specimens were distinguishable and this could be the best aspect in explaining the wear resistance result. The existence of oxygen could be related to retention of an oxide layer after the sliding process which led to the friction and wear reduction (47). The presence of zinc promoted the formation of a protective layer by creating a barrier to prevent metal to metal contact. Both oxide layer and zinc protective layer are important in minimising the metal to metal contact between contacting bodies (32, 48).

It was recorded that the amount of oxygen in the MO lubricated specimen was the highest (10.43 wt%) compared to others. This is associated with the lowest mass loss that the MO specimen produced. However, the amount of oxygen in the specimen lubricated with vegetable oils and vegetable oils-additive mixtures was not greatly retained. The amount of oxygen was slightly higher (1.43 wt%) found in the SBO lubricated specimen compared to the PO counterpart (1.17 wt%) and this was reflected in the result of the SBO wear performance, that was slightly better than PO. Although the oxygen detected in specimen lubricated with ZD:PO (2.25 wt%) and ZD:SBO (2.85 wt%) was higher than their pure oil state, they are about five orders of magnitude less than the oxygen amount detected in the MO lubricated surface and so higher wear was still produced. There were also a distinguishable amount of oxygen detected in hBN:PO (1.52 wt%) and hBN:SBO (1.71 wt%) compared to their pure oil state which presenting a slight wear reduction in their specimens. However, no boron compound was detected on the worn specimens which proves that the hBN particles have been flushed out in the lubricant during the sliding process. The relationship between the mass loss and the wt% of O and Zn is shown in Figure 12. It shows a non-linear relation between the mass loss and the weight % for both elements. Based on the graph (Figure 12), the small amount of zinc in weight % tremendously reduced the mass loss compared to oxygen, suggesting that the protective layer was more influenced by the zinc.

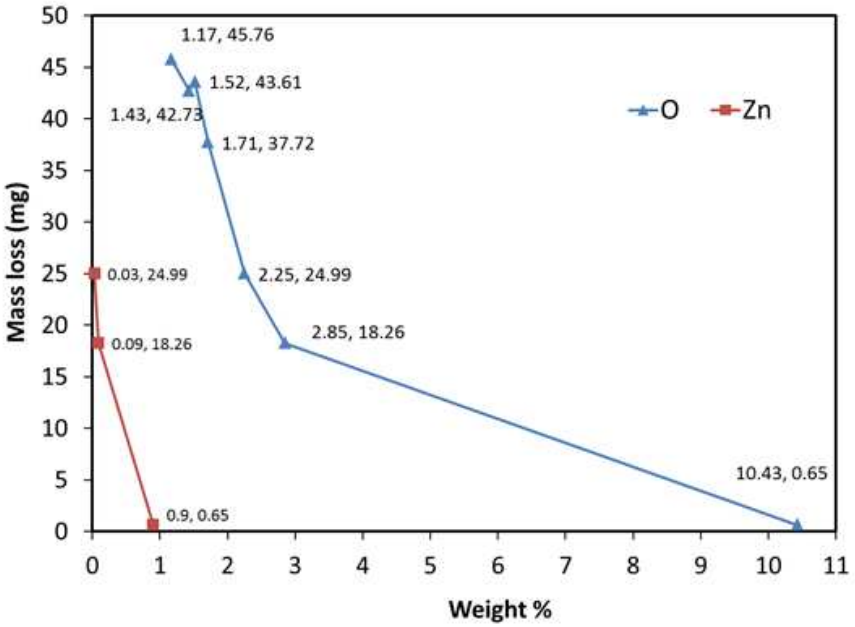

Figure 12 - Relation between the weight % of oxygen and zinc to the mass loss of specimens in relation to EDX analysis results in Table 4.

3.6 Oil Viscosity Analysis

Figure 13 shows the dynamic viscosity results measured at 40°C and 100 °C for fresh oil and used oil from the wear test rig. At both temperatures, the MO samples showed a higher viscosity compared to vegetable oils and vegetable oil-additive mixtures. As expected, all lubricants showed viscosity change with temperature (viscosity drops from a low to high temperature). However, the changes in viscosity over temperature for vegetable oils and vegetable oil-additive mixtures were found to be lower than from the MO sample. This low influence of temperature on viscosity for vegetable oils compared to MO suggests that the vegetable oils have a strong interaction between molecules that are resilient to temperature change.

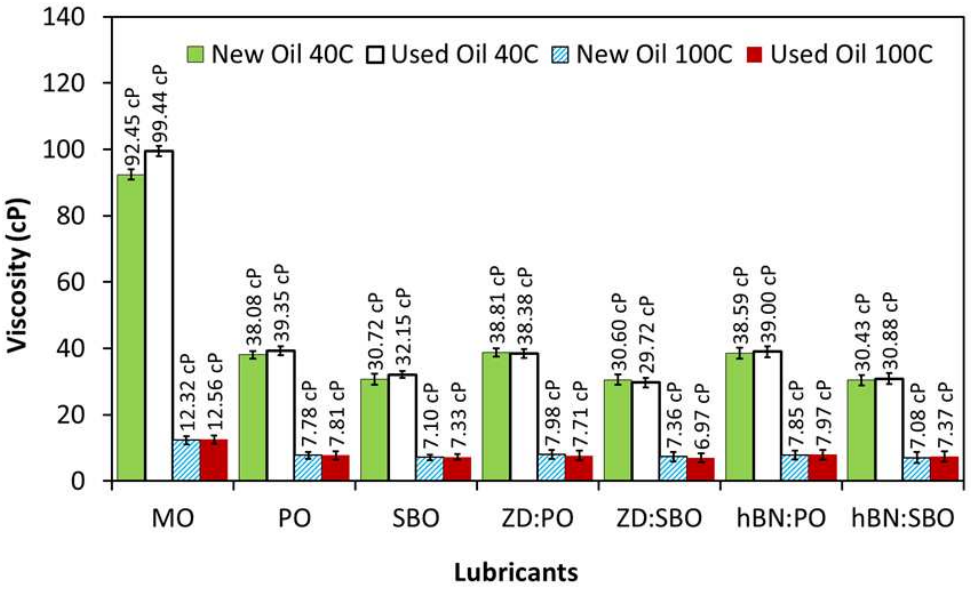

Figure 13 - Relation between the weight % of oxygen and zinc to the mass loss of specimens in relation to EDX analysis results in Table 4.

The viscosity value for all used oils after the wear test did not significantly change which indicates that no oil thickening process occurs during a sliding test. It is also noted that the addition of additives in the vegetable oils have not caused any significant changes in the oil viscosity value. A higher wear rate was reported for a sliding test in lower viscosity lubricant oil (49). Thus, the lower value of viscosity in vegetable oils compared to MO sample could probably be the reason to the lower wear resistance of their lubricated specimens. The minimum film thickness formula (28) is dependent on the oil viscosity, where higher viscosity oil promotes higher film thickness.

3.7 Oxidative Stability Analysis

The results of oxidation stability tests for all lubricants performed by the RPVOT test rig are depicted in Figure 14. The peak pressure shows the maximum pressure that the pressurised oil with oxygen can achieve in the pressure vessel before the pressure drops. The oxidation time reflects the oxidation stability which can be defined as a time taken for an oil to start to oxidise. It was found that the MO sample showed the highest stability in oil oxidation (270 min) and recorded a higher peak pressure (200 psi) compared to the vegetable oils. The antioxidant additive that exists in MO (ZDDP) could prevent the rapid oxidation process.

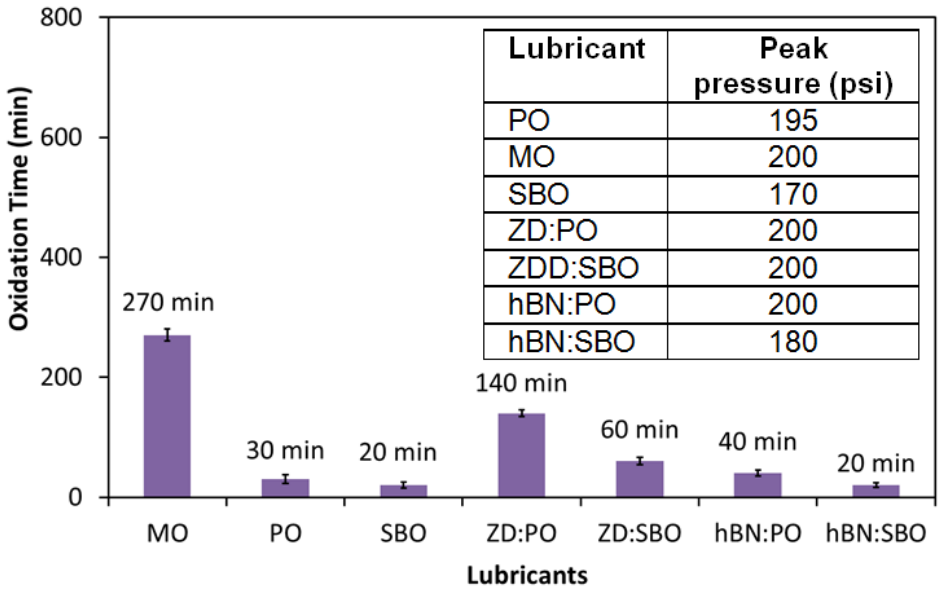

Figure 14 - Rotary pressure vessel oxidation test (RPVOT) result for mineral oil (MO), palm oil (PO), soybean oil (SBO) and their blends with additives.

The lower oxidation stability that the vegetable oils have may cause their poor wear performance (50). The lowest oxidation stability and lowest peak pressure indicates that the oxygen, that was pressurised in the pressure vessel of the machine, has reacted more quickly with the oil. In pure oil state, SBO exhibited the lowest oxidation stability (20 min) with the lowest peak pressure (170 psi).The higher amount of unsaturated fatty acids in SBO compared to PO has made it more susceptible to oxidation. The higher unsaturated fatty acids in SBO compared to PO has made it more susceptible to oxidation. The additions of additives in vegetable oils have led to an improvement in oxidation stability, especially in ZD:PO. This clearly indicates that the ZDDP was actively performing as an antioxidant agent in delaying the oxidation process in vegetable oils. The higher oxidation stability of ZD:PO could probably be the main factor that influenced to the reduction of wear. However, the oxidation stability of ZD:PO is relatively lower than the MO sample which recorded about 50% less than the MO's oxidation time.

The higher oxidation stability of ZD:PO compared to ZD:SBO was influenced by their based oil performance. The pure PO has higher oxidative stability compared to pure SBO. The oxidation results for ZD:PO and ZD:SBO was also exhibited a similar trend (ZD:PO was higher than ZD:SBO). A slight improvement in oxidation stability was also seen in hBN:PO which is likely attributed to the small volume of mineral oil in the mixture that acted as a carrier fluid for the hBN additive. Mineral oil performed well in oxidation stability.

In addition, there is no evidence found in literature that the hBN may act as an antioxidant agent.

3.8 Acid Number Analysis

The acid number (AN) for all lubricants tested in the form of fresh oil, used oil from wear test rig and used oil from the RPVOT test rig is depicted in Figure 15. AN is a measurement of oil acidity that is to quantify the amount of pottasium hydroxide (KOH) in miligram needed to neutralise one gram of oil. Measurement of AN is important in lubricant studies in order the monitor the oil oxidation level (ASTM D664-11a).

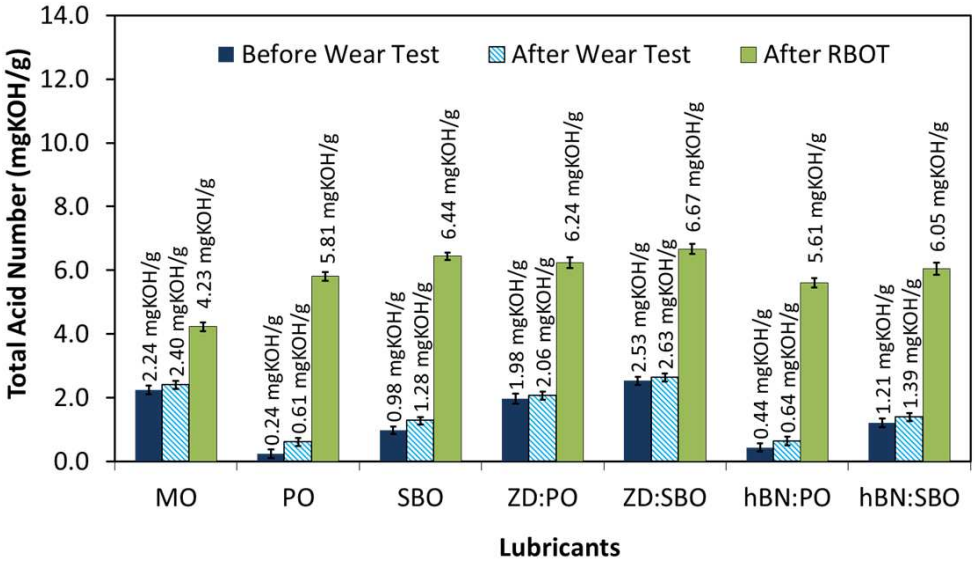

Figure 15 - Total Acid Number for Mineral Oil, Palm Oil, Soybean Oil and their blends with additives for fresh and used oils

In an oxidised oil, the hydroperoxide which is formed during propagation stage, may form oxygenated compounds like aldehydes and ketone which then may react further to form organic acids with the existence of oxygen (51). It can be seen that the pure vegetable oils (PO and SBO) exhibited the lowest AN compared to MO and their vegetable oil-additive mixtures in fresh oil state. It is also noted the MO sample and vegetable oil-additive mixtures recorded a higher AN. All of the used oils from wear test rig have also shown an increase in AN. However, the AN values for used oils from the wear test rig were relatively small compared the AN after RPVOT.

The higher AN value from fresh SBO (0.98 mgKOH/g) relative to PO (1.98 mgKOH/g) is possibly due to the higher acidity of the free fatty acid that is inherent in

unrefined oil (SBO). During the refining process most of the free fatty acids are removed (52). The higher AN in the MO sample and vegetable oil-additive mixtures could be attributed to certain additives like ZDDP that exist in lubricating oils that may increase the AN in a base oil (53). This was confirmed by the AN value of ZD:PO and ZD:SBO where significant increases in AN were seen when the ZDDP was added to pure PO and SBO. The highest AN recorded for oil samples taken from RPVOT test rig have confirmed that acids were produced during the oil oxidation process. This reinforces the earlier notion that an oxidised oil has a higher AN than the fresh oil sample and that the oils have been oxidised or started to oxidise after the wear test. This may also have contibuted to higher wear in ZD:PO and ZD:SBO compared to MO as ZDDP is less efficient as antiwear agent when it reacts with the peroxy radical that builds up in oxidised oil (54).

4. Conclusions

From the results presented of experiments conducted at severe contact conditions involving vegetable oils and their blends with additives (combined together and summarised in Table 5), the following conclusions can be drawn:

- The addition of 2% ZDDP in vegetable oils did not influence the fatty acid composition in vegetable oils. However, this level of additive has led to a significant improvement in wear, friction and oxidation stability.
- The amount of oxygen detected on worn specimens was found to be related to the amount of mass loss and the amount of zinc found on the worn surface was significantly related to the level of wear.
- The oxidative stability of oil and the surface waviness of the worn specimens are the factors most strongly related to the mass loss of specimens. The level of change in surface roughness of the specimen in the wear scar region was dependent on the friction coefficient during a particular test.
- The ZDDP was found to perform three tribological functions when used as an additive in vegetable oils: as an antiwear agent, as an antioxidant, and as a friction modifier.
- Of the additive-vegetable oil mixtures, the ZD:PO oil provided the best friction reduction while the ZD:SBO provided the best wear resistance

- The tribological performance of vegetable oil-additive blends was dependent on the tribological performance of its base oil.
- The function of hexagonal Boron Nitride as an antiwear additive is less effective when the particles size is greater than the surface roughness.
- In view of the presence of molybdenum and zinc and their contribution to the performance of the MO, a combination of ZDDP with MoDDP or MoDTC additive should be considered for future work aiming to improve the tribological performance of vegetable oil.
- Much more development needs to be done on formulating vegetable oil based lubricants for them to be viable alternatives to hydrocarbon-based lubricants.

Lubricants	Mass loss (mg)	COF	Surface Waviness, Wa (µm)	Surface Roughness at M2 point, Ra (µm)	Viscosity at 100 °C (cP)	Oxidation Time (min)	TAN (mgKOH/g)	Zn (wt%)	O (wt%)	Zn (ppm)	B (ppm)
MO	0.65	0.093	1.4	0.06	12.32	270	2.24	0.9	10.43	781	43
ZD:SBO	18.26	0.099	17.16	0.23	7.36	60	2.53	0.09	2.85	1129	0
ZD:PO	24.99	0.095	29.08	0.24	7.98	140	1.98	0.03	2.25	1153	3
hBN:SBO	37.72	0.116	30.88	0.38	7.08	20	1.21	-	1.71	65	357
SBO	42.73	0.112	36.29	0.27	7.1	20	0.98	-	1.43	3	1
hBN:PO	43.61	0.111	35.72	0.32	7.85	40	0.44	-	1.52	65	342
PO	45.76	0.105	41.43	0.26	7.78	30	0.24	-	1.17	1	2

Table 5- Summary of friction and wear results in relation to other experimental data

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