A Review on Tribological Properties of Various Lubricant Mixtures and Additives

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Abstract **–Reduction of wear of all kind of mating substance in engine or any kind of machine parts is the important task in engineering application, in which role of lubricant is very important, for this various lubricant are used. Now the trend is diverted towards bio lubricants so as to reduce pollution and increasing prices of commercial oil. Here study of different possible combination of lubricant and additives has been carried out. The author used mixtures of different lubricants with different properties. Also some of them added additives in base oils to improve tribological properties, hence the study deals with combination of HDEO, ATF, TMP, PE, addition of MoS_2 and SiO_2 in base oil, addition of Al_2O_3 and TiO_2 in engine oil. The standard procedures used in this study are ASTM D2270 for viscosity test method and ASTM D4172 for four balls tribology test method. Mixture of HDEO and ATF produces better friction resistance as compared to the original HDEO. The benefit of ATF can be used for engine lubrication. In this study, polyol ester was used as the source of a bio-lubricant. The trimethylolpropane(TMP) and pentaerythritol ester (PE) were produced from palm oil methyl ester; they are biodegradable and have high lubricity properties. Two different conditions of lubrication were investigated. Under these test conditions, the wear and friction characteristics of different ester samples were measured and compared. The esters derived from PE and TMP had comparable characteristics to the fully formulated lubricant (FFL) in terms of the coefficient of friction. In terms of the mixed lubrication condition, the PE ester has the lowest Coefficient of friction.**

Keywords - Lubricant, Additives, Viscosity Index, Coefficient Of Friction.

I. INTRODUCTION

Engine lubrication is the process or technique to reduce wear of one or both surfaces in close proximity and it moving relative to each other by interposing a substance called lubricant between the surfaces to carry the load which mean the pressure generated between the opposing surfaces. In the most common cases the applied load is carried by pressure generated within the fluid due to the frictional viscous resistance to motion of the lubricating fluid between the surfaces. Lubrication can also describes the phenomenon such reduction of wear occurs without human intervention. Adequate lubrication allows smooth continuous operation of equipment with only mild wear and without excessive stresses or seizures at bearings. When lubrication breaks down, metal or other components can rub destructively over each other causing destructive damage, heat and failure. The lubricants mixtures benefit from properties of various lubricants. They are useful lubricants that can give best protection to the engine and reducing wear and friction generated from sliding between two contact surface when engine in started condition. Currently, there is no research to analyze the performance of lubricant mixtures. Aluminum and titanium oxides (Al_2O_3 and TiO_2) nanoparticles are the most appropriate for many environmental applications due to their excellent tribological, chemical and thermal properties. The addition of TiO_2 nanoparticles with lubricant oil showed stable friction due to the formation of protective films on worn surfaces. Also drivers and mechanics performed trial and errors in order to get the perfect mixture ratio between HDEO and ATF. They applied the lubricant mixtures and tried on the vehicle engine and compared the performance by observation during actual vehicle operation. However, the results of experiment are nerely subjective to the person’s opinion and feeling toward engine vibration, engine ignition condition and after used lubricant condition. Therefore, to prove their claims on the benefit of lubricant mixtures, a study on the lubricant mixtures is performed. The purpose of this study is to improve the lubricant ability in term of viscosity and thickness that can operate under critical conditions such as high temperature, maximum speed and high loads. This study is also carried out to prove the hypothesis of the benefits of mixture of HDEO and ATF to the performance of petrol engine.

The present study aims to investigate the effect of SiO_2 and MoS_2 nanoparticles on lubricity for magnesium alloy forming fluids under reciprocating sliding motion using a ball-on-flat contact configuration. Three sets of contact conditions were used to evaluate the effect of concentration, the capacity of carrying load and the stability of the lubrication film, respectively. After friction test, the morphology and composition of worn magnesium alloy surfaces were characterized by means of field emission scanning electron microscopy (FESEM) and X-rayphoto-electron spectroscopy (XPS). Correlations between tribological properties and morphology and composition of worn surfaces were found, there by improving our understanding of the behavior of nanoparticle addition to lubricating system.

II. METHODOLOGY

A. Tribological test for nano-MoS_2 and nano-SiO_2

The tribological studies were performed using a reciprocating ball-on-flat tribometer (CSM Instruments, Peseux, Switzerland) under different lubrication conditions .A flat, 10×20×3 mm3 in size, made from AZ31 magnesium alloy with the hardness of Hv=66.7 kgf/mm2. In order to concentrate all the wear on the oscillating AZ31 magnesium alloy flat sample,a hardened AISI52100 bearing steel ball (Hv=697717kgf/mm2) was used as a stationary counter body. The test results were evaluated in terms of the AZ31 magnesium alloy flat's wear volume and the average steady-state coefficient of friction.The contact area was lubricated before operation.Three sets of contact conditions were used to evaluate the effect of concentration (TestA), the capacity of carrying load (TestB) and the stability of lubrication film (Test C) , respectively. In order to study the effect of nanoparticle concentration on friction and wear (TestA), the concentration of nanoparticles by weight fraction in the oil was changed from 0.2% to 1.0%.These concentration values were established from the results of bibliographic research, where concentration of nanopar- ticles was in the range of 0.1–1 wt%. The normal load was selected as 3N corresponding to a maximum Hertzian contact stress of 312 MPa atleast 30% higher than the yield strength of AZ31 magnesium alloy sheets. The sliding speed was selected as 0.08 m/s which corresponds to the drawing speed in the metal forming process. The duration of tests was 0.5h. Second, the capacity of carrying load tests (Test B) were performed with loadings of 1,3,5, and 8N, corresponding to maximum Hertz pressures of 223,312,381 and 446MPa, respectively. Finally, in order to determine the stability of the lubrication film (Test C), the load was increased to 8N, and the sliding speed was reduced to0.03 m/s.

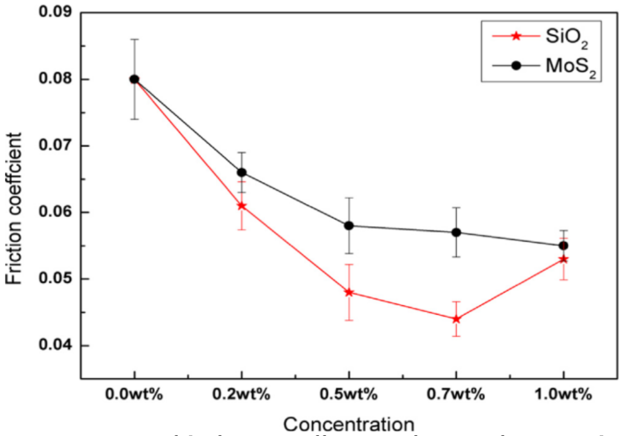

Fig. 2.1 Variation of the friction coefficients as function of nanoparticles concentra- tion. (3N, 0.08m/s, 30min).

During the test the friction coefficient was continuously monitored and an abrupt increase in the friction coefficient was taken as an indication of lubrication-film breakdown. Triplicate measures were done for each sample. Each experimental point represents an averageing of experiments.

B. Tribological test for Al_2O_3 and TiO_2

a).Materials-

Against the background that Al_2O_3 and TiO_2 are the most appropriate for many tribological applications (including solid lubricants) because of the excellent tribological behavior, these nanoparticles were chosen for the current investigation. Al_2O_3 and TiO_2 powders were purchased from Nanjing XFNANO Materials Tech Co., Ltd. The average sizes of the Al_2O_3 and TiO_2 nanoparticles were 8–12nm and 10nm, respectively. The varying concentrations of Al_2O_3 and TiO_2 used were 0.05, 0.1, 0.25 and 0.5wt% in the engine oil for each nanoparticle type. The tribological tests were conducted using of engine oil (Castrol EDGE professional A55W- 30, a commercial lubricant) to demonstrate the effect of using nanoparticles as engine oil additives. The compositions of the tested samples of Al_2O_3 and TiO_2 nano-lubricants.

b)Tribological test-

The important parameters which were measured and calculated to assess the tribological performance of nano-lubricants during experiments included the friction coefficient, power losses and the wear rate of the ring. To study the effects of load and speed on the tribological parameters between the piston ring/liner interface, the load was varied from 30 to 250N, which corres- ponds to contact pressures ranging from 0.65to5.43MPa,respectively, to clarify the lubrication regimes. However, this does not represent typically maximum pressures under normal running conditions for the engine. However, arrange of contact pressures (0.65 – 5.43 MPa) is represented the nominal radial pressure applied after combustion at 50% of maximum engine load. This is due to the combustion pressure in engine acting primarily on the piston crown and the back side and top surface of the first ring in the ring pack. To estimate the resulting contact force be- tween the ring to the liner is the difference between these pres- sures.The speed was varied from 50 to 800 r.p.m, corresponding to maximum mid-stroke velocities from $0.212ms^{-1}$ to $3.48\ ms^{-1}$, respectively. The stroke length was fixed at 65mm. The average reciprocating sliding velocity of the ring can be cal- culated with the known running speed, connecting rod length, and crank radius. The tribological experiments were conducted at an oil temperature of 100 °C, to simulate top dead center (TDC) position near the surface of the cylinder liner temperature. In this study, the compression ring was used for the tribological tests. The compression rings in the ring pack operate under oil starvation in most of the stroke because of the action of the oil scraper ring. This presents a prolonged mixed lubrication regime during the reciprocating stroke. In lubricant starvation, the.fig 2 The designed bench tribometer of the piston ring/cylinder liner interface.

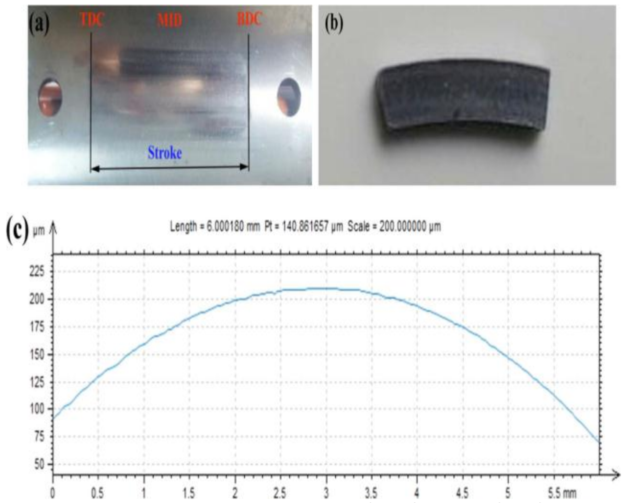

Fig. 2.2. The test specimens (a, b)and profile of running face for piston ring(c).

Pressure of the lubricant in the outlet region does go down dras- tically. Consequently, to simulate the characteristics of the compression ring lubrication under oil starvation, the amount of lubricant supplied to the interface between the ring and the liner should be a limited to a small amount (4ml). More over, the effect of lubricants tarvation greatly reduces the film thickness, and is likely that this starvation condition could help in confirming the effect nano-lubricants. Before testing for wear, piston ring specimens were ultrasonically cleaned in acetone for15min and dried to remove any contamination on surfaces. The wear results during this in- vestigation have been presented in terms of specific wear rate which were calculate dusing the following formula

$$\text{Specific wear rate} = V/Fn\ S$$

where, *V* is worn volume (mm3), *Fn* is the applied load on ring (N) and S is the sliding distance (m). The exten to f wear for the ring was determined via the profiles of the worn scar cross-section measured using a surface profilometer. A details description of this measurement was published. Each friction test was carried for duration of 20min. The friction and wear tests were carried out atleast three times under the same conditions in an attempt to replicate experimental results, after which the average results were taken to minimize measurement error.

C. Tribological test on mixture of HDEO and ATF

The properties of the lubricants are shown by .The mixtures of lubricants are homogenized using Wise Tis homogenizer HG-15D machine .The mixtures are content of percentages of ATF and HDEO as shown by The sample is mixed in 60 ml sample bottle and homogenized at 4000 rpm spinal speed. The viscosity of each sample is tested using standard ASTM D2270 practice. Viscosity meter is used to measure the kinematic viscosity at 40 ºC and 100ºC. The viscosity index is determined using Equation (1). The four-ball tester machine (Fig. 1c) is use following the ASTM D 4172 standard of tribology testing. The testing conditions are shown by Table 3. The three steel balls with 12.7 mm diameter are clamped together and covered with the lubricant mixtures. Different forces starting at 147 N and then 392 N are applied into the cavity formed by the three clamped balls for three point contact. The temperature of the test lubricants mixtures is set at 75□C and the top ball is rotated at 1200 rpm for duration of 60 min. The scar diameter is compared between all samples using inverted microscope.

$$VI = [(L - U) / (L - H)] \times 100 \ldots\ldots (1)$$

Where,
L = Kinematic viscosity at 40°C of a lubricant of 0 viscosity index having the same kinematic viscosity at 100°C.
H = Kinematic viscosity at 40°C of a lubricant of 100 viscosity index having the same kinematic viscosity at 100°C.
U = Kinematic viscosity at 40°C of the lubricant whose viscosity index is to be calculated.

D.Ttribological test of bio-based lubricant

a)Lubricant sample preparation

In this investigation, TMP ester and PE ester were compared to paraffin oil and fully formulated lubricant (FFL). Table 1 presents some of their physical properties. The TMP ester and PE ester were synthesized by the transesterification of methyl esters prepared from palm oils (POME) with TMP and PE respectively, as shown in Fig. 1 and Fig. 2. A 200 g volume of POME and a known amount of TMP and PE was placed in a 500 ml three neck reactor and constantly agitated using a magnetic stirrer. The weight of TMP and PE was determined based on the required molar ratio and the calculated mean molecular weight of POME. The mixture was then heated to the reaction temperature and the catalyst was added. A vacuum was gradually applied to the system until the desired pressure was reached. This pressure was maintained until the reaction reached completion. Table 2 shows the fatty acid content in the TMP ester.

TABLE I MAJOR PHYSICAL PROPERTIES OF DIFFERENT LUBRICANTS

Lubricant Type	Specific gravity at 15.6˚c (g/ml)	Viscosity (cSt)		Viscosity Index	TAN (mgKOH/g)
		40˚c	100˚c		
Paraffin oil	0.8283	30.61	5.26	110	-
FEL	0.8549	101.86	14.46	146	1.02
TMP	0.9021	40.03	9.50	194	0.44
PE	0.9300	68.40	12.70	183	0.20

TABLE II FATTY ACID CONTENT

Sources	Fatty acid (%)			
	Tetraester	Triester	Diester	Monoester
TMP	-	82	9	1
PE	52	36	-	-

b)Four-ball wear test

A four-ball machine was used to investigate the effect of esters under boundary and extreme pressure conditions. The four-ball wear tester is the predominant wear tester used by the oil industry to study lubricant chemistry. The device consists of three balls held stationary in a ball pot plus a fourth ball held in a rotating spindle, as shown in Fig. 1. The balls used in this study were steel balls, AISI 52-100, 12.7 mm in diameter, with a hardness of 64–66 RC. The balls were thoroughly cleaned with toluene before each experiment. The sample volume required for each test was approximately 10 ml.

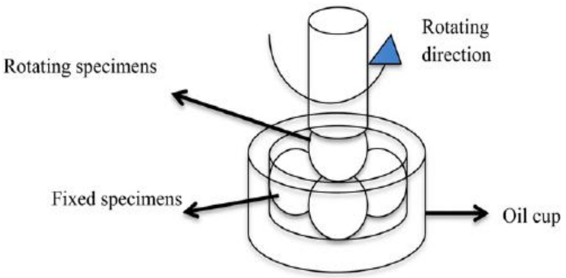

Fig. 2.3. Schematic of the four-ball test machine

To determine the anti-wear characteristics, the test conditions were a 392 N load, operation at room temperature, a rotational speed of 1200 rpm, and an operation time of 60 min. The wear produced on the three stationary balls was measured using a calibrated microscope and reported as the wear scar diameter (WSD)or calculated volume.

For the extreme pressure conditions, the test standard was ASTM 2783. In the machine, a vertical driving spindle rotated a chuck with a speed of 1770 rpm. The load was increased by 196 N every 10 second until the ball was welded. Seizure was indicated by a sharp rise in the coefficient of friction. A number of tribological parameters were determined using the standard procedures prescribed by the manufacturer. Each test was carried out three times to determine the experimental error. Error measurements specified in this experiment were based on the maximum deviation between three measurements.

III. RESULTS

A . Results of tribological test for MoS2 and SiO2

It has been noted before that friction coefficient of nanoparticles is highly dependent on concentration. Fig. 2 shows the friction coefficients of the dispersed oil with varying concentrations of nanoparticles. According to Fi, it can be seen that the friction coefficient decreased with increasing concentration of nano-MoS_2, where as the friction coefficient of SiO_2 nanolubricants decreased first and then increased with increasing content of nano-SiO_2. Therefore, when the amounts of nano-SiO_2 reach an optimal concentration, obvious friction-reduction effect is acquired. If excess nano-SiO_2 was added in to the base lubricant, nano-SiO_2 would tend to form irreversible agglomerates, and the agglomerates between the contact interfaces will result in worse friction reducing efficacy. The friction coefficient was reduced by 31.25% for 1.0 wt% MoS_2 nanolubricants and 47.5% for 0.7 wt% SiO_2 nanolubricants when compared to that found with the base lubricant. The outstanding friction reducing performance of SiO_2 nanolubricants could be attributed to the irnano-scale size and excellent dispersion in the base lubricant, and these characteristics allow the nano-SiO_2 to easily enter the contact area, there by preventing the rough surfaces from coming in to direct contact. In contrast, MoS_2 nanoparticles tend to aggregate due to their poor dispersion in the base lubricant, because no dispersants in our study were used in order to isolate the effects of the nanoparticles additives. On one hand, during the ball-on-flat contact, the central contact zone was pressed tightly, minimal MoS_2 nanoparticles could reach the center due to aggregation. On the other hand, the agglomerates between the contact interfaces will result in worse friction reducing efficacy. These are the main reason why the SiO_2 nanolubricants possess better friction reducing ability than that of the MoS_2 nanolubricants under the selected testing conditions.

B. Result for tribological test of Al_2O_3 and TiO_2

Tribological performance of Al_2O_3 and TiO_2 nano-lubricants presents the friction coefficient and frictional powerloss characteristics during one cycle of the crank shaft for an average sliding speed of 0.65ms^{-1} and 120N contact load using the best concentration of nanoparticles (0.25wt%). The variation in the friction coefficient with crank angle, represented by the negative part of the curveis due to the change in sliding speed direction during the reciprocating sliding motion. The mechanism of the friction different during one strokeowing to different lubrication regimes can occur in the stroke depending on running conditions. The boundary or mixed lubrication regimes occur near TDC and BDC, with hydrodynamic lubrication occurring at midstroke.

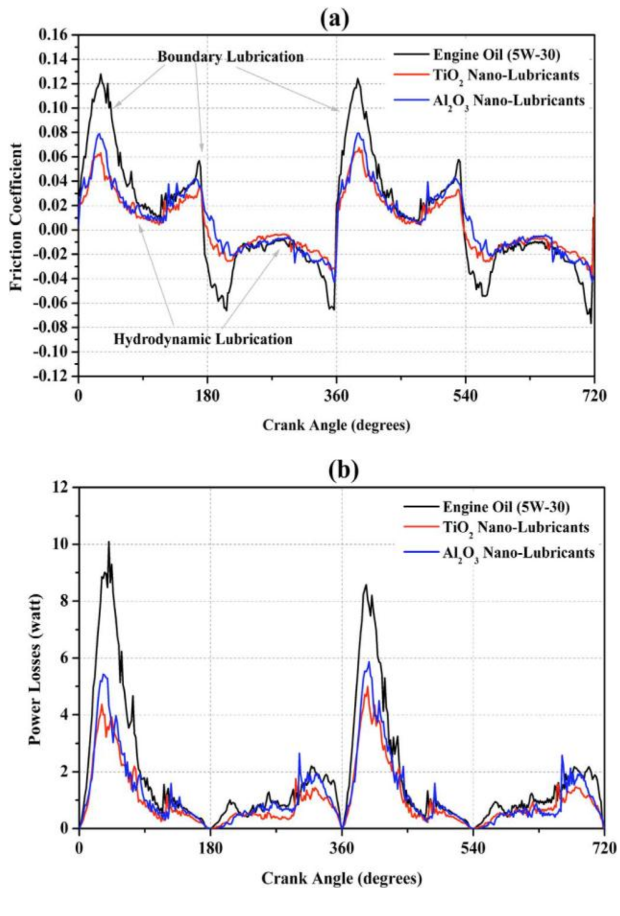

Fig. 3.1Tribological behavior of piston ring assembly versus crank angle with and without the use of nanoparticles as engine oil additives under the boundary lubrication regime:(a)Friction coefficient and (b)Frictional powerlosses.

The results showed that the maximum friction coefficient value was reached at TDC and BDC locations. The reason is related to the critically low sliding speed attained at dead centers, which pre- vents adequate access of the lube oil to these locations (boundary or mixed lubrication) and the increase in the metal contact be- tween worn surfaces (boundary lubrication). However, at the middle of the stroke minimum values of the friction coefficient were recorded because of the adequate access of the lube oil (hydrodynamic lubrication) as a result of the maximum sliding speed. In contrast, the maximum powerlosses were observed at mid-stroke location as shownin Fig. This might be due to the sliding speed reaching its maximum at mid-stroke causing an in- crease in the shear stress in the lubricant film, leading to an increase in the frictional powerlosses. This behavior reveal sanin- teresting aspect of the action of nano-lubricants.

C..Result for tribological test of HDEO and ATF

The value of VI was obtained by comparing the kinematic viscosity value of engine oil at 40ºC and 100 ºC, and the procedure for calculation is described in ASTM D 2770. Fig. 2 shows kinematic viscosity of the samples at 40ºC and 100ºC respectively. Fig. 3 shows the graph of viscosity index. From this figure, it shows that, the increment of percentage of ATF in the mixture reduce the viscosity index up until 50 %, but as the percentage of ATF increases from 60 % to 90%, the viscosity index is increase significantly. This is perhaps due to the property of ATF. At low percentage of ATF, the major contribution of viscous property is HDEO. However, ATF has reduced the viscosity within this range. At high percentage of ATF, the major contribution of viscous property is the ATF itself. Since ATF has better viscosity than HDEO, the major role in increasing the viscosity index comes from ATF. Fig. 4 shows the results of coefficient of friction for each sample. Zero % of ATF means 100 % of HDEO. From the graph, it is shown that, better friction resistance is at 20 % and 40 % of ATF mixtures. Other samples however, do not possessed significant improvement in friction resistance. Fig. 5 shows the graph of wear scar diameter for each sample. From this graph, it is shown that, the best result is at 40 % of ATF mixture where the scar is 454.36 m (Fig. 6), while full ATF lubricant produces 597.24 m and full HDEO lubricant produces 672.01 m (Fig. 7). From these results, the scar diameters are independent and not affected by percentage of lubricants in mixtures.

Table3 .Percentage of lubricants mixtures

Sample	HDEO(%)	ATF(%)
A	10	90
B	20	80
C	30	70
D	40	60
E	50	50
F	60	40
G	70	30
H	80	20
I	90	10
J	0	100
K	100	0

Table 4. Testing condition

Condition	I	II
Temperature	75±2oc	75±2oc
Speed	1200±60rpm	1200±60rpm
Duration	60±1min	60±1min
Load	147±2N	392±2N

D. Result for tribological test of bio based lubricant

The results will be divided into two different sections. The first section describes the extreme pressure condition and the second section describes the mixed lubrication condition. The experiments were repeated 3 times for each load to check its stability of the Coefficient of friction value. From the results, the value of mean and standard deviation for all lubricant, it is noted that when the load is fixed, the lubricant yielded consistent Coefficient of friction value over multiple runs. The maximum error is $8.58*10^{-3}$.

a)Extreme pressure condition

Fig. 2 shows the correlation of Coefficient of friction with different loads using paraffin oil. At low loads (below 392 N), the Coefficient of friction of paraffin oil is nearly unchanged. It shows that the thin film is formed can still sustain the load. However, as the load was increase, the thin film started to break down and the Coefficient of friction increased.

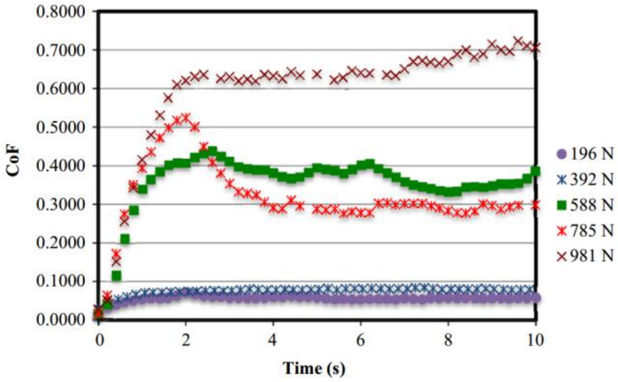

Fig.3.2. Variation in Coefficient of friction with load for paraffin oil (Error ± 0.02).

As the load increased up to 785 N, the Coefficient of friction increased sharply at the beginning and then decreased. This is possibly due to the “running-in” effect, in which the thickness of the oil film is too thin such that contact begins at the peak of the asperities, thus increasing both the Coefficient of friction and wear. This regime is known as boundary lubrication. In this regime, the contacting regions increase local pressures, which may lead to noise, fatigue damage, and high wear rates. The rubbing surfaces are thus smoothened and, at this latter stage, their wear rate is low and constant. At 981 N, the Coefficient of friction continued increasing until the ball welded. This occurred due to the high pressure and high temperature; the lubricant evaporates and causes the balls to weld together.

Fig. 3.3 shows the correlation of Coefficient of friction with different loads using FFL. Even at 981 N, the lubricant still did not encounter the initial seizure load. This shows that this lubricant has better extreme pressure characteristics compared to paraffin oil. It is believed that the extreme pressure additive package acted to maintain the low Coefficient of friction value.

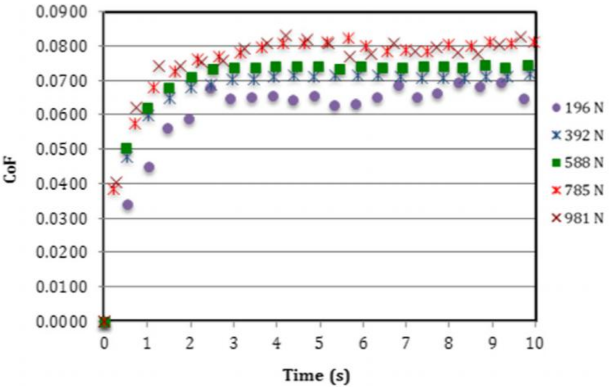

Fig. 3.3. Variation in Coefficient of friction with load for FFL (Error ± 0.02).

Fig. 4 shows the correlation of Coefficient of friction with different loads using TMP ester. It shows a similar trend to paraffin oil. However, the value of Coefficient of friction was lower compared to paraffin oil. The figure shows that the TMP ester had better extreme pressure characteristics compared to paraffin oil. However, TMP ester still had a higher Coefficient of friction compared to FFL.

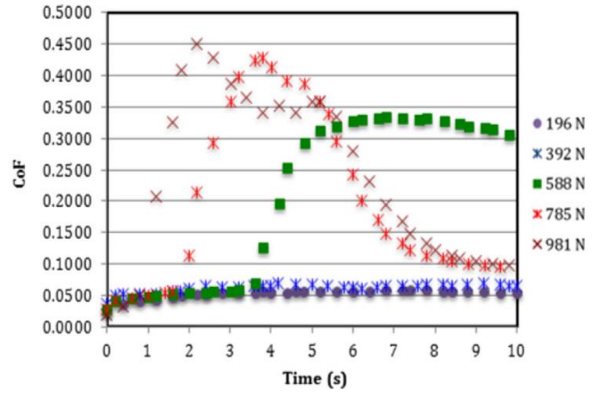

Fig. 3.4. Variation in Coefficient of friction with load for TML ester (Error ± 0.02).

In Fig. 3.5, it can be seen that as the load increased, the Coefficient of friction increased. In addition, the trend was also similar to paraffin oil and TMP ester. At low load, at 196 N and 392 N, the thin film formed by PE still can sustain the load applied. However, it can be seen that running-in effect started to occur. PE had the lowest Coefficient of friction and the best extreme pressure characteristics as compared to all other samples as the weld point for this case is higher than 981 N.

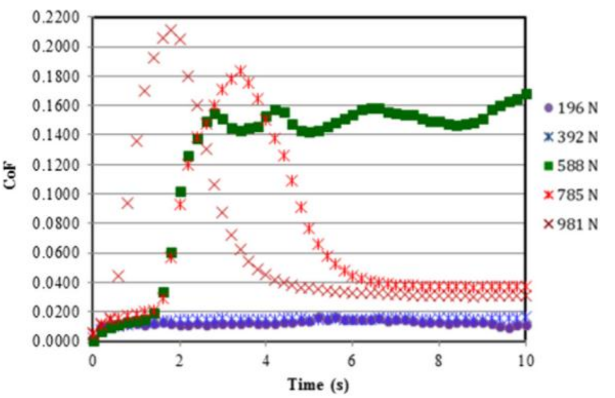

Fig.3.5. Variation in Coefficient of friction with load for PE ester (Error ± 0.02).

b)Mixed lubrication condition

From the above figures, as the load increased, the film thickness decreased, hence the lubrication regime changed from mixed lubrication to boundary conditions. At high contact loading, the stress intensity produced led to localized plastic deformation followed by initiation and the steep propagation of crack resulting in spall formation. The nominal film thickness formation is majorly dependent upon the lubricant viscosity, but at the same time the rheology and elastic and plastic surfaces deformation of interacting surfaces becomes significant at high contact temperatures. Such phenomenon results in instantaneous local film rise for even low viscosity lubricants as rubbing surfaces asperities are deformed to provide remaining reservoir of lubricant before the rapture of film. This may not be the case if the contact mechanism between interacting surfaces is changed. PE had the highest film thickness of around 0.054 µm, and paraffin had the lowest film thickness of around 0.028 µm. This could increase the life of steel ball with PE than that of with paraffin oil. Even though, FFL has low film thickness compared to TMP and PE esters, additive packages in the lubricant will help to protect the surfaces. Based on the lambda ratio, nearly all of the lubricants fall under mixed lubrication except for paraffin oil.

IV. CONCLUSION

1. .Nano-MoS_2 or nano-SiO_2 exhibit excellent lubrication properties as compared with the base lubricant .
2. Load carrying capacity of the base lubricant can be improved by the addition of the nanoparticles.The positive effect of the nano- MoS_2 is more pronounced under high contact pressures as compared with nano-SiO_2 because of extreme pressure effect.
3. The optimum concentration of Al_2O_3 and TiO_2 nanoparticles blended with the engine oil can reduced coefficient and wear rate of the ring by 11% and 2.6%, respectively.The frictional powerlosses were also reduced by 45% and 50% for the Al_2O_3 and TiO_2 nano-lubricants.
4. The wear rate of the piston ring was reduced by 21–29% for the use of TiO_2 and Al_2O_3 nano-lubricants respectively
5. The ATF had minor effect in reducing the viscosity of the mixture until 50 % of its content. . The mixture with 20 % and 40 % of ATF produce the best friction resistance compared to other mixtures, lubricant mixture resistance to friction is demonstrated by the result of coefficient of friction. The mixture with 30 % of ATF is superior in terms of wear resistance.
6. PE showed the lowest Coefficient of friction of around 0.025, even compared to ordinary lubricant at around 0.07.
7. From the above study, the bio based lubricant is more efficient than other lubricants and additives .Coefficient of friction is found to be minimum in bio based lubricant compare to HDEO , ATF and nano particle lubricant . In this study using TMP and PE as a bio based lubricant, under mixed lubrication PE shows lower most coefficient of friction than TMP. So PE ester is environmentally superior to mineral oil based lubricant.

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