Effects of Oil Additives on Friction and Wear Characteristics of DLC Coatings

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by

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A thesis submitted in partial fulfilment for the degree of
Doctor of Engineering

in the
DEPARTMENT OF MECHANICAL SCIENCE AND ENGINEERING
GRADUATE SCHOOL OF ENGINEERING

March 2019

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Abstract

One of the solutions to reduce friction between two sliding surfaces in automobile engine is by applying DLC coating to engine components. However, it is critical that the effect of lubricant additives to DLC coating to be clarified before hands as to avoid components failure. At the beginning, tribological friction test between SUJ2 balls and as-deposited plus UV irradiated a-C:H coatings was conducted to clarify the effect of ultraviolet irradiation to DLC coating in four different additives added lubricant oils. Atomic force microscopy (AFM, Nanopics 1000), nano-indentation hardness tester with Berkovich indenter (Elionix ENT-1100a), spectroscopic ellipsometery, non-contact three-dimensional scanning white light interferometry (Zygo, Newview), and energy dispersive spectroscopy-scanning electron microscopy (EDS-SEM, JEOL, JCM-5700NU) were used to investigate the effect of UV irradiation to a-C:H DLC before and after friction test. Prior the friction test, the results showed that UV irradiation presented no significant change in terms of hardness and roughness but the irradiation did penetrate into topmost surface of the a-C:H coating to several degree and could create dangling bonds to interact with lubricant additives elements. Friction test results showed that UV irradiated a-C:H coatings presented lower friction coefficient than as deposited a-C:H coatings. Worn surface analysis revealed that UV irradiated a-C:H coatings attracted more lubricant additives element to attach on its surface thus created thicker tribofilm on its own surface and its counter materials, resulted in lower friction coefficient than the as-deposited a-C:H coatings.

Subsequently, friction and wear behaviour of amorphous hydrogenated carbon (a-C:H) DLC coating slide against high carbon steel SUJ2, titanium carbide (TiC) and titanium nitride (TiN) mating material disks in Base and ZnDTP+MoDTC oils boundary

lubrication is comparatively investigated to determine the most favourable DLC/mating material/lubricant and interrelated tribofilm formation mechanism on each mating materials. Tribological tests were executed by utilizing roller on disk friction tester, nano-indentation hardness test, 3D optical surface profiler, and EDS-SEM were used to characterize the tribofilm formed on both worn roller and disk surfaces. The results showed that the wear volume of a-C:H/TiC tribo-pair in ZnDTP+MoDTC marked a tremendous wear volume reduction compared to than that of in Base oil. EDS investigation on tribofilm element investigation revealed that SUJ2 and TiN mating material disk attracted high concentration of Molybdenum at% on its surface that later caused high wear volume on both roller and disk sliding surfaces. TiC mating material disk however, formed a low at% yet helpful tribofilm consisting of a fraction of Zn (zinc) and P (phosphorus) from ZnDTP attached on both roller and disk which assisted the reduction of wear volume.

Furthermore, friction and wear properties of amorphous hydrogenated carbon (a-C:H) DLC coated bearing slide against alloy steel SAE4620, TiC and TiN mating material rings in Base and ZnDTP+MoDTC oils boundary lubrication was evaluated to identify the most suitable DLC/mating material/lubricant combinations by investigating the tribo-layers formation and compositions on each mating materials. Tribological tests were conducted by using the bearing on ring friction tester, 3D non-contact scanning white light interferometry, and EDS-SEM to characterize the tribofilm formed on the wear track of both bearing and ring surfaces. The results reveal that the a-C:H/TiC tribo-pair in ZnDTP+MoDTC gives the lowest friction and wear by providing the best lubrication mode for all three types mating material compared to than that of in Base oil. EDS analysis on tribo-layers element disclosed that SAE4620 and TiN mating material rings attract high concentration of Mo at% on its surface which reflected on the higher friction and wear results. Although traces of Molybdenum can also be detected on TiC mating material ring, significantly higher at% of Calcium from detergent on both bearing and ring helps to protect both the a-C:H and TiC coating thus further lower the friction and wear of the a-C:H/TiC tribo-pair.

Acknowledgements

First of all, I would like to express my sincere gratitude and respect to my supervisor, Prof. Dr. Noritsugu Umehara, for all I have learned from him and for his excellent guidance, continuous help, patience, motivation and support in all stages of this thesis. I would also like to thank him for being an open person to ideas, and for encouraging and helping me to shape my interest and ideas. Without his guidance and persistent help this dissertation would not have been possible.

I would like to thank my dissertation committee members, Prof. Dr. Kenji Fukuzawa, Prof. Dr. Hatsuhiko Usami, Assoc. Prof. Dr. Shintaro Itoh and Assoc. Prof. Dr. Takayuki Tokoroyama for sharing their ideas on the improvement of the thesis, and for their encouragement, insightful comments, and suggestions.

The success of this thesis is attributed to the extensive support and assistance from all members of Advanced Material and Manufacturing Laboratory. Especially, I would like to express my grateful gratitude and sincere appreciation to Assoc. Prof. Dr. Takayuki Tokoroyama, Asst. Prof. Dr. Motoyuki Murashima and Mr. Shinkoh Senda for their kindness in examining the research work and providing technical suggestions for improvement and encouragement during my time here.

My special thanks are given to my lab mates for their cheerful cooperation, encouragement, help and support and enjoyment during the course of my study. I hope our friendship will remain same in coming years.

This work is supported by Council for Science, Technology and Innovation (CSTI), Cross ministerial Strategic Innovation Promotion Program (SIP), "Innovative Combustion Technology" (Funding agency: JST). I would also like to thank Universiti Teknikal Malaysia Melaka (UTeM) and the Ministry of Higher Education (MOHE), Malaysia, for the financial support under the scholarship of Skim Latihan Akademik IPTA.

I would also like to offer my special thanks to my family, especially my mother and father for always believing in me, for their continuous love and their supports in my decisions. My special thanks are extended to my dearest wife, Alina Izura binti Salehuddin and my lovely children Aisy Syahmie, Faqihah Hannany and Umar Haruki. I am particularly grateful for the love and support, thank you very much for being in my life through hardness and through happiness. Without them, I could not have made it until this point.

Above all, I owe it all to Almighty ALLAH, creator and sustainer of the universe, for endowing me with wisdom, health, patience, and knowledge in exploring things to pursue this dissertation.

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1. Introduction

1.1 The importance of automotive tribology

Tribology is one of the specialty in the area of material science and mechanical engineering associating to the investigation of friction, wear and lubrication [1]. In the fields of transportation, industrial and power generation, significant quantity of energy was wasted merely to reduce friction and major economic losses as a result of parts and components wear and their substitution [2]. By implementing better tribological exercises in production industries, it is estimated that about 1.0 to 1.4% of total domestic product can be saved [3]. Hence, the continuation of great amount of investment in the tribology research is a necessity.

Based on the latest transport statistics by UK government, out of 36.5 million registered vehicles, 61% are petrol fueled, 38% diesel and the rest are hybrid and electric powered vehicles [4]. Fossil fuel currently enacts as main power source for typical internal combustion (IC) engine and expected to remain in the same position for another few decades. Even though IC engine is tremendously dependable and useful, it gives negative effects which affected the environment due to the harmful exhaust emission such as toxic particulate, nitrous oxide, hydrocarbon emissions and carbon dioxide that creates greenhouse effect [5]. Main engine parts such as piston assembly, valve train and journal bearings could cause significant energy degeneration due to unavoidable friction in relative motion. Frictional components will particularly experience high friction and severe wear during the stage of engine stalling and engine start-up.

As shown in in Figure 1.1, 33% of energy converted from fuel is consumed by the friction generated in and engine and 17% of that portion comes from engine and transmission friction losses [6]. Thus, it is necessary to enhance the tribological performance of IC engine for the sake of environmental and economic interests so that higher engine and fuel efficiency, lower harmful exhaust emission, higher durability and reliability engine can be achieved [7].

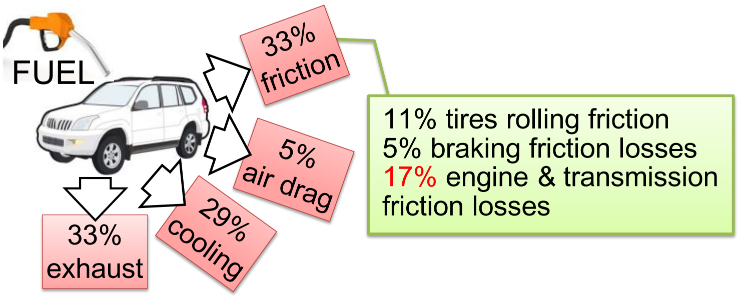


Figure 1-1 Vehicles fuel energy degeneration at approximated speed of 60 km/h [6]

To achieve high efficiency of machinery elements, a proper understanding of tribological concepts is important. As tribology examine mostly on sliding surfaces, appropriate surface engineering methods are needed most to enhance the tribological operation of a tribosystem and to lower the expense by utilizing low-cost substrate material [8]. Such engineering methods can be generally categorized into for parts: (1) Microstructural modification treatments [9]–[11]; (2) thermochemical diffusion treatments [12]–[14]; (3) surface topography modification treatments [15]–[17]; (4) surface coating treatments [18]–[20]. Due to the superior properties of diamond-like carbon (DLC) coating such as high in hardness, chemically inert, low in friction and highly wear resist both in dry and lubricated conditions makes it extensively recognized as adaptable protective coating material in automobile engine industry [21]–[23].

1.2 DLC coatings applications in automotive industry

DLC coating was initially utilized in the small scale surface thin film coatings to appliances such as microelectronics and magnetic hard disk. Thanks to the advancement of coating deposition technologies, the DLC coating application possibility has been widespread to large scale thick film coatings to automobile engine components. The deposition process of DLC coating can even be extended to be deposit on the low contact pressure frictional sliding components such as piston cylinder liner, valve lifter and cam follower as shown on Figure 1.2. For higher contact pressure frictional sliding component such as engine bearings, where the applied load keeps varying during the engine operation, DLC coating is expected to show outstanding tribological performance than any other coating material. However, in such operating condition, possible severe wear on the sliding surfaces could trigger seizure to occur and might leads to friction forces to increase abruptly. Seizure indicates to extreme adhesion between directly contacted surfaces which are in relative movement and can be activated at any sliding speed yet with high contact pressure [24]. In light of these mechanical demands, DLC coating is viewed as a favorable tribological material which can evade severe wear and preserve the low friction characteristics under the high load contact conditions, for example, engine bearings as shown in Figure 1.3.

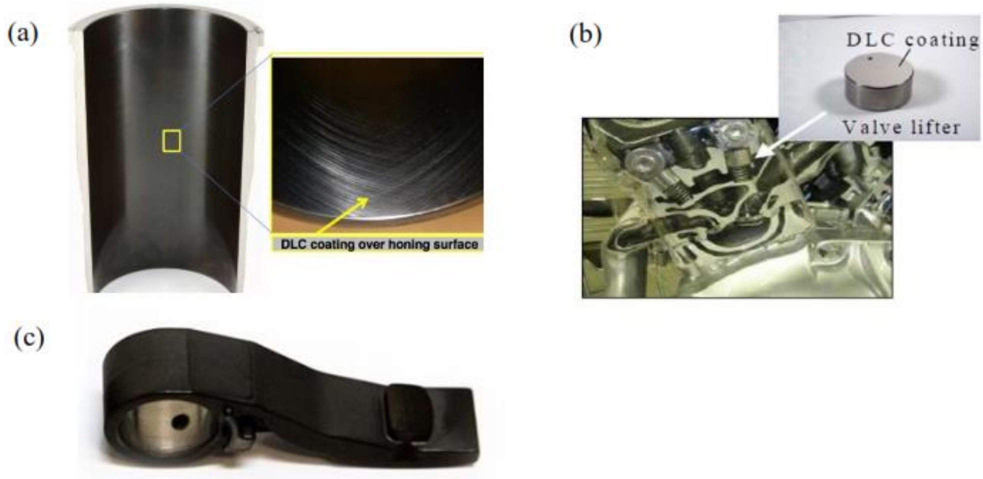


Figure 1-2 DLC coating on (a) cylinder liner, (b) valve lifter, (c) cam follower [25]

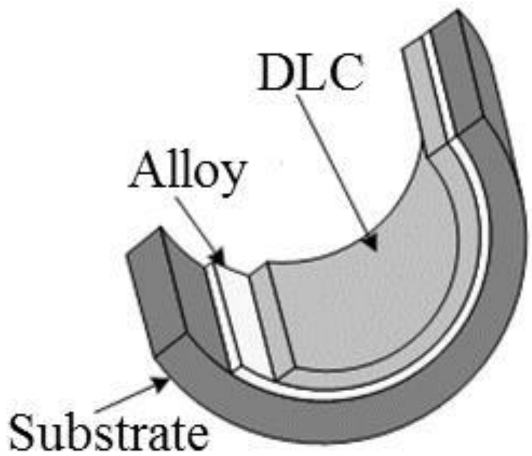


Figure 1-3 Inner surface of DLC coated engine main bearing

Friction and wear are defined as a tribo-system function and they are not a constant characteristic of materials can vary subjected to the working parameters (speed, load, temperature, humidity and so on), operating environments (dry, lubricated, oil with or without additives and so on) and type of mating materials [26], [27]. Inside one engine, typically engine bearing experiences variable high contact load at variable sliding speed in boundary lubrication conditions. Automotive industry at the present time tends to realize the ideas of light weight and less/zero emission vehicles. Hence, downsizing of petrol fuel engine capacity is thought to be one of the solutions [28], [29]. However, such downsized engines will normally couple with high air pressure induced turbo machinery to achieve the same output of torque curve of a modern, large-capacity engine. At such condition, the engine bearing will experience higher contact pressure and the possibility for seizure that caused high friction and wear or even breakdown to the engine bearing to happen is considerably high.

Real-world applications of specifically dedicated function engine components must be taken into account when executing tribological research. In this thesis, the engine bearing was selected to be the application models to elucidate the effect of several parameters on the tribological characteristics of DLC coatings. And by successfully executing this task, it is believed that DLC can be favorably applied for other harsh contact conditions.

1.3 Diamond-like carbon coatings

DLC film is an amorphous carbon thin film having both sp^3 bond composed of a diamond structure and sp^2 bond composed of a graphite structure. Young's modulus and hardness of DLC film are very similar to Young's modulus and hardness of diamond, and thermal conductivity is close to graphite. In addition to being high in hardness as mentioned above, it has excellent low friction characteristics, high wear resistance, etc., so it has been put to practical use in cutting drills, valve lifters for engines, etc. [21], [30]–[34]. In addition, Ferrari et al. classified the DLC by using a ternary diagram as shown in Figure 1.4 according to the differences in sp^2/sp^3 ratio and hydrogen content in DLC film [35].

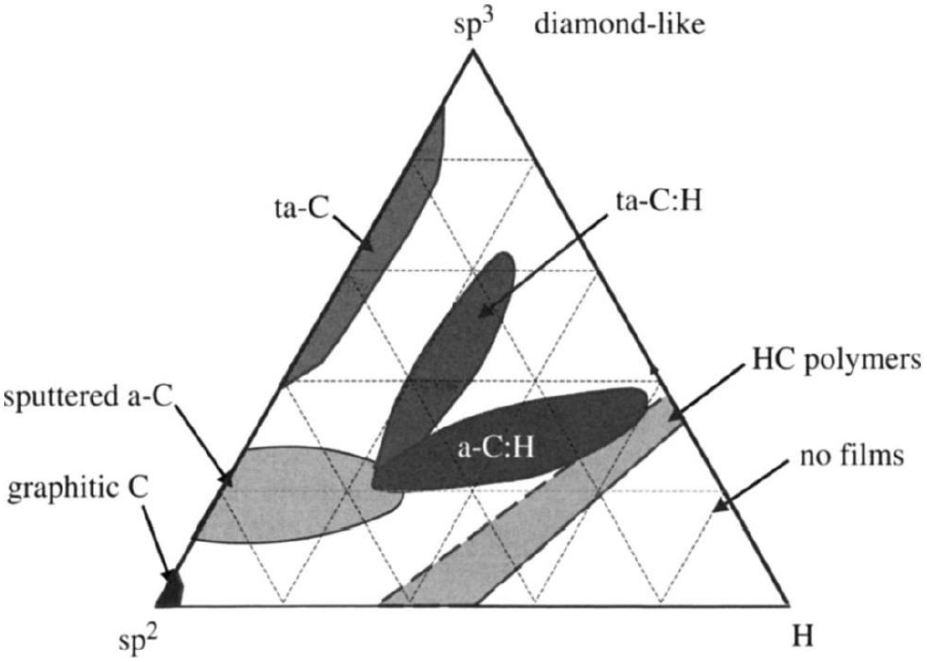


Figure 1-4 Classification of DLC film by sp^2/sp^3 ratio and hydrogen content [34]

Generally there are two main player in the world of DLC which are tetra-amorphous carbon (ta-C) and hydrogenated amorphous carbon (a-C:H). One of reports on excellent low friction characteristics and high abrasion resistance of DLC film are reported by Liu et al. They conducted a friction test in a dry environment using a various type of mating material for the DLC film. As a result, the coefficient of friction was 0.05 to 0.07 and the specific wear amount was 1.6×10^{-9} mm^3/Nm when the steel material was used as the mating material. Furthermore, Raman spectroscopic analysis reveals that the bonding structure of carbon in the DLC film is changed from the sp^3 structure to the sp^2 structure, and this lowered shear layer derived from graphite is the key factor of the low friction and high wear resistance property of the DLC film [36].

Many reports on excellent low friction characteristics and high wear resistance of DLC film in lubricating oil are also made. Podgornik uses a polyalphaolefin (poly-α-olefin, hereinafter referred to as PAO) as base oil and performs a friction test using a DLC film and a steel material under PAO lubrication, and it was reported that the DLC film shows higher wear resistance than the steel material [37]. In addition, Haci et al. conducted a friction test of SUJ2/SUJ2 tribo-pair and SUJ2/DLC tribo-pair under 4 types of oils that are PAO, PAO+GMO, PAO+ZnDTP and PAO+GMO+ZnDTP lubrication. Glycerol monooleate (GMO) and Zinc dialkyldithiophosphate (ZnDTP) are friction modifier and anti-wear agents oil additives respectively. As shown in Figs. 1.5 and 1.6, it was reported that the coefficient of friction of the SUJ2/DLC tribo-pair was lower than the SUJ2/SUJ2 tribo-pair with the lowest coefficient of friction of 0.03 [38].

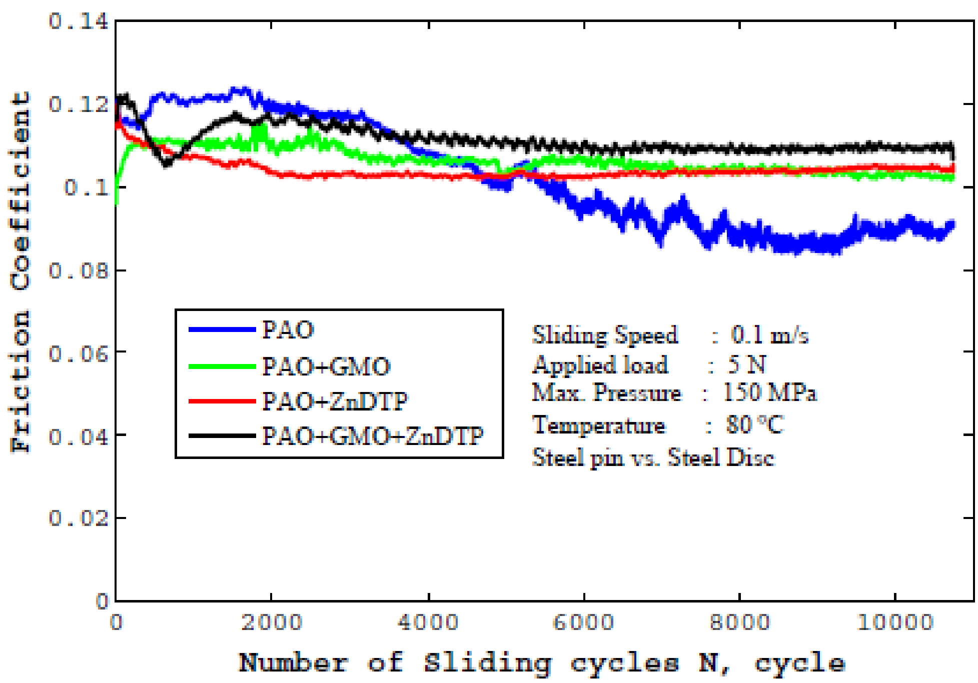


Figure 1-5 Friction coefficients of SUJ2/SUJ2 tribo-pair under PAO lubrication [37]

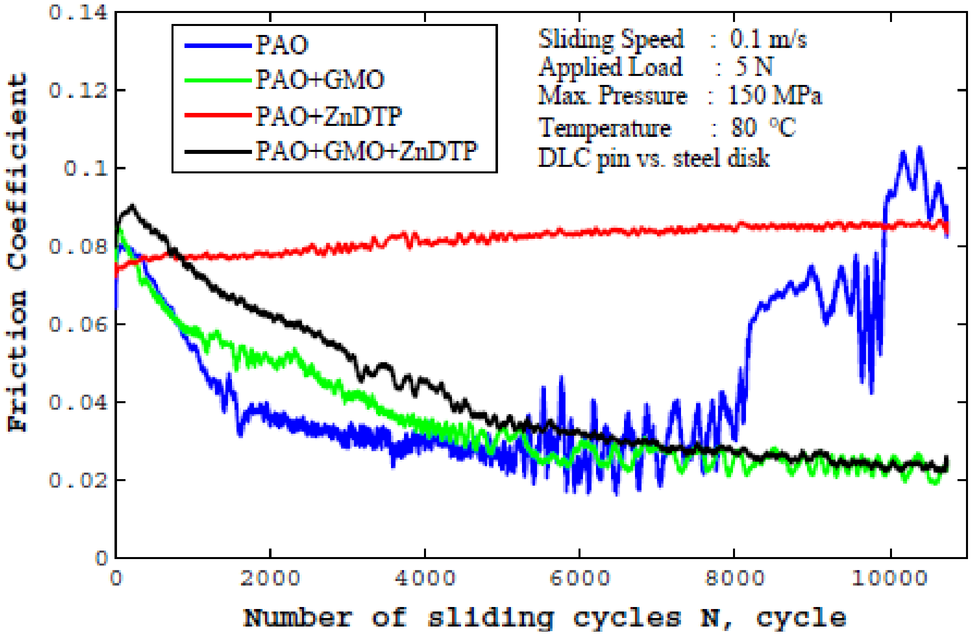


Figure 1-6 Friction coefficients of SUJ2/DLC tribo-pair under PAO lubrication [37]

Furthermore, Haci et al. carried out a friction test in PAO using four types of DLC films, and as shown in Figs. 1.7 and 1.8, the lowest coefficient of friction of 0.02 was obtained when the ta-C film was used, however the specific wear rate of Cr doped a-C:H (a-C:H:Cr), was significantly lower than the ta-C film [39]. In addition, Vengudusamy reported that the friction coefficient of the ta-C film was the lowest when the speed was low, however the wear resistance was much better when the a-C:H film was used [40].

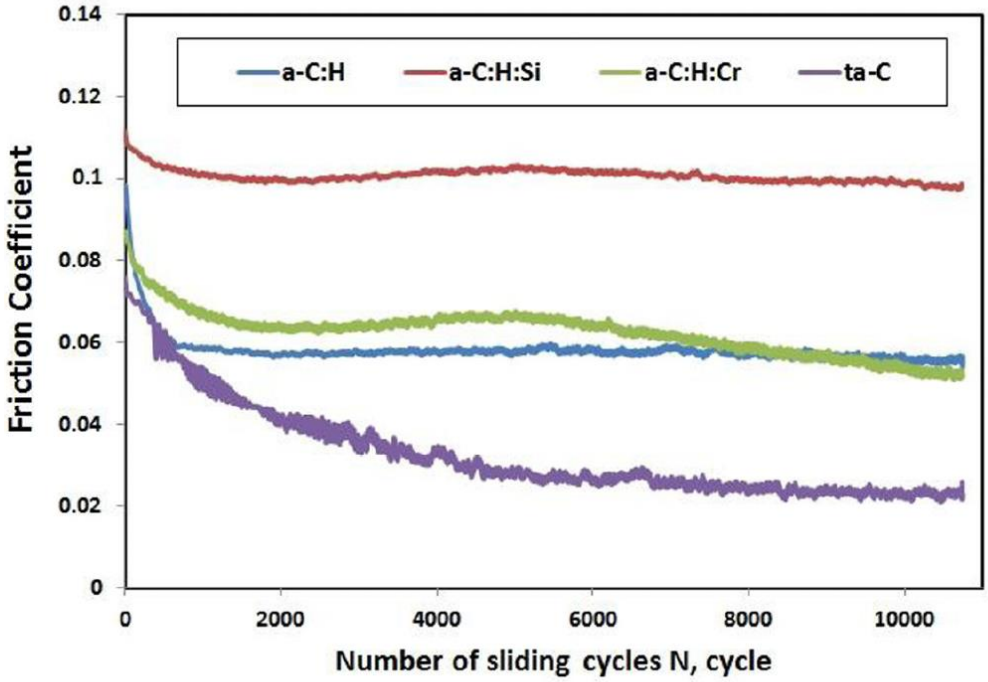


Figure 1-7 Friction coefficients of various DLC films under PAO lubrication [38]

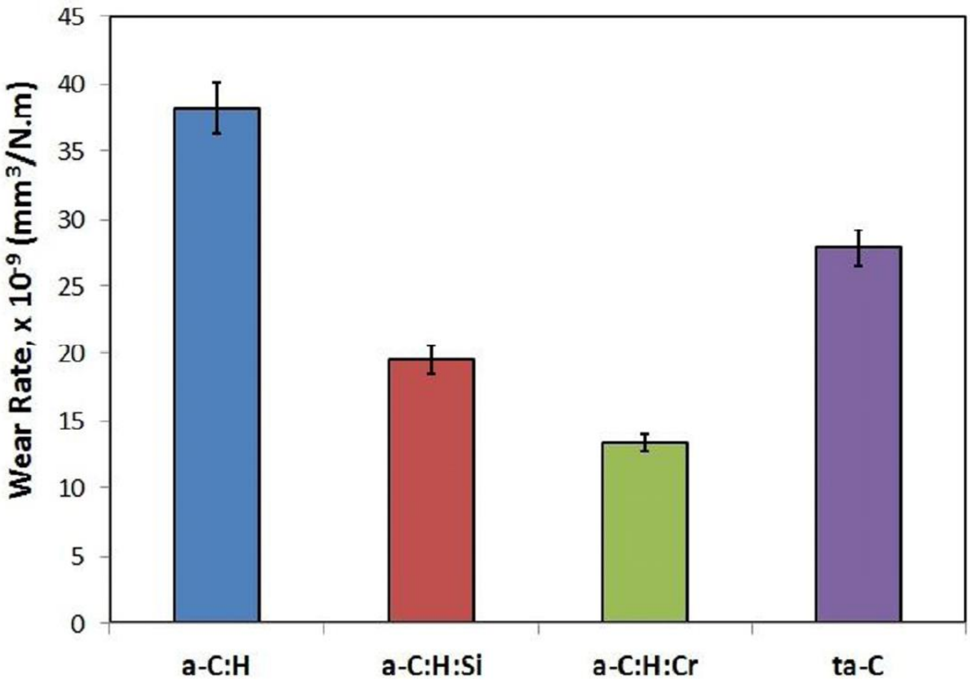


Figure 1-8 Specific wear rate of DLC film under PAO lubrication [38]

In the whole picture, ta-C coating shows high friction and wear in dry or vacuum condition but shows low friction and wear in humidity condition or additives-containing base oil boundary lubrication condition [38], [41]. Mabuchi et al. reported that the low frictional characteristic gained by the ta-C film was achieved thanks to the dangling bond that remains active without being terminated on the ta-C coating surface [42], [43]. However, due to its high hardness properties caused it to high in brittleness which then leads to high in wear. a-C:H on the other hand is a softer DLC and as result less wear happen during sliding. The hydrogen passivates the free dangling bonds on its surface and superior in dry sliding condition [44]. It was reported that a-C:H can show low friction and wear both in dry and vacuum condition however relatively higher friction and wear in the water and/or oxygen containing environments due to strengthened bonding at the sliding interface by oxidation of a-C:H films [45].

In this study, a-C:H coating was selected as the main DLC coating to be interacted with different oil additives added lubricant and mating materials. Main reason of the a-C:H selection among many other kinds of DLC coatings was to get closer to the real application condition in one engine where the deposition of the coating will be mainly on the non-flat curvy engine parts such as journal bearings and connecting rod bearings. The deposition process of such non-flat curvy 3D surface bearing requires for medium hardness coating such as a-C:H coating otherwise the coating layer will not be able to attach uniformly on the bearing surface causing one part to be thick and the others to be thin. Hard coating such as ta-C for an example mainly can be coated on flat surfaces.

1.4 Lubricant oil additives

Three main oil additives commonly formulated inside lubricant oil are and Zinc dialkyldithiophosphate (ZnDTP-anti-wear agent), molybdenum dithiophosphate (MoDTC-friction modifier) and Glycerol monooleate (GMO-friction modifier). Figure 1.9 shows the structure of the three additives. Previous study mentioned that ultra-low friction values achieved by hydrogenated DLC coatings under MoDTC contained lubricant is due to the formation of self-lubricating MoS_2 sheets [37], [46]. However, it caused higher wear rates than in pure base oil lubrication [47], [48]. However, with the presence of both MoDTC and ZnDTP in lubrication oil, the friction and wear properties of the DLC coatings can further be improved [49], [50].

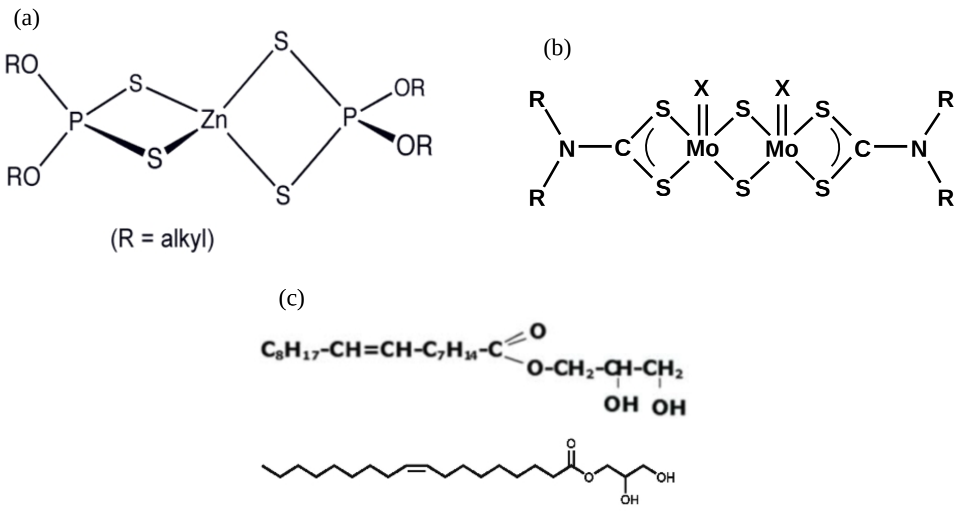


Figure 1-9 Structure of (a) ZnDTP, (b) MoDTC and (c) GMO additives

Another one type of friction modifier GMO gives more effect to stabilize friction and reducing wear of ta-C coating but shows not much difference for a-C:H coating [51]. For the hydrogenated DLC, the friction and wear progression is quite similar to the one obtained in pure PAO though both friction and wear appears to be marginally increased.

As for the hydrogen free DLC, the friction progression is significantly decreased lower than that of a-C:H as well as the wear rate however, stays higher than that of a-C:H. This indicates that GMO can act as anti-wear agent for ta-C coating.

Past study mentioned that anti-wear agent ZnDTP forms protective tribofilms on ferrous surface by the reaction of tribochemical [52]. On DLC coatings however, several reports indicates that weak tribofilm was formed on DLC coatings [53], [54] though some mentioned that no tribochemical reaction happens between ZnDTP and DLC coatings [37], [55], [56].

1.5 Purpose of this study

Main focus of this study is to find which approach can realize low friction and wear to a-C:H DLC. Previously there are various studies done on the effect of UV irradiation to DLC and being interacted either in dry condition or in PAO base oil. And previously there are various studies done looking on the effect of oil additives to DLC slide on metal mating material. However there are no study done looking on the effect of UV irradiated a-C:H in oil additives added lubricant oils. On top of that, no study has been done investigating on the effect of mating material, seizure load and sliding speed operated in additives added lubricant oil. So the main objectives of this study are as follows:

1. To clarify the effects of UV irradiation to a-C:H on friction and wear under oil additives added lubricant oil.
2. To clarify the effects of oil additives and mating materials to friction, wear and seizure of a-C:H coating.
3. To clarify the effects of oil additives, sliding speed and mating materials to friction and wear of a-C:H coating.

1.6 Outline of dissertation

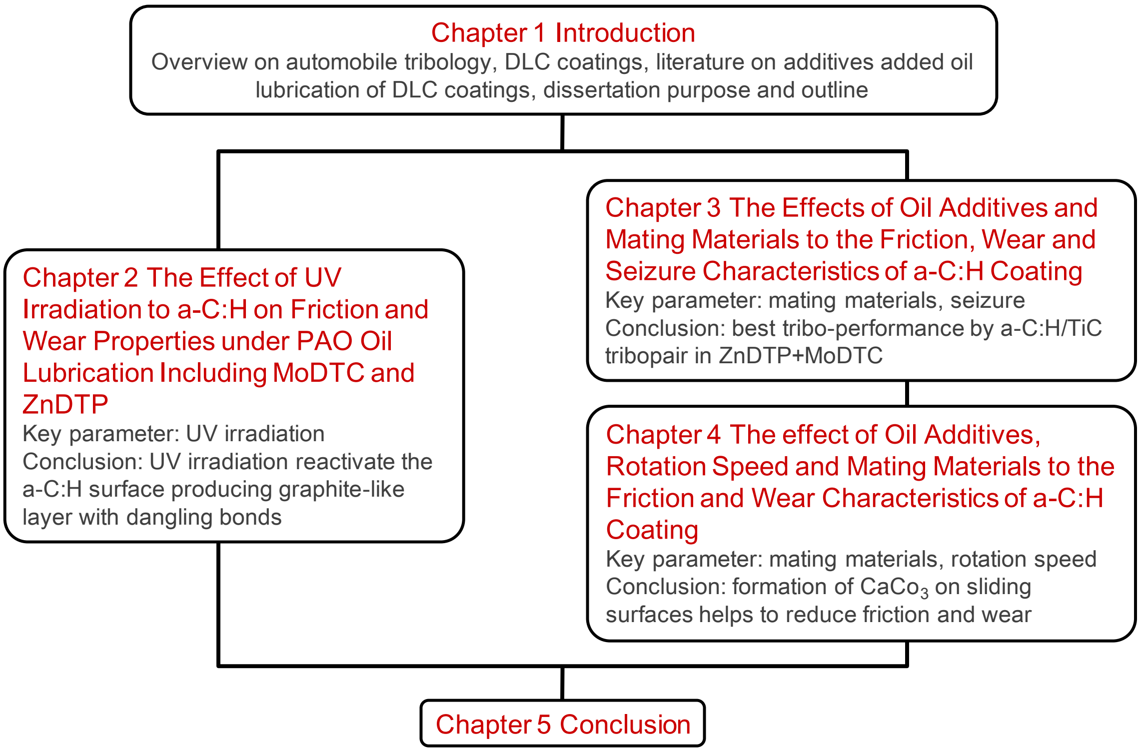


Figure 1-10 Organization of this dissertation

2. Effects of UV irradiation to a-C:H on friction and wear characteristics under oil additives added lubricant oils

2.1 Introduction

From the 100% of fuel that being poured into one vehicle, 33% of the chemical energy converted will be transformed into friction, and 17% of the previous percentage will be converted into engine and transmission friction losses [6]. One of the solutions to reduce these losses is by applying diamond-like carbon (DLC) to engine components so that higher engine performance, fuel efficiency and also harmful emission gas reduction can be achieved. DLC is an amorphous material which is a combination of both sp^2 and sp^3 structure and as a result, a superior material that has the properties of low in friction, high hardness, chemically inert and highly wear-resist. However, in order to apply DLC in engine components, one problem might happen which is the incompatibilities between DLC and the lubricant additives. This is due to current commercial lubricant containing various type of additives, designed only to cater the contact between metal to metal and not in between DLC and metal. If this problem is not solved, it ultimately will cause DLC coated parts failure.

Anti-oxidant and anti-wear properties of Zinc dialkyldithioposphate (ZnDTP) is one of oil additives that has been extensively used for a long time. In recent times, there are numerous studies regarding on the tribological characteristics of DLC films in ZnDTP oil lubrication [27], [37], [38], [53], [54], [57]–[59]. However, the reaction between DLC and ZnDTP are very much depending on the type of the DLC film used.

Studies showed that there was ZnDTP derived tribofilm formed on the DLC film [27], [53], [54], [58] and there was also some that reported on the non-existence of ZnDTP derived tribofilm on sliding surface of DLC film [37], [59].

Another studies reported that due to the existence of MoDTC in lubricant oils, the fraction of the anti-friction additives further accelerates the wear of DLC when rubbed against steel [49], [50], [60]–[64]. Haque et al. reported that the wears of DLC/steel contact were exceptionally high in MoDTC included lubricant oil however, the presence of anti-wear additive ZnDTP can dampen the effect of MoDTC thus reduce the wear [60]. The finding is consistent with findings of past studies by Tung et al., which summarized that in the lubrication environment of fully formulated oil, the availability of both MoDTC and ZnDTP can further reduce the friction and wear of DLC film compared to solely MoDTC included lubricant oil [61].

For the case of lubrication in glycerol mono-oleate (GMO), the mechanism for steel to steel contact is generally known as the Bowden-Tabor model. The friction modifier component comes from the hydrolysis product of GMO which then generates a long, straight chain of carboxylic acid. However, interestingly, this is contrary to some other studies reported that GMO produces a significant amount of friction reduction when contacted with DLC coating. Instead of forming carboxylic acid during the interaction, GMO contacted with DLC in the shape of ester plus the hydroxyl groups in the molecule enact an important part during the interaction [27], [65]. Although there were many researches about the reactions between DLC coatings and lubricant additives, only few focused on the effects lubricant additives to the ultra-violet (UV) irradiated DLC coating.

There have been several studies in the literature reporting on the effects of UV irradiation to DLC coatings. Tokoroyama et al. demonstrated that UV light will transforms the uppermost surface of DLC coating into graphite-like layer, resulting the light concentration to surpass the bonding energy of carbon to carbon, conjoins the produced dangling bonds, which in turn creates graphite-like layer at the uppermost surface of DLC [66]. The finding is consistent with findings of past studies by Zhang et al., which indicated that by conducting UV irradiation to DLC, the process escalates the carbon to carbon and carbon to nitrogen double bonding, and lessening the carbon to hydrogen bonding [67]. The research study by Gadallah et al. also found out that UV irradiation reduces the hydrogen composition and the ratio of sp^3 to sp^2 hybridization consequently produces a long graphene layers on the irradiated DLC coatings. They also discovered that graphite fibres forms on the processed DLC coatings [68]. In addition, according Ji et al., UV irradiation is able to lessen the cross-connection of the carbon affinity, and as a result reduces the friction and wear properties [44]. Again, it appears from the aforementioned investigations that numerous investigations have been conducted on the effects of UV irradiation to DLC coatings. Nonetheless, no attempt was made to investigate the effects lubricant additives to the ultra-violet (UV) irradiated DLC coating. In this investigation, UV irradiation process has been done to hydrogenated amorphous carbon (a-C:H), and their characteristics in terms of friction and tribofilm formation have been studied when lubricated by four types of additives added lubricant oil.

2.2 Materials and tests method

2.2.1 Hydrogenated DLC and lubricant additives

The a-C:H coating used in this study has 16% hydrogen content and was formed by a plasma enhanced chemical vapour (PECVD) method on the Si (100) substrate by about 1.8 μm. The surface roughness had a centre line average roughness Ra of about 8.2 nm and a maximum height roughness Ry of about 33.6 nm.

Four types of oil used in this study which is anti-wear ZnDTP included base oil, ZnDTP and anti-friction MoDTC included base oil, ZnDTP and anti-friction GMO included base oil and lastly unadulterated base oil. From this point onwards, these 4 types of oil will be referred as only ZnDTP, ZnDTP plus MoDTC, ZnDTP plus GMO and Base.

Base, ZnDTP, ZnDTP+MoDTC and ZnDTP+GMO oils are the four engine oils used as lubricant during the friction test. Inside all the additives added lubricant oils, apart from anti-wear agent from ZnDTP and friction modifier from MoDTC and GMO, the oils were also formulated with five common additives of detergent, anti-oxidant, foam inhibitor, dispersant and viscosity improver. Detail properties of each lubricant oils are tabulated in Table 2.1.

Table 2.1 Each lubricant properties

	Base	Base+ZnDTP	Base+ZnDTP +MoDTC	Base+ZnDTP +GMO
Viscosity mPa·s	4.25	5.90	5.92	5.90
Ca (wt%)	-	0.20	0.20	0.20
Mo (wt%)	-	-	0.07	-
P (wt%)	-	0.08	0.08	0.08
Zn (wt%)	-	0.09	0.09	0.09
S (wt%)	-	0.17	0.22	0.17
N (wt%)	-	0.09	0.10	0.09

2.2.2 UV irradiation and friction tester equipment

In this study, BioLink (Cosmo Bio, BLX-312) was used as a light source for generating ultraviolet rays. One type of discharge tubes (CST-8A) with spectral peaks of wavelengths 254 nm was used. The maximum UV irradiation energy was 99.99 Jules and the irradiation range was 260 mm × 300 mm. The atmosphere in the UV irradiation box was atmospheric air and the ambient temperature was room temperature.

Figure 2.1 shows a schematic diagram of the ball-on-disk friction test apparatus used in this research for the friction test under four types of lubrication. In the friction test, the load was 1.0 N corresponding to maximum initial Hertzian contact pressures of 455 MPa, the sliding speed of the two opposing surfaces was 6.28×10^{-2} m/s (200 rpm), and the atmosphere temperature was at room temperature. The atmosphere temperature at 24^{o}C was purposely picked to create the hardest environment for the tribofilm to be produced on the sliding surfaces which then allowing for significant differences to be seen between the as-deposited and UV irradiated DLC. The tests were then redone again at least 3 times for confirmation and reproducibility of outcomes. Before and after the friction tests, SUJ2 balls and the a-C:H coating disks were cleaned by acetone for fifteen minutes. The above mentioned experimental conditions for the ball-on-disk friction test and were then summarized in Table 2.1.

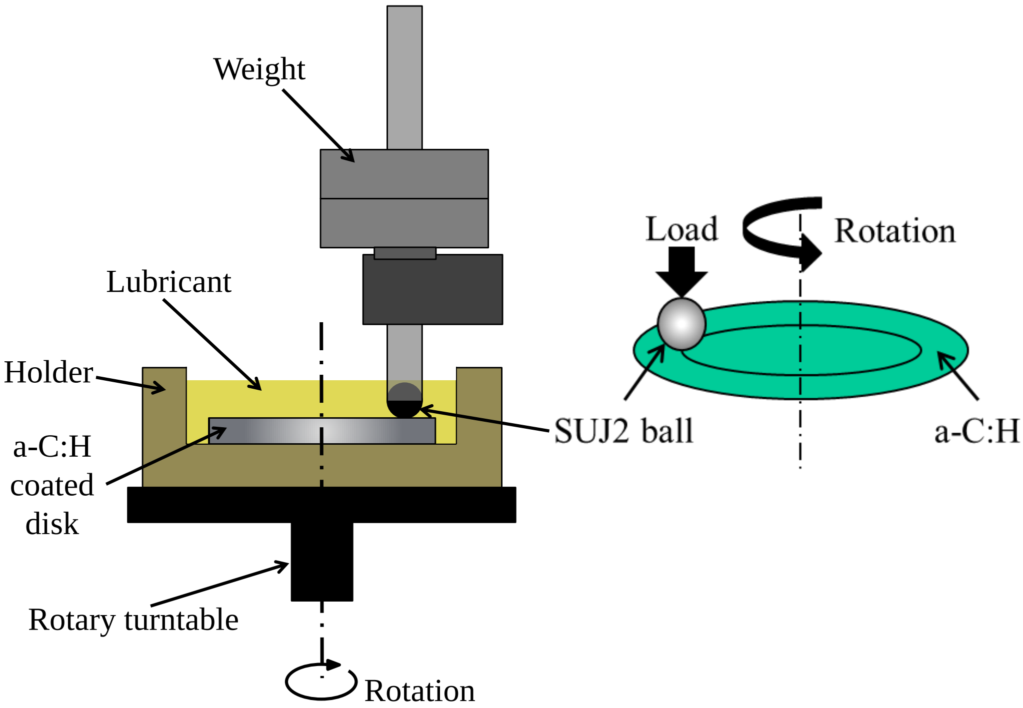


Figure 2-1 Schematics of ball-on-disk friction equipment

Table 2.2 Ball-on-disk friction test experimental conditions

Experimental conditions	
Ball	SUJ2
Disk	a-C:H on Si(100)
Load, N	1.0
Max. initial Hertzian contact pressure, MPa	455
Temperature, ^{o}C	24
Sliding speed, rpm	200
Sliding speed, m/s	6.28×10^{-2}
Duration, min	100

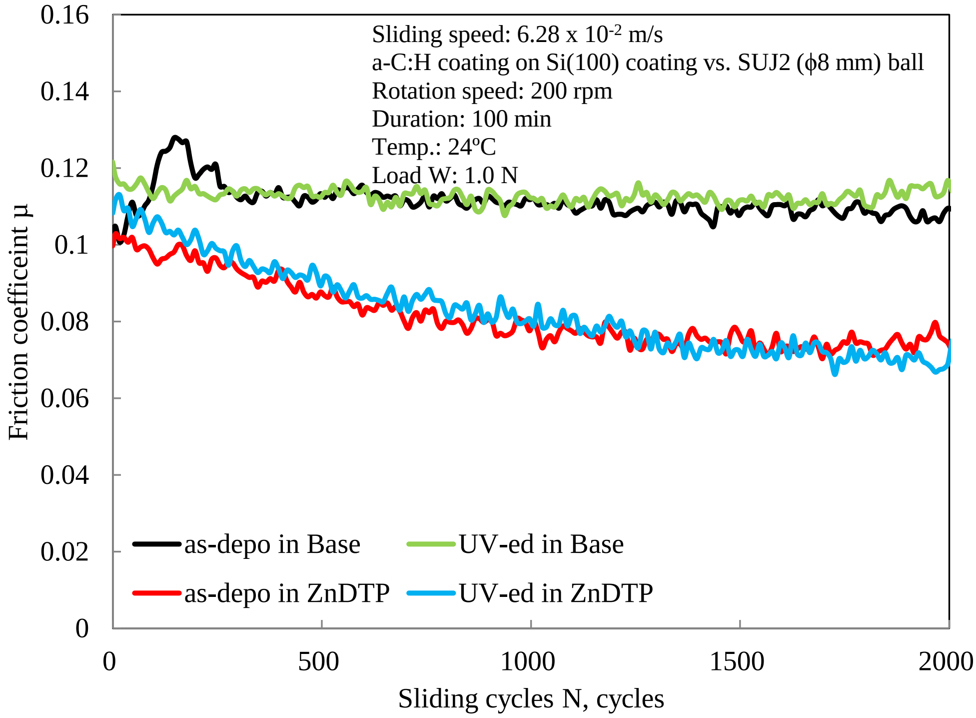
2.2.3 DLC surface and tribofilm analysis equipment

In this research, atomic force microscope (AFM) was used to measure the DLC coatings surface before and after the ultraviolet irradiation. For the indentation hardness test, nano-indentation hardness tester ENT-2100 manufactured by Elionix was used. To approximate the penetration depth of UV into the a-C:H, the coefficient of extinction and refractive index were calculated by utilizing ellipsometery (MART-102). Tribofilm formed on both DLC disks and mating material SUJ2 balls were studied using non-contact, three-dimensional, scanning white light interferometry (Zygo, Newview) and finally tribofilm element study was done by utilizing the energy dispersive X-ray spectroscopy (EDS) to analyse chemical composition of rubbed surfaces.

2.3 Results and discussions

2.3.1 Friction coefficient

To look on the effect of initial running in process to as-deposited and UV irradiated a-C:H disks, Figure 2.2 which focused on the cycles from 0 to 2000 were illustrated and the overall friction coefficients as a function of sliding cycles for SUJ2 balls contacted against as-deposited and UV irradiated a-C:H DLC in four types of additives added lubricant oils are shown in Figure 2.3. The UV irradiated a-C:H in ZnDTP oil showed the lowest friction coefficient, while as-deposited a-C:H showed the highest friction coefficient. For the case of friction test in Base oil, both as-deposited and UV irradiated a-C:H showed a gradual reduction of friction with sliding cycles that exhibited a reduction from initially 0.12 to 0.09 at the end of friction test and from initially 0.12 to finally at 0.08 for each as-deposited and UV irradiated a-C:H respectively. For the case of friction test in ZnDTP oil, the running in period for both as-deposited and UV irradiated was longer compared to the previous result in Base oil, which the steady state value gained at somewhere around 2000 cycles. The friction coefficient of as-deposited a-C:H gradually decreased from 0.11 to 0.055, and 0.11 to 0.04 reduction for UV irradiated a-C:H.



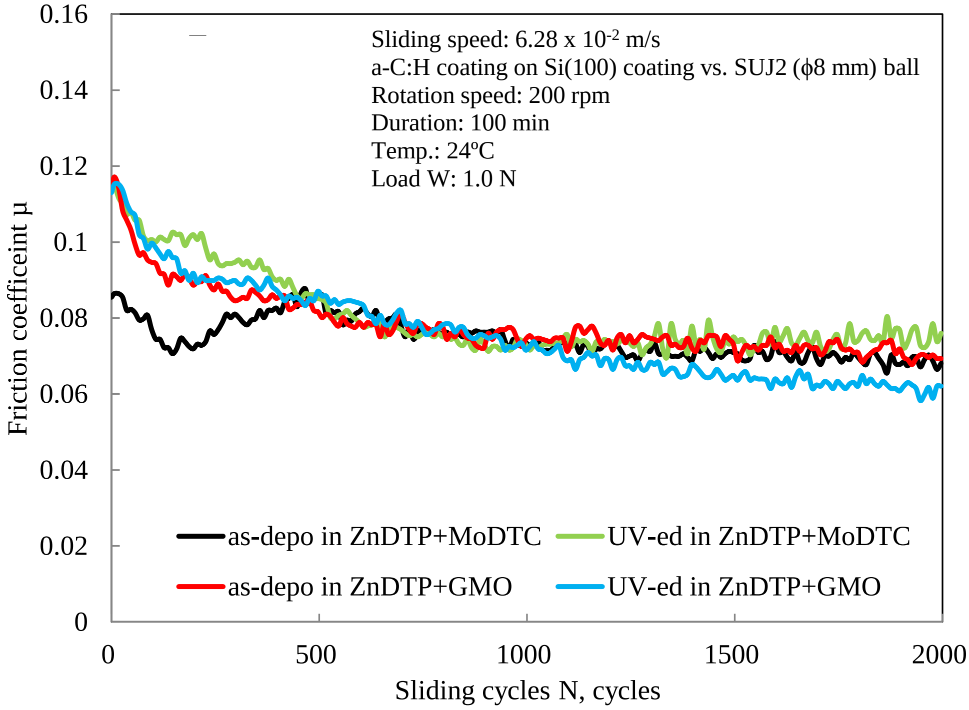


Figure 2-2 Friction coefficient of as-deposited and UV irradiated a-C:H coating under four types of lubricant oil lubrication at first 2000 cycles

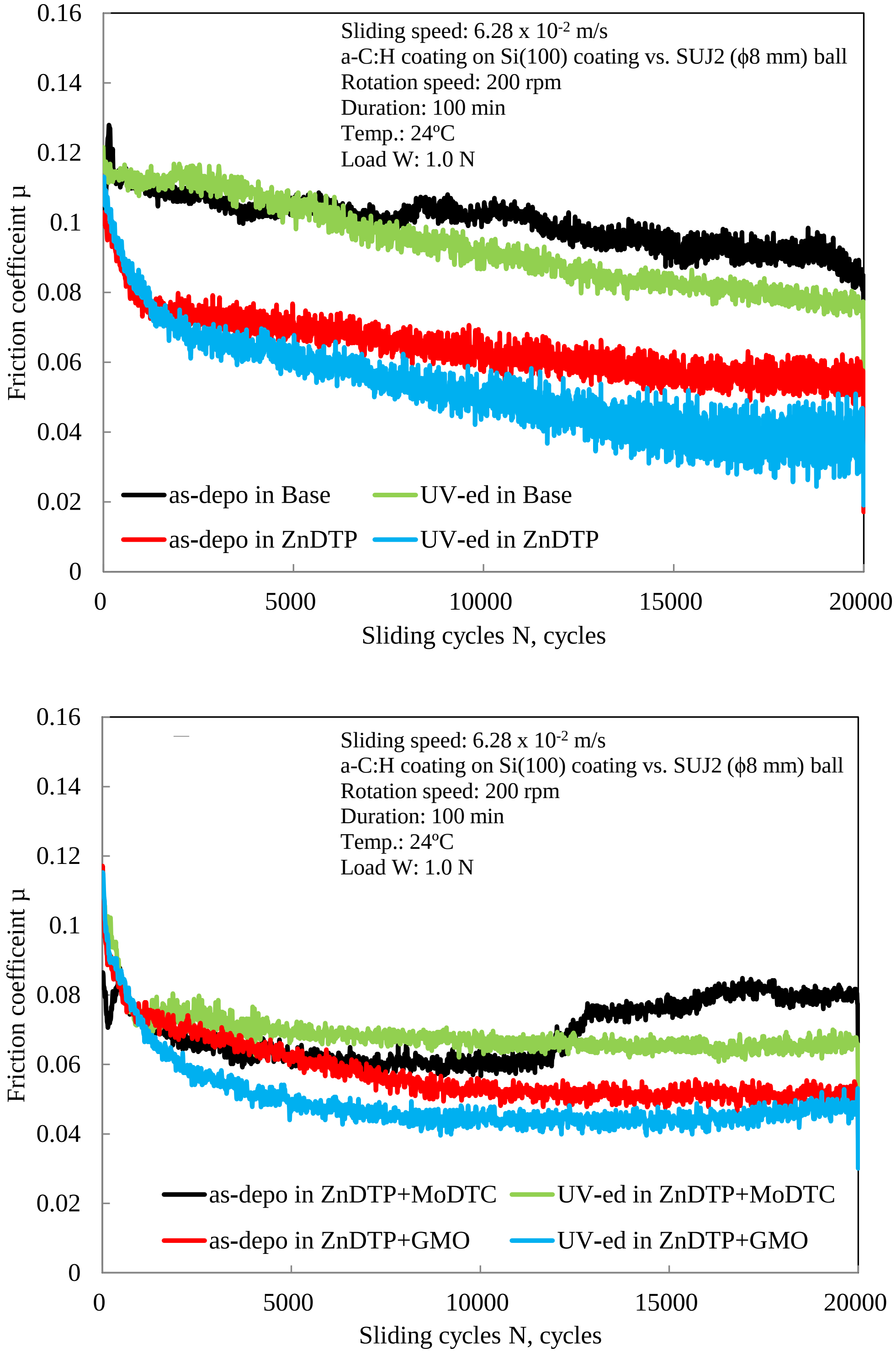


Figure 2-3 Friction coefficient of as-deposited and UV irradiated a-C:H coating under four types of lubricant oil lubrication for overall cycles

For the condition of lubrication in ZnDTP+MoDTC oil, friction coefficient of as-deposited a-C:H dropped from initially 0.09 to 0.07 at 500 cycles but bounced back to 0.09 at 1000 cycles then gradually reducing and remained almost constant at 0.06. However, at 12000 cycles, the friction coefficient increased back to around 0.09 until the end of friction test. This increment of friction coefficient at 12000 cycles might possibly be due to the increasing wear of the a-C:H disk became too high thus increased the friction coefficient. The effect of this increasing friction coefficient later can be seen on the wear track of as-deposited a-C:H disk surface where obvious consistent wear line can be observed along the wear track. However, the same effect had not occurred for the case of UV irradiated a-C:H disk. Although the initial friction coefficient was quite high at 0.115, the value rapidly reduced to 0.07 at 1000 cycles and remained almost constant until the end of friction test. It can be suggested that, UV irradiation process can lessen the effect of wear acceleration by MoDTC when being lubricated by ZnDTP+MoDTC oil as per reported by previous researchers [49], [50], [60]–[64].

Lastly, for the lubrication condition of ZnDTP+GMO oil, the running in phase of UV irradiated a-C:H was longer than as-deposited a-C:H. Both type of DLCs started the friction test with friction coefficient of 0.12. For as-deposited a-C:H, the value reduced swiftly to 0.075 at 1000 cycles, then gradually reduced to 0.05 at 8000 cycles and stayed almost steady from that point onwards until the end of the friction test, whereas in the UV irradiated a-C:H, the friction coefficient reduced to 0.06 at 2000 cycles, then slowly reduced and stayed at 0.045 at 8000 cycles for the rest of friction test.

To find which one of lubricant oil gives the lowest and the highest friction coefficient, the results of steady state friction coefficient in the last 5000 cycles of friction test are plotted and charted into a bar graph as shown in Figure 2.4. The tests of each configuration were repeated 3 times for confirmation and reproducibility of results and the error bar shown in the bar graph was calculated by utilizing standard deviation of that each configurations three tests friction coefficient results. From the result, it can be observed that for the as-deposited a-C:H, the highest friction coefficient was in Base oil, followed by in ZnDTP+MoDTC oil, then in ZnDTP oil and the lowest friction coefficient was in ZnDTP+GMO oil. UV irradiated a-C:H showed the first and second highest friction coefficients were in Base and in ZnDTP+MoDTC respectively which was the same like as-deposited a-C:H, but the lowest was in ZnDTP oil instead of in ZnDTP+GMO oil. In each type of lubricant oil, UV irradiated a-C:H showed lower friction coefficient than the as-deposited a-C:H with reduction from 0.091 to 0.080 in Base oil, 0.056 to 0.038 in ZnDTP oil, 0.080 to 0.065 in ZnDTP+MoDTC oil and 0.051 to 0.046 in ZnDTP+GMO oil.

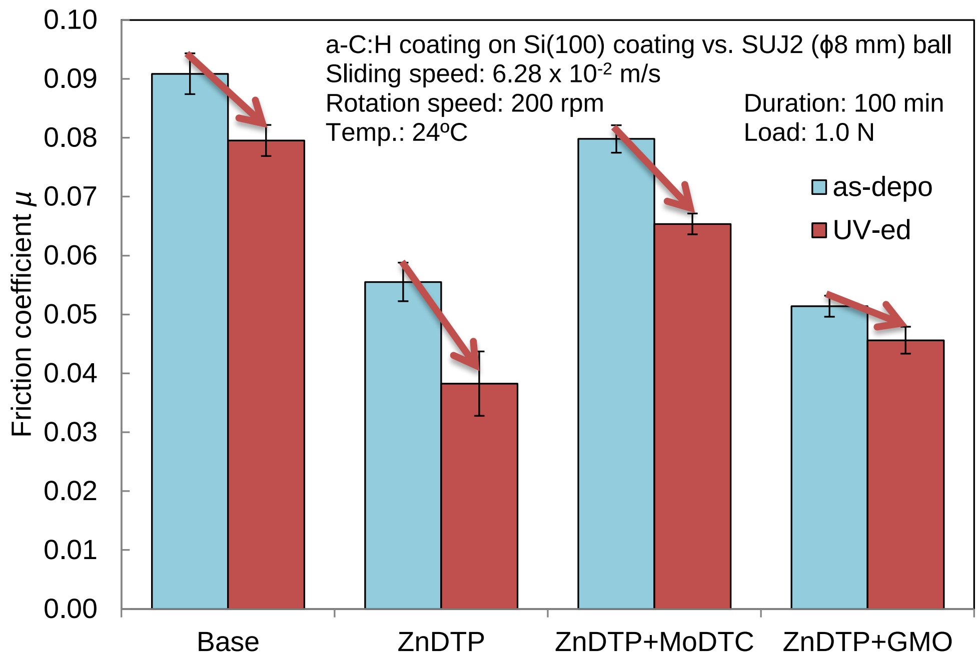


Figure 2-4 Average friction coefficient of as-deposited and UV irradiated a-C:H coating in four different types of oil

2.3.2 Wear rate

The wear rates of SUJ2 balls rubbed against as-deposited and UV irradiated a-C:H and wear rates of as-deposited and UV irradiated a-C:H disks are shown in Figure 2.5 and 2.6 respectively. Wear rates of SUJ2 balls in Base, ZnDTP and ZnDTP+GMO oils shows relatively high wear than in ZnDTP+MoDTC oil. Wear rates of UV irradiated a-C:H disks in Base and ZnDTP+MoDTC demonstrates significant reduction compared to the as-deposited a-C:H disks. The combination of UV irradiated a-C:H in ZnDTP+MoDTC able to accommodate an environment that can provide the lowest wear for both SUJ2 ball and a-C:H disk compared to the other combinations. ZnDTP and ZnDTP+GMO on the other hand capable to administer lower friction coefficient compared to the other two types of oils as can be seen in Figure 2.4, and also provide lower wear rate on both as-deposited and UV irradiated a-C:H disks. However, the wear rates of SUJ2 balls are comparatively higher than in ZnDTP+MoDTC.

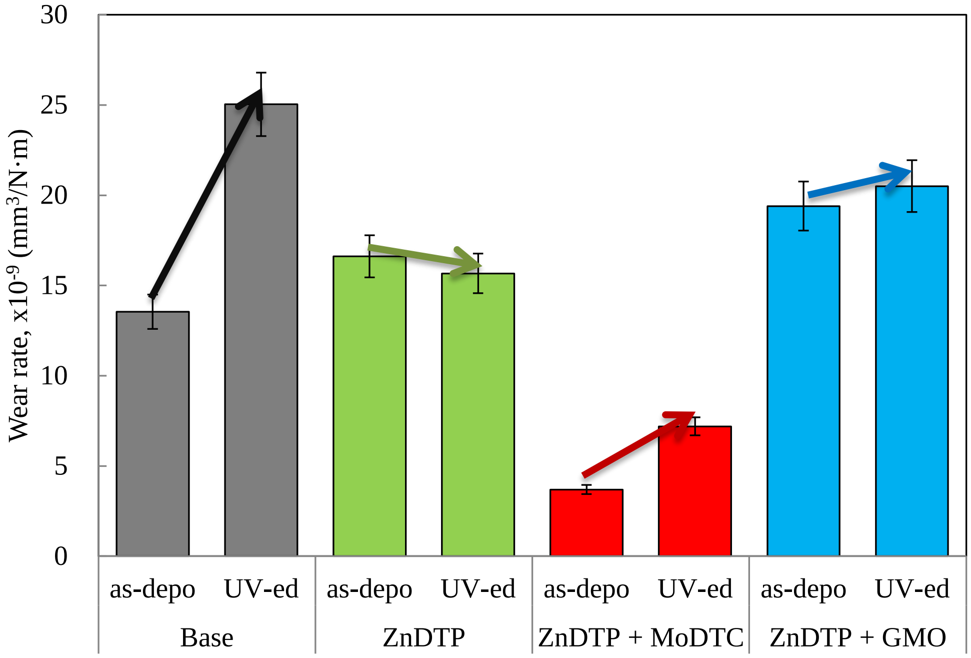


Figure 2-5 Wear rates of SUJ2 balls rubbed against as-deposited and UV irradiated a-C:H disks in four types of lubricant oil

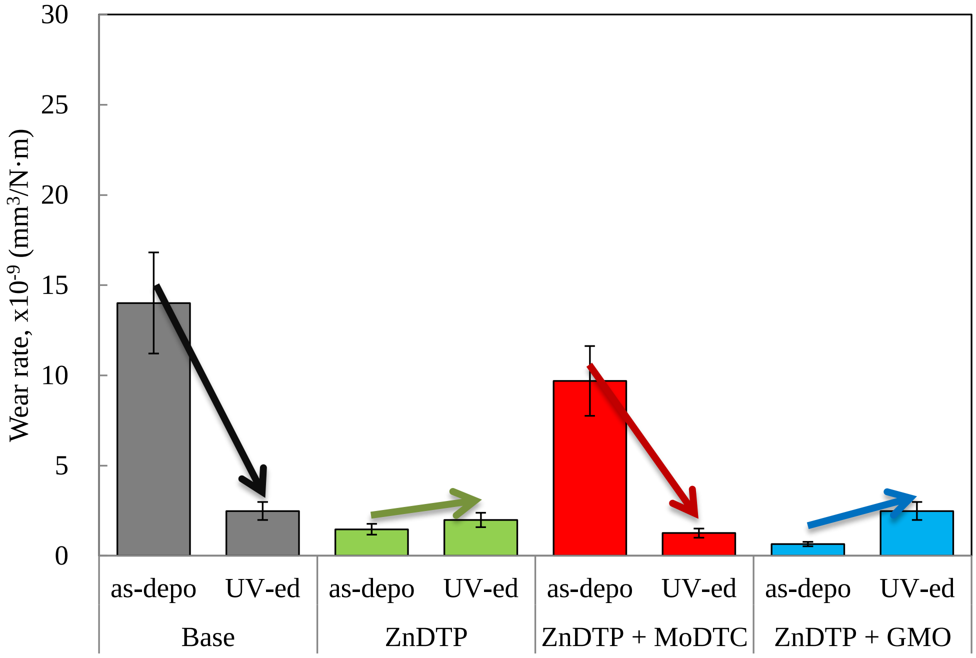


Figure 2-6 Wear rates of as-deposited and UV irradiated a-C:H disks rubbed against SUJ2 balls in four types of lubricant oil

2.3.3 Surface roughness and hardness

Figure 2.7 shows the AFM image of the a-C:H coating surface irradiated with ultraviolet light for 60 minutes. The center-line average roughness (R_a) of the as-deposited a-C:H coating was about 8.2 nm and the maximum height roughness (R_y) was about 33.6 nm. The surface roughness of the a-C:H coating irradiated with ultraviolet rays of 254 nm for 60 minutes was about 8.1 nm in the center-line average roughness (R_a), and about 34.3 nm in the maximum height roughness (R_y).

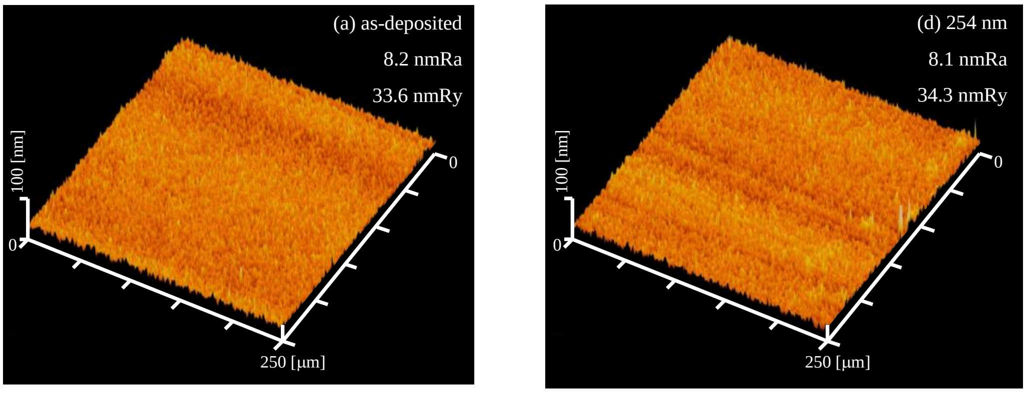


Figure 2-7 AFM images of as-deposited and UV irradiated a-C:H coating

In order to clarify the change in the hardness of the a-C:H coating by ultraviolet irradiation, the a-C:H coating irradiated with ultraviolet rays of 254 nm wavelength for 60 minutes was subjected to indentation hardness test by a micro indentation hardness tester. The indentation load was set to 49 μN to confirm the change in the hardness of only the topmost surface of the a-C:H coating. Table 2 shows the hardness and Young's modulus of the topmost surfaces of the as-deposited and UV irradiated a-C:H coating. The findings suggest that UV irradiation gave no significant change to a-C:H coating in terms of roughness and hardness.

Table 2.3 The hardness and Young's modulus of as-deposited and UV irradiated a-C:H coating

Coating type	a-C:H	
UV wavelength	As-deposited	254 nm
Hardness *H*, GPa	16.7	16.0
Hardness standard deviation, GPa	1.0	0.7
Young’s modulus *E*, GPa	15.2	15.2
Young’s modulus standard deviation, GPa	4.7	1.6

2.3.4 UV irradiation penetration depth

Previous study done by Tokoroyama et al. found that the UV irradiation time of 60, 120, 180 and 240 minutes do not shows significant changes among them and they also clarified that the effect of UV irradiation by calculating penetration depth of three types of UV light wavelength into a-C:H coating by utilizing ellipsometery. The penetration depth d_p of light is expressed by the following equation

$$d_p = 1/\alpha \tag{2-1}$$

In this formula, α represents the absorption coefficient of the material and is obtained by the following equation

$$\alpha = \frac{4\pi k}{\lambda} \tag{2-2}$$

Here, λ is the wavelength of light, and k is the extinction coefficient. Since ultraviolet wavelengths are 365, 312 and 254 nm, it is possible to estimate the penetration depth of ultraviolet rays by clarifying the extinction coefficient of the a-C:H coating. As a result of the ellipsometry measurement, extinction coefficients of the a-C:H coating are about 2.19. Ultraviolet penetration depths to the a-C:H coating at each wavelength were calculated by using the extinction coefficients of each and the previous two equations, and are shown in Table 3. In the a-C:H coating, the penetration depth of over 9 nm at any wavelength was calculated at any wavelength [66].

Table 2.4 The ultraviolet penetration depth to the a-C:H coating and the a-C film at each wavelength

Wavelength	Penetration depth d_p, nm
	a-C:H
365 nm	13.3
312 nm	11.3
254 nm	9.2

2.3.5 Ball and disk wear track surface profile observation

Figures 2.8 and 2.9 shows the optical microscope images of SUJ2 balls contacted with as-deposited and UV irradiated a-C:H disks. From the images, it can be observed that SUJ2 balls contacted with UV irradiated a-C:H showed darker traces compared to the as deposited a-C:H contacted SUJ2 balls. These traces found on the SUJ2 ball surfaces are likely to be the tribofilm as a result of the rubbing between the two surfaces. And since the traces were darker on the UV irradiated counter material surfaces, it can be concluded that a-C:H disks exposed to UV light are capable of producing thicker tribofilm compared with a-C:H disks without exposure to UV light. To support this claim, non-contact, three-dimensional, scanning white light interferometry, Zygo was utilized to acquire the surface profile of tribofilm formed on the SUJ2 balls.

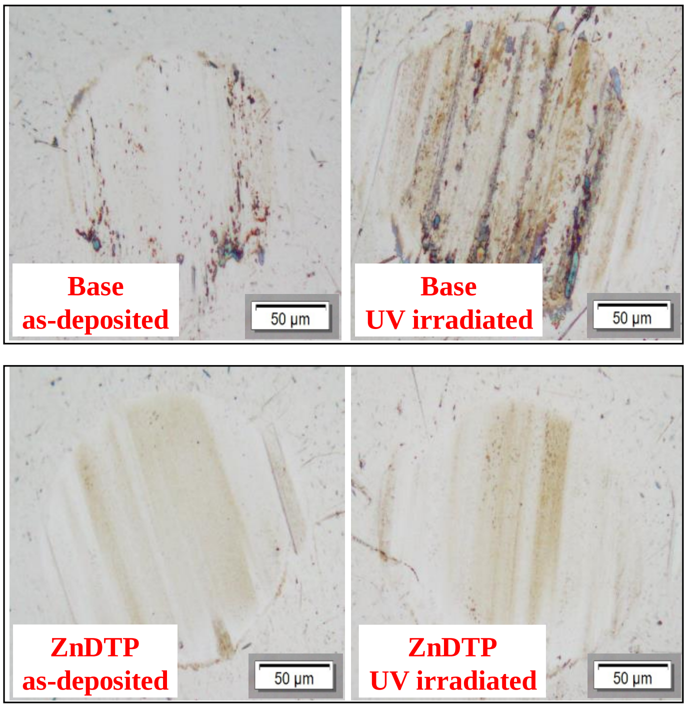


Figure 2-8 Optical images of SUJ2 balls after friction test under Base and ZnDTP lubrication

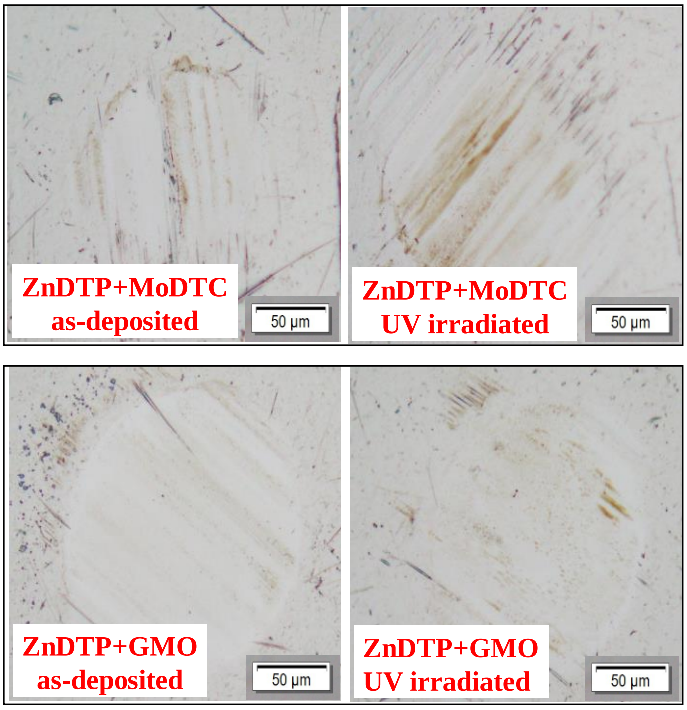


Figure 2-9 Optical images of SUJ2 balls after friction test under ZnDTP+MoDTC and ZnDTP+GMO lubrication

Figures 2.10, 2.11, 2.12 and 2.13 shows the Zygo images and surface profile graphs of as-deposited and UV irradiated a-C:H disks mating material SUJ2 ball in Base, ZnDTP, ZnDTP+MoDTC and ZnDTP+GMO oils respectively. The results then compiled and converted into bar graph shown in Figure 2.14, where the UV irradiated a-C:H disks mating material exhibited higher tribofilm height than the as-deposited disks mating material with an increment from 21 to 72 nm in Base oil, 10 to 12 nm in ZnDTP oil, 6 to 20 nm in ZnDTP+GMO oil, except in ZnDTP+MoDTC oil where the height decrease from 77 to 72 nm. This reduction of tribofilm height can be explained by looking at the results of EDS-SEM on SUJ2 balls in the next section where the amount of Sulphur reduced for the case of lubrication in ZnDTP+MoDTC for the UV irradiated a-C:H and the rest type of oils showed increment of oil additives at% for the UV irradiated a-C:H. These findings suggest that the higher the value of surface profile height, the thicker the thickness of tribofilm attached on the SUJ2 balls. The result also revealed that UV irradiated a-C:H disks made the thickness of the tribofilm higher on SUJ2 balls than the as-deposited a-C:H disks.

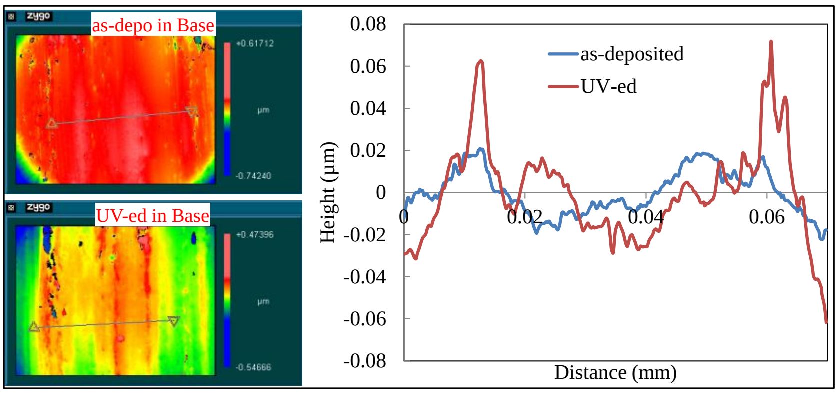


Figure 2-10 Zygo images and surface profiles of SUJ2 balls after friction test under Base lubrication

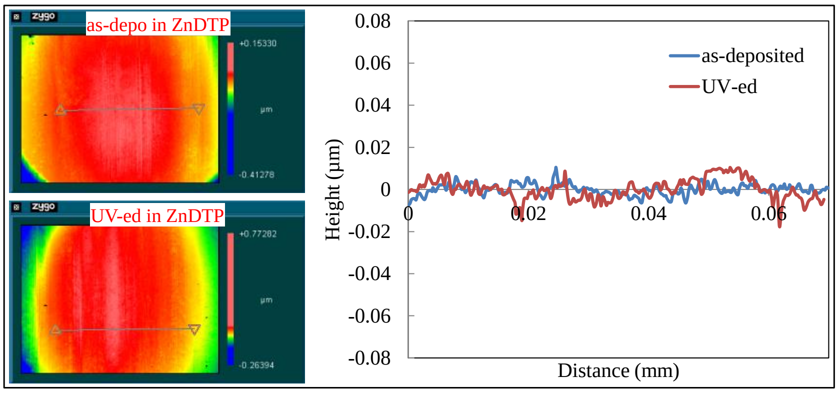


Figure 2-11 Zygo images and surface profiles of SUJ2 balls after friction test under ZnDTP lubrication

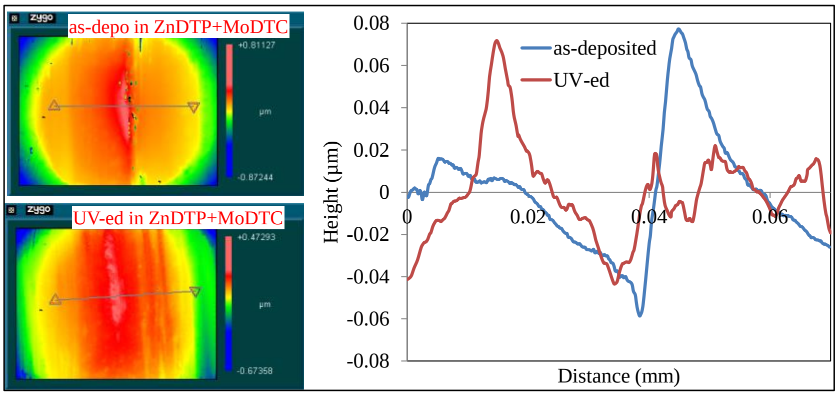


Figure 2-12 Zygo images and surface profiles of SUJ2 balls after friction test under ZnDTP+MoDTC lubrication

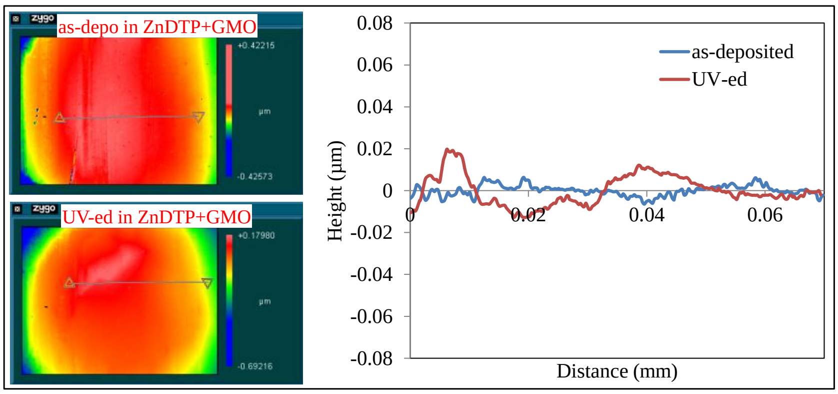


Figure 2-13 Zygo images and surface profiles of SUJ2 balls after friction test under ZnDTP+GMO lubrication

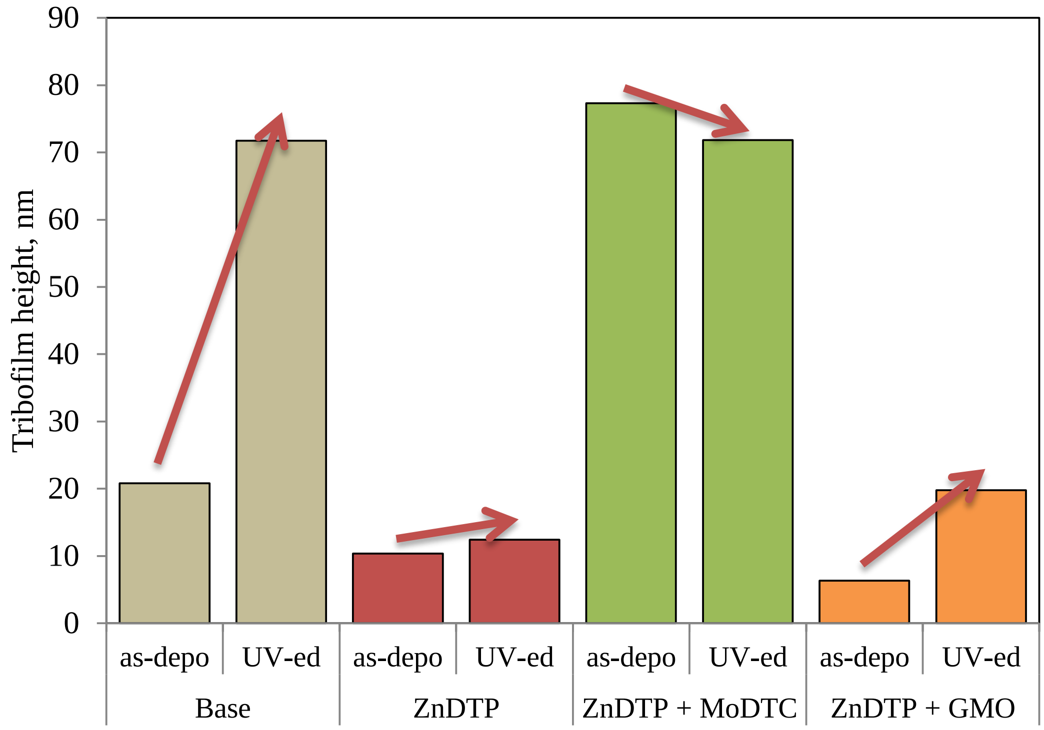


Figure 2-14 Tribofilm height on SUJ2 balls after rubbed against as-deposited and UV irradiated a-C:H disks in four types of lubricant oil

The analysis of a-C:H disks wear track was done next by utilizing Zygo images and surface profile graphs of as-deposited and UV irradiated a-C:H disks in the four different types of oil and the results are shown in Figures 2.15, 2.16, 2.17 and 2.18. The results then compiled and converted into bar graph shown in Figure 2.19. Compared to the results of SUJ2 balls, the tribofilm height formed of a-C:H disks were much more lower compared to the ones formed on the SUJ2 balls. In general, UV irradiated a-C:H disks exhibited slightly higher tribofilm height than the as-deposited a-C:H disks with an increment from 2.2 to 2.5 nm in ZnDTP oil and 2.2 to 3.6 nm in ZnDTP+GMO oil. However, for the case in Base and ZnDTP+MoDTC, the tribofilm height reduced slightly from 5.0 to 3.6 and 6.5 to 4.9 nm respectively. Except for the case of Base oil, the rest of results show the same trend as SUJ2 balls where the UV irradiated disks formed thicker tribofilm than as-deposited disks. And the reduction of tribofilm height in ZnDTP+MoDTC for the UV irradiated disks was probably due to the reduction of elements such as Molybdenum and Sulphur attachment that will be explain later on the upcoming section.

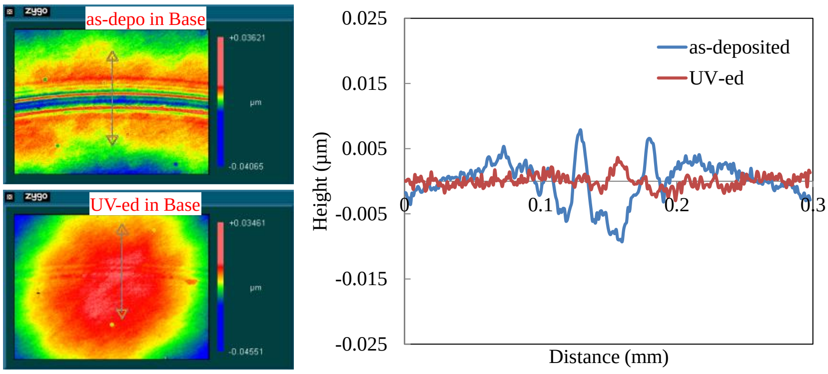


Figure 2-15 Zygo images and surface profiles of as-deposited and UV irradiated a-C:H disks after friction test under Base lubrication

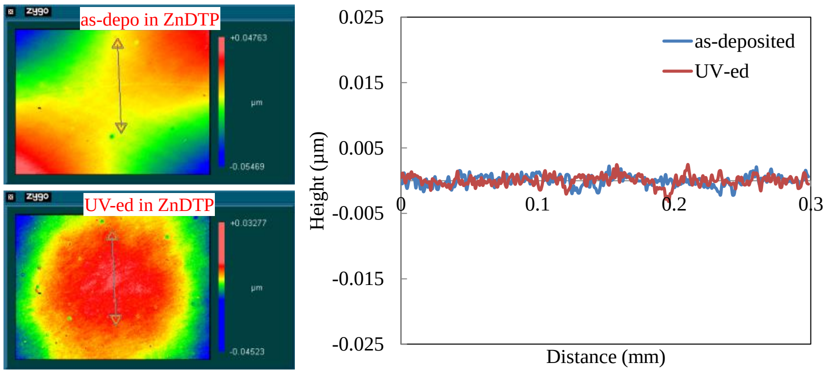


Figure 2-16 Zygo images and surface profiles of as-deposited and UV irradiated a-C:H disks after friction test under ZnDTP lubrication

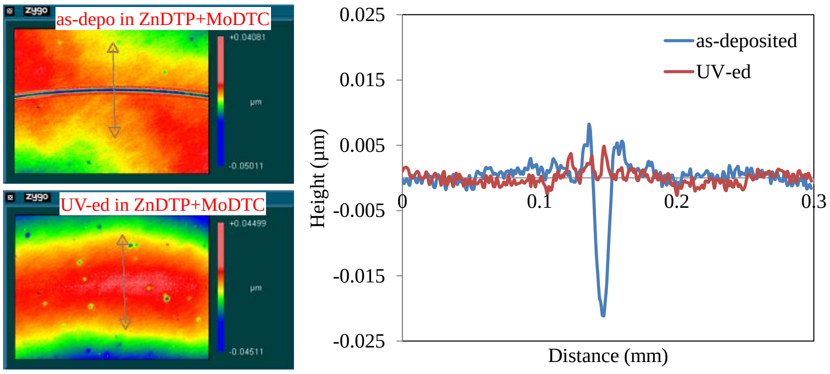


Figure 2-17 Zygo images and surface profiles of as-deposited and UV irradiated a-C:H disks after friction test under ZnDTP+MoDTC lubrication

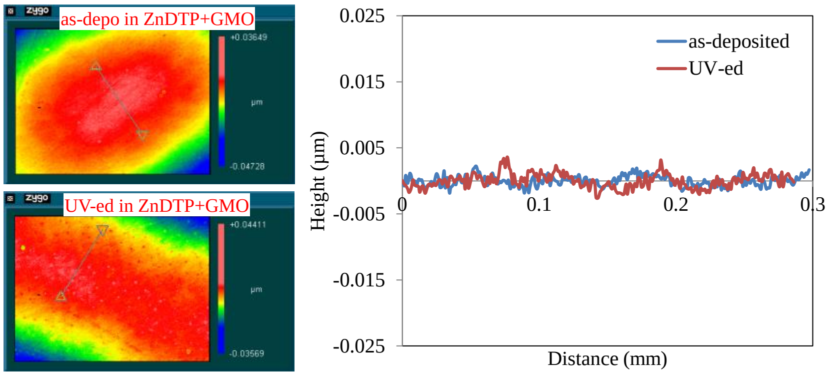


Figure 2-18 Zygo images and surface profiles of as-deposited and UV irradiated a-C:H disks after friction test under ZnDTP+GMO lubrication

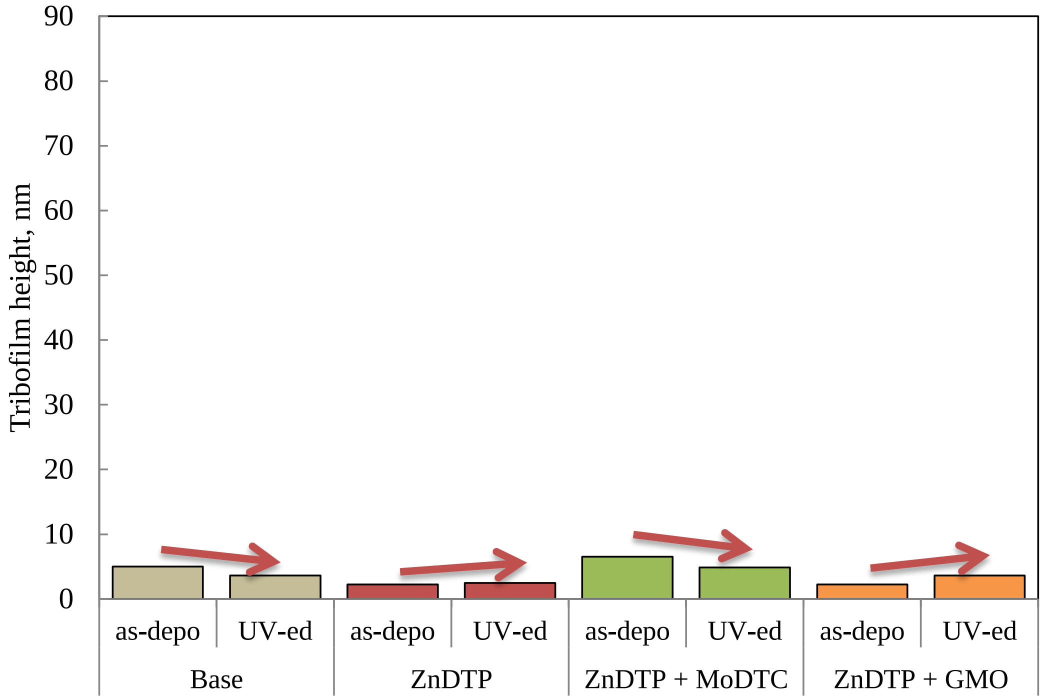


Figure 2-19 Tribofilm height on as-deposited and UV irradiated a-C:H disks after rubbed against SUJ2 balls in four types of lubricant oil

2.3.6 Tribofilm height validation by confocal laser scanning microscope

To validate the tribofilm height formed on both sliding surfaces, the wear track of SUJ2 balls was reinvestigated again by utilizing confocal laser scanning microscope (Olympus LEXT OLS5000). Figure 2.20 shows the height and intensity profile images of SUJ2 ball wear tracks paired with as-deposited and UV irradiated a-C:H in Base oil. When the ball wear track of both cases were observed closely, some part of the surface can be seen rise up building a layer with peaks which can be considered as tribofilm.

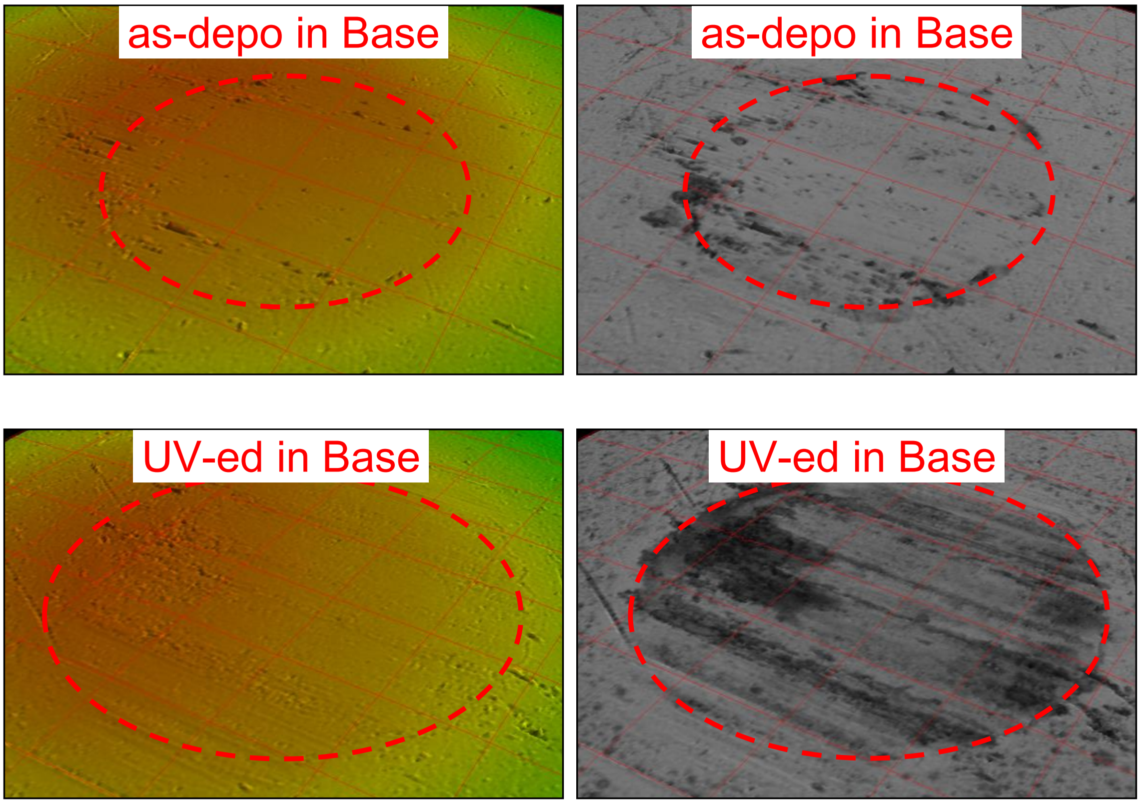


Figure 2-20 SUJ2 balls wear track height and intensity images

Figure 2.21 shows the surface profile of SUJ2 ball wear tracks for both cases and compared with SUJ2 ball surface before friction test in Base and ZnDTP+MoDTC oil. The results show that the upper surface of the balls worn and forming flat surface with majorly peaks and some valleys. Much more clear presence of the peak can be observed for the case in ZnDTP+MoDTC lubrication.

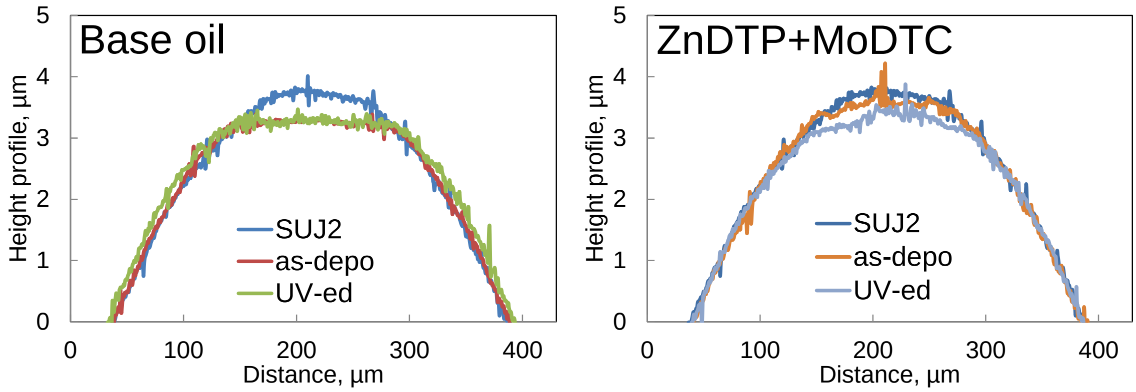


Figure 2-21 Surface profiles of SUJ2 balls paired with as-deposited and UV irradiated a-C:H disks in Base and ZnDTP+MoDTC oils

Next, the average value of the height of the summit from the highest to the fifth highest among the peaks in the reference area (wear track flat surface) S5p as shown in Figure 2.22 was gained by utilizing the three-dimensional system surface roughness parameters (ISO 25178-2:2012) and the result was shown in Figure 2.23. The results revealed almost the same trends as the results gained by Zygo in the previous section which validated all the results gained by it.

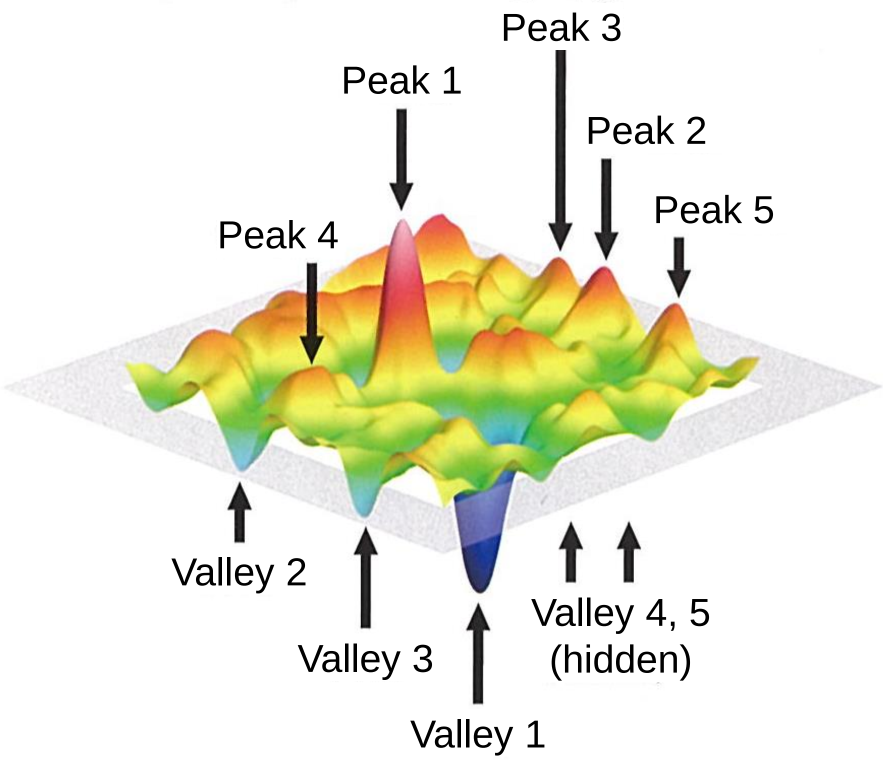


Figure 2-22 Five point average height of the peaks, S5p

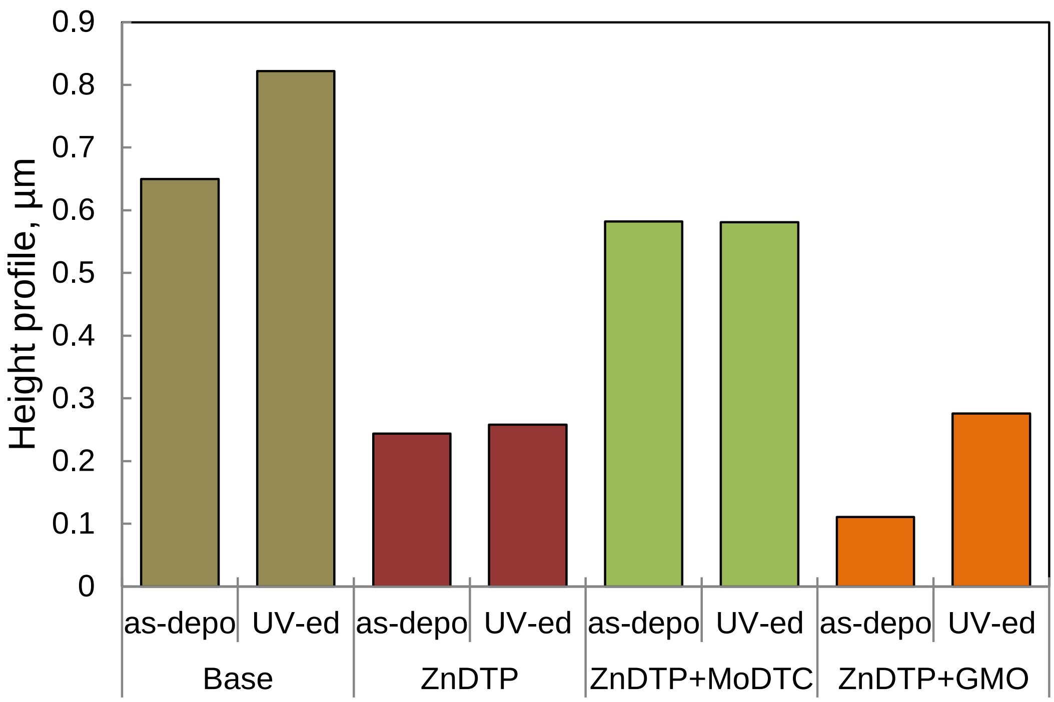


Figure 2-23 Tribofilm height on SUJ2 ball wear tracks results by 3D optical microscope

2.3.7 Tribofilm element investigation

To identify which oil additives element attached on both sliding surfaces, an energy dispersive X-ray spectroscopy (EDS) was used to carry out qualitative element analysis for both sliding surfaces. Figure 2.24 and 2.25 show the SEM images location area of the EDS scanning for SUJ2 balls and both as-deposited and UV irradiated a-C:H disks after friction tests. Figure 2.26 and 2.27 shows the concentration of Carbon element attached on SUJ2 balls and as-deposited and UV irradiated a-C:H disks. The source of this carbon that attached on both sliding surfaces mainly originated from two sources which are carbon derived from lubricant oils and carbon from the wear particles of graphite-like layer produced from the UV irradiation process.

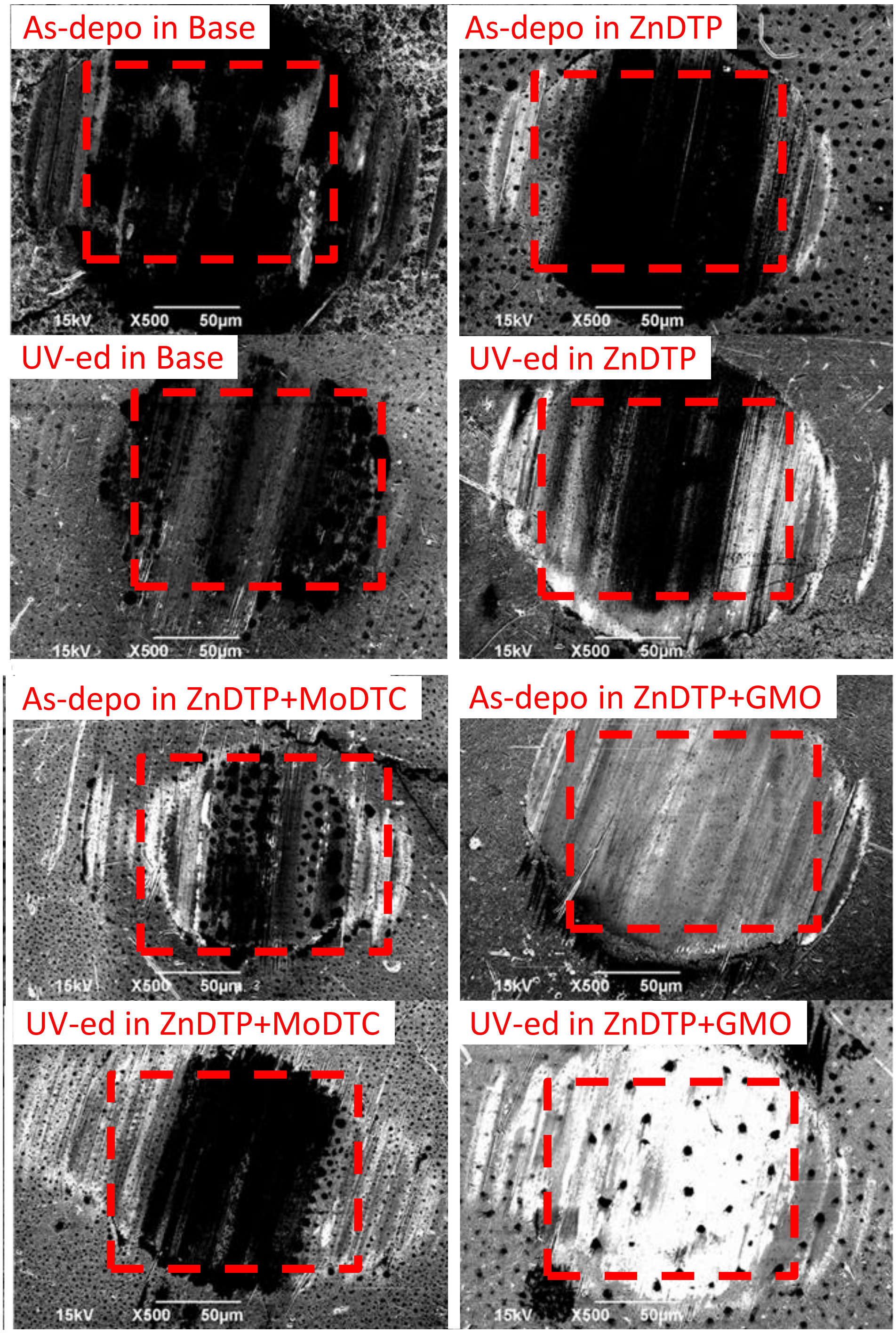


Figure 2-24 SEM images location area of the EDS scanning for mating material SUJ2 balls contacted to as-deposited and UV irradiated a-C:H disks in four types of lubricant oil

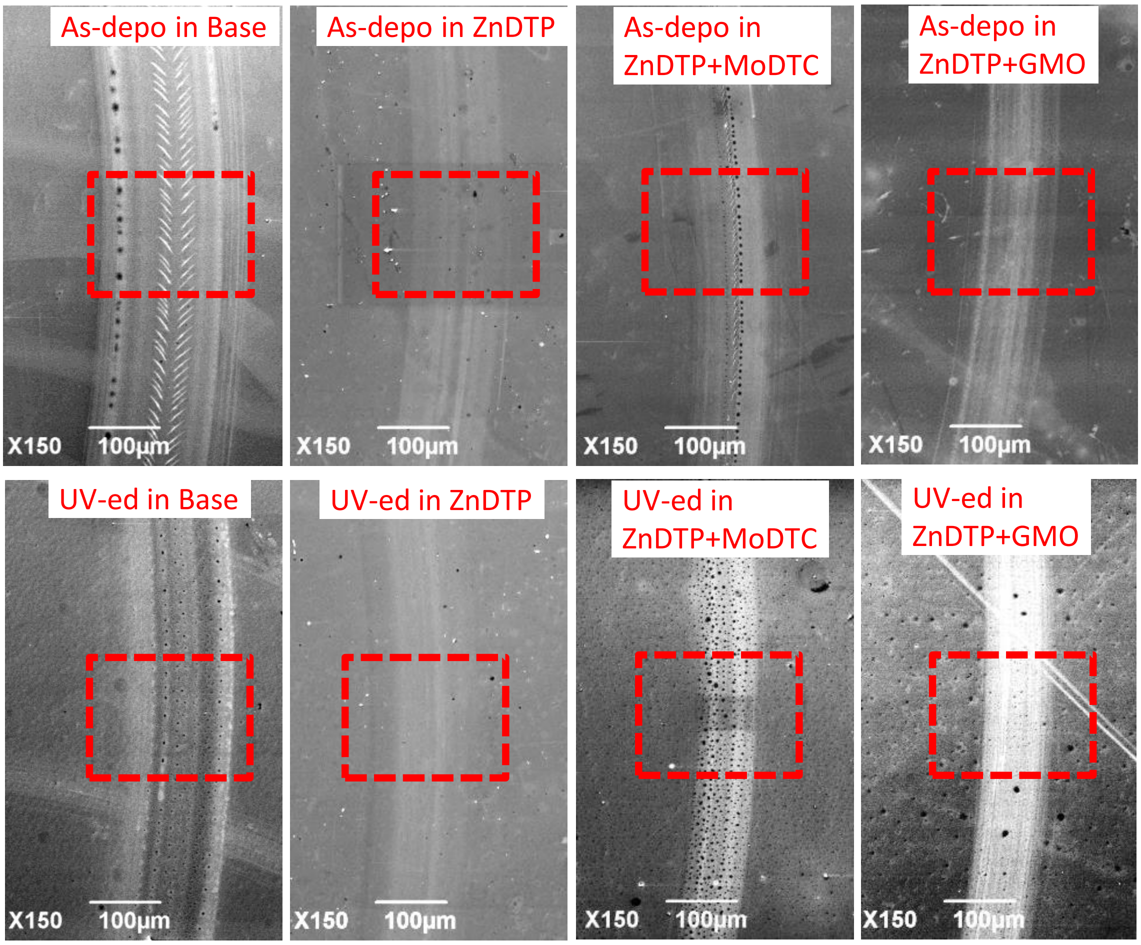


Figure 2-25 SEM images location area of the EDS scanning for both as-deposited and UV irradiated a-C:H disks in four types of lubricant oil

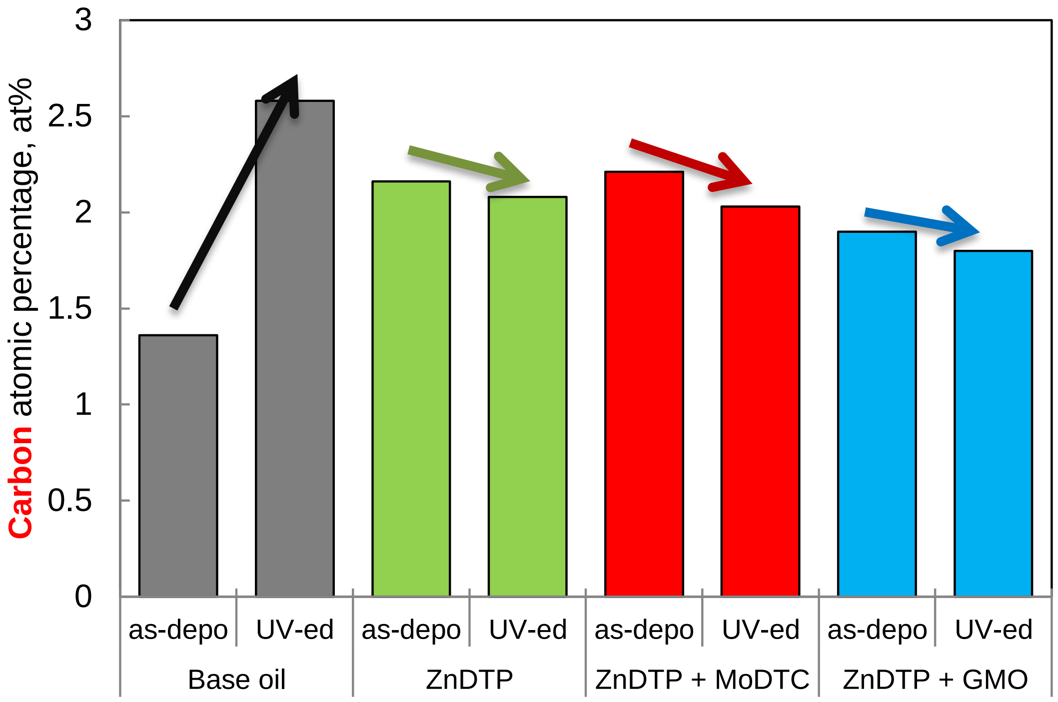


Figure 2-26 Carbon element analysis by EDS on SUJ2 balls

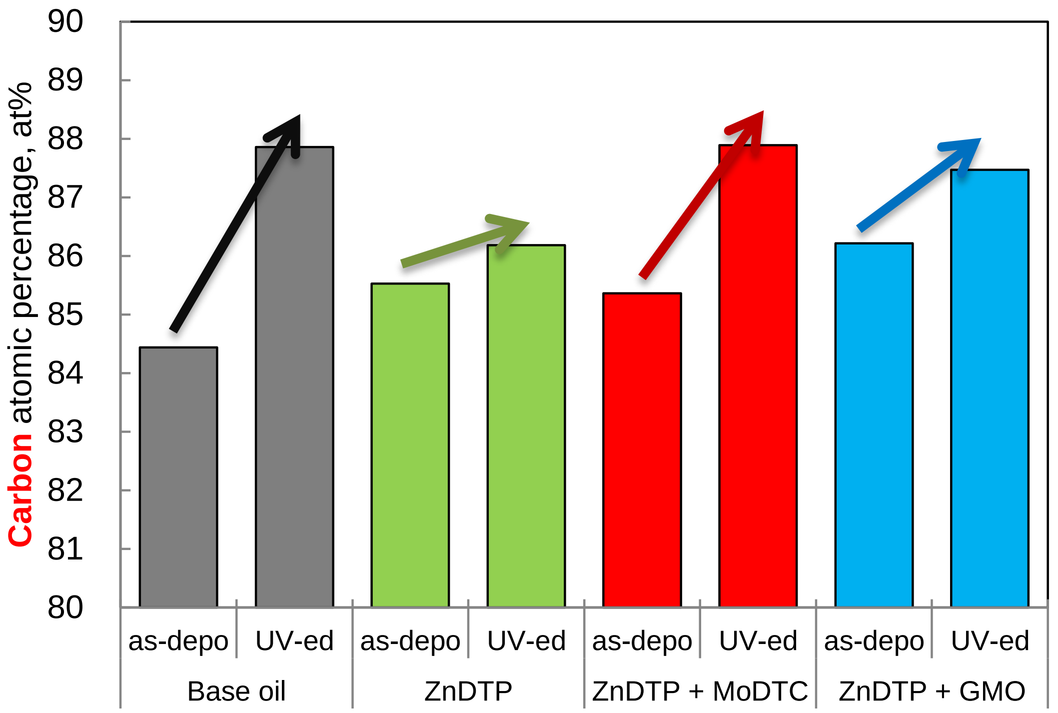


Figure 2-27 Carbon element analysis by EDS on as-deposited and UV irradiated a-C:H disks

Except for the case in Base oil, the attachment of carbon element on SUJ2 when being rubbed against UV irradiated a-C:H disks was lower than when being rubbed against as-deposited a-C:H disks in ZnDTP, ZnDTP+MoDTC and ZnDTP+GMO lubricant oils. The increment of carbon when rubbed against UV irradiated a-C:H in Base oil, the finding highlights that the wear particles of graphite-like layer from a-C:H disk adhered to the SUJ2 ball surface and then accumulates with carbon elements came from Base oil. However, for the other three types of additives added lubricant oils, elements that came from the oil additives such as Zinc, Sulphur, Phosphorus and Molybdenum substitutes some portion of carbon place explaining the logic behind the reduction of carbon attachment on SUJ2 balls when rubbed against UV irradiated a-C:H. Carbon attachment on a-C:H disks however exhibits an increment from as-deposited to UV irradiated a-C:H disks in all type of lubricant oils. The finding is consistent with findings of past studies by Zhang et al., which indicated that by conducting UV irradiation to DLC, the process escalates the carbon to carbon and lessening the carbon to hydrogen bonding [67], explaining the higher concentration of carbon at% on UV irradiated a-C:H disks despite the type of lubricant oils.

Main elements of ZnDTP, MoDTC and GMO lubricant additives which are Phosphorus, Sulphur, Zinc and Molybdenum and also Calcium from detergents were selected to be investigated. The at% concentration values then converted into bar graphs as shown in Figure 2.28 and 2.29 to evaluate the effect of UV irradiation to tribofilm and lubricant additives elements attachment on both sliding surfaces. It was clear that there are no lubricants additives element detected on SUJ2 balls lubricated with Base oil, however in ZnDTP and ZnDTP+GMO lubrication, higher traces of lubricant additives was detected on SUJ2 ball contacted to UV irradiated a-C:H disks. Lubrication in

ZnDTP+MoDTC however, reveals that no Sulphur was traced on SUJ2 ball of UV irradiated a-C:H disk, while the rest of the elements showed higher atomic percentage compared to the case when paired with as deposited a-C:H disk.

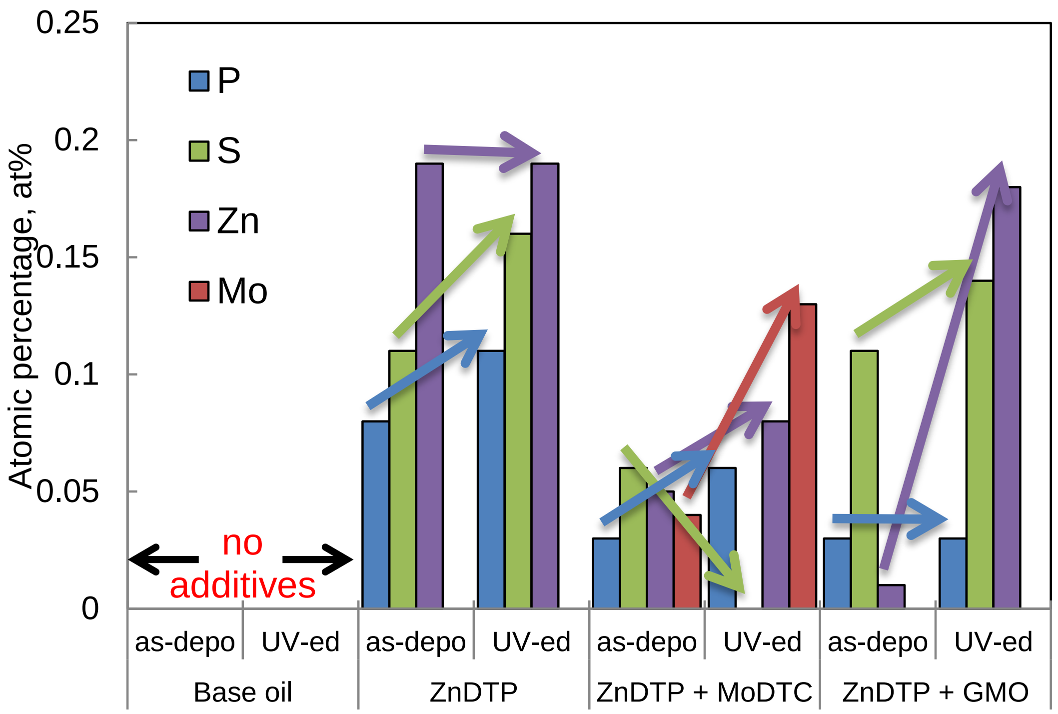


Figure 2-28 Lubricant additives element analysis by EDS on SUJ2 balls

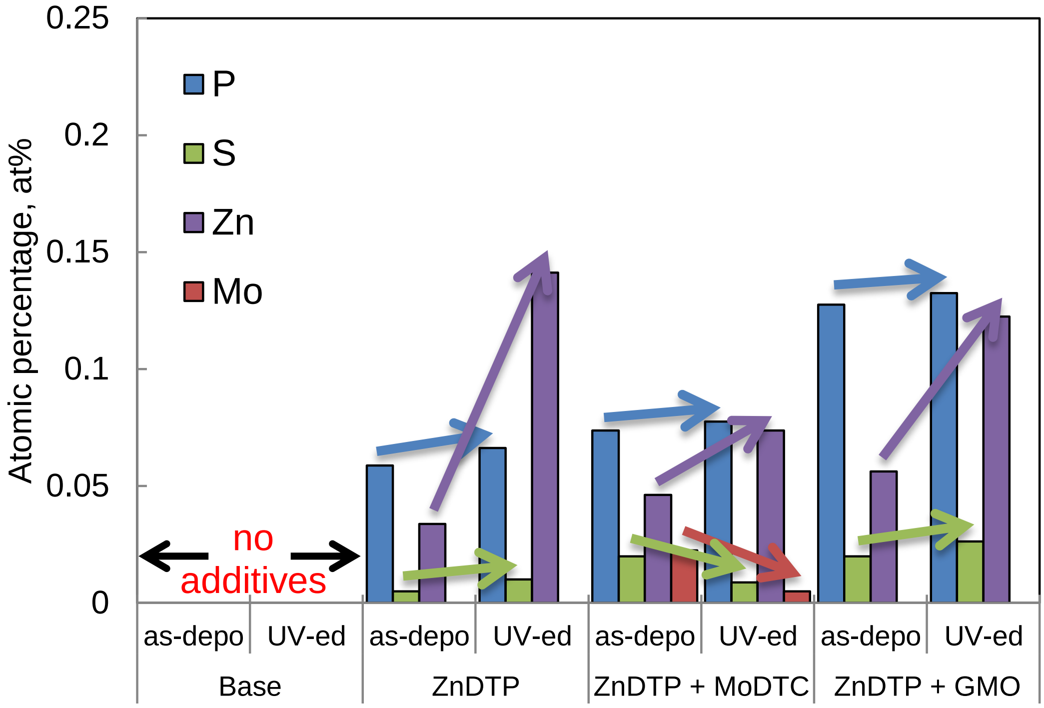


Figure 2-29 Lubricant additives element analysis by EDS on as-deposited and UV irradiated a-C:H disks

Similar to the result on the SUJ2 ball, no lubricants additives element can be found on both as-deposited and UV irradiated a-C:H disks when lubricated with Base oil either. As same with previous SUJ2 results, UV irradiated a-C:H disks showed higher lubricant additives attachment compared to the as-deposited a-C:H disks. Except for the case of lubrication in ZnDTP+MoDTC where the Sulphur and Molybdenum elements decreased on UV irradiated a-C:H disk, all the other lubricant additives elements attached more on UV irradiated than as-deposited a-C:H disks.

Based on these results, the findings suggest that UV irradiation process has helped to generate thick tribofilm on both UV irradiated a-C:H and its counterpart SUJ2 balls. These were made possible by the dangling bonds and thin graphite-like layer formed on the topmost surface of a-C:H disk and is consistent with findings of past studies [44], [67], [68]. The thin graphite-like layer and dangling bonds that was produced by the UV irradiation process somehow able to reduce the ability of Sulphur to attach on both sliding surfaces. Molybdenum however found to be attached more on the SUJ2 ball paired with UV irradiated a-C:H disk. Molybdenum and Sulphur both are the main elements contained in MoDTC and as being reported by Haque et al., the wears of contact between DLC and steel were exceptionally high in MoDTC included lubricant oil [60]. Thanks to the the reduction of both element attachment on the sliding surfaces, the wear rate of UV irradiated a-C:H disk was significantly reduced compared to the as-deposited disk.

Figures 2.30 and 2.31 shows the at% of Oxygen and Calcium on both ball and disk. From the figures it is suggested that the possibilities of $CaCO_3$ from detergents formed only on a-C:H disk. And except for the case of UV irradiated a-C:H in ZnDTP+GMO oil, the other two type of oils shows reduction of Calcium. However, in the overall, the difference shown from mating material to another is small. Therefore, the results indicates that Calcium from detergents do not show obvious difference to the sliding interfaces.

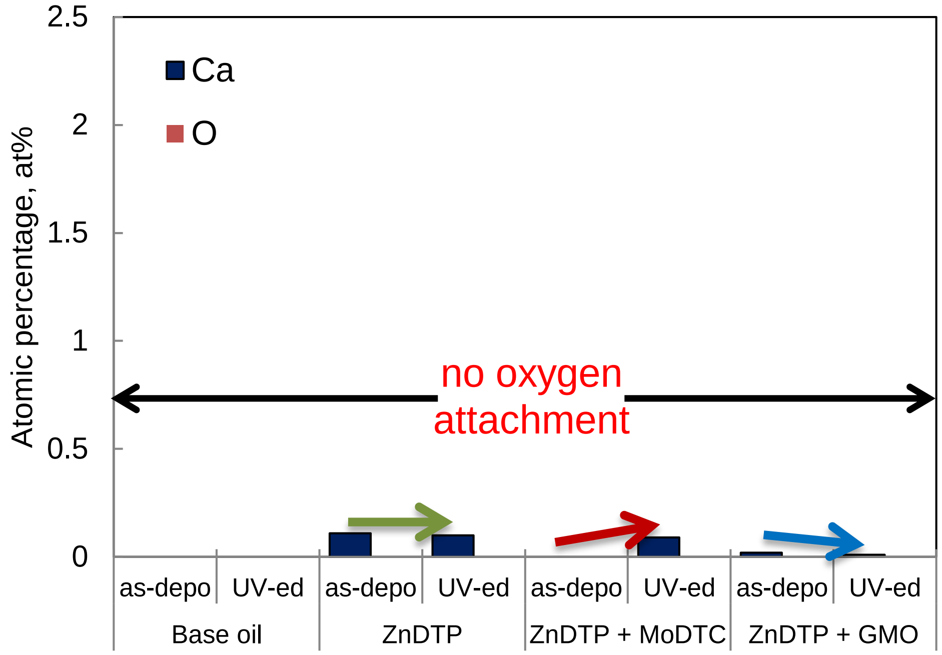


Figure 2-30 Calcium and Oxygen at% on SUJ2 balls

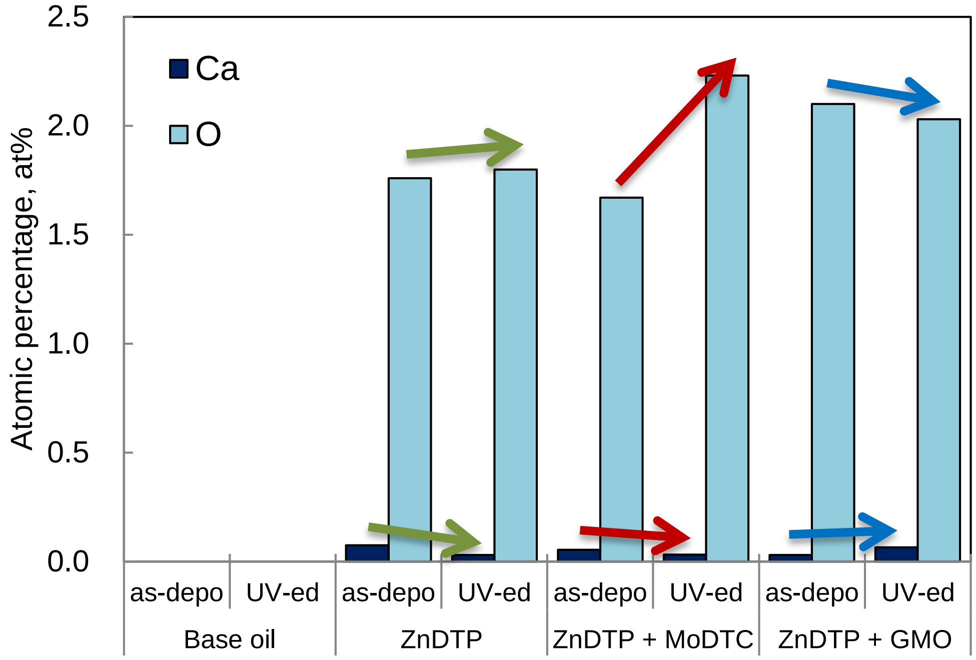


Figure 2-31 Calcium and Oxygen at% on as-deposited and UV irradiated a-C:H disks

2.3.8 Tribofilm formation on SUJ2 balls, as-deposited and UV irradiated a-C:H disks

Based on the entire results before, Figure 2.32 and 2.33 was illustrated to propose on the tribofilm formation phase on as-deposited and UV irradiated a-C:H disk. For the case of contact between SUJ2 ball and as-deposited a-C:H disk, the first image shows the initial contact condition between SUJ2 ball and as-deposited a-C:H disk. At the initial phase of sliding process, tribofilm formed on only on SUJ2 balls and not on a-C:H disk due to its chemically inertness. Along the time of friction test, tribofilm formed on SUJ2 ball was transferred and attached to counter material a-C:H disk. This explains the small traces of lubricant additives element found on as-deposited a-C:H disk and its counter material SUJ2 ball.

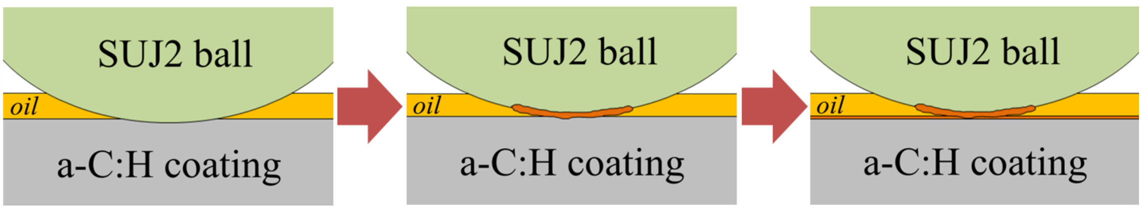


Figure 2-32 Tribofilm formation phase on SUJ2 ball and as-deposited a-C:H disk

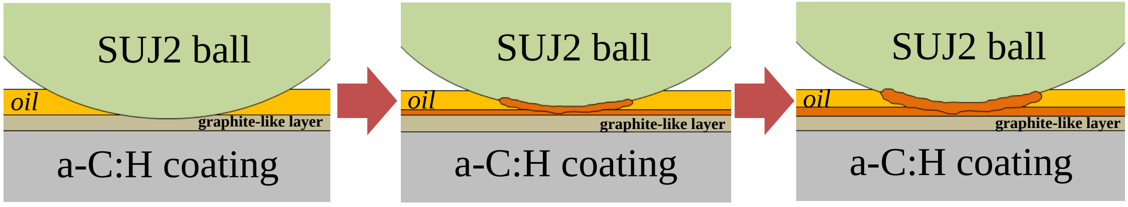


Figure 2-33 Tribofilm formation phase on SUJ2 ball and UV irradiated a-C:H disk

Next, for the contact between SUJ2 ball and UV irradiated a-C:H disk, the initial contact during the start-up was actually between SUJ2 ball and graphite-like layer formed on the topmost surface of a-C:H disk. Thanks to the graphite-like layer and dangling bonds made available by UV irradiation, thin tribofilm then formed on both SUJ2 ball and a-C:H disks. As a result of cyclic process, tribofilm formed on both on SUJ2 ball and a-C:H disk had accumulated and thicker tribofilm comprises of carbon and lubricant additives elements was formed on both SUJ2 ball and UV irradiated a-C:H disk. This justifies the earlier EDS results of higher carbon and lubricant additives elements on found on both SUJ2 ball and UV irradiated a-C:H disk which was consistent with findings of past study by Gadallah et. al. [68].

2.3.9 Base, ZnDTP, ZnDTP+MoDTC and ZnDTP+GMO oils tribofilm formation mechanism on as-deposited and UV irradiated disks

To get better understanding on what exactly are the tribofilm of Base, ZnDTP, ZnDTP+MoDTC and ZnDTP+GMO are made of, Figure 2.34 (a and b) also Figure 2.35 (a and b) was illustrated to explain the mechanism on how the tribofilm can be produced on as-deposited and UV irradiated sliding surfaces in Base and additives added oils (ZnDTP, ZnDTP+MoDTC and ZnDTP+GMO) respectively. For the case in Base, the tribofilm formed on both sliding surfaces can be attributed to the solid derived tribofilm and oil derived tribofilm. At the initial process of friction test in Base for the as-deposited DLC, both surfaces contacted and by the effects of adhesive wear, the worn particles of a-C:H DLC asperities attached and adhered on the SUJ2 ball surface.

These wear particles then became the solid derived tribofilm originated from the DLC. Then, due to no additives added inside the Base, the oil derived tribofilm which was mainly the hydrocarbon originated from Base attached to the surface of SUJ2 ball. Possibly, no oil derived tribofilm attached to the DLC disk initially due to its chemical inertness properties. But, as a result of repeated process, the tribofilm formed on the SUJ2 ball accumulated and then transferred to the DLC surface which explain the small traces of lubricant additives elements found on the as-deposited a-C:H disk.

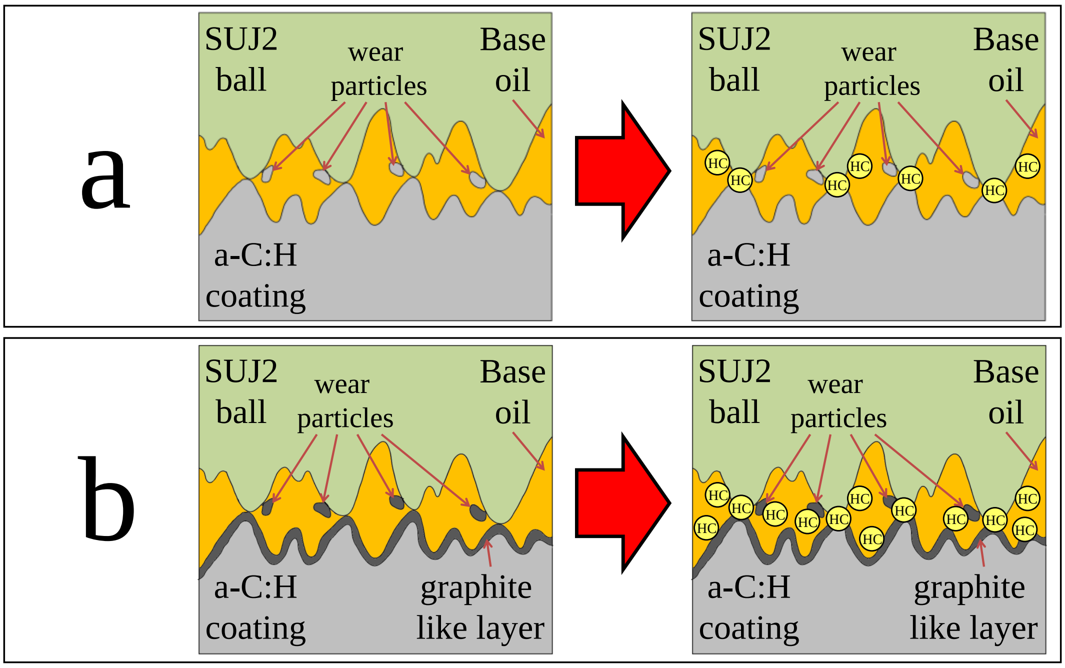


Figure 2-34 Tribofilm formation mechanism on SUJ2 ball and (a) as-deposited (b) UV irradiated a-C:H disk in Base oil

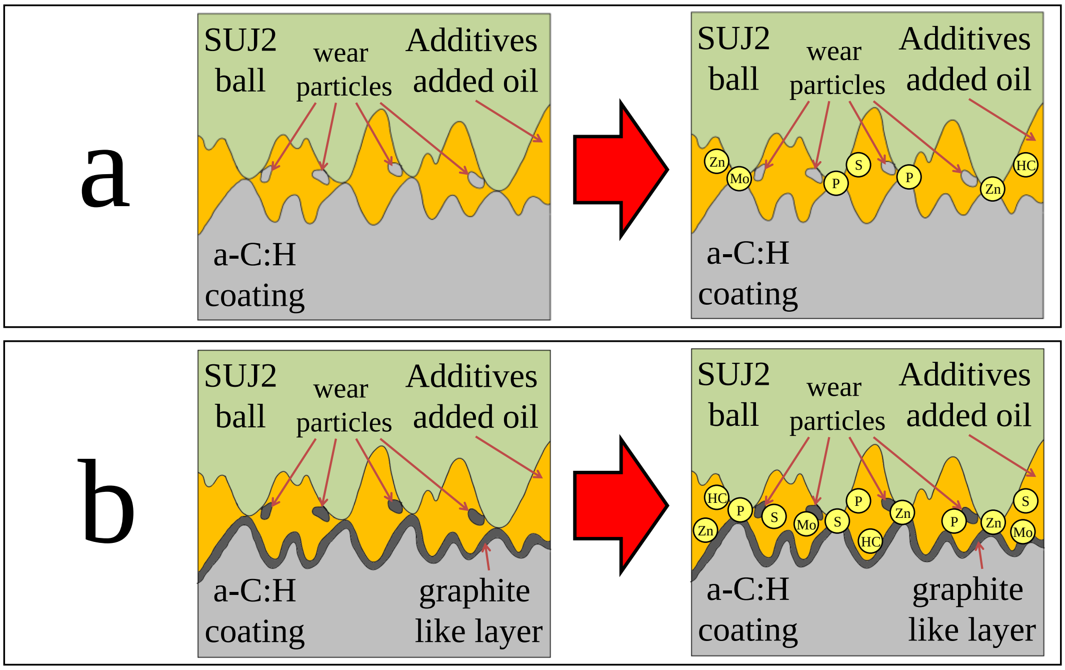


Figure 2-35 Tribofilm formation mechanism on SUJ2 ball and (a) as-deposited (b) UV irradiated a-C:H disk in additives added oils

However, for the case of friction test for the UV irradiated DLC in Base, the wear particles that wear during the sliding process was actually the DLC graphite-like layer that contains dangling bonds. These wear particles then attached to the SUJ ball making both disk and ball surfaces available for the oil elements to attach to. Hydrocarbon from the oil then attached to three surfaces which are the ball surface, graphite-like layer wear particles surface and graphite-like layer on UV irradiated disk surface thus producing thick tribofilm between the ball and disk that further reduce the friction coefficient.

Next, the mechanism of tribofilm formation on as-deposited and UV irradiated sliding surfaces in additives added oils. The overall process of tribofilm attachment is quite similar with the Base. The difference is, instead of only hydrocarbon, elements such as Zinc, Sulphur, Phosphorus and Molybdenum were also detected attached on the sliding surfaces. For the case of ZnDTP and ZnDTP+GMO lubrication, the tribofilm produced mainly consist of hydrocarbon, Zinc, Sulphur and Phosphorus elements. The tribofilm for these two types of oil then generates thin and smooth surface between the sliding surfaces. The UV irradiated DLC however exhibits thicker tribofilm thickness than the as-deposited DLC. This represents that the dangling bond on graphite-like layer attracted more beneficial wear and friction reduction additives elements to affix on its surface which then reflected to the result of lower friction for the UV irradiated DLC.

ZnDTP+MoDTC on the other hand, produced thicker tribofilm compared to the other two previous lubricant oils. The tribofilm comprise of hydrocarbon, Zinc, Sulphur and Molybdenum elements. Tribofilm thickness on SUJ2 ball for the UV irradiated DLC was thinner than on the as-deposited DLC, which probably due to the lower amount of Sulphur attached on the ball. The same trend of reduction of element attachment such as Sulphur and Molybdenum can also be seen on the on the UV irradiated DLC disk. This indicates that the graphite-like layer produced by the UV irradiation process is capable to reduce the ability of wear accelerating elements in MoDTC such as Molybdenum and Sulphur to attach on the DLC surface contributing to lower friction and wear for the UV irradiated DLC [60].

Tribofilm formation on the surface of SUJ2 ball paired with UV irradiated a-C:H disk in ZnDTP+MoDTC however, due to the graphite-like layer seems to be unfavourable for the Sulphur and Molybdenum to attach on its surface, cause high portion of Molybdenum to attach on the SUJ2 ball surface. The attachment of Sulphur on the other hand remains lower on the SUJ2 ball. One possible explanation for this is unlike Molybdenum, Sulphur attachment on SUJ2 ball might be depending on the amount of attachment Sulphur on the mating disk. So the lower the attachment of

Sulphur on the a-C:H disk, the lower the Sulphur detected on the SUJ2 ball. Further investigations are required to confirm this.

Figure 2.36 shows the wear mechanism possibly caused by the SO_x on a-C:H coatings. As being mentioned before in the section 2.3.6, for the case of lubrication in ZnDTP+MoDTC oil, the reduction of Sulphur element was observed. And reduction of wear rate of UV irradiated a-C:H can also be seen. From that, it is believed that the amount of Sulphur at% difference play some role in reducing the wear. One possible explanation is the excessive amount of Sulphur on UV irradiated a-C:H in ZnDTP and ZnDTP+GMO oils reacted with the Oxygen inside the oils and remaining Hydrogen on the graphite layer and produces corrosive sulphuric acid like compound [69]. This compound possibly caused chemical wear on the UV irradiated a-C:H explaining the higher wear under the two type of oil lubrication.

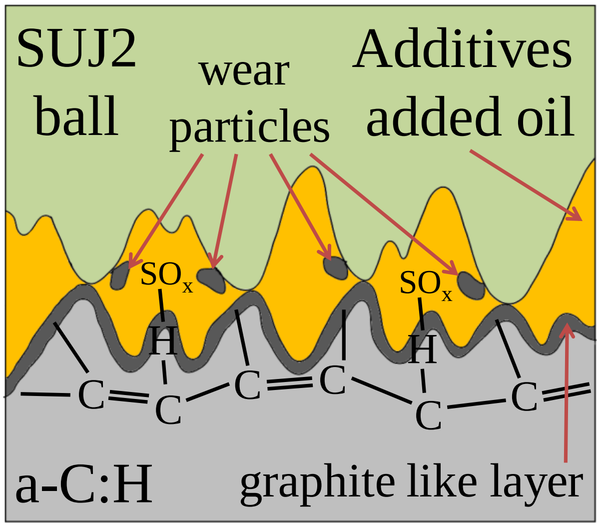


Figure 2-36 Wear mechanism caused by SO_x

2.4 Conclusions

The purpose of this chapter is to examine the effect of UV irradiation on the a-C:H film on the friction and wear characteristics when oil with additives is used and to discloses the nature and composition of the tribofilm produced after the interactions. The conclusions can be summarized as follows:

(1) By doing UV irradiation to a-C:H coating, the friction coefficient of UV irradiated a-C:H shows lower friction coefficient than as-deposited a-C:H despite the type of lubricant oil. Specifically in ZnDTP oil, the friction coefficient decreased from 0.06 to 0.04. Largest reduction of specific wear rate was shown by UV irradiated a-C:H in ZnDTP+MoDTC oil from 9.69 x 10^{-9} mm^3/Nm to 1.26 x 10^{-9} mm^3/Nm.

(2) The tribofilm formed on both a-C:H disks and SUJ2 balls was measured by EDS-SEM and 3D interferometry. It was revealed that the film thickness did not change very much on a-C:H coating but it was observed that by doing UV irradiation, the oil additives elements from each lubricant oils attached more on the UV irradiated a-C:H. In particular, all lubricant oils show an increase of selected oil additives elements at% except for ZnDTP+MoDTC oil where a reduction of Molybdenum and Sulphur was observed.

(3) On the mating material SUJ2 balls, it was revealed that the tribofilm thickness increased by UV irradiation except for ZnDTP+MoDTC oil where reduction observed probably caused by the reduction of Sulphur. In the overall, ZnDTP+MoDTC forms thicker tribofilm on SUJ2 ball which around 70 nm to 75 nm than the other two additives added oil which is around 10 nm to 20 nm.

(4) In the overall, UV irradiated a-C:H in ZnDTP+MoDTC considered as the best combination in terms of specific wear rate reduction on the sliding interfaces and

the reason are as follows. Generally UV irradiation helps to attract more oil additives elements to attach on the sliding interfaces, however particularly for ZnDTP+MoDTC oil, UV irradiation reduces the attachment of wear producer Molybdenum and Sulphur. Combined with the formation of thicker tribofilm formed by ZnDTP+MoDTC oil on the mating material SUJ2 balls further helps to improve the friction and wear of the combination.

3. Effects of oil additives and mating materials to friction, wear and seizure properties of a-C:H coating

3.1 Introduction

It is estimated that over 30% of the chemical energy converted from engine fuel is to be transformed into friction between bearing parts under oil boundary lubrication conditions [70]. Deposition of diamond-like carbon (DLC) to engine parts is one of the methods to scale down these losses so that higher fuel and engine efficiency can be achieved. With a combination of both sp^2 and sp^3 structures, DLC is one amorphous material that has the characteristics that is of low in friction, high hardness, chemically inert and highly wear resist [34], [71], [72]. However, before depositing DLC coating to engine parts, the problem of incompatibilities between DLC and lubricant additives needs to be solved first to avoid components or parts failure. This is because fully formulated commercial lubricants oils consist of various type of additives were designed to serve the interaction between metal to metal and not in between DLC and metal.

Progressive amounts of analytical investigations related to the friction and wear characteristic of DLC coatings under lubricated environments have been carried out over the past few decades [12], [73], [74]. One of the study is the existence of self-lubricating MoS2 sheets in friction modifier Molybdenum Dithiocarbamates (MoDTC) contained lubricant oil, enables the hydrogenated DLC coatings to gain ultra-low friction coefficient [46], [75]. However, there are also studies reported that hydrogenated DLC coatings in lubricants with MoDTC marked higher wear rates than in Base oil lubrication [48], [63]. [49], [50] manifested that the friction and wear of DLC coatings can further be reduced when boundary lubricated with MoDTC and Zinc Dialkyldithiophosphate (ZnDTP) contained lubricant oil. By means of tribochemical reactions, ZnDTP produces wear protective tribofilm on top of ferrous surface and has ever since been used extensively as anti-wear additive in lubricant oil [52]. There are some studies denoted that ZnDTP is incapable to play its role as anti-wear on DLC surface due to its chemical inertness property [55], [56] however, note that there are also studies claiming about the construction of thin ZnDTP tribofilm, on DLC coatings [53], [76].

Apart from the utilization of Titanium Carbide (TiC) and Titanium Nitride (TiN) in extending the lifespan of cutting tools, both materials also used as a coating on machine elements such as sliding bearings, seals, and valves [77]. [78], [79] reported that in dry surface friction test, the wear rate of TiN coated specimen is lower than TiC coated specimen, however the friction coefficient is relatively higher than that of the TiC film. [80] indicated that in PAO oil boundary lubrication friction test, the wear rate of a-C:H/TiC and a-C:H/steel tribo-pairs denoted the lowest wear rate compared to the other four tribo-pairs. Previous study by [81]–[83] has demonstrated the effects of different mating materials in dry air environment to the friction and wear of diamond-like carbon (DLC) by altering the types and hardness of the mating materials.

However, no attempt is made to investigate the effects of both lubricant additives and mating materials to DLC coating. In this study, tribological test between hydrogenated amorphous carbon (a-C:H) DLC slide against three type of mating materials of uncoated SUJ steel disk, Titanium Carbide (TiC) and Titanium Nitride

(TiN) coated SUJ2 steel disk in Base and ZnDTP+MoDTC oils have been done, and their characteristics in terms of friction and tribofilm formation have been investigated.

3.2 Materials and test method

3.2.1 Hydrogenated DLC and lubricant oil additives

The hydrogenated amorphous carbon (a-C:H) coatings used in this study were supplied by Daido Metal Co. Ltd with a hydrogen content of 30 at%. They were deposited by a plasma enhanced chemical vapour (PECVD) method on the high carbon chrome steel (SUJ2) cylinder roller substrate with a thickness of 4.0 μm. The top surface of the DLC coating was polished during the finishing process to eradicate the droplets and particles possibly attached on the coating surface. Atomic force microscopy (SEIKO, Nanopics 1000) and Nanoindenter (NANOPICS 1000 Elionix ENT-1100a) was used to determine the surface roughness, hardness and Young’s modulus of the DLC coating. Three variations of mating material disks used in this study were uncoated SUJ2 disk, and also Titanium Carbide (TiC) and Titanium Nitride (TiN) coated SUJ2 disks. Detailed properties of DLC coated roller and mating material disks are listed in Table 3.1.

Table 3.1 Properties of mating material disks and DLC roller

Properties	Roller	Disk		
	a-C:H	SUJ2	TiC	TiN
Dimension (mm)	Ø5 x 5	Ø22.5 x 4	Ø22.5 x 4	Ø22.5 x 4
Substrate	SUJ2	-	SUJ2	SUJ2
Thickness (μm)	4	-	1	1

Based on the results from chapter 2, ZnDTP+MoDTC shows the best results in terms of specific wear rate reduction compared to the other two ZnDTP and ZnDTP+GMO oil additives added lubricants. Therefore in this chapter, ZnDTP+MoDTC oil was selected as the main oil additives added lubricant oil and Base oil was selected to be the point of reference for comparison purpose of the friction test results. For the ZnDTP+MoDTC oil, apart from anti-wear agent from ZnDTP and friction modifier from MoDTC, the oil was also formulated with five common additives of detergent, anti-oxidant, foam inhibitor, dispersant and viscosity improver. Detail properties of each lubricant oils are tabulated in Table 3.2.

Table 3.2 Each lubricant properties

	Base	Base+ZnDTP +MoDTC
Viscosity mPa·s	4.25	5.92
Ca (wt%)	-	0.20
Mo (wt%)	-	0.07
P (wt%)	-	0.08
Zn (wt%)	-	0.09
S (wt%)	-	0.22
N (wt%)	-	0.10

3.2.2 Friction tester equipment

Figure 3.1 shows a schematic diagram of the roller-on-disk friction tester used in this research for the friction test against three types of mating material in two types of lubrication oils. In the friction test, four incremental-fixed loads of 10, 20, 30, 40 and 50 N (corresponding to maximum initial Hertzian contact pressures of 170, 240, 295, 340 and 380 MPa respectively for each load) were applied above the roller with the time interval of 20 minutes in between each load. The sliding speed of the two opposing surfaces was set at 100 rpm equivalent to 6.80×10^{-2} m/s at the centre of the roller. Therefore there is a linear distribution of velocity from 4.71×10^{-2} m/s to $8.90. \times 10^{-2}$ m/s due to the radius range. The test temperature was set at 80°C. The tests were then repeated again 3 times for confirmation and reproducibility of results. Before and after the friction tests, all the mating materials and the a-C:H coated rollers were cleaned by acetone for 15 minutes. The above mentioned friction test experimental conditions were then summarized in Table 3.3.

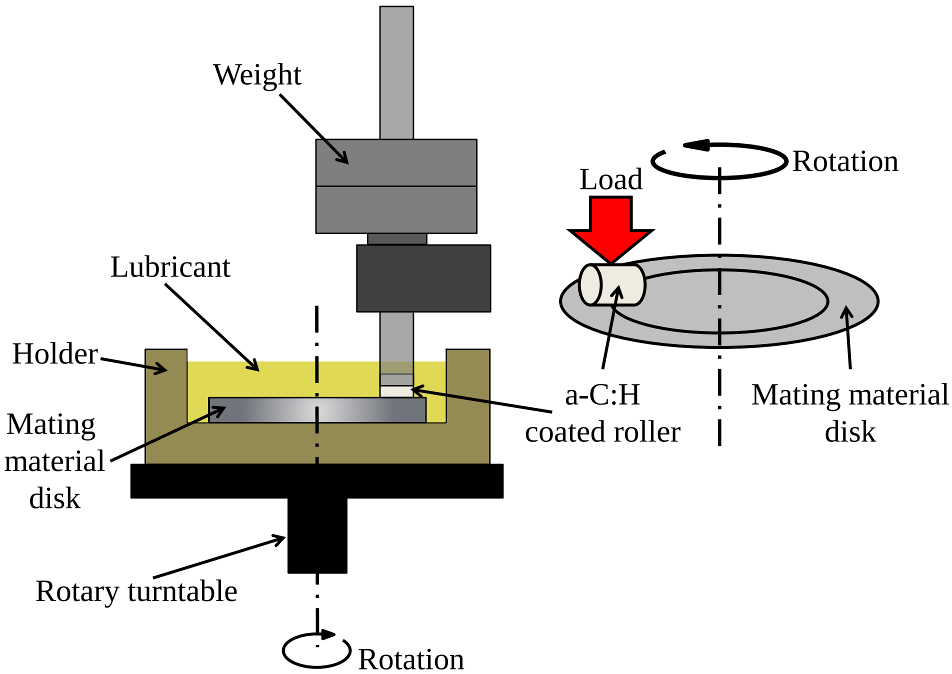


Figure 3-1 Schematics of roller-on-disk friction tester

Table 3.3 Roller on disk friction test experimental conditions

Experimental conditions	
Roller	a-C:H
Disk	SUJ2, TiC, TiN
Load, N	10, 20, 30, 40, 50
Max. initial Hertzian	170, 240, 295,
contact pressure, MPa	340, 380
Temperature, ^{o}C	80
Sliding speed, rpm	100
Sliding speed, m/s	6.80×10^{-2}
Duration, min	100 20 min/load

3.2.3 DLC surface and tribofilm analysis equipment

In this research, nano-indentation hardness tester ENT-2100 manufactured by Elionix was used to execute the indentation hardness test on the mating material disks before and after friction tests. Surface morphology of tribofilm formed on mating material disks were studied using non-contact, three-dimensional, scanning white light interferometry (Zygo, Newview) and elemental study were done by utilizing the energy dispersive X-ray spectroscopy (EDS) to analyse the tribofilm chemical composition of the worn disk and roller surfaces.

3.3 Results and discussions

3.3.1 Friction coefficient

Seizure test was conducted by applying incremental-fixed load, and seizure manifestation was observed in the form of large mass flow on the disc, steep accretion of friction coefficient, and uncommon noise and vibration originated from the roller on disk friction tester. Figure 3.2, 3.3 and 3.4 shows the typical test results of each a-C:H/SUJ2, a-C:H/TiC and a-C:H/TiN tribo-pairs in Base and ZnDTP+MoDTC oils.

Figure 3.2 shows the friction coefficient as a function of cycle numbers and applied force for a-C:H/SUJ2 tribo-pair under boundary lubrication condition. At the initial stage of friction test, the rapidly decreased friction coefficient reveals that the tribo-pair encountered a running-in period, and identical phenomenon appeared at every fixed load phases for both type of lubricant oils. As shown on the figure, friction coefficient decreased deliberately with the increment of applied force and number of sliding cycle. However, in comparison, the a-C:H/SUJ2 tribo-pair in Base oil showed lower friction coefficient of 0.05 than 0.08 in ZnDTP+MoDTC oil at the end of friction test.

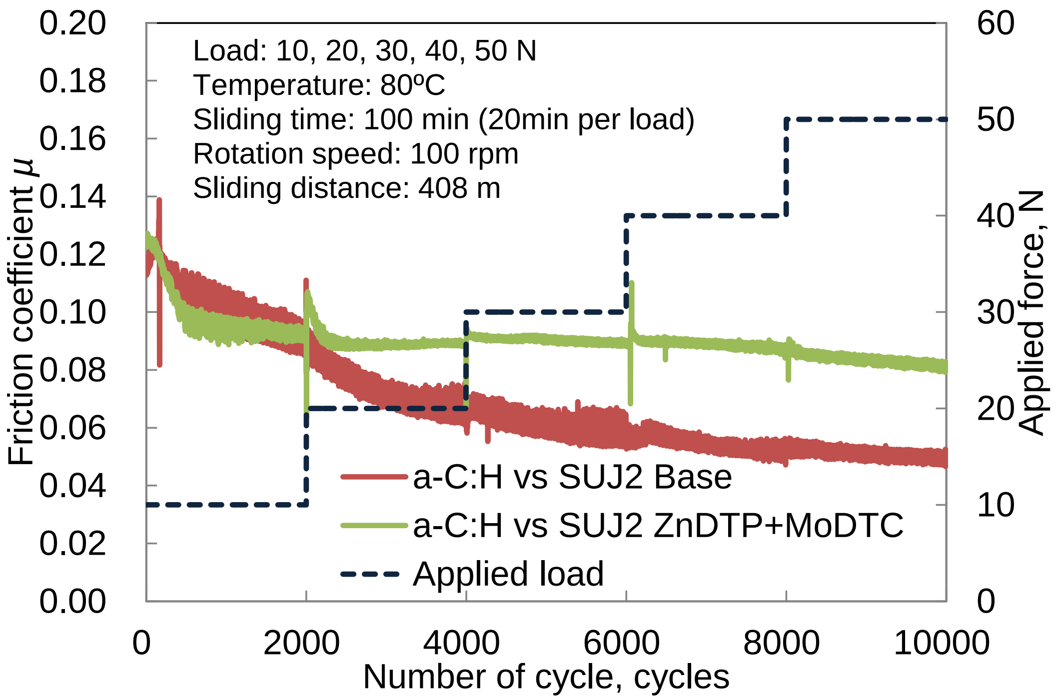


Figure 3-2 Friction coefficient of a-C:H/SUJ2 tribo-pairs in Base and ZnDTP+MoDTC oils

Figure 3.3 exhibits the friction coefficient as a function of cycle numbers and applied force for a-C:H/TiC tribo-pair under boundary lubrication condition. It is revealed that there was no significant change of friction coefficient with the rising of incremental-fixed load for a-C:H/TiC tribo-pair in ZnDTP+MoDTC. The friction coefficient value stayed almost stagnant at 0.09 from start to the end of friction test. The friction coefficient of a-C:H/TiC tribo-pair in Base oil however was unstable and kept on fluctuating from the start of the friction test. During 40 N incremental-fixed loads, as the usual running in phenomenon taking place, at 6500 cycle, the friction coefficient bounced and gradually increased. At 50 N incremental-fixed load, croaking noise and vibration was observed hence, the test was brought to a halt promptly.

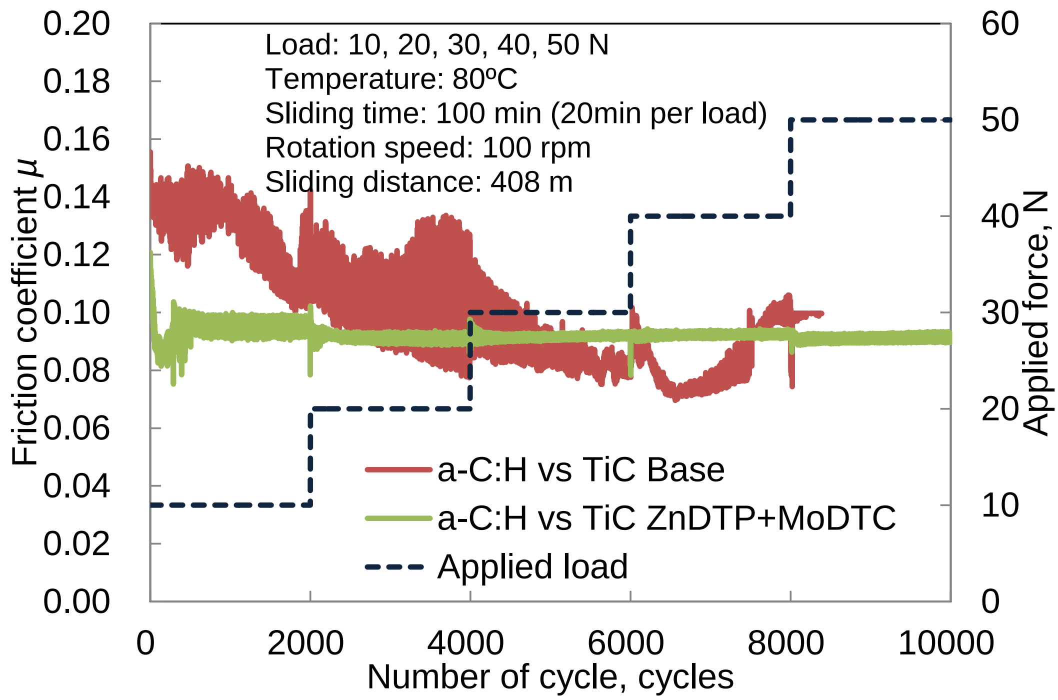


Figure 3-3 Friction coefficient of a-C:H/TiC tribo-pairs in Base and ZnDTP+MoDTC oils

Figure 3.4 exhibits the friction coefficient as a function of cycle numbers and applied force for a-C:H/TiN tribo-pair under boundary lubrication condition. With uniform pattern of running-in cycles, friction coefficient of a-C:H/TiN tribo-pair in ZnDTP+MoDTC decreased gradually with the increment of applied force and number of sliding cycle. Although the friction coefficient of a-C:H/TiN tribo-pair in Base oil was unsteady and kept on fluctuating, no signs of seizure occurrence found.

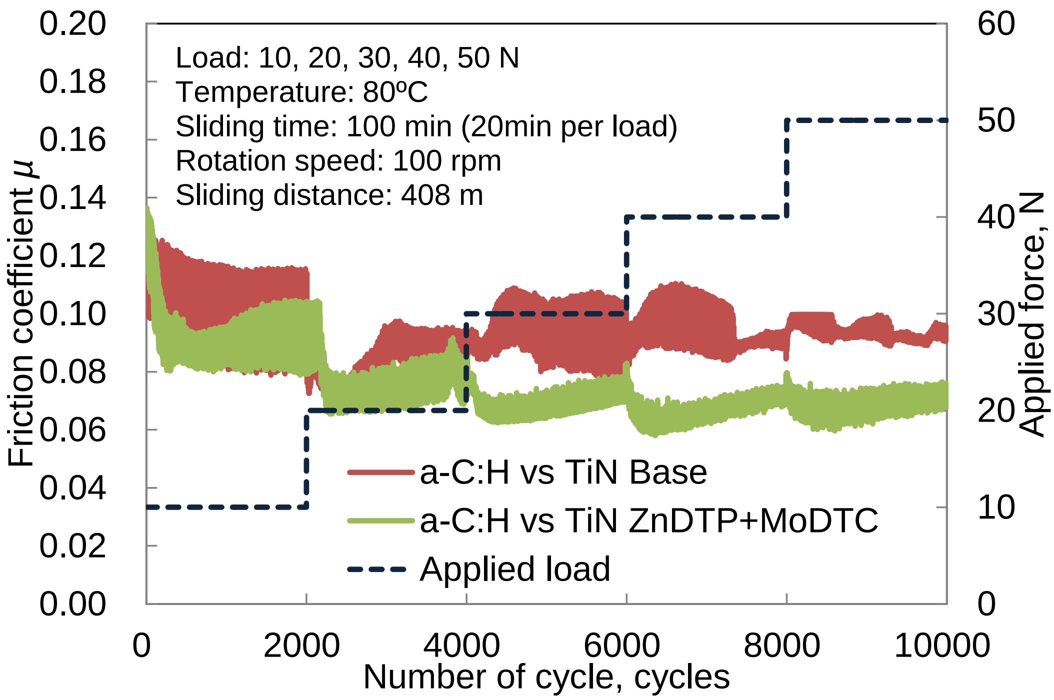


Figure 3-4 Friction coefficient of a-C:H/TiN tribo-pairs in Base and ZnDTP+MoDTC oils

To make comparison of which lubricant oil gives the lowest and the highest friction coefficient, the results then concluded into one bar graph as shown in Figure 3.5 by taking the average of steady state friction coefficient between 4000 to 8000 cycles. As shown in the figure, a-C:H/SUJ2 tribo-pair in Base oil marked the lowest friction coefficient except for a-C:H/TiN tribo-pair in ZnDTP+MoDTC oil that recorded the second low friction coefficient, the rest tribo-pair in both type of oils logged the maximum value of friction coefficient of approximately 0.09.

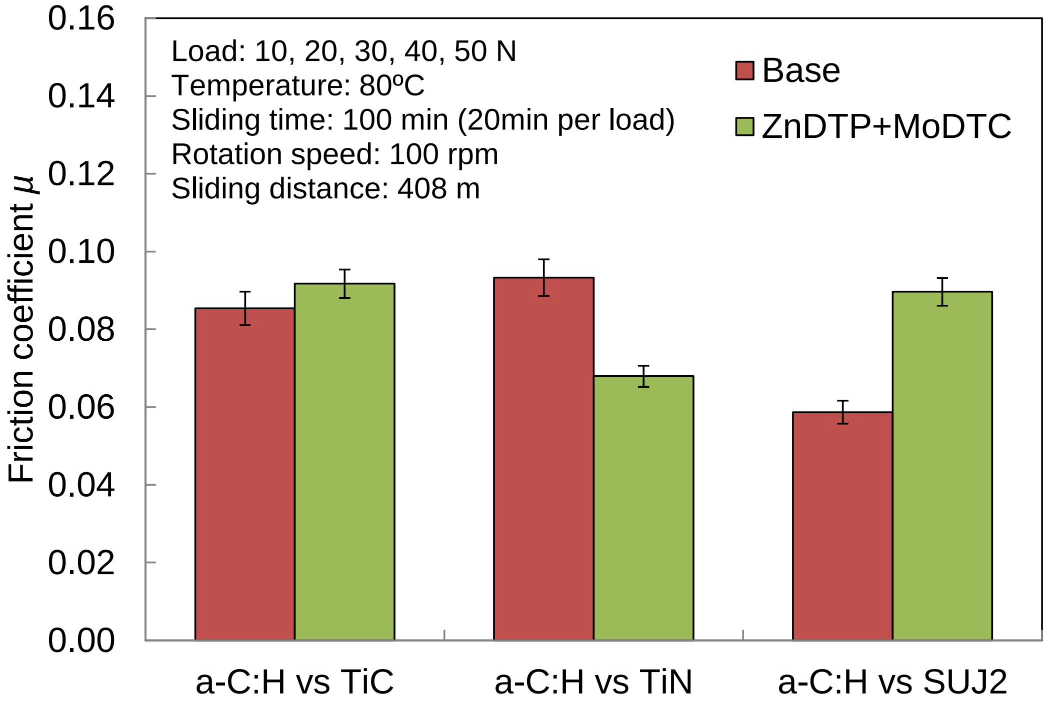


Figure 3-5 Friction coefficient of all three tribo-pairs in Base and ZnDTP+MoDTC oils

3.3.2 Wear volume

Wear volume of a-C:H for each tribo-pair in Base and ZnDTP+MoDTC oils are shown in Figure 3.6. The highest and lowest wear volume of a-C:H is denoted by the same a-C:H/TiC tribo-pair in Base and ZnDTP+MoDTC oils respectively. The distinction between the two tribo-pair is compelling with 99.6% of reduction from Base to ZnDTP+MoDTC oil. Comparatively, a-C:H/TiN tribo-pair manifested high wear volume with significant 47.8% reduction from Base to ZnDTP+MoDTC oil. The a-C:H/SUJ2 tribo-pair wear volume however increased 44% higher from Base to ZnDTP+MoDTC oil.

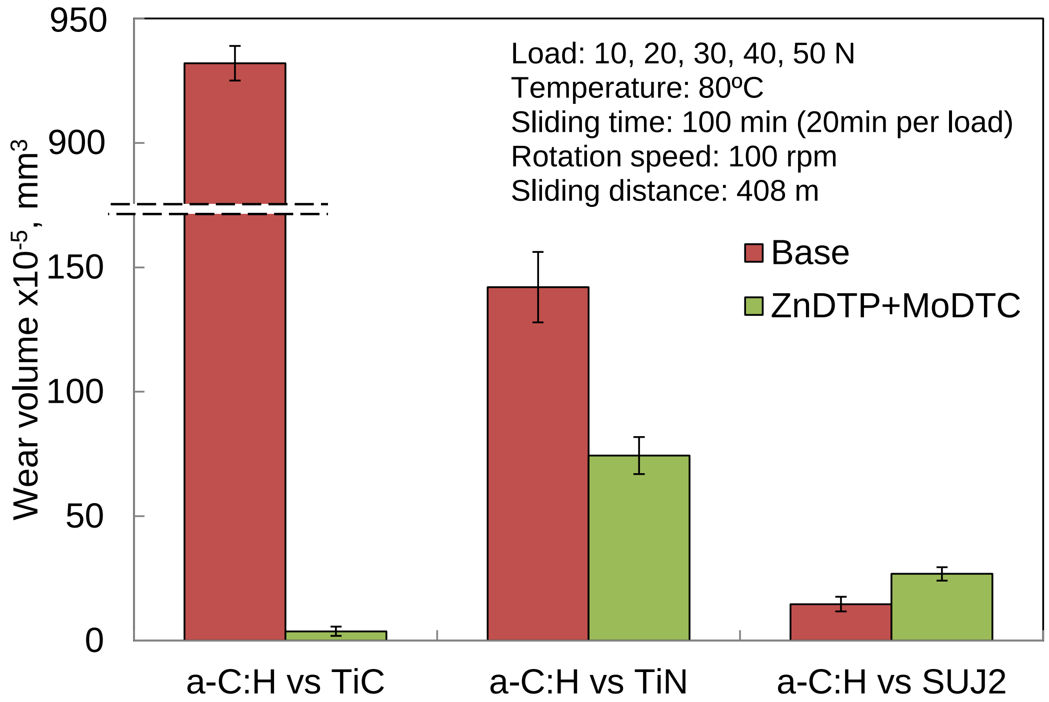


Figure 3-6 Wear volume of all three tribo-pairs in Base and ZnDTP+MoDTC oils

3.3.3 Seizure occurrence observation on roller and disk

Figure 3.7 shows the optical microscope images of a-C:H/SUJ2, a-C:H/TiC and a-C:H/TiN tribo-pairs in Base oil. For the case of a-C:H/SUJ2 tribo-pair, the top surface of DLC roller wear has produced a polished mirror-like surface contributing to low friction coefficient. Because of the mating material was an uncoated SU2 steel, no sign of spalling from neither the roller nor the disk was observed. The finding suggests that no abrasive wear particles existed during the contact and as a result low wear volume obtained. Next, the arrangement of a-C:H/TiC tribo-pair disclosed the widest DLC wear width compared to the other tribo-pairs. Figure 7 (c) and (d) shows that the TiC coating on the disk peeled off and the DLC coating on the roller spalled and worn out. This led to metal to metal contact between both surfaces due to the excessive load imposed. Consequently, initial stage of seizure happened where irregular noise and vibration were noticed coming from the friction tester. TiN coated disk on the other hand, was the hardest mating material disks compared to the other two. Consequently, the DLC coating for the a-C:H/TiN tribo-pair wore heavily and spalled, causing the high wear volume of the DLC roller.

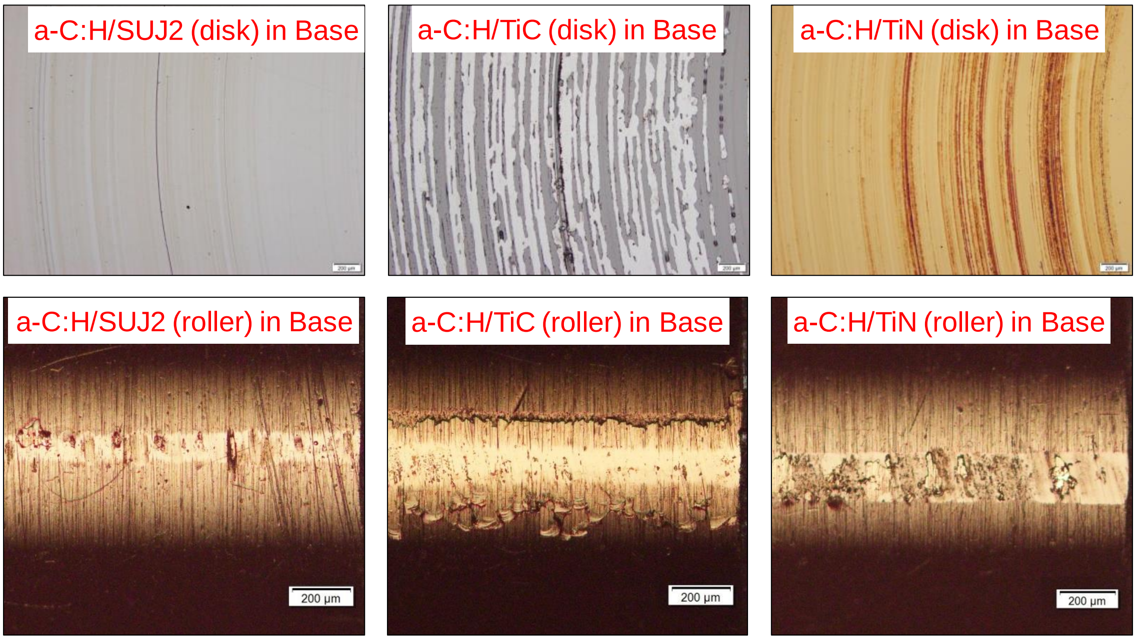


Figure 3-7 Optical microscope images of all three tribo-pairs Base oil

Figure 3.8 shows the optical microscope images of a-C:H/SUJ2, a-C:H/TiC and a-C:H/TiN tribo-pairs in ZnDTP+MoDTC oil. As can be seen in the figure, all three tribo-pairs disk exhibited wear track with traces possibly tribofilms as a result of the rubbing between the two surfaces. And, all three tribo-pairs showed no spalling on the a-C:H rollers. Consistent with findings of past studies, wears of DLC/steel contact were especially high in MoDTC included lubricant oil [48], [63]. This is reflected on the configuration of a-C:H/SUJ tribo-pair where high wear volume of a-C:H roller plus, blue and brownish wear pattern observed on the mating disk. High hardness of TiN disk further increased the wear volume of a-C:H/TiN tribo-pair with dark orange pattern formed on the disk wear track. a-C:H/TiC tribo-pair revealed the smallest a-C:H wear width with brownish wear pattern observed on the mating disk.

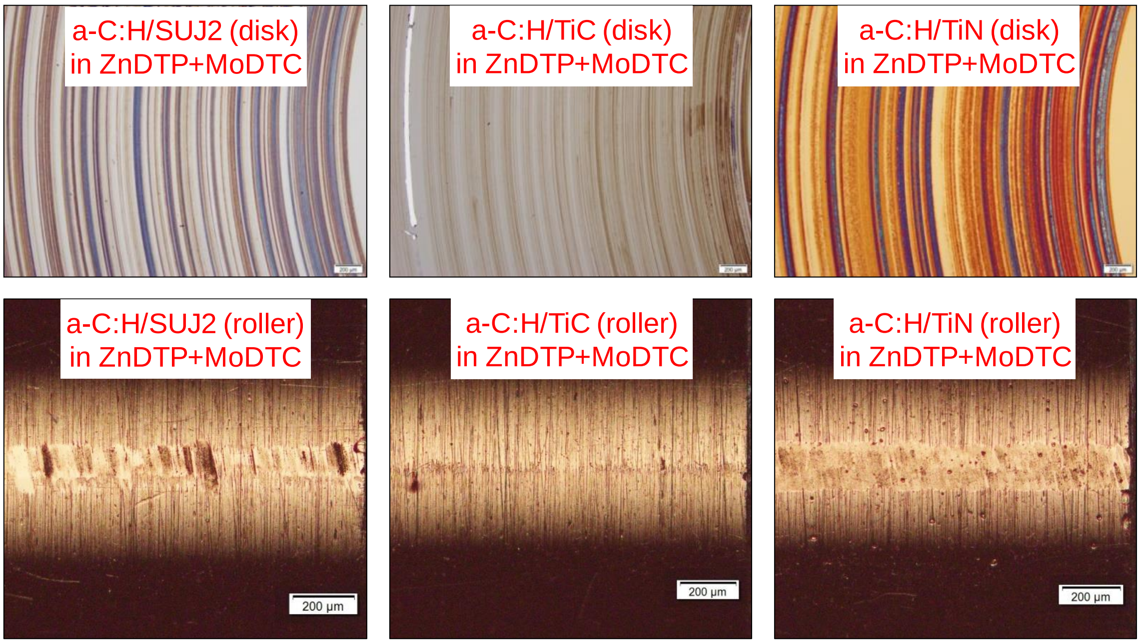


Figure 3-8 Optical microscope images of all three tribo-pairs ZnDTP+MoDTC oil

Seizure is basically attributed to exceptional micro-welding situated in the interfaces. It is inwardly overwhelmed by the nature of mating materials themselves and outwardly activated by applied stress instead of relative velocities [84]. In this study, all the three mating materials could administer seizure resistance particularly in ZnDTP+MoDTC lubricant oil. Although the Molybdenum inside the oil tends to cause high wear on DLC, it can suppress the effect of peeling off on both DLC and mating material coatings. Arrangement of a-C:H/TiC in Base oil however, came out to be the most unsuitable combinations due to the lack of anti-wear additives causing high wear and peeling off on both roller and disk coating materials that later led to the seizure occurrence.

3.3.4 Tribofilm elemental investigation

SEM element analysis area images of wear scar on roller and disk for each tribo-pair in Base and ZnDTP+MoDTC oils are shown as Figure 3.9 and Figure 3.10 respectively. An energy dispersive X-ray spectroscopy (EDS) was utilized to perform a qualitative element analysis of which elements of additives oils that appended on both roller and disk contact surfaces. Zinc, Phosphorus, Sulphur and Molybdenum were the main elements of ZnDTP and MoDTC lubricant additives and also Calcium from detergents was selected to be investigated. Common elements coming out from both oil additives and mating materials that were Carbon, Oxygen, Nitrogen and Iron were also monitored during the investigation. Atomic concentration values gained were then translated into bar graphs as shown in Figure 3.11 (a) and (b) also Figure 3.12 (a) and (b) to evaluate the differences in between each tribo-pair by observing the changes of lubricant additives' atomic concentration on both sliding surfaces. Oxygen atomic percentage on both roller and disk for each tribo-pair were about equal to each other and higher compared than that of Base oil. This indicates that Oxygen that coexisted in both ZnDTP and MoDTC further increased the Oxygen attachment on rollers and disks.

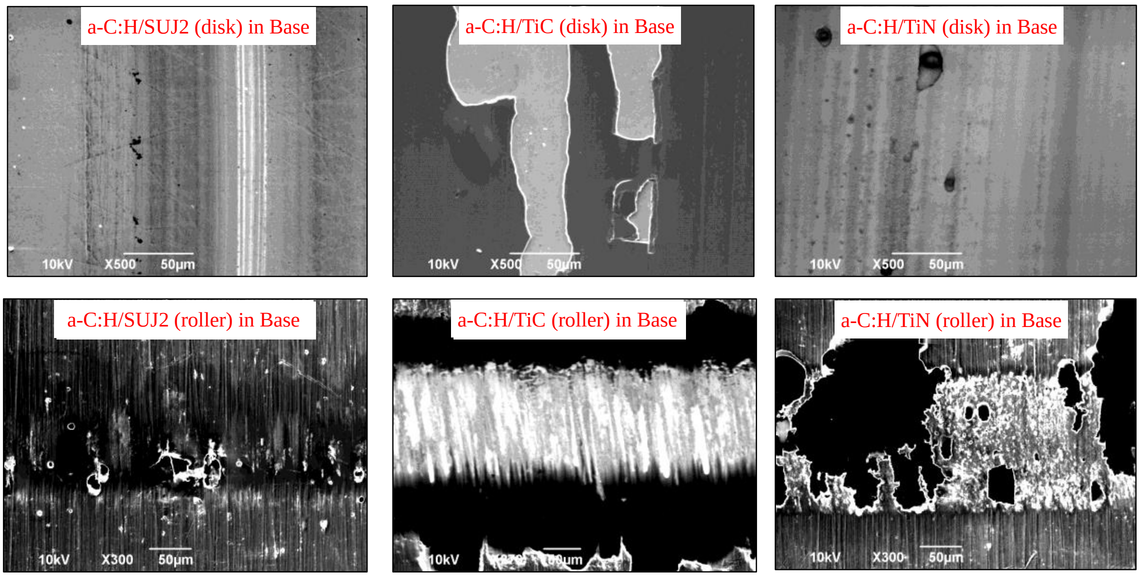


Figure 3-9 SEM images of EDS analysis area of all three tribo-pairs Base oil

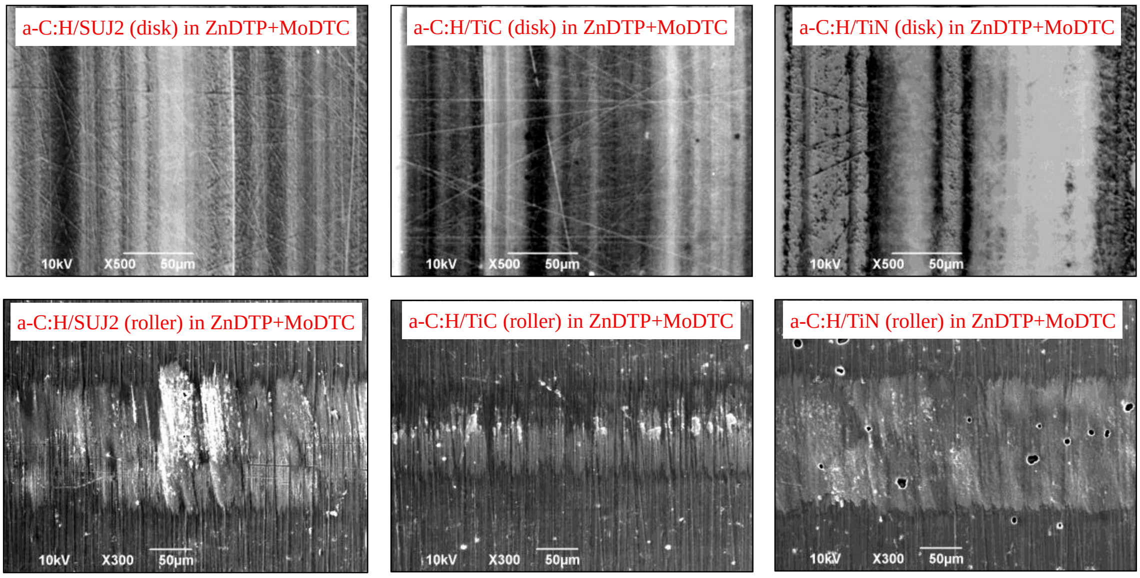


Figure 3-10 SEM images of EDS analysis area of all three tribo-pairs ZnDTP+MoDTC oil

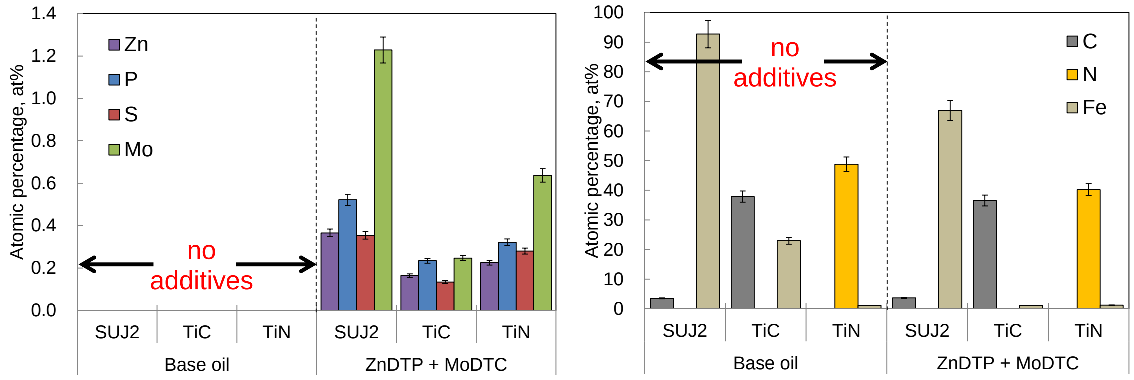


Figure 3-11 Lubricant additives elements analysis by EDS on mating material disks

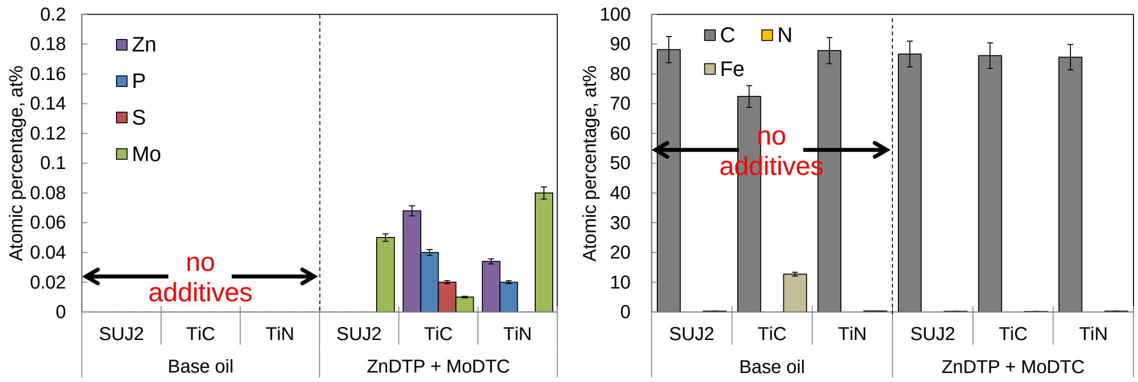


Figure 3-12 Lubricant additives elements analysis by EDS on a-C:H rollers

For the case in Base oil, the findings suggest that high atomic percentage of Carbon, Iron and Nitrogen represents the value of a-C:H rollers and SUJ2, TiC and TiN disks main material atomic percentages. Generally, because of there was no lubricant additives included inside Base oil; there was no Zinc, Phosphorus, Sulphur and Molybdenum detected on each tribo-pairs disks and rollers for the case of friction test in Base oil. Oxygen detected on a-C:H/SUJ2 and a-C:H/TiC tribo-pairs roller and disk indicates oxidation occurred on both sliding wear surfaces. Except for a-C:H/TiN tribo-pair, Oxygen only discovered on DLC roller surface. Traces of Carbon possibly originated from a-C:H/SUJ2 tribo-pair DLC roller suggests that small transferred layer formed on SUJ2 disk. a-C:H/TiC tribo-pair exhibited high concentration of Iron on both roller and disk surfaces indicates that peeled TiC coating as well as worn out a-C:H coating have exposed the Iron substrate underneath both surfaces due to exponentially high wear volume for this a-C:H/TiC tribo-pair. There was also peeling off observed on a-C:H/TiN tribo-pair DLC coating but not as severe as in a-C:H/TiC tribo-pair. This was reflected by the detection of Iron on TiN disk which transferred from the DLC worn substrate particles to the TiN disk.

For the case in ZnDTP+MoDTC oil, a-C:H/SUJ2 tribo-pair signified the highest atomic percentage of Zinc, Phosphorus, Sulphur and Molybdenum on SUJ2 disk and intermediate amount of Molybdenum traced on the DLC roller. a-C:H/TiC tribo-pair on the other hand, disclosed the smallest atomic percentage of Zinc, Phosphorus, Sulphur and Molybdenum on TiC disk. The all four elements also found on the DLC roller with the least in Molybdenum and the highest in Zinc and Phosphorus. a-C:H/TiN tribo-pair marked the second highest atomic percentage of Zinc, Phosphorus, Sulphur and Molybdenum on TiN disk. Highest concentration of Molybdenum was also observed on DLC roller with traces of Zinc and Phosphorus.

Based on all the above results and description, the findings suggest that no beneficial tribofilm to reduce wear and friction produced on the sliding surfaces of the three tribo-pairs in Base oil. Because of that, a-C:H/TiC tribo-pair cannot withstand high load causing both roller and disk coatings were peeled under the given load. a-C:H/TiN tribo-pair DLC roller was also largely worn out due to the rubbings against harder TiN coated disk. a-C:H/SUJ2 appears to be the best candidate in Base oil with lower wear volume but relatively still high compared to a-C:H/TiC in ZnDTP+MoDTC. The wear of DLC under high load can further be reduced by finding the best match for a-C:H mating material in ZnDTP+MoDTC oil. The criterion is tribo-pairs that can dampen the wear accelerative effect of MoDTC and fully taking advantage on the presence of anti-wear ZnDTP inside the oil.

In ZnDTP+MoDTC, all mating material SUJ2, TiC and TiN can absorb the oil additives elements. a-C:H/SUJ2 and a-C:H/TiN tribo-pairs both revealed high atomic percentage of Molybdenum both on disk and roller which led to high wear volume on DLC roller. a-C:H/TiC tribo-pair on the contrary demonstrated smaller yet complete set of Zinc, Phosphorus, Sulphur and Molybdenum oil additives elements, found on both the roller and the disk. The finding provides evidence that TiC disk is able to accommodate a surface that attracts low concentration of oil additives elements on its surface and proved to be favourable to reduce wear of DLC coating.

Figure 3.13 shows the Calcium and Oxygen attachment on rollers and disks under both type of oil lubricant. Generally, the at% of Calcium on a-C:H rollers for all type of mating materials are about the same concentration. On the mating materials, TiC and TiN shows quite similar concentration to each other however on SUJ2, the at% value was higher than the previous two. Based from the results, Calcium from detergents do not show obvious difference to each other except for the case on SUJ2 disk where the at% was slightly higher.

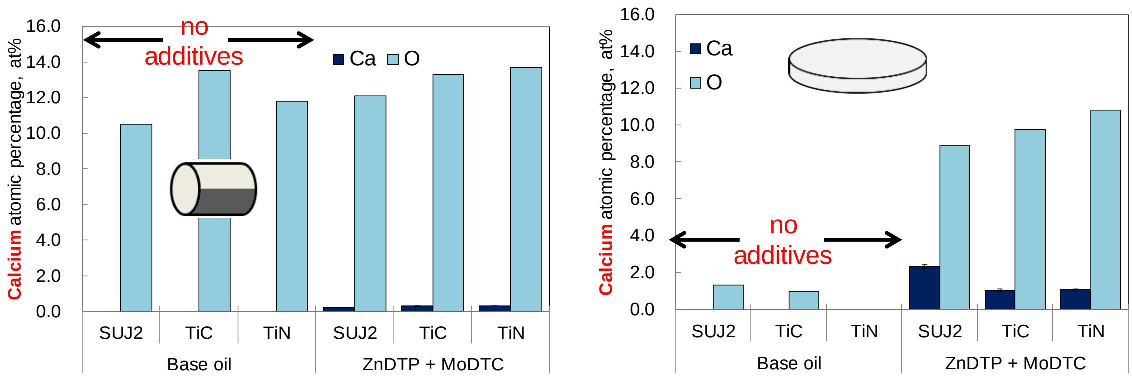


Figure 3-13 Calcium and Oxygen attachment on rollers and disks

3.3.5 Mating material coatings and tribofilms hardness and location

Because of no additives included inside Base oil, the observation and analysis of the effects of oil additives and mating materials to the formation of tribofilm was only done to the SUJ2, TiC and TiN disks in ZnDTP+MoDTC oil. Table 3.3 shows the results of hardness and Young's modulus of SUJ2, TiC and TiN mating material disks. All the three mating materials were subjected to indentation hardness test by a nano-indentation hardness tester to clarify the hardness of each mating material disks. The indentation load was set to 500 and 1000 μN. Lower 500 μN load was selected to verify whether the load can properly measure the hardness of the each mating materials disk surfaces. The same 500 μN was later used to determine the hardness of wear track formed on each mating material disks. The results suggest that both indentation loads can appropriately measure the hardness of each mating material disks with the highest hardness of 28 GPa for TiN, followed by TiC and SUJ2 with the hardness of 17 and 15 GPa respectively.

Table 3.4 Hardness and Young's modulus of all three mating materials

Mating material	SUJ2		TiC		TiN	
Indentation load, µN	500	1000	500	1000	500	1000
Hardness *H*, GPa	14.6	14.7	17.0	16.9	29.0	27.7
Hardness standard deviation, GPa	0.7	0.6	0.9	1.6	3.1	3.2
Young's modulus *E*, GPa	272.8	255.0	185.8	173.4	516.9	432.7
Young's modulus standard deviation, GPa	23.6	9.0	15.3	8.8	38.5	19.4

Figure 3.14 shows the nano-indentation location area of each mating material disks in ZnDTP+MoDTC oil. Ten selected indentation spot which are three on the bright spot of the wear track and the other seven on the darker spot of the wear track. The results of those ten hardness values were then converted into one single bar graph for both bright and dark spot hardness and shown in Figure 3.15. The results revealed that on the bright spot of the wear track, the hardness of each SUJ2, TiC and TiN were 14, 13 and 30 GPa which quite identical to the hardness values of the mating materials themselves. This suggests that on the bright spot of the wear track, there are no tribofilm formed on the area. On the darker area of the wear track however, the results varied from 3, 4 and 6 GPa for SUJ2, TiC and TiN accordingly. This indicates that the tribofilm on each wear track for each mating materials formed on darker area of wear track. Next investigation by 3D optical surface profiler was done to identify what basically these bright and darker areas of wear track represent, whether it is the ridges or grooves of the wear track.

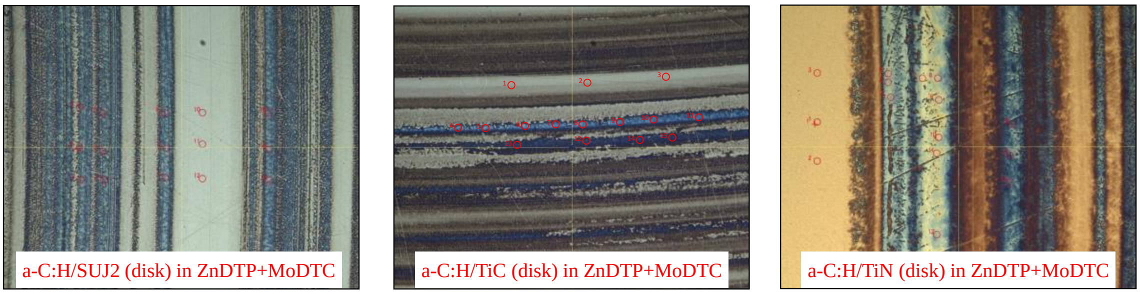


Figure 3-14 Nano-indentation analysis spots of all three tribo-pairs ZnDTP+MoDTC oil

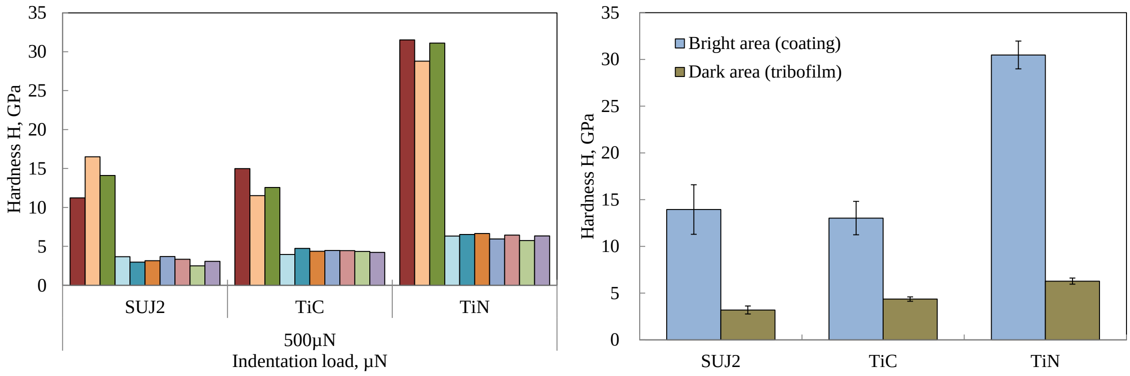


Figure 3-15 Hardness of tribofilm on mating materials bright and dark area

3.3.6 Wear track surface morphology

Figure 3.16 and Figure 3.17 shows the 3D optical surface profiler images and surface profile graphs of SUJ2, TiC and TiN after friction test in ZnDTP+MoDTC oils respectively. Table 3.4 shows the SUJ2, TiC and TiN disks wear track ridge height and groove depth and also roughness gained from the surface profile graph. As shown in Figure 3.17 and Table 3.4, TiC disk wear track exhibited the lowest roughness but on the contrary, both SUJ2 and TiN disks show high roughness of wear track.

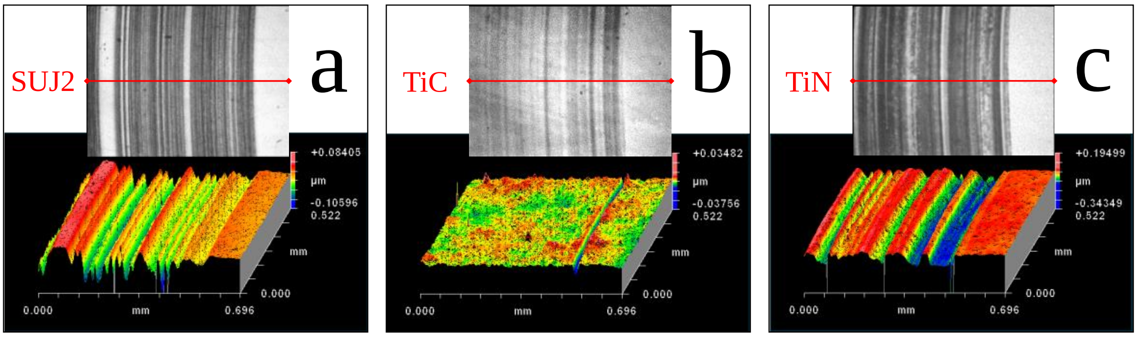


Figure 3-16 3D optical surface profiler wear tracks images of all three mating material disks lubricated with ZnDTP+MoDTC

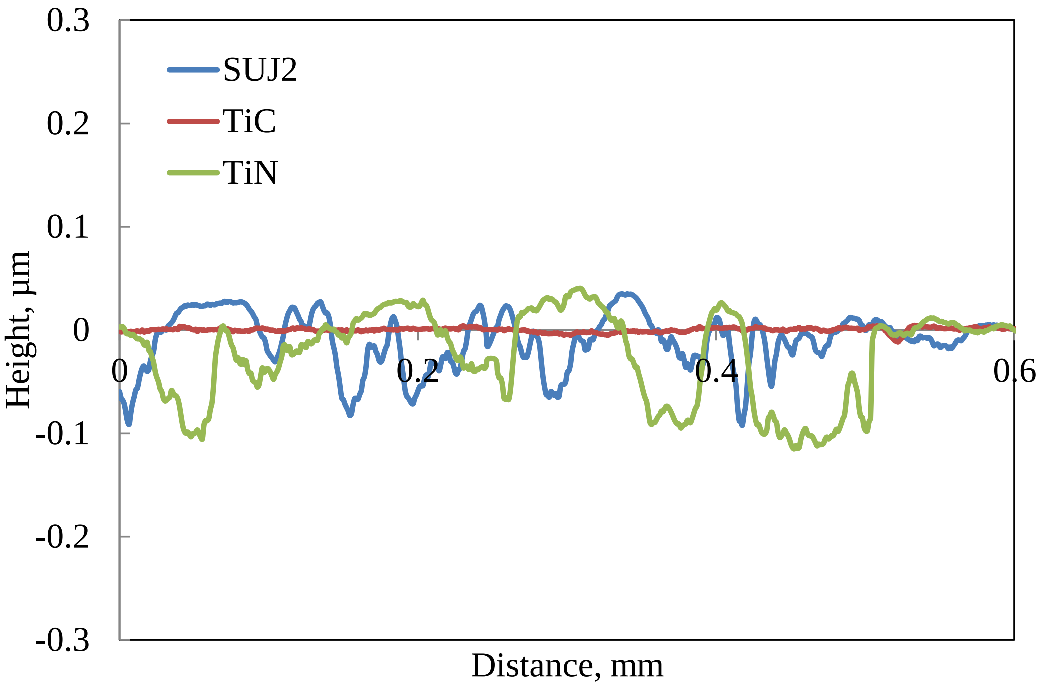


Figure 3-17 Surface profiles of all three mating material disks lubricated with ZnDTP+MoDTC

Table 3.5 Wear track roughness of all three mating material disks lubricated with ZnDTP+MoDTC

Mating material	SUJ2	TiC	TiN
Ridge height, nm	35.0	4.5	40.4
Groove depth, nm	92.2	11.6	115.0
Roughness, nm	23.0	2.0	37.0

Figure 3.16 (a) and (c) 3D images show the high roughness and severely worn out SUJ2 and TiN disk surfaces. The above black and white wear track images revealed that the bright and dark curve represents the ridges and grooves of the wear track. TiC disk 3D image as shown in Figure 3.16 (b) however, exhibited low roughness and wear on its surface without no obvious ridges and grooves. The black and white wear track image evinced that the bright and dark curve formed uniformly on the smooth surface of the disk. By referring back to the hardness result in the previous section, the finding suggests that the tribofilm of ZnDTP+MoDTC oil formed on the grooves of the wear track for the mating materials of SUJ2 and TiN. TiC disk however, the composed tribofilm scattered consistently all over the smooth TiC disk surface.

3.3.7 Tribofilm formation mechanism on a-C:H/SUJ, a-C:H/TiC and a-C:H/TiN tribo-pairs

Previous study by de Barros' Bouchet et al. [46] and Haque et al. [55] claimed that ZnDTP anti-wear additive oil will decompose into several forms which are Zinc phosphate, ZnO and ZnS. The ZnDTP main wear reduction agent of zinc phosphate does not construct on high hydrogen content of hydrogenated DLC coatings, as it would only remained as ZnO/ZnS in the tribofilm. MoDTC on the other hand forms a low shear strength hexagonal MoS_2 layer that acts as multi-layer solid lubricant which gives low friction on both ferrous and nonferrous surfaces. MoO_3 also another type of tribofilm forms from MoDTC which caused high friction due to its abrasive sharp edge crystalline properties [85], [86].

Figure 3.18 (a), (b), and (c) is illustrated to explain the mechanism of tribofilm formation on a-C:H/SUJ, a-C:H/TiC and a-C:H/TiN tribo-pairs. Figure 3.18 (a) indicates that higher friction coefficient and wear volume of a-C:H/SUJ2 tribo-pair in ZnDTP+MoDTC than in Base oil suggests that the tribofilm formed on both roller and disk consisted an abrasive MoO_3 that caused both sliding surface to wear out heavily. There was also Zn phosphate and ZnS present on the tribofilm however, the ability to reduce wear was not functional due to intensely high MoO_3.

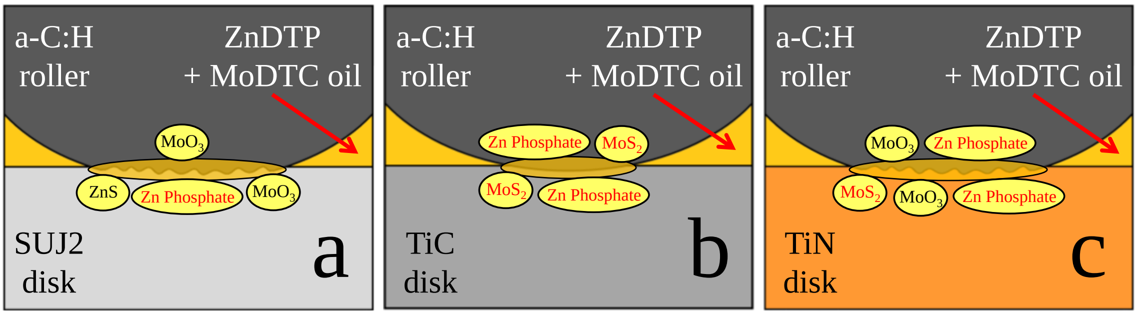


Figure 3-18 ZnDTP+MoDTC tribofilm formation mechanism on each mating material disks

Although the wear pattern of a-C:H/TiN tribo-pair seemed similar to a-C:H/SUJ2 tribo-pair as shown in Figure 3.18 (c), the interaction was eminently different. This was due to the friction coefficient and wear volume of a-C:H/TiN in ZnDTP+MoDTC was lower than that of in Base oil. The findings suggest that tribofilm formed on roller and disk contained both MoO_3 and Zinc Phosphate therefore, the act of abrasive wear of MoO3 was balanced out by the Zinc phosphate. The MoS_2 found on the disk part of the tribofilm has helped to reduce the friction coefficient.

Figure 3.18 (b) shows the best scenario of a-C:H/TiC in ZnDTP+MoDTC oil which exhibited the least concentration of Molybdenum at% than the other two tribo-pairs. Compared to the a-C:H/TiN in Base oil, the wear of both roller and disk was remarkably low. The finding provides evidence that no MoO_3 and only MoS_2 derived tribofilm formed on both roller and disk. However, the too low concentration of MoS_2 cannot fully play the part of reducing the friction.

3.4 Conclusions

The purpose of this chapter is to clarify the influence of additives on friction, wear and seizure load when changing the counter material against a-C:H. The conclusions can be summarized as follows:

(1) In the friction of ZnDTP and MoDTC containing oil, the influence of different mating material ring on the friction, wear and seizure characteristics of a-C:H coating was clarified. Specifically, the coefficient of friction slightly increased with the inclusion of additives in the case of SUJ2 steel, but not so much difference in the case of TiC and slightly decreased in the case of TiN. On the other hand, the wear amount remarkably changed depending on the counterpart disks material. Specifically, the inclusion of additives increased the wear amount to 1.4 times for SUJ 2 steel, but in the case of TiN and TiC, the wear reduction remarkably decreased to 1/2, 1/258 respectively depending on the inclusion of additives.

(2) Detailed analysis of SEM and EDS was conducted. As a result, it was revealed that the thickness and composition of the tribofilm derived from the ZnDTP+MoDTC oil additives are differed depending on the material of the opponent disk material. In particular, compared to the lowest Molybdenum on TiC, SUJ2 and TiN discloses about 5 times and 3 times higher value of the same elements on their surfaces. The same pattern also observed on the a-C:H rollers where TiC denoted the lowest attachment of Molybdenum on its surface.

(3) In the overall, a-C:H roller mated with TiC disk in ZnDTP+MoDTC considered as the best combination in terms of specific wear volume reduction on the sliding interfaces and the reason are as follows. Molybdenum on the TiC disk was balanced out by the ZnDTP derived elements while on the a-C:H roller, ZnDTP derived

elements was detected higher than the Molybdenum. It is suggested that wear agent ZnDTP able to execute excellent role in this exact arrangement.

(4) ZnDTP+MoDTC lubricant oil is able to suppress seizure by concealing the effect of peeling off on both DLC and mating materials coatings. Compared to Base oil, the running in phase at each applied force in ZnDTP+MoDTC was much steadier and quickly balances out.

4. Effects of oil additives, sliding speed and mating materials to friction and wear characteristics of a-C:H coating

4.1 Introduction

About one-third of chemical energy converted from engine fuel will be wasted in the form of friction between sliding parts under boundary oil lubrication [70]. One of the means in reducing this kind of waste is by applying diamond-like carbon (DLC) coated engine parts with the aim to reduce friction and wear so that higher fuel consumption and engine operation efficiency can be obtained. DLC is superior materials which has the properties of high in hardness, chemically inert, low in friction and highly wear resist thanks to the structure combination of sp^2 from graphite and sp^3 from diamond [34], [71], [72]. However, before the actual application of DLC coating to engine components, the compatibilities between DLC and oil additives need to be confirmed promptly to evade parts and components breakdown. The reason is that commercially formulated lubricant oils comprise different kind of additives aimed to cater the interaction between ferrous to ferrous and not in between ferrous and DLC sliding interfaces.

Friction modifier Molybdenum Dithiocarbamates (MoDTC) and anti-wear agent Zinc Dialkyl-dithiophosphates (ZnDTP) are two of the most regular additives that commonly formulated in lubricant oils normally used for ferrous material surfaces. During the tribological contacts in boundary lubrication conditions, MoDTC will decompose into several forms including low shear strength, low friction MoS_2 crystal sheets providing low friction [87]–[89]. Sulphide and phosphate tribofilms formed from ZnDTP bestows anti-wear properties at ferrous material surfaces [88]–[90]. There was also some study reported that the MoS_2 sheets construction and stability was furthermore enhanced by the existence of ZnDTP [12], [91]. In the recent trends, researchers have begun to investigate the reactions between different non-ferrous material DLC coatings with lubricant additives under boundary lubrication. There were some contradicted reports stated that DLC coatings shows no reaction to MoDTC+ZnDTP containing oil however there was also reports indicated that MoS_2 sheets and ZnDTP derived compounds formed on DLC coating resulting low friction and wear under boundary lubrication conditions [46], [55], [60], [92]–[95].

Calcium Carbonate ($CaCO_3$) over-based detergents are one type of oil-soluble nanoparticles oil additive [96], [97]. They have the structure of calcium carbonate in the core and surfactant in the outer shell. Detergents act to stabilize dirt and debris in oil formulations and neutralize possibly formed corrosive acids and to contribute to engine cleanliness. Previous researchers reported that by utilizing nanoparticles of $CaCO_3$ in poly-alpha-olefin (PAO) oil as an alternative green additive can enhance the friction and wear reduction properties and also the load carrying capabilities and extreme pressure characteristics [98]–[101].

Titanium Carbide (TiC) and Titanium Nitride (TiN) not only can be used to lengthen the lifecycle of cutting tools, they also can be utilized as a protective coating on machinery parts for example sliding bearings, seals, and valves [77]. The effect of different types and hardness of mating materials in dry air friction condition to the friction and wear of DLC coating by various researchers [81]–[83]. Guu et al. reported that the wear rate of TiN coated test piece was lower than TiC coated test piece yet higher in terms of friction coefficient in dry condition friction test [78], [79]. In oil lubrication, a-C:H/TiC and a-C:H/steel tribo-pairs exhibited lower wear rate compared to the other tribo-pairs in PAO oil boundary lubrication. However, no effort was made to examine the effects of lubricant additives, sliding speed and mating materials to DLC coating. In this study, tribological investigation between hydrogenated amorphous carbon (a-C:H) DLC slide against uncoated SAE4620 steel ring, TiC and TiN coated SAE4620 steel rings mating materials in Base and ZnDTP+MoDTC oils was performed and the friction, wear and also tribo-layers compositions properties have been evaluated.

4.2 Materials and test method

4.2.1 Hydrogenated DLC, mating materials and lubricant oil additives

Hydrogenated amorphous carbon (a-C:H) coatings provided by Japan ITF Co. Ltd. utilized in this study was deposited by using the plasma enhanced chemical vapour (PECVD) method on aluminium alloy bearing substrate with a thickness of 4.0 μm. Three different kinds of mating materials was used to be mated with a-C:H coated bearing during the friction test. They are unpolished uncoated SAE4620 ring and the other two are 1.0 μm thickness of Titanium Carbide (TiC) and Titanium Nitride (TiN) coated on the unpolished SAE4620 ring. Table 4.1 shows the detail properties of a-C:H coated bearing and mating material rings.

Table 4.1 Properties of a-C:H bearing and mating material rings

Properties	Bearing	Rings		
	a-C:H	SAE4620	TiC	TiN
Substrate	Aluminium	-	SAE4620	SAE4620
Thickness (μm)	4	-	1	1

Base oil and ZnDTP+MoDTC oil is the two engine oils used as lubricant during the friction test. For the ZnDTP+MoDTC oil, apart from anti-wear agent from ZnDTP and friction modifier from MoDTC, the oil was also formulated with five common additives of detergent, anti-oxidant, foam inhibitor, dispersant and viscosity improver. Detail properties of each lubricant oils are tabulated in Table 4.2.

Table 4.2 Each lubricant properties

	Base	Base+ZnDTP +MoDTC
Viscosity mPa·s	4.25	5.92
Ca (wt%)	-	0.20
Mo (wt%)	-	0.07
P (wt%)	-	0.08
Zn (wt%)	-	0.09
S (wt%)	-	0.22
N (wt%)	-	0.10

4.2.2 Friction tester equipment

Figure 4.1 shows the schematic diagram of the bearing on ring friction. The a-C:H bearing was fixed at the bottom of the load cell and the mating material ring test pieces were fixed at the rotating shaft. Both bearings and rings were ultrasonically cleaned with benzene and acetone for 15 minutes before and after friction test. An oil bath was installed under the ring test piece, and the oil temperature was set to 80°C by a heater installed in the lower part of the oil bath. The frictional force between the bearing and the ring caused by the sliding is transmitted to the load cell, and the frictional force is measured from the voltage change of the load cell. The vertical load was given by the weight on the bearing. As for the mating materials, three kinds of ring which are SAE4620 ring, TiC and TiN coated ring as per explained in 2.1 was used. The sliding speed was set to be change at every fixed time of 5 minutes during the friction test. The summarizations of all the above mentioned friction test experimental conditions were shown in Table 4.3.

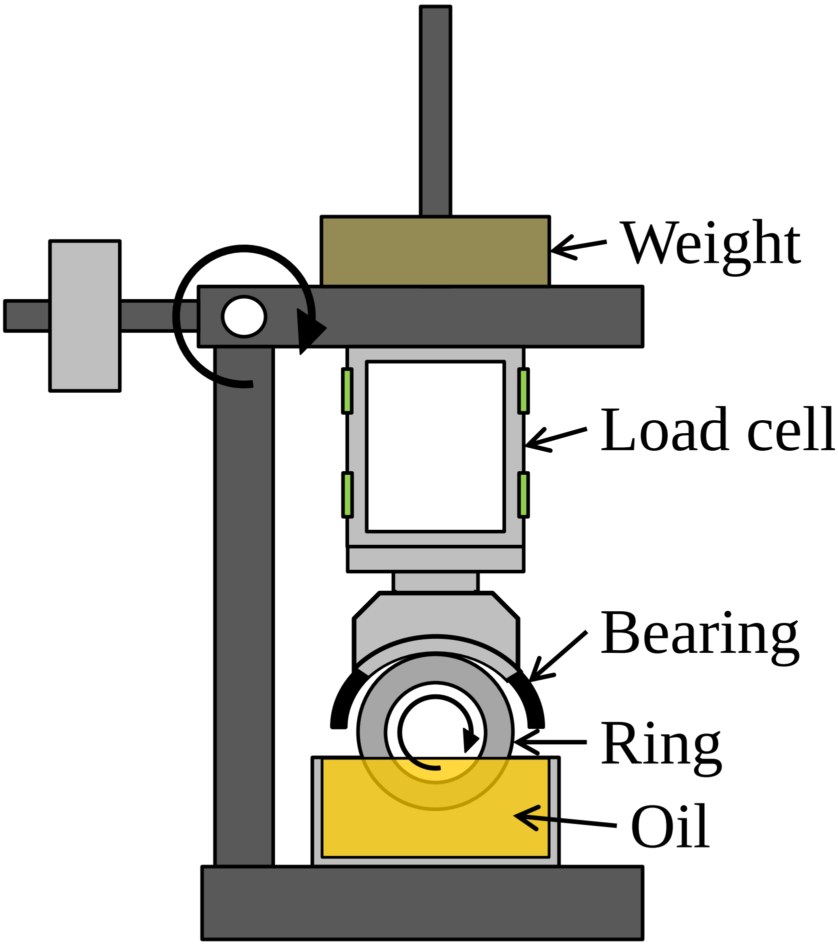


Figure 4-1 Schematics of bearing-on-ring friction tester

Table 4.3 Bearing on ring friction test experimental conditions

Experimental conditions	
Bearing	a-C:H
Ring	SAE4620, TiC, TiN
Load, N	5
Temperature, ^{o}C	80
Sliding speed, rpm	250, 150, 75, 30, 10
Duration, min	50 (5 min/rpm)

4.2.3 DLC surface and tribofilm analysis equipment

Three dimensional non-contacts, scanning white light interferometry (ZYGO, Newview) was utilized to observe the surface morphology of the wear track as well as the tribo-layers formed on the wear track by measuring the roughness and constructing the 3D images of the aforementioned surface. Next, to understand the chemical element attachment on the tribo-layers of the wear track, an energy dispersive X-ray spectroscopy (EDS) was used to execute the task by measuring the weight percentage as well as the atomic percentage of each element concentration on the aforementioned surface.

4.3 Results and discussions

4.3.1 Friction coefficient

Friction test was conducted in four configurations with the first two configurations of full test run with the complete set of decreasing and increasing of the sliding speed and the latter two configurations of the middle test stop at the sliding speed of 10 rpm. Table 4.4 shows the details of each four friction test configurations. This was done to measure the roughness of both bearing and ring wear tracks at the middle of the test during the lowest sliding speed. Next, to observe the lubrication mode during the friction test, the lambda value was calculated by utilizing the measured roughness results of before, middle and after the friction test.

Table 4.4 Friction test configurations

Test name	Sliding speed, rpm	Load, N	Temperature, ^{o}C	Sliding time t, min	Lubricant
A	250,150,75,30,10	5	80	10x5	Base
B	250,150,75,30,10	5	80	10x5	ZnDTP+MoDTC
C	250,150,75,30,10	5	80	5x5	Base
D	250,150,75,30,10	5	80	5x5	ZnDTP+MoDTC

The frictional behaviours of a-C:H coating lubricated with Base oil (configuration A) as a function of sliding time and sliding speeds are shown in Figure 4.2. a-C:H/TiN tribo-pair marked the lowest friction coefficient and then followed by the a-C:H/SAE4620 tribo-pair. The a-C:H/TiC however exhibited unstable pattern of friction coefficient and keep on fluctuating at the initial stage of the friction test, however starting from the minutes of 20 and above, the friction curve started to stabilize and maintained at the most same value despite changes of sliding speed.

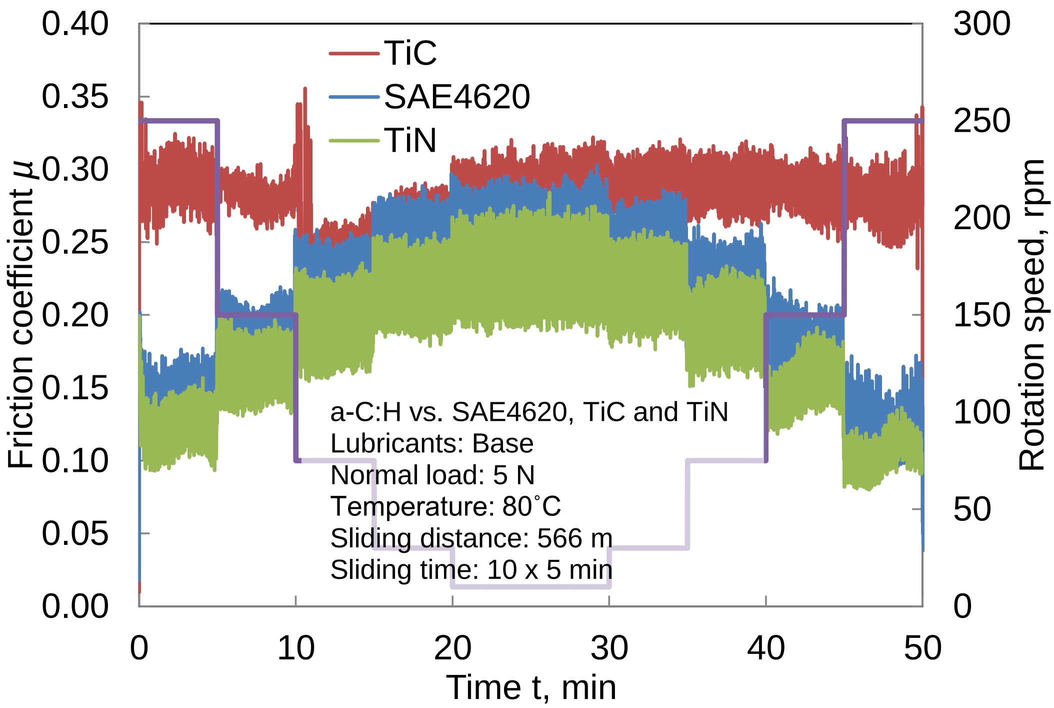


Figure 4-2 Friction coefficients of each tribo-pairs in Base oil

The frictional behaviours of a-C:H coating lubricated with ZnDTP+MoDTC (configuration B) oil as a function of sliding time and sliding speeds are shown in Figure 4.3. Opposite to the case in Base oil, a-C:H/TiC in ZnDTP+MoDTC oil demonstrated the lowest friction coefficient and then followed by a-C:H/SAE4620 and a-C:H/TiN tribo-pairs as the second and the highest friction coefficient respectively. In the overall, friction coefficient of each mating materials in ZnDTP+MoDTC oil denoted lower value than in Base oil lubrication.

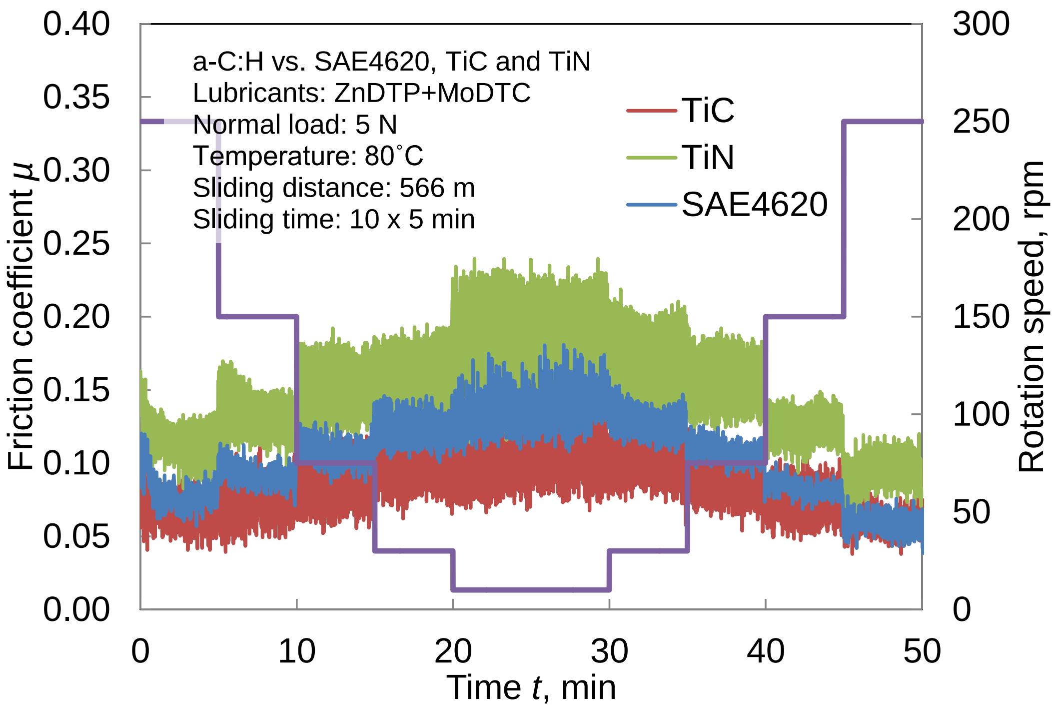


Figure 4-3 Friction coefficients of each tribo-pairs in ZnDTP+MoDTC oil

The average steady state friction coefficient at the lowest sliding speed of 10 rpm at the middle of the friction test from minutes 20 to 30 are presented in Figure 4.4. As shown in the figure, a-C:H/TiC tribo-pair marked the biggest difference of friction coefficient from Base to ZnDTP+MoDTC oils from 0.29 to 0.10 with 64% reduction and then followed by a-CH/SAE4620 from 0.25 to 0.14 and a-C:H/TiN tribo-pairs from 0.23 to 0.18 with 46% and 22% of reduction respectively.

Friction test in Base oil lubrication with the sliding speed changed at every 5 minutes reveals low friction coefficient of 0.14 and 0.12 for SAE4620 and TiN coatings respectively at high speed of 250 rpm. As the sliding speed gradually reduced to the lowest speed of 10 rpm at the middle of the test, the friction coefficient increased along with the sliding speed reduction with 0.25 and 0.23 for SAE4620 and TiN coatings respectively. TiC mating material however did not show the same trend as the former two mating materials where the friction coefficient remains nearly constant at 0.28 despite the changes in the sliding speed.

Friction test of all three mating materials in ZnDTP+MoDTC oil lubrication with the sliding speed changed at every 5 minutes reveals lower friction coefficient than in Base oil with 0.08, 0.06 and 0.11 for SAE4620, TiC and TiN coatings respectively at high speed of 250 rpm. As the sliding speed gradually reduced to 10 rpm at the middle of the test, the friction coefficient increased to 0.13, 0.10 and 0.18 for SAE4620, TiC and TiN coatings respectively. The results suggest that the differences of friction coefficient when the sliding speed changes are related to the mode of lubrication where the lowest friction coefficient possibly occurred in mixed lubrication and the highest friction coefficient in boundary lubrication.

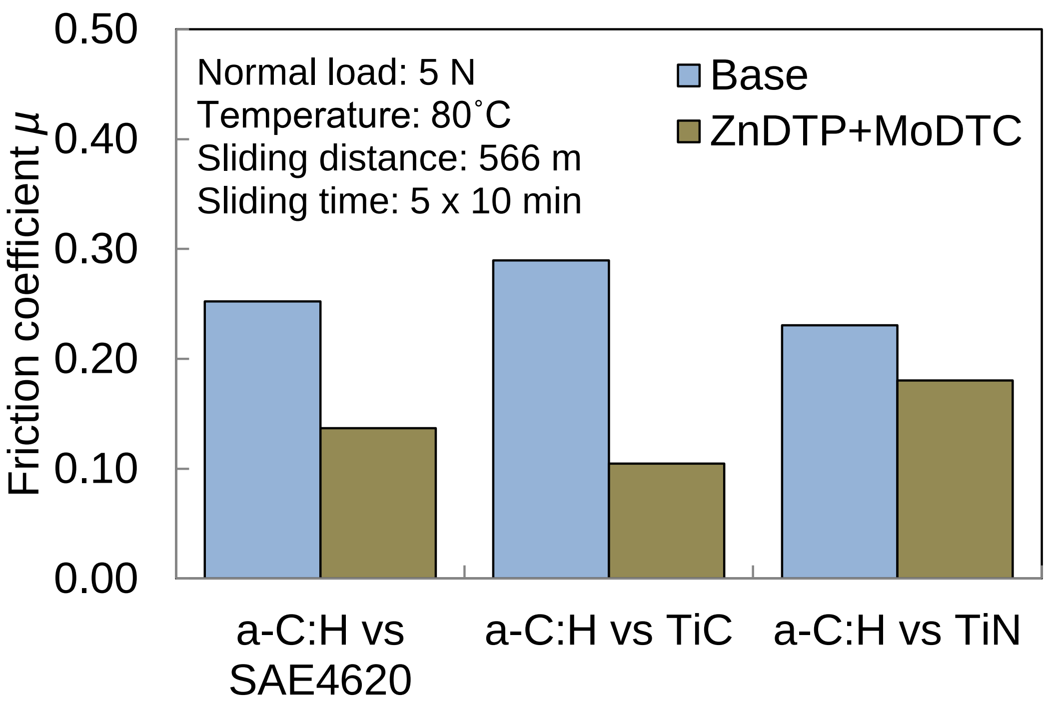


Figure 4-4 Average steady state friction coefficient of each tribo-pairs in both oils

Figure 4.5 and Figure 4.6 shows the frictional behaviours of a-C:H coating as a function of sliding time and sliding speeds for the other two configuration of C and D. The result reveals that the friction curve for both configurations are quite identical to than that of A and B configurations.

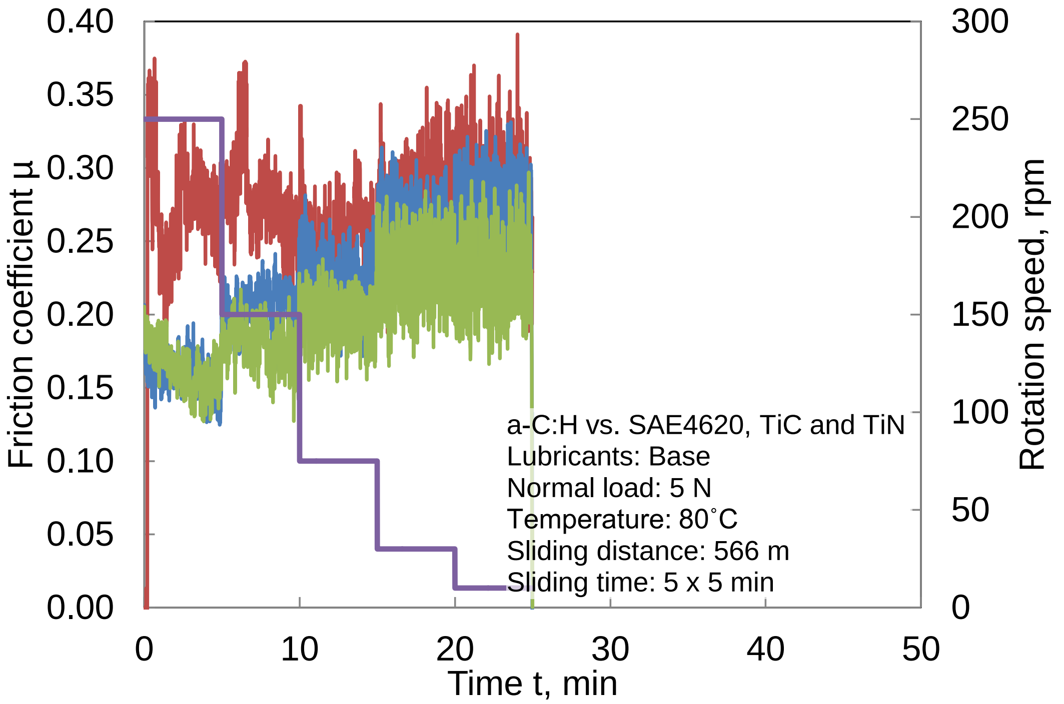


Figure 4-5 Friction coefficients of each tribo-pairs in Base oil (middle test stop)

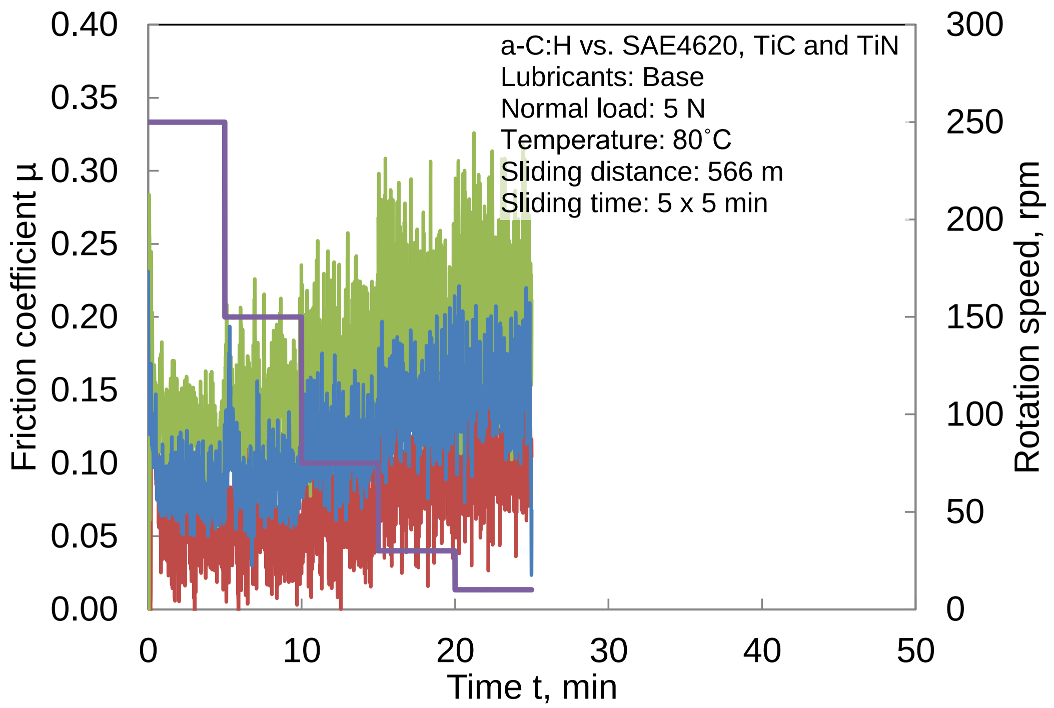


Figure 4-6 Friction coefficients of each tribo-pairs in ZnDTP+MoDTC oil (middle test stop)

4.3.2 Wear rate

Figure 4.7 shows the optical microscope images of a-C:H/SAE4620, a-C:H/TiC and a-C:H/TiN tribo-pairs in Base and ZnDTP+MoDTC oil. In general, both a-C:H bearings and mating material disks in Base oil reveals higher wear compared than in ZnDTP+MoDTC oil except for the a-C:H/TiN in ZnDTP+MoDTC where the wear observed to be much more severe compared to when lubricated in Base oil. And particularly for the case of a-C:H/TiC in Base oil, the wear of both a-C:H bearing and TiC ring was severely worn and exposing the metal substrate underneath. This is consistent with the findings from previous study by Taufik et al. where in the study, they found that the a-C:H roller and its counter material TiC disk was severely worn with seizure occurrence during sliding process when lubricated with Base oil. However, when lubricated with ZnDTP+MoDTC oils, the occurrence of seizure was suppressed and lower amount of friction and wear gained [102].

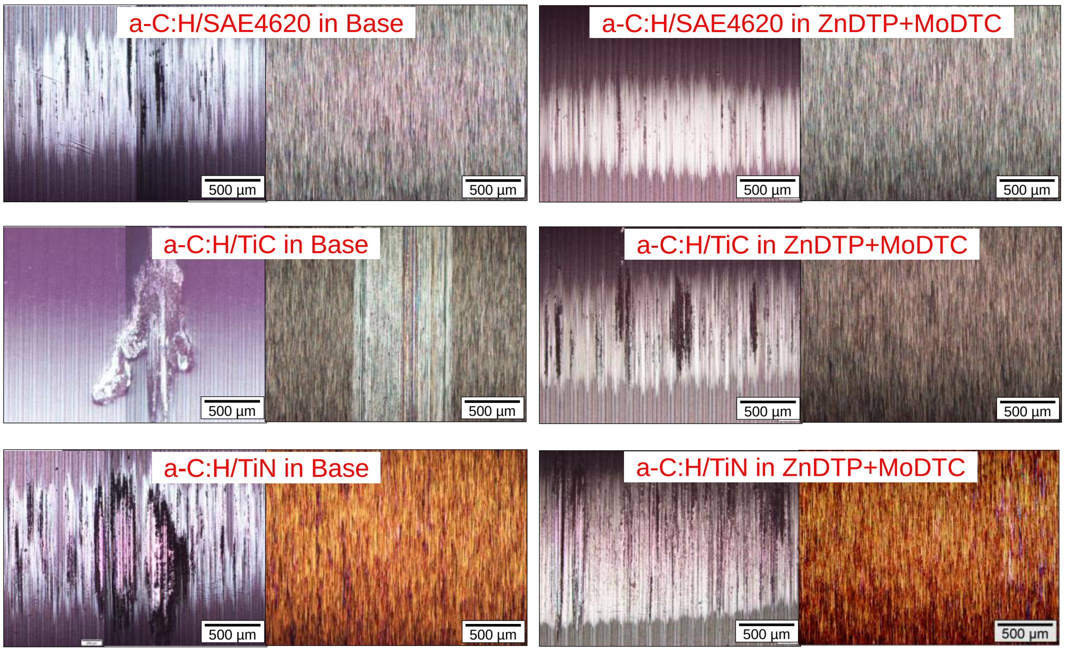


Figure 4-7 Optical microscope images of each tribo-pairs wear track in both oils

Figure 4.8 shows the specific wear rates of a-C:H for each tribo-pairs in Base and ZnDTP+MoDTC oils. As appeared in the figure, except for the case of a-C:H/TiN tribo-pair where we can see 77% of wear rate increase from Base to ZnDTP+MoDTC oils, the other two a-C:H/SAE4620 and a-C:H/TiC tribo-pairs disclosed a 51% and 52% of wear rates reduction respectively.

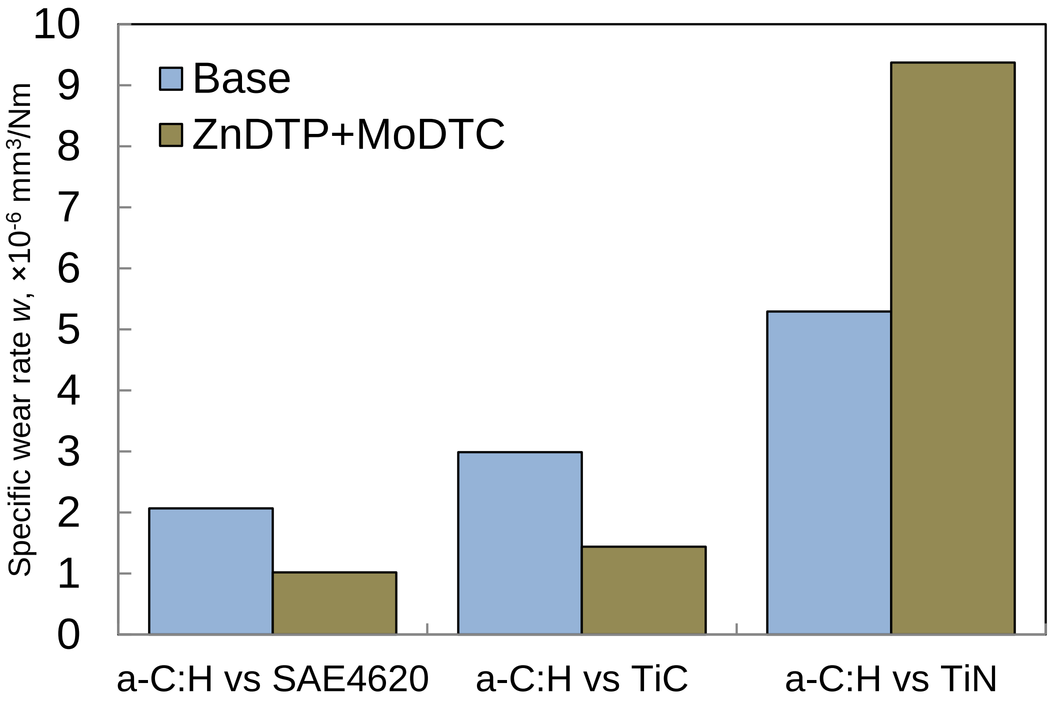


Figure 4-8 Specific wear rates of a-C:H for each tribo-pairs in both oils

4.3.3 Film thickness ratio (Λ value)

The film thickness ratio Λ was calculated to estimate the lubrication state during the friction test. The lubrication state in the friction test in the lubricating oil is classified into the boundary, mixed and hydrodynamic lubrication state. The film thickness ratio is the ratio of the minimum oil film thickness to the synthetic roughness shown in the formula (4-1). In order to calculate the minimum oil film thickness, the equation (4-2) showing the minimum oil film thickness under line contact proposed by Hamrock et al. was used [103]. To calculate the composite roughness σ, the circumferential root mean square roughness R_q of both bearing and ring wear track were measured by white light interferometry scanner (ZYGO, Newview).

$$\Lambda = \frac{h_0}{\sigma} \tag{4-1}$$

$$h_{min} = 1.806(\omega'_z)^{-0.128}(\eta_0\tilde{u})^{0.694}\xi^{0.568}{R_x}^{0.434} \tag{4-2}$$

$$R_x = \frac{R_1 R_2}{R_1 + R_2} \tag{4-3}$$

Λ : Film thickness ratio

h_{min} : Minimum film thickness, m

$\tilde{u}$: Average sliding speed, m/s

ξ : Viscosity pressure coefficient, m^2/N

R_1 : Ring radius, m

σ : Synthetic roughness, m

ω'_z : Load per unit width, N/m

η_0 : Atmospheric pressure viscosity, Pa·s

R_x : Equivalent radius including slip direction coordinate, m

R_2 : Bearing radius, m

To estimate the lubrication state by using the film thickness ratio, relationship between film thickness ratio of contact faces and noncontact time ratio as per reported by Johnson et al. was used [104]. Figure 4.9 shows the relationship between film thickness ratio and noncontact time ratio. When $\Lambda<1$, the friction surface is almost in direct contact at all times, resulting in a boundary lubrication state. When $1\leq\Lambda\leq3$, the non-contact time increases between the friction surfaces, resulting in a mixed lubrication state. When $\Lambda>3$, there is almost no direct contact between the friction surfaces, resulting in a hydrodynamic lubrication state.

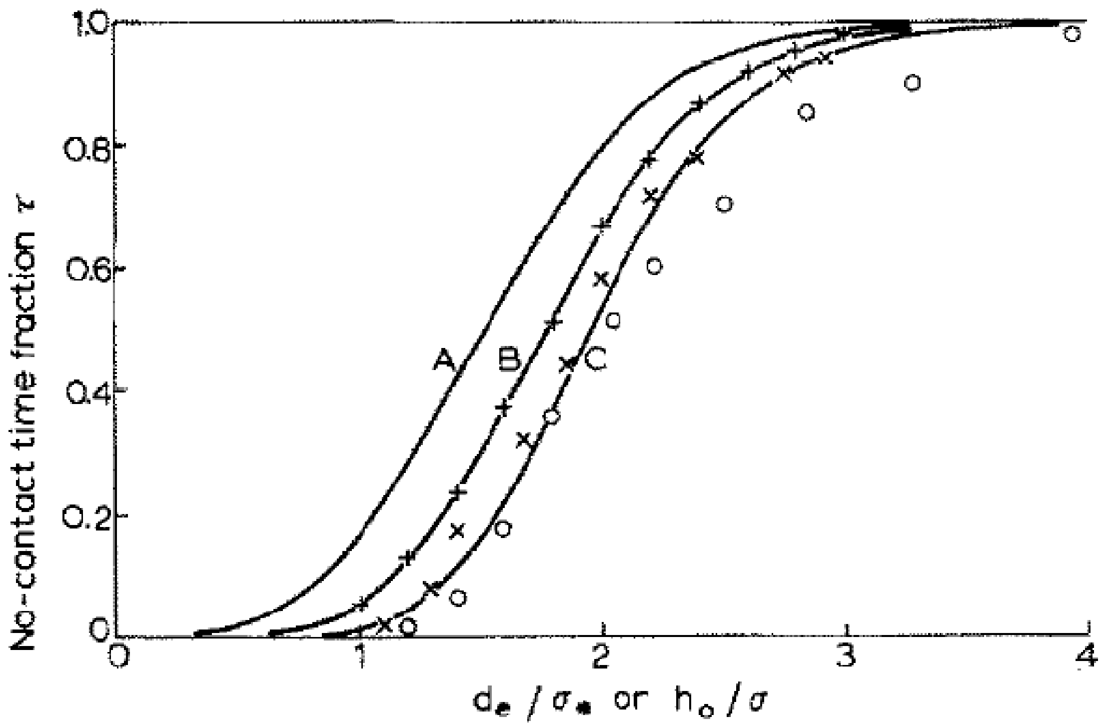


Figure 4-9 Relationship between film thickness ratio (h_0/σ) and non-contact time ratio [103]

Figure 4.10 exhibits the 3D images each tribo-pairs wear track in both type of oils after the friction test. By utilizing the roughness results of each tribo-pairs gained from the Zygo observation for the initial, middle and after friction test wear tracks, the Λ value was calculated. Figure 4.11, 4.12 and 4.13 shows the Λ value of each tribo-pairs in each type of lubricant oils. In the whole, ZnDTP+MoDTC oil provides better lubrication mode for all type of mating materials at every stages of sliding speed of the friction test. However TiC mating material in particular, shows obvious distinction of Λ value between the two types of oil with 80% and 89% of increment at the middle stage (10 rpm) and at the final stage (250 rpm) of friction test respectively. The finding suggests that TiC mating material able to provides better lubrication mode by offering higher oil film thickness during the sliding process both in low and high sliding speed.

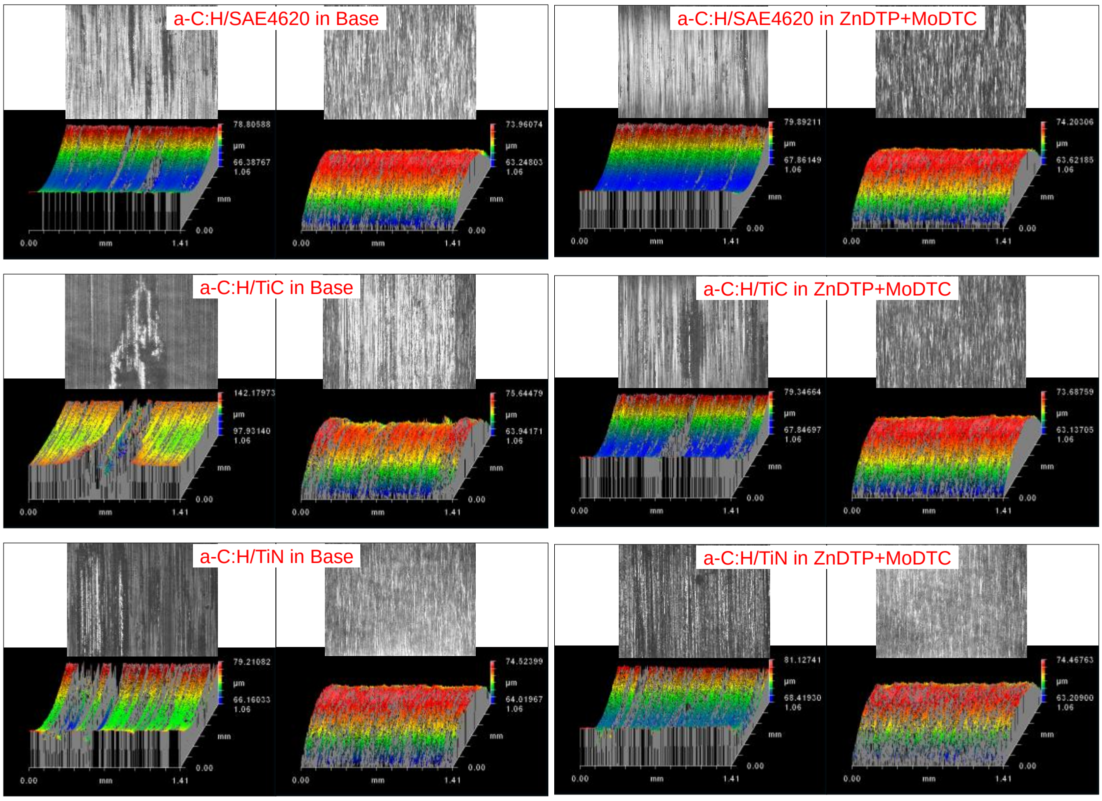


Figure 4-10 3D optical surface profiler of wear track images for each tribo-pairs in both oils

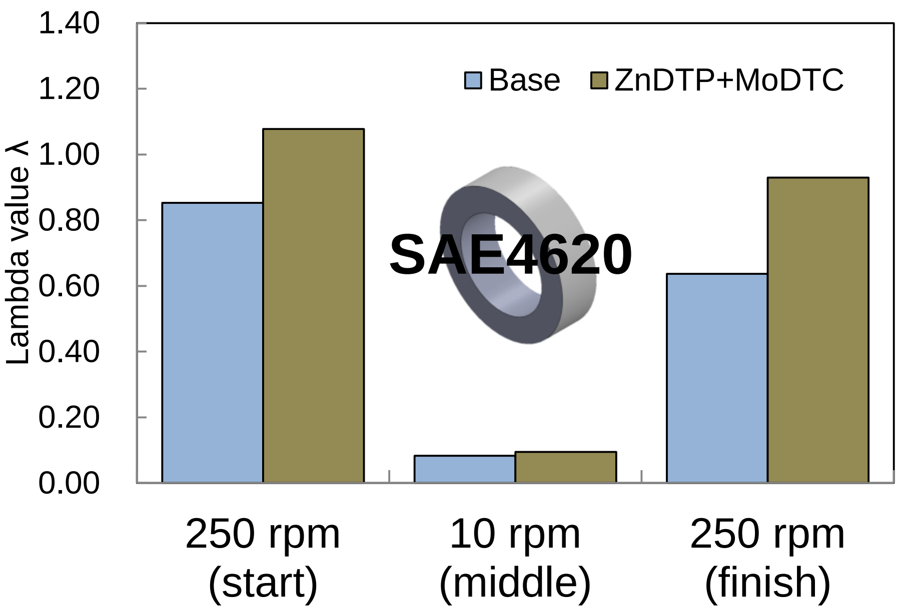


Figure 4-11 Λ value of a-C:H/SAE4620 tribo-pair at each stage of friction test in both oils

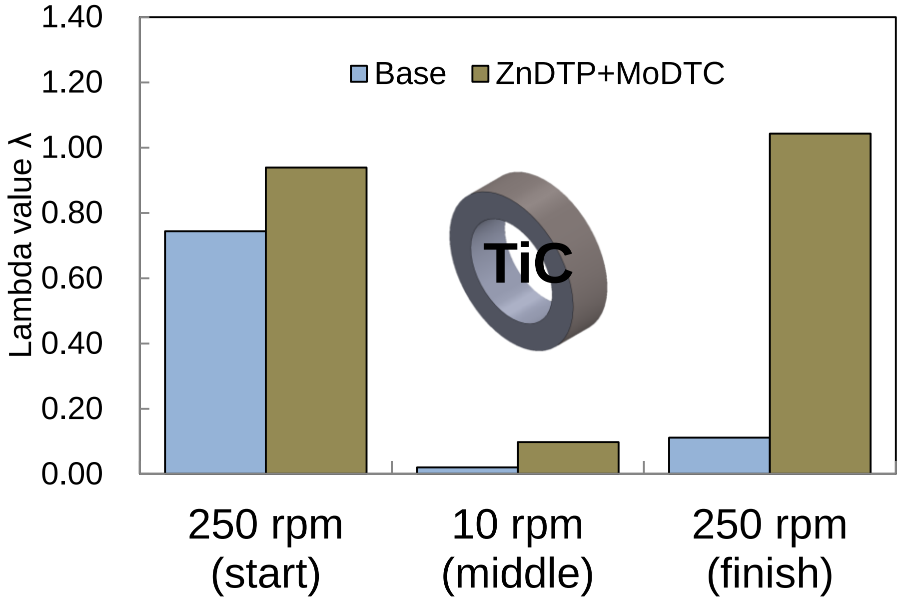


Figure 4-12 Λ value of a-C:H/TiC tribo-pair at each stage of friction test in both oils

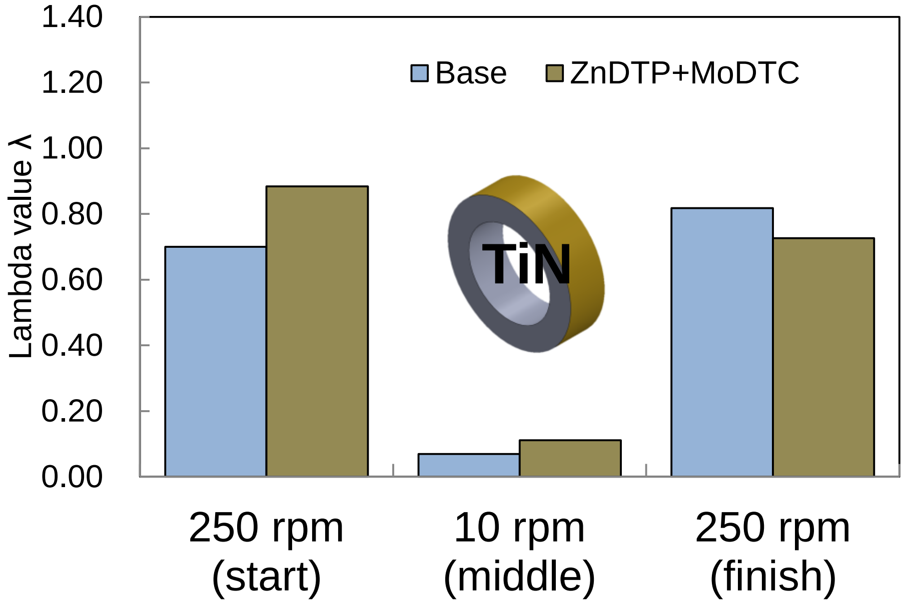


Figure 4-13 Λ value of a-C:H/TiN tribo-pair at each stage of friction test in both oils

4.3.4 Tribo-layers elemental investigation

Figure 4.14 exhibits the wear tracks SEM images of the analysis area on both bearings and rings in Base and ZnDTP+MoDTC oils. To understand what kind of effects given by both type of oils to a-C:H bearings and each mating material rings, an energy dispersive X-ray spectroscopy (EDS) was used to measure the oil additives chemical elements attachment on both bearing and ring wear tracks. Main chemical elements from ZnDTP and MoDTC oil additives which are Zinc, Phosphorus, Sulphur and Molybdenum and also Calcium from detergents was selected to be investigated. Carbon and Oxygen that is coexisted in the aforementioned oil additives was also examined during the investigation.

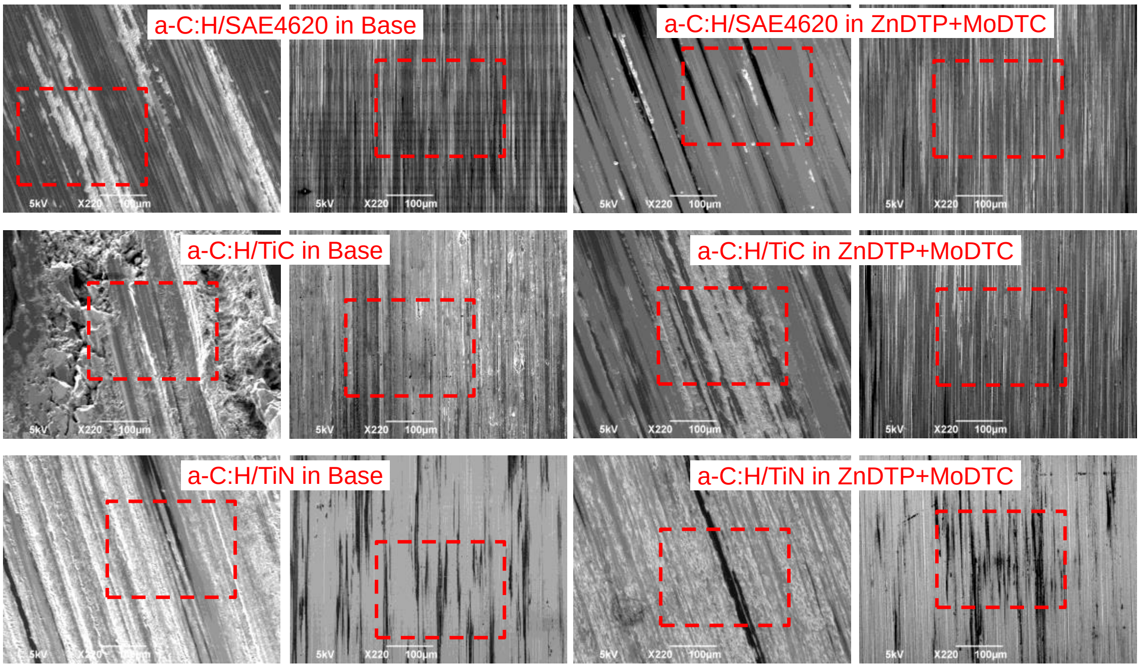


Figure 4-14 EDS analysis area on each tribo-pairs wear tracks SEM images

Figure 4.15 shows the atomic percentages of each oil additives elements. Generally, quite similar concentration of Carbon and Oxygen attachment both on bearing and ring wear tracks observed for both types of oils. However, exclusively for the case of a-C:H/TiC tribo-pair in Base oil, due to high wear on both sliding surfaces, the Carbon concentration was lower and the Oxygen concentration was higher than in ZnDTP+MoDTC oil. This indicates that heavily worn a-C:H bearing and TiC ring in Base oil caused the reduction of the Carbon at% value and oxidation also occurred on both wear track based on the increment of Oxygen at% value.

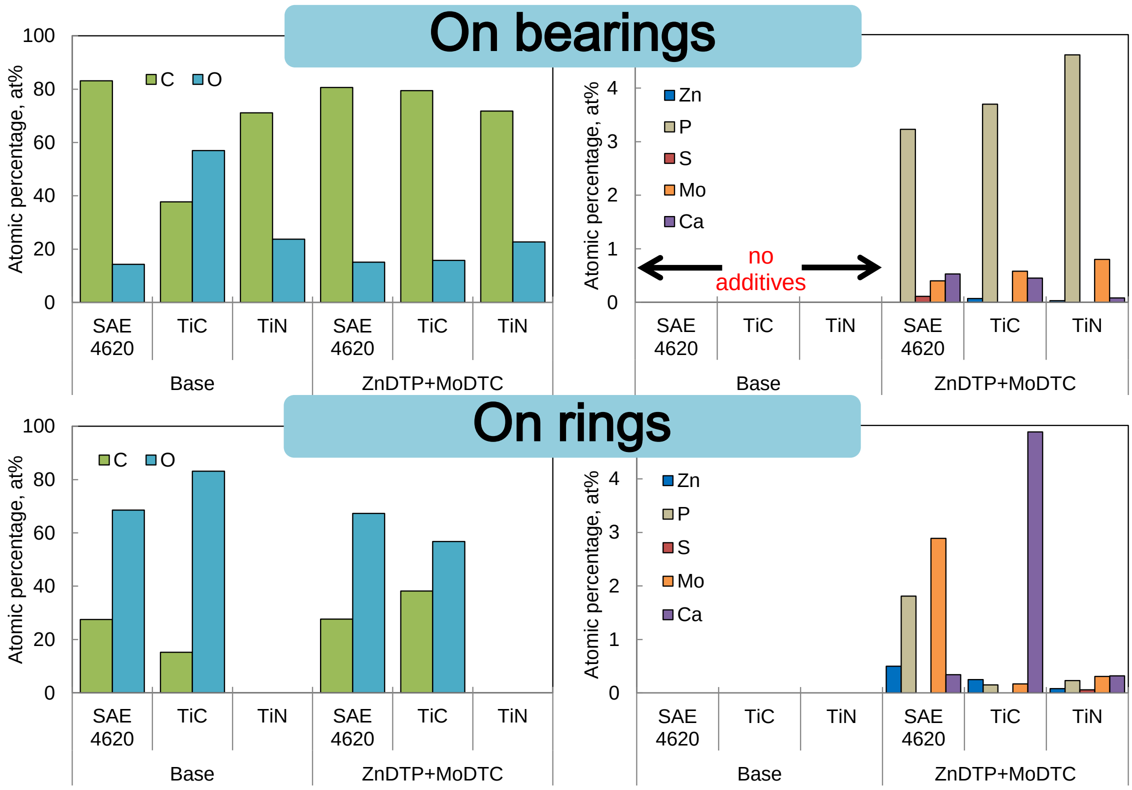


Figure 4-15 Element analysis of each tribo-pairs bearing and ring wear tracks results

Next, for the case of main oil additives elements of Zinc, Phosphorus, Sulphur, Molybdenum and Calcium, obviously because of no such elements were included inside Base oil, they were not detected on both bearings and rings. Obvious differences could be seen for the case in ZnDTP+MoDTC oil are there is exceptionally high concentration of Calcium on TiC ring and Molybdenum on SAE4620 ring detected. High traces of Phosphorus detected on a-C:H bearings for all tribo-pairs however only SAE4620 shows high at% value for mating material rings. Zinc and Sulphur shows lower at% values compared to the other elements however on SAE4620 ring, relatively higher at% of Zinc was detected on its surface and then followed by TiC and TiN rings.

Figure 4.16 shows the relationships between each element at% values to the friction coefficient and specific wear rates tendency to increase and decrease. What can be understand from the figure is that Carbon, Calcium and Zinc gives positive effect in reducing friction and wear on a-C:H and each mating materials. However Phosphorus, Molybdenum and Oxygen did not gives the same effects as the aforementioned elements. For the case on each mating materials, Phosphorus and Molybdenum did not gives significant effect on both friction and wear, Oxygen however gives progressive influence which is opposite to the case of on a-C:H bearings.

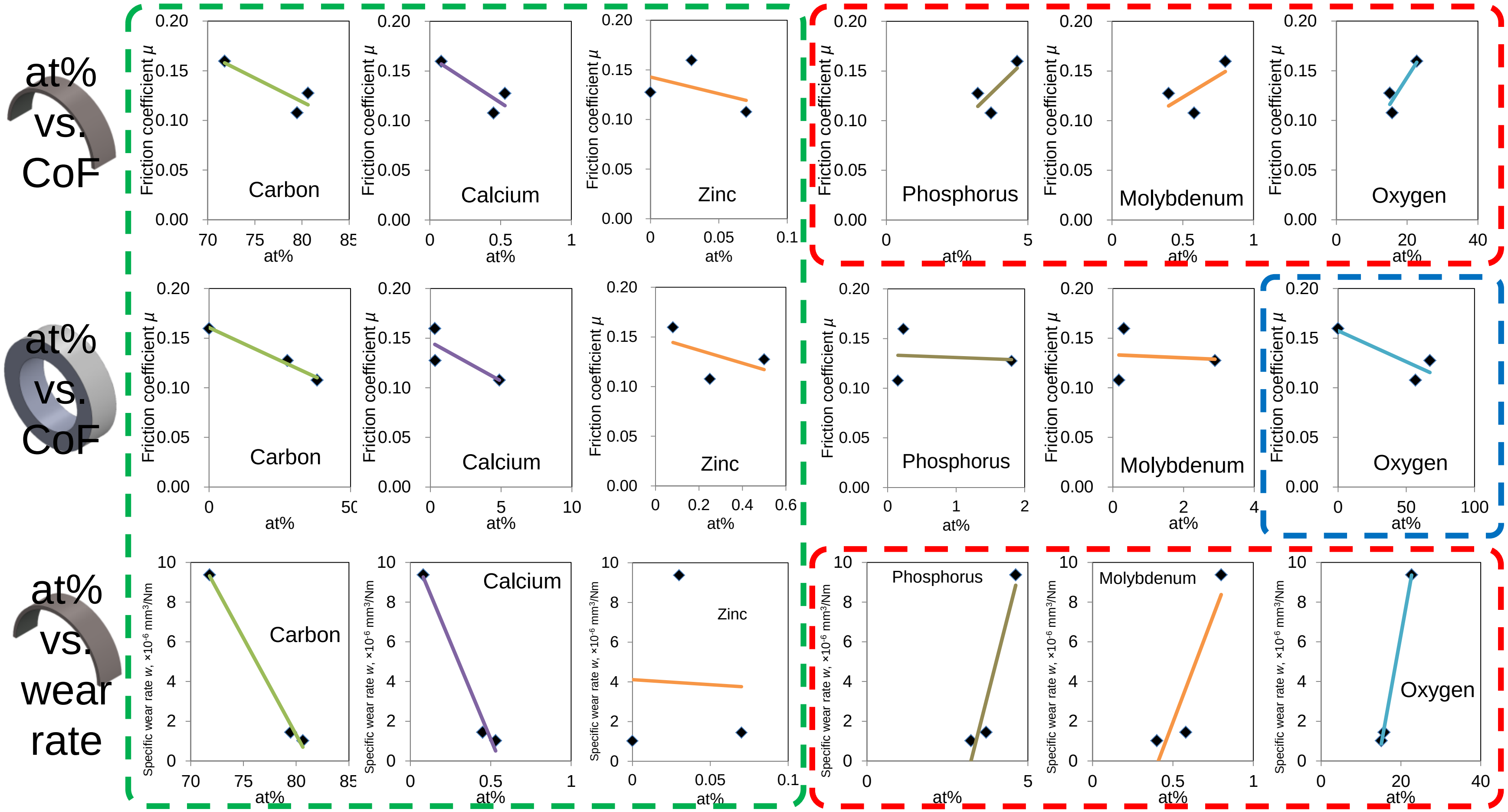


Figure 4-16 Relationships between each element at% values to the friction coefficient and specific wear rates

From all the above stated results and descriptions, the outcomes propose that no constructive tribofilm formed for the sliding in Base oil lubrication which caused the high friction and wear for the a-C:H/TiC tribo-pair. The sliding of a-C:H bearing on harder TiN ring also caused the DLC coating to heavily worn. From all the mating materials, SAE4620 ring appears to be the best companion to be paired with a-C:H DLC in Base oil. ZnDTP+MoDTC lubrication in contrast substantially aids the reduction of friction and wear for a-C:H/SAE4620 and a-C:H/TiC tribo-pairs. These were translated by the over half amount of friction and wear reduction from Base to ZnDTP+MoDTC oils. a-C:H/TiN on the contrariwise did shows some reduction of friction coefficient in ZnDTP+MoDTC oil however higher wear revealed on the a-C:H bearing makes the TiN to be not suitable to be paired with the DLC coating in both type of oils.

4.3.5 Oil additives tribo-layers on a-C:H and mating materials compositions

Haque et al. [55] and de Barros' Bouchet et al. [46] highlighted that lubricant oil anti-wear additive ZnDTP will deteriorated into several structures of Zinc phosphate, ZnS and ZnO with the Zinc phosphate being the main agent to reduce wear during the interactions between the two sliding surfaces. de Barros' Bouchet et al. also mentioned that during friction test under heating, MoDTC will decomposes into molybdenum disulphides (MoS_2) sheets and molybdenum oxide (MoO_3) [105], [106]. The low shear strength hexagonal MoS_2 layer performs as multi-layer solid lubricant which gives low friction on both ferrous and nonferrous surfaces. MoO_3 conversely causes high friction due to its abrasive sharp edge crystalline properties [85], [86]. Zhang et al. indicated that $CaCO_3$ nanoparticles which originated from detergents can drastically enhance the load carrying limit and also improve the properties of friction and wear reduction of PAO base oil [100]. Figure 4.17 was illustrated to describe the tribo-layers compositions on a-C:H/SAE4620, a-C:H/TiC and a-C:H/TiN tribo-pairs in ZnDTP+MoDTC oil with the size of each oval roughly represents the at% concentration of each elements.

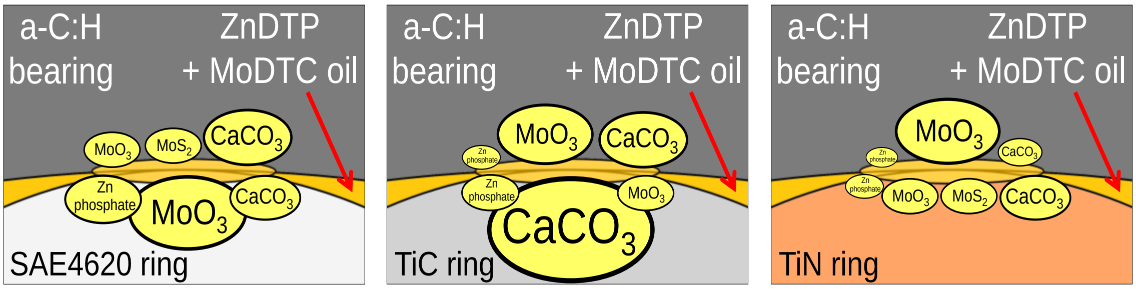


Figure 4-17 Tribo-layers compositions of each tribo-pairs in ZnDTP+MoDTC oil

For the case of a-C:H/SAE4620 tribo-pair, the finding suggests that both MoS_2 and $CaCO_3$ act to reduce the friction and wear on a-C:H bearing and dampen the effect of MoO_3. There are ZnDTP derived elements and $CaCO_3$ that being overshadowed by the higher at% of MoO_3 that probably cause wear on SAE4620 bearing. Next, for the case of a-C:H/TiC tribo-pair, the substantially high concentration of $CaCO_3$ helps to protect the TiC ring from wear by weakening the effect of MoO_3. High traces of MoO_3 formed on a-C:H bearing caused wear on its surface but was controlled by the $CaCO_3$. There was also ZnDTP derived elements detected on both surface but was dominated by the overwhelmingly higher traces of the others. High wear on a-C:H/TiN tribo-pair was probably caused by the high concentration of MoO_3 on a-C:H bearing outshined the effect of smaller traces of $CaCO_3$ and the ZnDTP derived elements. On the ring side however, MoS_2 and $CaCO_3$ protect the ring from wear by minimizing the effect of MoO_3. Highly worn a-C:H bearing sliding on the harder TiN ring further caused the DLC coating to wear.

Although similar combinations of oil additives and mating materials as chapter 3 was used in this chapter 4, the tribofilm formation mechanism was quite different especially on the contribution of $CaCO_3$ to reduce friction and wear. The differences in the test method (roller on disk and block on ring) and parameters (fix load, incremental load, fix sliding speed, incremental sliding speed) possibly caused the difference to happen. Further investigations on the effect of $CaCO_3$ with various test method and parameters are necessary to confirm this.

4.4 Conclusions

The purpose of this chapter is to clarify the effect of additives on friction between the a-C:H film and various counterpart ring materials when changing the sliding speed and changing the lubrication state. The conclusions can be synopsized as follows:

(1) The effect of assorted mating material ring, sliding speed on the friction and wear properties of a-C:H coating under ZnDP+MoDTC lubrication was clarified. The friction and wear amount remarkably changed depending on the counterpart disks material. Particularly, each mating materials unveils a reduction in friction coefficient from Base to ZnDTP+MoDTC lubrication with the biggest friction coefficient reduction was denoted by TiC with 64% of reduction. Wear rate of a-C:H paired with TiN on the other hand 77% increased while the other two SAE4620 and TiC decreased 51% and 52% respectively from Base to ZnDTP+MoDTC lubrication.

(2) SEM and EDS analysis was conducted on both bearing and ring wear track. The results indicated that the properties of the tribofilm derived from the ZnDTP+MoDTC oil are varied subject on the mating material rings material. Generally, it was revealed that the oil additives element at% did not change very much on a-C:H bearings except for the pair of TiN where the Calcium was remarked relatively lower. On mating material rings however, compared to TiC which exposes the lowest Molybdenum on its surfaces, about 17 times higher Molybdenum was detected on SAE4620 surface. As for the Calcium attachment, TiC marked 15 times higher value compared to the other two.

(3) a-C:H bearing paired with TiC ring in ZnDTP+MoDTC believed to be the best combination in terms of friction reduction between the sliding surfaces and the rationale are as follows. The coexistence Calcium and low Molybdenum on a-C:H bearing and remarkably high Calcium on TiC ring suggests that detergents additives effectively works in reducing friction and wear for this combination.

(4) ZnDTP+MoDTC oil is capable to provide better lubrication mode both in mixed and boundary lubrication regime for all three type of mating materials especially TiC with the biggest different in friction and wear than in Base oil.

5. Conclusions and Future Outlook

In this thesis, the tribological performance of a-C:H coatings in oil additives added lubricant oils was clarified to provide a design guideline for applying DLC coating to engine bearing. Therefore, the effect of lubricant oil additives, surface modification by UV irradiation, mating materials and sliding speed to the seizure and lubrication mode of a-C:H coatings under high contact pressure boundary lubrication condition were investigated. From the tribological tests and the surface analysis, the main findings of this thesis can be summarized as follows:

1. Tribological properties of UV irradiated a-C:H DLCs sliding against steel under boundary lubrication condition in various oil additives added lubricant oil were investigated in order to determine the effect of UV irradiation on friction and wear behavior. The following conclusions are as follows:
    a. By doing UV irradiation to a-C:H coating, the friction coefficient of UV irradiated a-C:H shows lower friction coefficient than as-deposited a-C:H despite the type of lubricant oil. Specifically in ZnDTP oil, the friction coefficient decreased from 0.06 to 0.04. Largest reduction of specific wear rate was shown by UV irradiated a-C:H in ZnDTP+MoDTC oil from 9.69 x 10^{-9} mm^3/Nm to 1.26 x 10^{-9} mm^3/Nm.
    b. The tribofilm formed on both a-C:H disks and SUJ2 balls was measured by EDS-SEM and 3D interferometry. It was revealed that the film thickness did not change very much on a-C:H coating but it was observed that by doing UV irradiation, the oil additives elements from each lubricant oils attached more on the UV irradiated a-C:H. In particular, all lubricant oils show an increase of

selected oil additives elements at% except for ZnDTP+MoDTC oil where a reduction of Molybdenum and Sulphur was observed.

c. On the mating material SUJ2 balls, it was revealed that the tribofilm thickness increased by UV irradiation except for ZnDTP+MoDTC oil where reduction observed probably caused by the reduction of the Sulphur. In the overall, ZnDTP+MoDTC forms thicker tribofilm on SUJ2 ball which around 70 nm to 75 nm than the other two additives added oil which is around 10 nm to 20 nm.

d. In the overall, UV irradiated a-C:H in ZnDTP+MoDTC considered as the best combination in terms of specific wear rate reduction on the sliding interfaces and the reason are as follows. Generally UV irradiation helps to attract more oil additives elements to attach on the sliding interfaces, however particularly for ZnDTP+MoDTC oil, UV irradiation reduces the attachment of wear producer Molybdenum and Sulphur. Combined with the formation of thicker tribofilm formed by ZnDTP+MoDTC oil on the mating material SUJ2 balls further helps to improve the friction and wear of the combination.

2. Tribological properties of a-C:H DLCs sliding against four different type of mating materials under boundary lubrication condition in various oil additives added lubricant oil with incremental loads were investigated in order to determine the seizure characteristics, friction and wear behavior. The following conclusions are as follows:

   a. In the friction of ZnDTP and MoDTC containing oil, the influence of different mating material ring on the friction, wear and seizure characteristics of a-C:H coating was clarified. Specifically, the coefficient of friction slightly increased with the inclusion of additives in the case of SUJ2 steel, but not so much difference in the case of TiC and slightly decreased in the case of TiN. On the other hand, the wear amount remarkably changed depending on the counterpart disks material. Specifically, the inclusion of additives increased the wear amount to 1.4 times for SUJ 2 steel, but in the case of TiN and TiC, the wear reduction remarkably decreased to 1/2, 1/258 respectively depending on the inclusion of additives.

   b. Detailed analysis of SEM and EDS was conducted. As a result, it was revealed that the thickness and composition of the tribofilm derived from the ZnDTP+MoDTC oil additives are differed depending on the material of the opponent disk material. In particular, compared to the lowest Molybdenum on TiC, SUJ2 and TiN discloses about 5 times and 3 times higher value of the same elements on their surfaces. The same pattern also observed on the a-C:H rollers where TiC denoted the lowest attachment of Molybdenum on its surface.

c. In the overall, a-C:H roller mated with TiC disk in ZnDTP+MoDTC considered as the best combination in terms of specific wear volume reduction on the sliding interfaces and the reason are as follows. Molybdenum on the TiC disk was balanced out by the ZnDTP derived elements while on the a-C:H roller, ZnDTP derived elements was detected higher than the Molybdenum. It is suggested that wear agent ZnDTP able to execute excellent role in this exact arrangement.

d. ZnDTP+MoDTC lubricant oil is able to suppress seizure by concealing the effect of peeling off on both DLC and mating materials coatings. Compared to Base oil, the running in phase at each applied force in ZnDTP+MoDTC was much steadier and quickly balances out.

3. Tribological properties of a-C:H DLCs sliding against four different type of mating materials under various lubrication condition in various oil additives added lubricant oil with various sliding speeds were investigated in order to determine the effect of sliding speed and lubrication mode, friction and wear behavior. The following conclusions are as follows:
   a. The effect of assorted mating material ring, sliding speed on the friction and wear properties of a-C:H coating under ZnDP+MoDTC lubrication was clarified. The friction and wear amount remarkably changed depending on the counterpart disks material. Particularly, each mating materials unveils a reduction in friction coefficient from Base to ZnDTP+MoDTC lubrication with the biggest friction coefficient reduction was denoted by TiC with 64% of reduction. Wear rate of a-C:H paired with TiN on the other hand 77% increased while the other two SAE4620 and TiC decreased 51% and 52% respectively from Base to ZnDTP+MoDTC lubrication.
   b. SEM and EDS analysis was conducted on both bearing and ring wear track. The results indicated that the properties of the tribofilm derived from the ZnDTP+MoDTC oil are varied subject on the mating material rings material. Generally, it was revealed that the oil additives element at% did not change very much on a-C:H bearings except for the pair of TiN where the Calcium was remarked relatively lower. On mating material rings however, compared to TiC which exposes the lowest Molybdenum on its surfaces, about 17 times higher Molybdenum was detected on SAE4620 surface. As for the Calcium attachment, TiC marked 15 times higher value compared to the other two.
   c. a-C:H bearing paired with TiC ring in ZnDTP+MoDTC believed to be the best

combination in terms of friction reduction between the sliding surfaces and the rationale are as follows. The coexistence Calcium and low Molybdenum on a-C:H bearing and remarkably high Calcium on TiC ring suggests that detergents additives effectively works in reducing friction and wear for this combination.

d. ZnDTP+MoDTC oil is capable to provide better lubrication mode both in mixed and boundary lubrication regime for all three type of mating materials especially TiC with the biggest different in friction and wear than in Base oil.

In the future, in order to further extend the potential and possibilities of a-C:H DLC coating applications, the process of overcoat CN_x coating on top of a-C:H DLC is highly recommended. CN_x is a softer, low internal stress material. Previous study by Sakakibara et al. deposited CNx film and other DLC film on both friction surfaces and rubbed them under PAO lubrication. As a result, it was reported that the lowest coefficient of friction is exhibited when the CN_x film is formed on both friction faces and the friction coefficient is less than 0.05 [107]. Tagami et al. measured the oil film thickness using a reflective spectroscopic film thickness meter when a sapphire hemisphere was pressed against the CN_x and the DLC film in PAO oil. As a result, it was reported that the CN_x coating forms an oil film thicker than the DLC coating and can reduce direct contact during friction [108]. So by using the same approach as this study that is varying the mating material to be interacted with the CN_x over coated on the a-C:H coating, it is expected that ultra-low friction coefficient and wear rate can be achieved, and of course the attention will be much more on the TiC mating material.

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