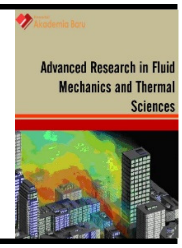
Journal of Advanced Research in Fluid Mechanics and Thermal Sciences 33, Issue 1 (2017) 1-13

Penerbit Akademia Baru

Journal of Advanced Research in Fluid Mechanics and Thermal Sciences

Journal homepage: www.akademiabaru.com/arfmts.html
ISSN: 2289-7879



Tribological properties of biodegradable nano-lubricant

Open Access

Darminesh Sathuramalingam Pillay [1,*], Nor Azwadi Che Sidik [1]

[1] Faculty of Mechanical Engineering Universiti Teknologi Malaysia, 81310 Johor, Malaysia

ARTICLE INFO

Article history:
Received 21 March 2017
Received in revised form 31 May 2017
Accepted 20 June 2017
Available online 24 June 2017

Keywords:
Biodegradable lubricant, nano lubricant, tribological properties

ABSTRACT

The biodegradable or vegetable oil possess good chemical properties competitive with mineral oil which can used as alternative lubricant. However, the vegetable oil has poor performance of tribological characteristics at high temperature and oxidation which causes the vegetable lubricant not used widely in industrial sector. To optimize lubrication, the vegetable oil can be mixed with hybrid additives. In this paper, RBD palm olein and soybean oil was mixed with single and hybrid additives which has been tested to determine its lubricating properties. The additives which has been used for the study was zddp and copper oxide nanoparticles. The mixing percentage of zddp has been fixed with 1% optimum whereas the copper oxide nanoparticles varies from 0.75% to 1% of the total mass. Testing has been conducted using fourball tribotester based on ASTM D4172 standard condition. The result shows that formulated palm olein lubricant with hybrid additive with zddp and CuO nanoparticles at 0.75% and 1% respectively provided 54.6% of WSD reduction, 29.2% COF reduction and smooth surface roughness compared with base RDB palm olein and soybean oil. However, in term of WSD and surface roughness, the mineral lubricant possesses better performance expect COF value of hybrid additive lubricant possess better value. From this results, it can be concluded that the performance of vegetable lubricant could be better enhanced with hybrid additives and its tribological characteristics competitive with conventional mineral lubricant.

1. Introduction

The environment threat provided by the mineral oil as lubricant causes the vegetable oil becomes the next alternative solution. The vegetable oil based lubricants have its own merits and demerits. Vegetables oils are promising alternatives oils because of its several advantages such as renewable, environmental-friendly, easily manageable, simple manufacturing process and cheap. It has all the qualification as lubricants with its outstanding physical properties but poor thermo-oxidation property which has causes restriction for vegetable oil as lubricant at elevated temperatures [1]. One of the research conducted to investigate the base vegetable lubricant, the 100% palm oil fatty acid

* *Corresponding author.*
E-mail address: darminesh9108@yahoo.com.my (Darminesh Sathuramalingam Pillay)

(PFAD) has been tested on four ball tester which provides larger size of wear scar diameter compared with conventional hydraulic oil and mixture of PFAD + Hydraulic oil [2]. In the similar research, a comparison made with commercial stamping oil with Jatropha oil, RBD Palm Olein and PFAD which proven that nature condition of vegetable oil reflects greater wear scar diameter on ball tester bearing under extreme pressure compared with commercial lubricant [3]. Both results reflect in such manner because base vegetable lubricant has oxygen bond which cause oxidation on the four ball tester ball bearing and made the structure brittle with producing higher wear scar diameter.

Most of the research for the vegetable oil lubricant has been conducted to improve the thermo-oxidation property by chemical process or additives to enhance the characteristics equivalent or higher compared to mineral oil based lubricant. In recent days, many research has been conducted on the improvement method to enhance the performance of vegetable oil based lubricant. As the oxidation stability is necessary for the vegetable lubricant, ZDDP is the appropriate additive which improves the anti-oxidant and its excellent anti wear properties has been quickly recognized and many research has conducted investigation on tribology effect due to ZDDP addition. The 1% concentration of zddp with base oil on actual engine piston ring and its cylinder has enhanced the tribological properties at room temperature compare to base oil [4]. Moreover, the pure polyalphaolefine (PAO) lubricant with 1% concentration of zddp on cylinder-on-plate tribotester has shown 20% reduction of COF compared with base lubricant [5]. Other than that, the PAO with WS2 nanoparticles on reciprocating pin-on-flat tribotester has shown reduction of 70% of WSD and COF reduction and further addition of 1% zddp has further enhanced the friction reduction and anti-wear effect of the base lubricant [6].

The nanoparticles additive also exhibits good anti-wear and anti-friction properties on vegetable based lubricant. Copper oxide nanoparticles have been used widely in many researches as additive since it carries outstanding tribological properties, self-repairing, create a formation of protective film effect which reduce friction & wear and mainly its environmental friendly [7]. The coconut oil extracted lubricant added with optimum concentration CuO nanoparticles has reduce the COF and has smooth worn surface [8]. In the other hand, the palm oil based lubricant added with CuO nanoparticles have enhanced of AW and EP ability compared to chemically modified palm oil lubricant [9]. The CuO added with rapeseed oil has provided 31% enhancement on friction factor compared with SiO2 and conventional lubricant for metal forming process [10].

Furthermore, research conducted with 0.75 wt% concentration of hybrid nanoparticles or hybrid additives, TiO_2/SiO_2 with palm oil extracted TMP ester has exhibited improved tribological properties under EP compared with base oil and single additive nanoparticle of TiO2 and SiO2 [11]. This shows that hybrid additives have high potential to enhance the tribological properties of base vegetable lubricant. The purpose of this work is to determine the tribological effect of hybrid additives on base vegetable lubricant and conduct the comparison with conventional mineral lubricant.

2. Experimental Method

The experimental conduct has been divided into three main categories as shown in Figure 1. The first stage covers the base vegetable oil used, type of additives used and its preparation method. Then, the second stage the experiment with four ball tribotester conducted for the base vegetable oil and formulated vegetable oil. Based on the results, the tribological characteristics has been evaluated. Finally, the vegetable based lubricant compared with conventional mineral lubricant.

2.1 Preparation of Testing Materials

In this research, Refined Bleached Deodorized (RBD) Palm oil and Soybean oil has been used as base vegetable lubricant. The both vegetable lubricant has been added with two different type of additives which are zinc dithiophosphate (ZDDP) and copper oxide (CuO) nanoparticles. The ZDDP (T_20_3) has been supplied by Green Scientific Enterprise and it comes in liquid form which provides better homogenization with the base oil whereas the CuO nanoparticles has been supplied by mkNano with 99% purity. The concentration of the additives added into base lubricant are based on weight percentage (wt%) basis. The high performance dispersing instrument, Ultra-Turrax T25 has been used for the lubricant mixture after the preparation of base vegetable oil with required wt.% additives. The homogenizer speed set at 12000 rpm and maintain at 35℃ constantly throughout the mixture period of 30 minutes. The formulated lubricants shown in Table 1 used for the experiment conduct and classification based on the label provided.

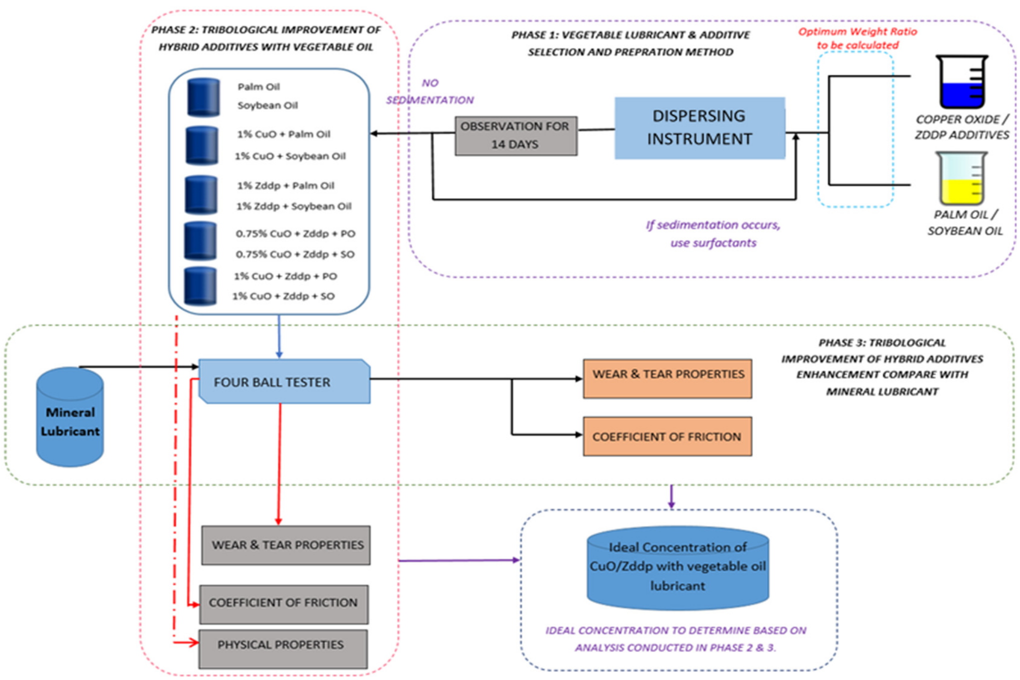


Fig. 1. Experiment conduct framework

2.2 Chemical Properties Analysis

The physical properties such as kinematic viscosity, viscosity index and density of base and formulated lubricants are important parameters to conduct comparison with conventional lubricant. The density of lubricant measured using Anton Paar DMA4100 density meter accordance to ASTM D1298-85(90) standard. Whereas, the kinematic viscosity determined according to ASTM D445-94 using the Townson & Mercer viscosity bath and reference to the kinematic viscosity at 40℃ and 100℃ the Viscosity Index (VI) of lubricants calculated based on ASTM D2270.

Table 1
Lubricant and its label

Label	Lubricant
S1	RBD Palm Olein
S2	RBD Soybean Oil
S3	PO + Zddp 1%
S4	SO + Zddp 1%
S5	PO + CuO 1%
S6	SO + CuO 1%
S7	PO + CuO 0.75% + ZDDP 1%
S8	SO + CuO 0.75% + ZDDP 1%
S9	PO + CuO 1% + ZDDP 1%
S10	SO + CuO 1% + ZDDP 1%

2.3 Tribological Testing and Surface Analysis

The COF was measured from four ball tribotester, Figure 2 shows diagram of tribotester used to evaluate friction coefficient of raw vegetable oil, formulated oil and conventional mineral lubricant. The tribotester connected with data acquisition system to set the desired running temperature and also to obtain the frictional torque created during the experimentation. The load applied on the ball bearing are manually based on the required load for the experiment conduct. The experiment conducted according to ASTM D4172 condition. The standard states that the three ball bearing with diameter of 12.7mm or 1/2 inch clamped and submerge with the lubricant. The fourth 12.7mm steel ball or referred as top ball pressed with force of 392 N into the cavity form by the three clamped balls for three-point contact. The temperature of the test lubricant regulated at 75℃ and the top mounted ball rotated at 1200 rpm constantly for 60 minutes.

The data acquisition system will provide the average COF after the experiment conduct completed for 3600s. However, during the experiment start-up, there will be high peak obtain in the frictional torque which cause the average COF result inaccurate. To obtain accurate results, the frictional torque obtain at steady state can be average and used to calculate the COF based on Equation 1.

$$\mu = \frac{T\sqrt{6}}{3\,W\,r} \tag{1}$$

where
μ: the COF,
T: frictional torque (kg.mm),
W: applied load (kg),
R: distance from centre of contact surface on lower balls to the axis of rotation

The wear scar diameter of steel ball has been analyses using the high power microscope connected with computer to capture the image of wear scar diameter. In this experiment, the Motic BA310 series microscope with high quality optical tube lens used to present good result and ease of comparison.

In the other hand, the depth of the wear scar diameter also measured to evaluate the performance of lubricants using the Mitutoyo Absolute Digimatic Heightgage 570 series comes with smooth slider which measures the arithmetical mean roughness (Ra) used to determine the smooth or rough surface of the wear scar on the steel ball.

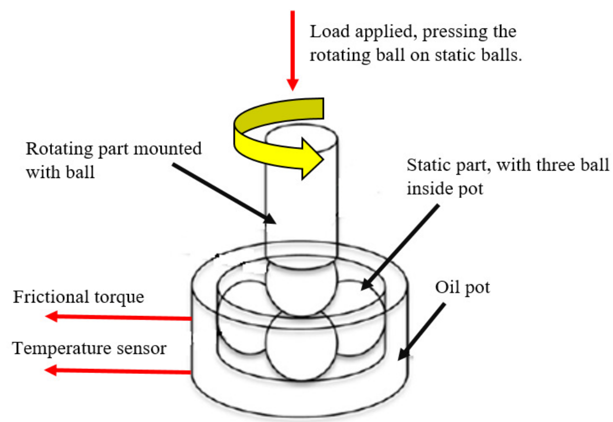


Fig. 2. Schematic diagram of four ball tribotester

3. Result and Discussion

3.1 Chemical Properties

Table 2 presents the information on test lubricants and also the conventional mineral lubricant. It has been found all the formulated lubricants possess very low kinematic viscosity at 40°C and 100°C than the mineral lubricant which has 150 cSt and 15 cSt. In this chemical properties testing, the base lubricant possesses high kinematic viscosity compared with other formulated expect the S7 lubricants which has similar visocity value. It has observed that the additive added slightly decrease the visocity. The reason of this issue is the lubricants preparation method which has used homogenizer at 35°C at 12000 rpm cause the reduction in the viscosity value.

The mineral lubricant possesses high kinematic viscosity but it has lowest viscosity index, 95 as compared with base lubricant and formulated lubricant which holds approximate nine times better viscosity index. This shows that the mineral lubricant is less stable at high temperature, as the lubricant tends to be thin as the temperature increases. This conclude that vegetable based lubricant are stable lubrication layer at elevated temperature condition.

3.2 Wear Scar Diameter (WSD)

Both of the base vegetable oil lubricant creates larger WSD compared with formulated vegetable lubricant with additives. This phenomenon occurs because oxidation reacts with steel balls cause the material to become brittle and generates high WSD. This oxidation can be clearly visualized in Figure 3(a) has the surrounding and also on the scar surface a lot of steel ball material chipped off due to steel ball material becomes brittle. The similar phenomena of material brittle can be visualize on Figure 3(b) steel ball which has been tested 1% CuO vegetable lubricants. However, the nanoparticles additive acts as protective film for base vegetable oil has reduced the WSD by 21.6% - 24%.

Table 2
Chemical properties of lubricants

Test Lubricant	Kinematic Viscosity @ 40°C, cSt	Kinematic Viscosity @ 100°C, cSt	Viscosity Index	Density @ 15°C,kg/m³
RBD Palm Olein	41.841	8.47	915.7	185
RBD Soybean Oil	31.571	7.535	923.7	221
PO + Zddp 1%	39.54	8.649	916.5	206
SO + Zddp 1%	32.164	7.878	923.9	232
PO + CuO 1%	40.89	8.382	917.1	187
SO + CuO 1%	32.677	7.625	925.2	215
PO + CuO 0.75% + ZDDP 1%	41.514	8.418	917.7	185
SO + CuO 0.75% + ZDDP 1%	32.58	7.468	925.8	208
PO + CuO 1% + ZDDP 1%	40.233	8.414	917.5	192
SO + CuO 1% + ZDDP 1%	31.604	7.606	926.2	223
Mineral lubricant	150	15	95	887

Other than that, the vegetable lubricant with 1% zddp presents lower WSD, reduced by 46.9% compared with base vegetable lubricant. This is because the zddp acted as anti-oxidant agent which enhance the tribological properties of vegetable lubricant as shown in Figure 3(c). Whereas the hybrid additive S7 and S8 lubricant shown in Figure 3(d) shown smaller WSD compared with single additive and base vegetable lubricant with presented 54.6% - 60.5% of WSD reduction and S9 and S10 lubricant shown in Figure 3(e) presented slightly higher WSD with reduction at 51.7% - 57.6%. The hybrid additives with 0.75% CuO and 1% zddp exhibits better tribology properties under this condition and it has eliminated the oxidation issue and also increase the film thickness of vegetable lubricant which provides less scar depth and smaller WSD.

3.2.1 Comparison between modified vegetable oil and mineral lubricant

The comparison between vegetable oil and mineral lubricant has been presented on Figure 4. The mineral lubricant has been created as base line to conduct the comparison. The results show that mineral lubricant has smaller WSD compared with hybrid additive added vegetable lubricant. This is because the mineral has been added with several additives to enhance its tribological properties. However, the different in WSD of mineral lubricant compared with S7 (palm oil + 0.75% CuO + 1% zddp) is only in average of 50µm which is minimum. Other than that, Figure 3(f) shows that surface smoothness of each lubricant is similar and no oxidation detected as both lubricant contains the anti-oxidant additives. Thus, in term of oxidation, WSD and surface smoothness, the S7 is competitive enough with S11, mineral lubricant. 3.2 Wear Scar Diameter (WSD).

Both of base vegetable oil lubricant creates larger WSD compared with formulated vegetable lubricant with additives. This phenomenon occurs because oxidation reacts with steel balls cause the material to become brittle and generates high WSD. This oxidation can be clearly visualized in Figure 3(a) has the surrounding and also on the scar surface a lot of steel ball material chipped off due to steel ball material becomes brittle. The similar phenomena of material brittle can be visualize on Figure 3(b) steel ball which has been tested 1% CuO vegetable lubricants. However, the nanoparticles additive acts as protective film for base vegetable oil has reduced the WSD by 21.6% - 24%.

Other than that, the vegetable lubricant with 1% zddp presents lower WSD, reduced by 46.9% compared with base vegetable lubricant. This is because the zddp acted as anti-oxidant agent which enhance the tribological properties of vegetable lubricant as shown in Figure 3(c). Whereas the hybrid additive S7 and S8 lubricant shown in Figure 3(d) shown smaller WSD compared with single additive and base vegetable lubricant with presented 54.6% - 60.5% of WSD reduction and S9 and S10 lubricant shown in Figure 3(e) presented slightly higher WSD with reduction at 51.7% - 57.6%. The hybrid additives with 0.75% CuO and 1% zddp exhibits better tribology properties under this condition and it has eliminated the oxidation issue and also increase the film thickness of vegetable lubricant which provides less scar depth and smaller WSD.

3.2.2 Comparison between modified vegetable oil and mineral lubricant

The comparison between vegetable oil and mineral lubricant has been presented on Figure 4. The mineral lubricant has been created as base line to conduct the comparison. The results show that mineral lubricant has smaller WSD compared with hybrid additive added vegetable lubricant. This is because the mineral has been added with several additives to enhance its tribological properties. However, the different in WSD of mineral lubricant compared with S7 (palm oil + 0.75% CuO + 1% zddp) is only in average of 50µm which is minimum. Other than that, Figure 3(f) shows that surface smoothness of each lubricant is similar and no oxidation detected as both lubricant contains the anti-oxidant additives. Thus, in term of oxidation, WSD and surface smoothness, the S7 is competitive enough with S11, mineral lubricant.

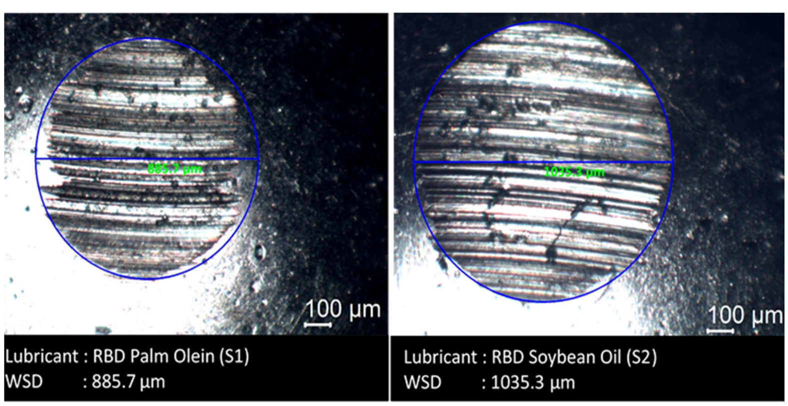


Fig. 3(a). WSD of S1 and S2 lubricants

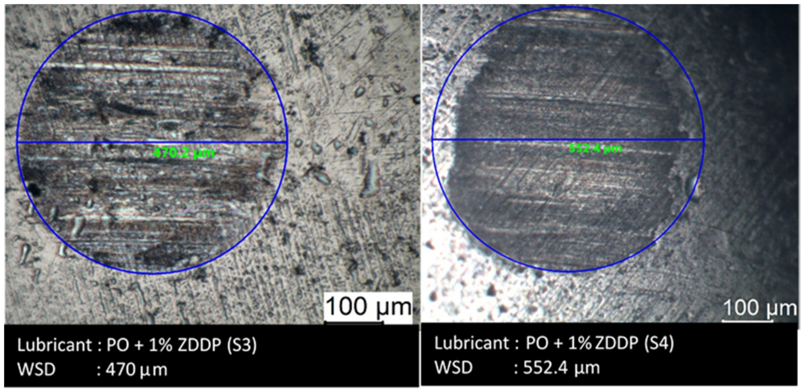


Fig. 3(b). WSD of S3 and S4 lubricants

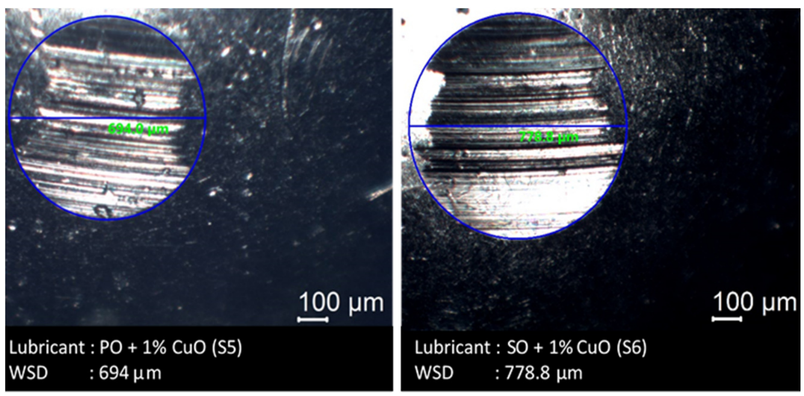


Fig. 3(c). WSD of S5 and S6 lubricants

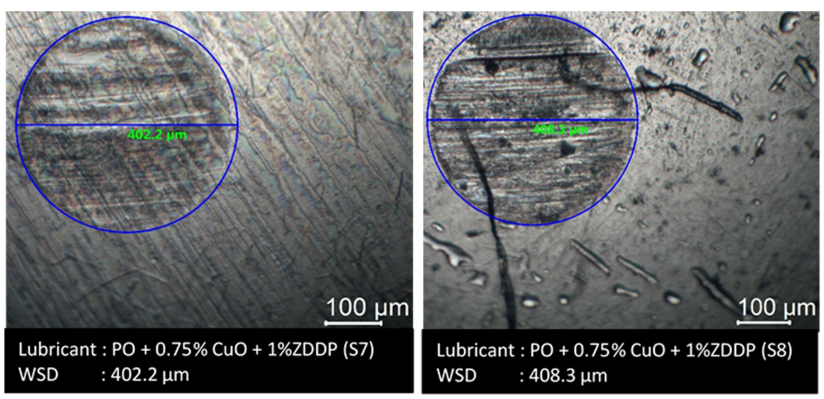


Fig. 3(d). WSD of S7 and S8 lubricants

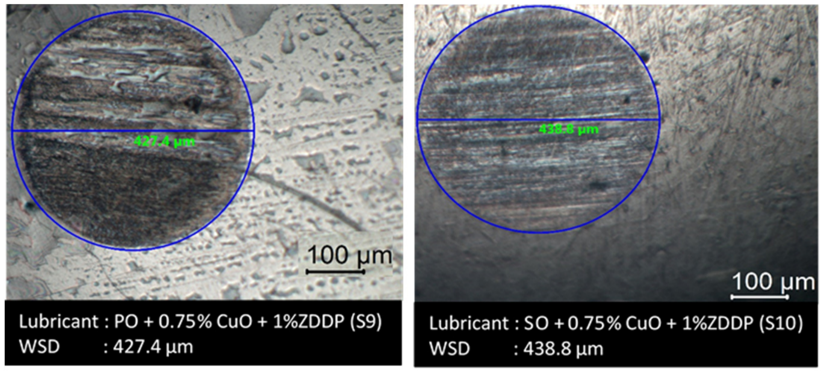


Fig. 3(e). WSD of S9 and S10 lubricants

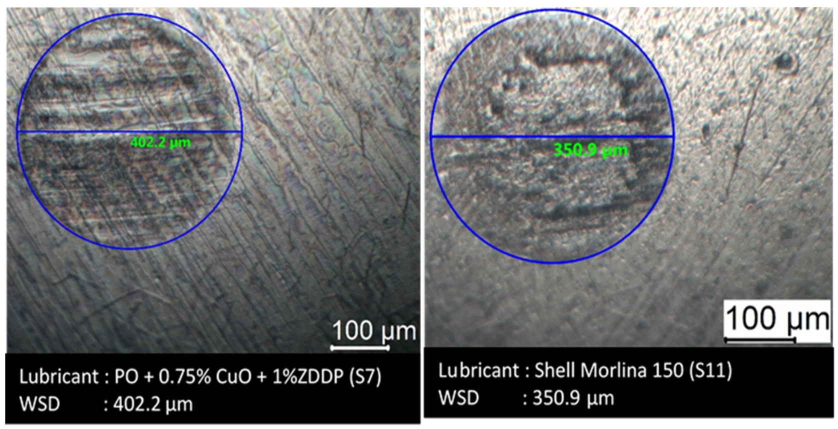


Fig. 3(f). WSD of S7 and mineral lubricants

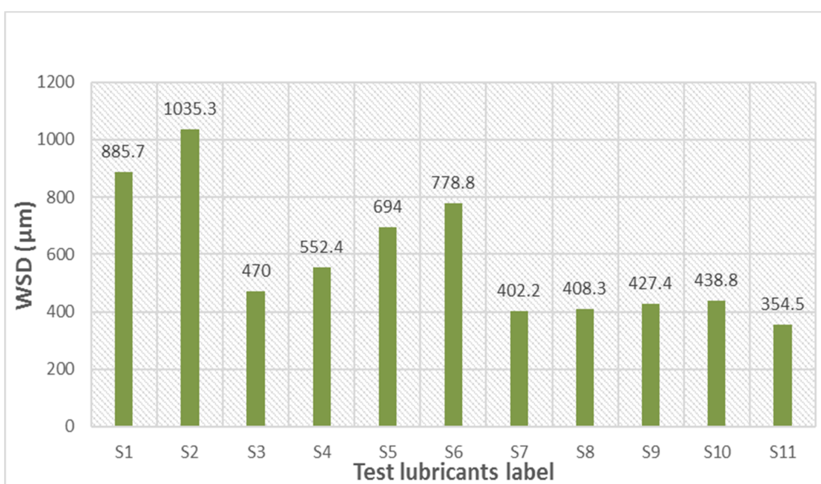


Fig. 4. WSD of vegetable based and mineral lubricant

3.3 Coefficient of Friction (COF)

The results computed by the system was the average COF and the steady state COF calculated based on Equation 1. The comparison of both average and steady state COF creates maximum difference of 6.7% only. This indicates that the average COF computes by the data acquisition system after experiment completion are valid for discussion. The results appear in Figure 5 represents the value of average COF but both COF charts has been presented.

The S3 and S4 lubricants shown higher COF compare other formulated lubricants. The COF results tabulated does not have any correlation with the WSD obtained. This is because the S3 and S4 provided better WSD compared with S1, S2, S5 and S6 lubricants. This is because the concentration of zddp increase in base oil creates weak interface between contacting surfaces, which offers less resistance to the applied tangential load and generates higher COF. However, the results of base oil show lower COF because the high scar depth causes the lubrication trapped inside the scar grooves which works as oil reservoir on mating surface and generates low COF. This phenomenon will be discussed further in surface roughness results section. However, the vegetable oil with CuO nanoparticles shown that the quasi spherical creates rolling effect mechanism between the two metal contact surface that causes low COF. In this COF performance, the S7 has exhibits lower COF compared with mineral lubricant. This results shows that 1% of CuO additive acts as abrasive agents giving rise to three body abrasion phenomenon causes higher COF compared with 0.75% CuO. The RBD palm olein with hybrid additives of 0.75% Cu0 and 1% zddp is the most competitive with mineral lubricant. However, this COF performance cannot be concluded as the surface roughness or grooves formation effects the COF results which will be discussed on the next section.

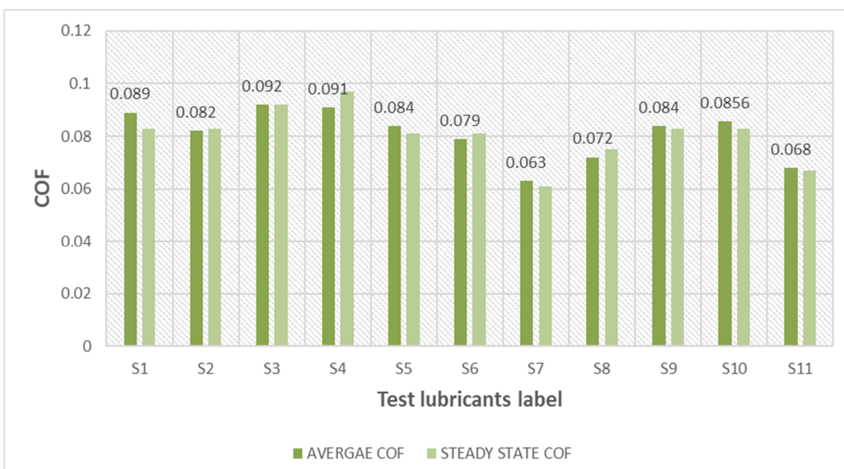


Fig. 5. COF of vegetable based and mineral lubricant

3.3 Surface Roughness

The steel ball arithmetic roughness value, Ra of about 0.029 µm before the experiment conduct. After the experiment in fourball tribotester, the worn track was observed carefully using the profiler to ensure that no wear particles or debris on the ball can influence the result. The surface pattern and average values of arithmetic roughness value, Ra has been measured after each individual test and all recorded and as shown in Figure 6 and 7 respectively.

In this surface roughness, the results of based lubricant, hybrid additive and mineral lubricant only has been studied. The main purpose of this conduct to evaluate the actual performance of hybrid additive vegetable lubricant compares with mineral lubricant. The groove depth shown in Figure 6 reflects great impact on the COF value. In the graph pattern Figure 7 shows that the S1 and S2 lubricant has lower COF compared with S3, S4, S9 and S10 lubricants because the deep groove on wear scar surface becomes lubricant reservoir causes reduction in COF value as shown in Figure 5. Other than that, the results indicate that 1% of CuO nanoparticles has created larger scar groove as it's because the hybrid additives with 1% concentration creates high abrasive reaction.

Theoretically, surface with high roughness, Ra has deep asperities or grooves while surface with low roughness has shallow groove or asperities. This relationship can be well related with Figure 6 and Figure 7 as the S1, S2, S9 and S10 has shown deep groove with high surface roughness. This can be concluded that COF results of those lubricant are slightly lower due to the grove acts as the lubrication reservoir. However, in other hand, the S7 prevails with smooth surface and low roughness compared to other vegetable based lubricant but the conventional mineral lubricant has low roughness, Ra. However, the surface roughness value difference between S7 and mineral lubricant is very minor which makes the S7 as competitive lubricant under ASTM D4172 condition.

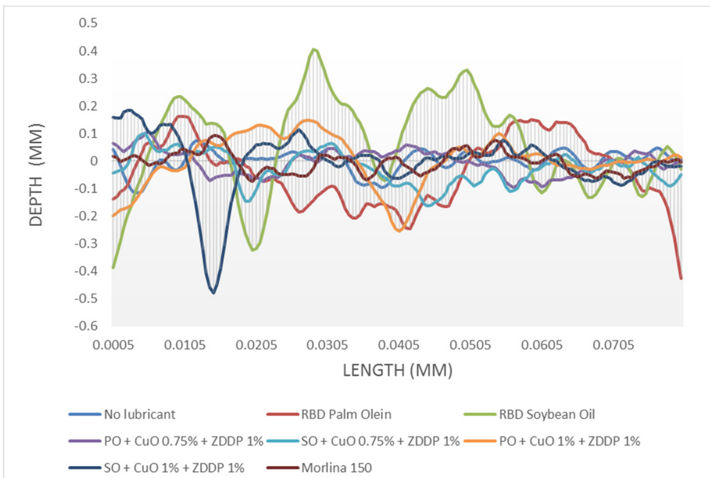


Fig. 6. Groove depth of WSD

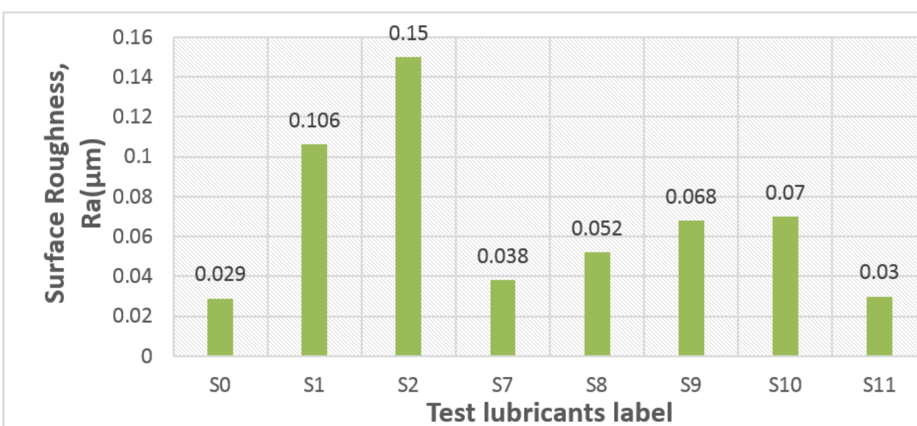


Fig. 7. COF of vegetable based and mineral lubricant

4. Conclusion

The conclusion of the research conducted as per below:

a) Under ASTM D4172 condition, it has been concluded that RBD palm olein based lubricant with 0.75% CuO and 1% zddp (S7 test lubricant) has improved the base lubricant performance with WSD reduction by 54.6%, COF reduction by 29.2% and lowest surface roughness with the smooth and shallow asperities on the wear scar. However, in term of WSD reduction the best enhancement was the RBD soybean oil based lubricant with 0.75% CuO and 1% zddp (S8 tested lubricant) reduction by 60.5%.

b) Under ASTM D4172 condition, it has been concluded that RBD palm olein based lubricant with 0.75% CuO and 1% zddp (S7 test lubricant) is a competitive lubricant with the conventional mineral lubricant. However, in term of WSD and surface roughness, the mineral lubricant possesses upper hand with 12.7% and 21% better performance respectively compared with S7 test lubricant. But, in term of COF, the S7 test lubricant prevails 7% lower COF value compared with mineral lubricant.

The overall conclusion is RBD palm olein based lubricant with 0.75% CuO and 1% zddp (S7 test lubricant) is competitive lubricant with good tribological properties compared with mineral lubricant under ASTM D4172 condition. However, the S7 lubricant should be tested on extreme pressure, various speed and various temperature. This experiment conduct is very crucial to understand the capability of the biodegradable lubricant with hybrid additive compares with mineral lubricant.

Acknowledgement
The authors wish to thank Universiti Teknologi Malaysia and the Malaysian Government for supporting this research activity.

Reference
[1] Mang, T., and Wilfried Dresel. "Lubricants and Lubrication Second, Completely Revised and Extended Edition." (2007).
[2] Syahrullail, S., M. A. M. Hariz, MK Abdul Hamid, and AR Abu Bakar. "Friction Characteristic of Mineral Oil Containing Palm Fatty Acid Distillate Using Four Ball Tribo-tester." *Procedia Engineering* 68 (2013): 166-171.
[3] Syahrullail, S., S. Kamitani, and A. Shakirin. "Performance of Vegetable Oil as Lubricant in Extreme Pressure Condition." *Procedia Engineering* 68 (2013): 172-177.
[4] Qu, Jun, Huimin Luo, Miaofang Chi, Cheng Ma, Peter J. Blau, Sheng Dai, and Michael B. Viola. "Comparison of an oil-miscible ionic liquid and ZDDP as a lubricant anti-wear additive." *Tribology International* 71 (2014): 88-97.
[5] Ito, Kosuke, Jean-Michel Martin, Clotilde Minfray, and Koji Kato. "Low-friction tribofilm formed by the reaction of ZDDP on iron oxide." *Tribology international* 39, no. 12 (2006): 1538-1544.
[6] Aldana, Paula Ussa, Fabrice Dassenoy, Beatrice Vacher, Thierry Le Mogne, and Benoît Thiebaut. "WS 2 nanoparticles anti-wear and friction reducing properties on rough surfaces in the presence of ZDDP additive." *Tribology International* 102 (2016): 213-221.
[7] Yu, H. L., Y. Xu, P. J. Shi, B. S. Xu, X. L. Wang, Q. Liu, and H. M. Wang. "Characterization and nano-mechanical properties of tribofilms using Cu nanoparticles as additives." *Surface and Coatings Technology* 203, no. 1 (2008): 28-34.
[8] Thottackkad, Manu Varghese, Rajendrakumar Krishnan Perikinalil, and Prabhakaran Nair Kumarapillai. "Experimental evaluation on the tribological properties of coconut oil by the addition of CuO nanoparticles." *International journal of precision engineering and manufacturing* 13, no. 1 (2012): 111-116.
[9] Gulzar, M., H. H. Masjuki, M. Varman, M. A. Kalam, R. A. Mufti, N. W. M. Zulkifli, R. Yunus, and Rehan Zahid. "Improving the AW/EP ability of chemically modified palm oil by adding CuO and MoS 2 nanoparticles." *Tribology International* 88 (2015): 271-279.
[10] Zareh-Desari, Behrooz, and Behnam Davoodi. "Assessing the lubrication performance of vegetable oil-based nano-lubricants for environmentally conscious metal forming processes." *Journal of Cleaner Production* 135 (2016): 1198-1209.

[11] Gulzar, M., H. H. Masjuki, M. A. Kalam, M. Varman, N. W. M. Zulkifli, R. A. Mufti, Rehan Zahid, and R. Yunus. "Dispersion Stability and Tribological Characteristics of TiO2/SiO2 Nanocomposite-Enriched Biobased Lubricant." *Tribology Transactions* (2016): 1-11.