TRIBOLOGICAL INVESTIGATION OF TETRAHEDRAL DIAMOND-LIKE CARBON (ta-C DLC) COATINGS USING VEGETABLE OIL CONTAINING ANTI-WEAR ADDITIVES

ABDUL MANNAN

FACULTY OF ENGINEERING
UNIVERSITY OF MALAYA
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ABDUL MANNAN

DISSERTATION SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF ENGINEERING SCIENCE

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ORIGINAL LITERARY WORK DECLARATION

Name of Candidate : Abdul Mannan

Matric No : KGA150053

Name of Degree : Master of Engineering Science

Title of Thesis : Tribological investigation of tetrahedral diamond-like carbon (ta-C DLC) coatings using vegetable oil containing anti-wear additives

Field of Study : Energy

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Friction and wear are considered as the nuance for machineries and need to reduce as much as possible. Use of proper lubricants and the treatment of interfacial surfaces can be a way of reducing both friction and wear. This study is about the tribological performance of tetrahedral diamond-like carbon (ta-C DLC) coating where the investigations were performed in Steel/Steel, Steel/DLC and DLC/DLC contacts in the presence of canola oil with and/or without additives. The Steel/Steel contact was investigated as the reference contact. The results varied between contacts and oils such as the coefficient of friction (COF) in Steel/Steel, Steel/DLC and DLC/DLC contacts under base oil was 0.062, 0.059 and 0.048, and under additivated oil was 0.066, 0.067 and 0.058 respectively. Both oils showed lowest wear in Steel/Steel contact and the Steel/DLC and DLC/DLC contact showed approximately 76% and 8% higher wear than Steel/Steel contact respectively when tested with base oil. The wear reduced in all contacts under additivated oil and this was higher in metal containing contacts such as approximately 79% in Steel/Steel, 66% in Steel/DLC and 60% in DLC/DLC contact. The wear reduction by additives might be due to the chemical absorption with steel and physical absorption with DLC surface as DLCs are known as “non-reactive”. The agglomeration of transferred particles in Steel/DLC under base oil was not found when tested with additivated oil. The damage of coating in DLC/DLC was not present when tested with additivated oil. Therefore, it can be said that the tribological properties can be improved applying DLC coating and further improvement can be done by additivating the base oils.
ABSTRAK

Geseran dan haus adalah sesuatu tidak dinilai didalam mesin dan ianya mestilah dikurangkan sebanyak mungkin. Pengunaan pelincir dan saduran yang sesuai boleh mengurangkan kedua-dua masalah ini. Di dalam kajian ini, keupayaan tribologikal bagi saduran tetrahedral diamond-like carbon (ta-C DLC) dikaji di antara permukaan sentuh keluli/DLC dan permukaan sentuh DLC/DLC dengan kehadiran minyak canola dengan additives dan tanpa additives. Sentuh antara keluli/keluli dikaji untuk dijadikan sebagai rujukan. Keputusan yang berbeza diantara permukaan sentuh dan minyak seperti pekali geseran (COF) dalam sentuh Steel / Steel, Steel / DLC dan DLC / DLC di bawah minyak asas adalah 0.062, 0.059 dan 0.048, dan di bawah minyak additives ialah 0.066, 0.067 dan 0.058. Kedua-dua minyak menunjukkan haus yang paling rendah dalam permukaan sentuh Steel / Steel dan permukaan sentuh Steel / DLC dan DLC / DLC menunjukkan kira-kira 76% dan 8% lebih tinggi pakai daripada permukaan sentuh keluli / Steel apabila diuji dengan minyak asas. Haus dikurangkan dalam semua permukaan sentuh di bawah minyak additives dan ini lebih tinggi dalam permukaan sentuh menagndungi logam kira-kira 79% dalam Steel / Steel, 66% dalam Steel / DLC dan 60% dalam hubungan DLC / DLC. Pengurangan haus oleh bahan tambah mungkin disebabkan oleh penyerapan kimia oleh keluli dan penyerapan fizikal oleh permukaan DLC sebagai DLC dikenal sebagai "tidak reaktif". Aglomerasi zarah-zarah yang dipindahkan dalam Keluli / DLC di bawah minyak asas tidak dijumpai apabila diuji dengan minyak additives. Kerosakan saduran di DLC / DLC tidak hadir semasa diuji dengan minyak tambahan. Oleh itu, dapat dikatakan bahawa sifat-sifat tribologi dapat ditingkatkan dengan menggunakan
saduran DLC dan peningkatan selanjutnya dapat dilakukan dengan menambah minyak asas.
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CHAPTER 1: INTRODUCTION

1.1 Overview

In the recent years, the industrial awareness of the importance of good tribological design has been increased largely because of its economic benefits and increased machine durability. Friction is defined as the resistance between two surfaces in relative motion and this is a major cause of energy loss in the machine. Some estimations say that USA alone counts the losses of approximately 4% of gross national product because of poor tribo-system and friction, directly or indirectly, is the cause of approximately one-third of world energy consumption (Bhushan, 2013b). Few other studies (Holmberg, Andersson, & Erdemir, 2012; Holmberg, Andersson, Nylund, Mäkelä, & Erdemir, 2014) have estimated that approximately one-third of input energy in passenger car as well as heavy duty vehicles are consumed just to overcome friction, which is a staggering loss of energy for this modern society. The purpose of research on tribology is to eliminate the wear and friction totally, or to minimize as much as possible. The world is in a stage of technology where every aspect of sliding contacts must be investigated critically; especially, the highly sophisticated machines (e.g. supersonic aircraft and nuclear submarine, etc.) always demand the appropriate solution of tribological problems. And, most of the tribology related problems can be solved with the currently available technology, i.e. a significant amount of money savings are possible just through applying currently available technology (Abdul-Mahdi, 1987).

Generally, a tribosystem is consisted of four main elements: two contacting surfaces, interfacial medium, which lies between the contacting surfaces, and the operating parameters, see Figure 1.1 (YONG, 2014). The operating parameters are the forces
involved, type of motion, temperature, relative speed and the stresses present at the contacts and moreover, the tribological processes can be physical, physicochemical (e.g. adsorption, desorption), or chemical in nature. Generally, different types of lubricants are available which act as the interfacial medium, and finally the whole phenomenon is shortened as input: operating variables and output: wear and friction.

Figure 1.1: The main elements of a tribo-system.

1.2 Problem Statement

If sliding takes places between two contacting surface, several chemical and mechanical changes occur on the surface. In this process, energy dissipates in various forms and one of them is termed as friction which has already been defined in the previous section. A large portion of input energy is required to overcome this friction such as one-third in automotive engine, which is already mentioned before. On the other hand, wear (i.e. material consumption) must take place if sliding between two contacting surfaces continues. It is well known that steel is dominantly used in machines and the hardness of steel quite high and satisfactory, but the adhesion of steel surfaces is relatively high, which can increase both friction and wear. In order to reduce the energy and material consumption, further modification of the contacting surfaces are required.
such as increasing surface hardness, reducing surface roughness, selection of proper material combinations, etc. Hence, the steel surfaces should be coated with a material of extreme hardness and low adhesion strength. Tetrahedral diamond-like carbon (ta-C DLC), constituted of very high amount of SP³ bond, is such a material which exhibits hardness value close to diamond and very low adhesion strength. DLC is also well known for their superior friction and wear properties in both dry or lubricated conditions (Sharma et al., 2012).

On the other hand, the use of proper lubricants can also reduce both friction and wear noticeably. For decades, the petroleum products were the main supply of lubricants, but the sources of petroleum are limited. In contrary, the lubricant consumption around the world is increasing following the expansion of industrialization (Research, 2016). Figure 1.2 shows how the lubricant demand is increasing around the word in different sectors. It is important to note that the petroleum-based-oils are harmful for the environment. Therefore, new lubricant sources are required that would be able to supply the increased demand without harming environment and one alternative source would be the vegetable oil as the sources are renewable and oils are biodegradable. Moreover, the addition of different chemical agents to the vegetable oil can improve many of its properties, especially friction and wear properties. The most popular lubricant additive around the world is the zinc dialkyldithiophosphates (ZDDP), which perform very well with steel surface. Moreover, a tribosystem can be operated under three lubricated condition: Hydrodynamic Lubrication (HL), Elasto-Hydrodynamic Lubrication (EHL), and Boundary Lubrication (BL). The friction and wear properties vary among these lubrication regimes. This study is basically based on the BL in which region, the friction and wear are relatively higher than other two regions. In this study, tetrahedral diamond-like carbon (ta-C DLC) is chosen as coating material and canola oil was
chosen as the base oil. This study is basically based on how ta-C DLC perform against canola oil with and without ZDDP at boundary condition, which is yet to be done, so that, the ta-C DLC coatings with the base oils and additives can become an effective means of controlling friction and wear.

**Figure 1.2:** Global lubricants market volume by product, 2012 – 2022 in million tons (Research, 2016).

**1.3 Objectives of This Study**

In this study, tetrahedral diamond-like carbon (ta-C DLC) coated AISI 440 C steel is the main targeted material for the observation of tribological properties. The commercially available canola oil is chosen as the base oil which is additivated with zinc dialkyldithiophosphates (ZDDP). ZDDP is well known for their anti-wear performance of steel surface, but however, it is attempted here to know how DLC perform against ZDDP. The objectives of this study are summarized below-

1. To study the tribological performance of Steel/Steel, Steel/DLC and DLC/DLC contacts in the presence of canola oil (as base oil) at boundary condition.
2. To study how ta-C DLC performs against Steel and ta-C DLC if lubricated with ZDDP-added base oil at boundary condition.
1.4 Thesis Outline

This thesis has five chapters including the current one. The each chapter of this thesis is outlined as follows:

Chapter 1: This chapter presents the brief introduction of the research topic. The chapter begins with a short overview on energy consumption due to friction. The chapter is followed by the problem statement as well as research objective.

Chapter 2: This chapter will present literature review on the topics relevant to this thesis such as the background of tribology, lubrication theory, friction and wear, and the DLC coatings from the previously published work.

Chapter 3: In this chapter, the sample materials such as steel ball, DLC coatings, base oil and additives, etc. and their properties will be presented. In addition, the experimental methodology as well as the test parameters used in this study will be presented.

Chapter 4: This chapter will present all the results obtained from the tribology tests, FESEM-EDX analysis, Raman analysis and the surface roughness along with discussion.

Chapter 5: This is the final chapter of this thesis where all the findings will be summarized.
CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

This chapter presents a brief literature review on the topics relevant to this study. The literature review begins with a historical background of friction and wear where the scientists and their contributions are presented chronologically because without their role it would be hard for this branch of technology to be an art and to design many sophisticated machines. Moreover, the successive sections will focus on the lubrication theory, vegetable oil and additives, and finally the chapter will be ended up with briefing on the structure, properties and applications of the DLC coating.

2.2 Historical Background of Tribology

The friction and wear in traditional form is an integral part of human history. The motivation to study friction and wear is the facilitation of everyday activities by the controlled friction and wear. A handful documents have been revealed which show that the friction was a concerning issue among the ancient peoples and their attempt to develop bearings as well as surfaces of low friction by their own way. Some 5000 years before peoples made bearings and wheels, and they used bitumen to reduce friction (G. Stachowiak & Batchelor, 2013). There are some ancient paintings (1800 BC) which show that the use of lubricants by Egyptians, see Figure 2.1 (Leong, 2015; Mang, Bobzin, & Bartels, 2011). Fig. 2.1 shows a large cart of heavy statue being pulled by many slaves, and one, standing on the cart supporting the statue, is pouring lubricant (most probably water) in front of the cart to reduce the resistance to the movement. However, knowledge of friction and machine elements have been developed chronologically from the ancient time to the middle ages and then current time and one of the amusing paradigms was the transition of materials such as bronze and iron
replaced wood and stone. A brief chronological history as well as industrial significance of tribology is given in the following paragraph.

Figure 2.1: Tribology in ancient Egypt. Scores of slaves pull a plate carrying a large sculpture, while one pours a liquid as a lubricant to reduce friction between the plate and the ground. Credit: Layard, A.G. 1853 (Leong, 2015).

The field of friction and wear is commonly expressed as tribology and Dr. H. Peter Jost used this term for the first time in 1966. The word “tribology” is derived from the two Greek words: *tribos* meaning rubbing or sliding; and the suffix *logy* meaning “study of” or “knowledge of” (Bhushan, 2013a). Therefore, the literal translation of tribology is “the study of rubbing or the science of rubbing”. Dictionaries define “tribology” as the science and technology of interacting surfaces in relative motion which includes the whole area (from learning to industrial application) of friction, wear and lubrication (Shah, 2011). Although the phenomenon of friction is older than the recorded history but it was not until the 15th century the scientific study of friction started. The first scientific study was conducted by Leonardo da Vinci, a great painter, an architect and an engineer, who deduced the two important laws of friction: the coefficient of friction is proportional to the normal load, and independent of the apparent contact area.
(Bhushan, 2013a). Although, it is thought that Leonardo da Vinci started first quantitative investigation of friction but his work was not revealed until the commencement of classical mechanics or the time of Newton. Actually, the scientific study of friction in broad manner was started by French in seventeenth century. Leonardo’s work on friction was rediscovered by a French physicist Guillaume Amontons in 1699 and sometimes Leonardo’s laws of friction are also called as Amontons’ laws of friction. Amontons explained the friction in terms of surface asperities and force required to lift the weight that keeps the surfaces in contact (Barber, 2013). He believed that all surfaces contain notched edges; when surfaces come in contact, the notched edges from one surface penetrate into the grooves of opposite surface (Sincell, 2001). If the upper surface is required to slide, a lateral force is needed to raise the teeth from the grooves and this force is termed as friction force or static friction force. Following Amontons, an English scientist, John Theophilus Desaguliers (1683-1744), studied friction and he explained friction from completely different viewpoint that was an adhesion concept of friction. Desaguliers observed that very smooth surfaces can also result higher friction and roughness theory of friction is unable to explain it. He proposed that the adhesion between the contacting surfaces play a role in friction but was unable to correlate this concept with the laws of friction. Another scientist, Charles-Augustin Coulomb (1736 – 1806) repeated and verified the Amontons’ works, and he added one more law that is friction force does not rely on sliding velocity once motion starts (Bhushan, 2013a). Charles Coulomb explicitly distinguished the static friction from the kinetic friction and tribologists remember him for this contribution much more than any other of his work.

The industrialization and human consciousness about energy and material conservation have directed researchers to search for better solution of the tribology
related problem, which tremendously expanded the knowledge in almost all areas of tribology (Helena Ronkainen, 2001). Some common tribo-systems are internal combustion engine, bearing, gear, clutches, artificial hip implants and prostheses, etc. (Tasdemir, 2014; YONG, 2014). The concept of wear is too young compared to the concept of friction. The scientific study on wear was started few decades before, and Ragnar Holm was one of the few earliest researchers who worked on wear (Bhushan, 2013b). However, every day the field of tribology is moving forward and something more precious is adding to it. Now, the field is so advanced that it is classified into several branches depending on the applications such as - (i) bio-tribology, which comprises the study of friction, wear and lubrication mechanisms inside either human body or animals and (ii) nano-tribology, where the tribology is studied at nano-scales.

2.3 Friction

Friction is defined as the force resisting the relative motion between two contacting surface (Helena Ronkainen, 2001). In machine, friction is considered as the nuisance and a concerning issue because of high power loss to overcome it such as in a motor car approximately 20% power is lost to overcome friction (Holmberg et al., 2012). The real problem is the damage done by friction – the wear or seizure of some important components of machine. However, the different viewpoints of the phenomena of friction are illustrated in the next paragraph.
On a microscopic scale, friction arises due to the electromagnetic forces between atomic particles (Persson & Spencer, 1999) and from the thermodynamic standpoint, friction is an energy dissipation process which might happen due to an irreversible process of heat conduction, chemical and structural transformations (e.g. plastic deformations, surface fracture, or delamination) (Amiri & Khonsari, 2010). Friction is more comprehensive on the macroscopic scale and macroscopically the friction is the force required to overcome the various adhesive and abrasive processes as well as to initiate and/or continue the movement. There are some fundamental laws of friction which are given below.

- The frictional resistance is directly proportional to the load acting normal to the sliding surfaces.
- The friction force is independent of apparent area of sliding surfaces under constant load
- The frictional resistance is independent of the sliding velocity once motion takes place.

The above laws are by no means to be considered as natural laws, but rather they are simplified models and descriptions to make easy the understanding of friction in general.

Figure 2.2: Schematic diagram of friction.
terms. Friction force is generally explained through a dimensionless parameter called the coefficient of friction ($\mu$), which is defined as the ratio of friction force ($F$) to normal force ($N$) and is shown in Equation 2.1 (Braun and Naumovets, 2006).

$$\mu = \frac{F}{N} \quad (2.1)$$

2.4 Wear

Wear includes many scientific disciplines and principles but wear itself is not exactly science. Wear between two contacting surfaces is inevitable if relative motion is present. The wear is defined as the removal of materials in gradual process from one or both surfaces when one surface slides over other in a relative motion (Zmitrowicz, 2006). The total prevention of wear is not possible, but however minimization can be done using some techniques such as the use of proper lubricant in the contact, coating of contacting surfaces with appropriate materials, etc. (Zmitrowicz, 2006). Therefore, the main purpose of research on wear is to minimize it as much as possible. The research on wear is moving forward aiming to know the true cause of it and how to control it, etc. Wear is classified into different categories based on its causes and features such as abrasive wear, adhesive wear, corrosive wear, oxidative wear, etc. A brief description of the different types of wear mechanism is presented in the following subsections.

2.4.1 Abrasive Wear

Abrasive wear is the most common wear mechanism in the industry. It takes place when rubbing or sliding happens between the surfaces of relative hardness under high load or pressure. Based on the systematic boundaries, the abrasive wear are classified into two groups such as the two body abrasion and the three body abrasion (Li). In two body abrasion, the asperities on the harder surface plough through the softer surface, see Figure 2.2(a). On the other hand, in three body abrasion, extraneous harder particles
may embed in the softer surface and cause wear on the opposite harder surface, or they trap into the sliding interface and abrade one or both surfaces, see Figure 2.2(b). Since asperities are inevitably present on the engineering surfaces even after extreme polishing, so the possibility of two body abrasions will always remain. Generally, two body abrasions cause higher wear over three body abrasions because in three body abrasions, loose foreign particles tend to roll over the softer surface during the movement of the surfaces.

Moreover, the abrasive wear is mostly seen in the ductile metals. Based on the attack angle and shear strength of contacting surfaces, the abrasive wear modes in ductile metals are classified into the following three modes (Institute, 2016):

**Ploughing:** Wear tracks are formed on the sliding surfaces. The material is just shifted to the sides of the wear track but no removal of the material from the surface is resulted.

**Cutting:** A long ribbon-like chip forms in front of the cutting asperity and the materials equivalent to the volume of the wear track is removed from the surface.

**Wedges:** In this category of abrasive wear mode, a short wedge is formed in front of the cutting asperity.

In all cases, the wear particles are formed when the accumulated materials on the side of wear track, wedges and chips are fractured and detached from the underlying surface, most probably because of the delamination process.
2.4.2 Adhesive Wear

Adhesion is defined as the aptitude of unlike particles or surfaces to stick together. When two surfaces slide over each other under high compressive load and/or high temperature, micro-junctions can be formed due to the cold welding of asperities between contacting surfaces, and thereby material may remove from the less wear-resistant surface (see Figure 2.3). Adhesive wear are often classified as galling, scuffing, welding or smearing (Bhushan, 2013b). The following measures can be taken to prevent adhesive wear.

- Selecting metal combinations which do not tend to bond together very easily.
- Contaminating the interfacial surfaces by oils, water, etc.
- Increasing the oil film thickness.
- Formation of a layer on the sliding surface of low shear strength.
2.4.3 Corrosive Wear

Generally, corrosive wear is a combined act of chemical reaction and mechanical action on the sliding surface. The main reason is the chemical reaction between sliding surface and corroding medium (air/lubricant/chemical reagent) (Kato & Adachi, 2001; NPTEL, 2016) which generally form a reaction layer on the sliding surface. Alongside of forming reaction layer, the movement of the counter surface can remove the layer partially. And thus, relative growth rate and removal rate determine the net wear rate in case of corrosive wear.

2.4.4 Oxidative Wear

Oxidative wear generally take places when dry metallic surfaces slide in the presence of oxygen/air. However, non-dry oxidative wear can also occur if the sliding is in the presence of liquid oxygen dissolved lubricant. If the applied load and speed are high enough to produce the frictional temperature of several hundred degrees Celsius, the debris particles transformed from metallic iron to iron-oxides (G. W. Stachowiak & Batchelor, 1993). It is hypothesized that the formation of thick oxide films on the wear
track means the prevailing wear is the mild wear and the broken down or absence of oxide layers is the sign of severe wear (Archard & Hirst, 1956). The feature of oxidative wear is the smooth worn surface and small oxidized debris particles. Oxidative wear can be found where the process temperature is high enough to cause rapid oxidation and formation of oxide particles (G. W. Stachowiak & Batchelor, 1993).

2.5 Lubrication Theory

Sliding under dry conditions generally cause high friction and high wear, and the consequence is the high loss of energy and material (H Ronkainen, Varjus, & Holmberg, 1998; Yan, 2014). One way to prevent this high friction and high wear is the use of lubricants at the contact during sliding. Moreover, the lubricants can play few secondary role as well: cooling the system, reducing vibration, carrying away the debris, etc. (Renman, 2012). The lubricants can be either solid such as graphite and molybdenum disulfide or liquid such as oil, grease and water. The use of liquid lubricants is very high compared to the solid lubricants, and thereby the lubrication theories are basically developed considering the application of oil lubricants. Based on the viscosity, velocity and applied load, the lubrication condition is divided into three parts: Hydrodynamic lubrication (HL), Elastrohydrodynamic lubrication (EHL) and Boundary lubrication (BL). Moreover, there is transitional regime between EHL and BL which is termed as the Mixed Lubrication (ML). The frictional behavior varies among the lubrication regime which is graphically illustrated in Figure 2.4 using the so called Stirebeck curve (Tasdemir, 2014). In the Striebeck curve, the friction coefficient is presented as the function of a dimensionless parameter \( \frac{Viscosity \times Speed}{Load} \). All the lubrication regimes shown in Figure 2.4 are discussed briefly in the following sections.
2.5.1 Hydrodynamic Lubrication (HL) Regime

In hydrodynamic lubrication condition, the fluid film thickness is greater than the roughness height and under this condition, the lubricant itself carries the total applied load (He; Renman, 2012). Hence, the obtained friction is caused by the lubricant viscosity and is independent of the interacting surfaces. Both of the friction and wear are very low under hydrodynamic lubrication regime.

2.5.2 Elasto-Hydrodynamic Lubrication (EHL) Regime

In elasto-hydrodynamic lubrication mode, the fluid film thickness is equivalent to the height of surface roughness. EHL condition occurs in lubricated non-conformal contacts where the fluid film thickness is largely influenced by the elastic deformation of solid surface (Lugt & Morales-Espejel, 2011). EHL is a leading lubrication mode in many critical and heavily loaded machine components such as ball or rolling element bearings, gears, cams and followers, etc. It also plays an effective role in some
considerably deformable bearing system such as seals, elastomeric bearings (Dowson, 1995). The elastic deformation properties of contacting surfaces are the result of high contact pressure and this high pressure can also increase the lubricant viscosity to several order of magnitude (Lugt & Morales-Espejel, 2011; Tasdemir, 2014). In summary, both of the elastic deformation of contacting surface and the increased lubricant viscosity has a positive influence on the lubricant film thickness.

2.5.3 Mixed Lubrication (ML) Regime

Mixed lubrication regime lies between Elasto-hydrodynamic and boundary lubrication regime. In this lubrication condition, the quantity of lubricant present between contacting surfaces is not high enough to keep the surfaces completely separated. Thus, the insufficient quantity of lubricants allows the asperities from both surfaces to come in contact and cause increased friction coefficient as well as wear rate. Mixed lubrication regime is also called as an “unstable” lubrication regime and under this lubrication regime the viscosity can be very low if heavy load is applied.

2.5.4 Boundary Lubrication (BL) Regime

Boundary lubrication takes place when other two principle lubrication modes such as HL and EHL fail to occur (Bhushan, 2013b). BL is defined as the lubrication mode where two contacting surfaces are in direct contact and the total load is supported by the asperities of the interfacial surfaces. Under high applied load or when the machine starts from an idle condition, however, in most of the cases, the bulk of lubricant squeezed out, but a few molecules thick adherent surface film remains which can prevent the seizure of interfacial surfaces and allows them to slide over each other (Halling, 1976). The fundamental characteristics of BL are as follows (Hironaka, 1984) -

(i) The frictional surfaces are in direct contact at micro-asperity level.
(ii) The asperity-asperity and/or the asperity-lubricant (including additives) contacts lead the tribological properties.

(iii) The lubricant bulk properties such as viscosity or the hydrodynamic properties have little effect on the tribological properties.

2.6 Lubricants

Lubricants are generally considered as the substances which can reduce the friction and wear of a contact if applied on it. Lubricants are formulated end products composed of 75-99% base oil (or base stock) and 1-25% different additives depending on the application (Theodori, Saft, Krop, & Broekhuizen, 2003). The additives are generally designed to improve the specific properties of base oil where the base oil works as a solvent for the additives, which control the bulk and surface properties.

2.7 Vegetable Oils as Base Oil

The base oil, which can be either mineral or synthetic, or vegetable oil, must be viscous enough to maintain a lubricant film under the required working conditions. Moreover, they should perform some additional functions such as keep the system cool, no power loss due to viscous drag, the ability to dissolve the additives and high thermal as well as oxidative stability.

The vegetable oils are the esters of glycerol and triglyceride extracted from different plants (e.g. sunflower oil, soybean oil, palm oil, canola oil, etc.). A typical structure of triglyceride is shown in Figure 2.5. Even though the vegetable oils are used for cooking purpose, they are highly appreciated for lubricant purposes as vegetable oil contain high amount of polar groups and un-saturated molecules (M. Kalin, Vižintin, Vercammen, Barriga, & Arnšek, 2006). Oils with high polar groups have more sites to react and
adsorb with metal surfaces and thus can form a film in boundary condition (Hsien, 2015). A lubricating film with tight bonding to the surfaces and sufficient cohesive interaction among lubricant molecules can effectively reduce the wear and friction. The most favorable lubricants are those which maintain low wear and friction over a wide range of temperature preventing the shear degradation, and exhibit superior boundary lubrication properties through strong chemical and physical adsorption with sliding surfaces (Hsien, 2015). Vegetable oils show few additional properties- high viscosity index, high flash/fire points, etc. (Hsien, 2015; Lubrication, 2016). In contrast, due to the higher level of unsaturation, vegetable oils show some drawbacks such as poor thermal and oxidative stability (N. J. Fox & Stachowiak, 2007). Few other drawbacks of vegetable oils which must be improved for extensive application are precipitation, cloudiness, poor flow and solidification upon long-term exposure to the cold temperature (Erhan, Sharma, & Perez, 2006; Rhee, Velez, & Von Bernewitz, 1995).

**Figure 2.6**: A typical structure of triglycerides (Low Carb Steve, 2015).

Reeves, C.J. et al (2015) studied the tribological properties of different types of vegetable oils and found the tribological properties varies among the oils according to the level of unsaturation of each oil. Especially, the high oleic acid concentrations improve friction and wear performance by establishing densely packed monolayers on the lubricating surface. Kalin, M. et al (2006) claimed that oils with higher level of
polarity and unsaturated molecules have more sites to react and can provide good boundary lubrication properties. Moreover, the authors have also reported that the vegetable oils are more important for the tribological properties of DLC coating due to their high unsaturation and polarity. It is important to mention that they used hydrogenated diamond like carbon for their research. Among all vegetable oil, canola oil contain extremely high amount of polar and un-saturated molecules (Zambiazi, 2007), therefore canola oil can be an effective lubricant and study of the tribological properties of canola oil have significance. A broad review on the preparation and tribological properties of bio based oils can be found here (Chan, Tang, Mohd, Lim, Yeong and Idris, 2018; Heikal, Elmelawy, Khalil and Elbasuny, 2017; Syahir, Zulkifli Masjuki, Kalam, Alabdulkarem, Gulza, Khuong and Harith, 2017). Moreover, a literature reviews on the tribological properties of different types of DLC coatings (e.g. a-C:H DLC, ta-C DLC, metal/non-metal DLC) under different oils (e.g. both vegetable and mineral oils) is done by Zahid, R. et al (Zahid, 2015). In this paper, authors have concluded that both frictional and wear performance of vegetable oils were better than mineral oils.

2.8 Motivation to Work with Vegetable Oils

Lubricants are essential in almost all machine as they accomplish some critical functions such as reduction of friction and wear, carry away debris particles, keep the system cool, minimization of vibration/noise, etc. (Renman, 2012). The commonly used lubricants are automotive lubricants, transmission fluids, industrial gear oils, greases, hydraulic fluids, metal working fluids, cold rolling oils, fire resistant hydraulic fluids, etc. (Nagendramma & Kaul, 2012). A market research report has mentioned that every year the lubricant consumption is increasing and it is estimated that the lubricants usage would be approximately 43 million tons by 2022 which was 36.36 million tons in 2014.
According to Theo Mang *et al* (Mang & Dresel, 2007), in 2004 only, 37.4 million tons of lubricants were consumed around the world: 53% consumed by automotive sectors, 32% consumed by industrial sectors, 5% consumed by marine and 10% consumed by other sectors, and most of the consumed lubricants are the non-biodegradable mineral-oil based. A big portion of that consumed mineral-oil-based lubricants are entering into our environment and polluting water, air, soil and thus posing a threat to the plant and animal life (Erhan, Sharma, Liu, & Adhvaryu, 2008; Salimon, Salih, & Yousif, 2010). Human consciousness about the safeguard of environment and its belongings from any threat posed by petroleum products have directed peoples to search for new types of environment friendly lubricant i.e. renewable and properly biodegradable (N. J. Fox & Stachowiak, 2007). Typically, mineral oil-based lubricants are derived from crude oil through distillation, solvent extraction as well as the cracking process of base oil, and it is composed of base oil, coloring agents, diluents and additives such as friction modifier, viscosity modifier, anti-oxidants, anti-wear, etc. (Sripada, 2012). All these constituents determine the total manufacturing costs and after that the selling price is decided. However, the price of mineral oil-based lubricants is increasing in regular basis for many reasons such as increased demand, limited resources, increased labor costs, etc (Sripada, 2012). Hence, alternative sources of ecofriendly and cheap lubricants are highly necessary. Vegetable oils can be the viable alternative sources of lubricants which are generally biodegradable and capable to confront the threat posed by mineral-oil based lubricant as well as fulfill the future lubricant demand.

### 2.9 Viscosity and Density of Lubricants

Viscosity is the single most important property of lubricant which is defined as the internal resistance of fluid to flow and also sometimes it is called the fluid friction
All real fluids have some resistance to stress and therefore are viscous, but a fluid which has no resistance to shear stress is known as inviscid fluid. Viscosity is a basic property of any lubricants which always plays a greater role in lubricity of contact. Viscosity is always an important property that must be taken into account in choosing a lubricant especially for hydrodynamic lubrication. Extremely high and low viscosity, both are inefficient. If the viscosity of lubricant is too high, high forces are required to overcome its own intermolecular forces in sliding motion between devices. Oppositely, if viscosity of lubricant is too small, it will cause surfaces between the devices to be rubbed directly and further damage the devices (Ting & Chen, 2011). A good study on the effect of viscosity improver on tribological properties can be found in (Quinchia, Delgado, Reddyhoff, Gallegos and Spikes, 2014).

2.9 Lubricant Additives

The chemical compounds which are mixed with the base oils to improve one or more specific properties of base oils are called additives (Ahmed & Nassar, 2011). The lubricant performance relies collectively on base oil, additives and their formulation. Besides promoting the existing properties, additives sometimes offer new properties to the lubricants, inhibit the undesirable changes in lubricants which may occur during operation. The use of additive started around 1920 and since then the use is increasing remarkably. The commonly used lubricant additives are- antioxidants, corrosion inhibitors, viscosity modifiers, extreme pressure additives, friction modifiers, anti-wear agents, etc. (Ahmed & Nassar, 2011; YONG, 2014). However, some of the additives exhibit more than one property; for instance, the most widely used additive zinc dialkyl dithiophosphates (ZDDP) offer anti-wear, antioxidant and extreme pressure properties. A brief description of different types of additives and their functions are given below.
2.9.1 Corrosion Inhibitor: Typically, corrosion inhibitors are compounds with high polar groups and long alkyl chains which have high affinity to metal surfaces (Ahmed & Nassar, 2011; YONG, 2014). They form a hydrophobic layer on the metal surfaces and thus prevent oxygen, water and other substances from being adsorbed by the metal surfaces. The two well-known corrosion inhibitors are sulphonates and carboxylic acid.

2.9.2 Viscosity Modifier: viscosity modifiers are long chain, polymer like molecules which increase the relative viscosity of oil more at high temperature compared to a low temperature (Zainal, Zulkifli, Gulzar and Masjuki, 2018; Machinery Lubrication, 2017). The typical viscosity index improvers are hydrogenated styrene-butadiene, olefin copolymer, polyalkylmethacrylate, etc.

2.9.3 Friction modifiers (Ahmed & Nassar, 2011; YONG, 2014): In general, the friction modifiers are the polar molecules and non-polar linear hydrocarbon molecules. The primary purpose of a friction modifier is to reduce the friction when added to the base oils. Typically, the polar molecules of friction modifiers are adsorbed by the solid surfaces and the non-polar hydrocarbon molecules extend themselves into the oil. The most widely used friction modifiers are glycerol mono-oleate (GMO) and molybdenum dithio-carbamates (MoDTC).

2.9.4 Extreme pressure: If the sliding surfaces operate under very high pressure and speed, the local temperature can increase to very high. And, in such situations, liquid lubricants fail to stick to the surface and may decompose as well as evaporate. To overcome these extreme pressure conditions, special types of additives have been formulated, which is called extreme pressure additives (Lubricants, 2016). These additives are able to form much durable films on the solid surfaces. The examples of EP
additives are molybdenum disulfide, graphite, sulfurized olefins and dialkyldithiocarbamate complexes, etc.

2.9.5 Antioxidant additives: Generally, all lubricants are dubious to oxidation. Oxidation reduces the working life of a lubricant through decomposition, oil thickening, sludge and varnish formation as well as the corrosive acid formation (YONG, 2014). Therefore, for proper operation a lubricant must have high oxidation stability (Ahmed & Nassar, 2011). Oxidation generally occurs when hydrocarbons expose to oxygen at high temperatures. The examples of antioxidant additives are aromatic amines and hindered phenols, phosphates, etc.

2.9.6 Anti-wear (AW) agents (Ahmed & Nassar, 2011; YONG, 2014): In the mixed and boundary lubrication condition, the lubricating performance of the oil is controlled by the anti-wear (AW) additives. The main elements for the anti-wear action is the phosphorous (Naveira Suarez, 2011) and the mostly used anti-wear additive is the Zinc dialkyl dithiophosphates (ZDDP). The ZDDP compound is constituted of Sulfur (S), Phosphorous (P), Zinc (Zn) and aryl/alkyl group (RO). Among all these elements, Phosphorous mainly the wear of a contact (Okubo, Watanabe, Tadokoro, & Sasaki, 2016). The anti-wear and extreme pressure agents show similar protection mechanism but the activation temperature for anti-wear agents is less compared to extreme pressure agents. The wear preventive mechanisms of ZDDP are as follows- (i) formation of mechanically protective layer, (ii) removal of corrosive peroxides and (iii) by digesting hard and abrasive iron-oxides particles.
2.10 Diamond-like Carbon (DLC) Coatings

In machineries, ranging from spacecraft to household appliance, lower friction and lower wear is always a prime requirement to minimize the energy and material consumption as well as to increase the longevity of machine. Alongside using appropriate lubricants, the coating of contacting surfaces with appropriate materials is a useful technique of reducing friction and wear. Diamond-like carbon (DLC) coatings have drawn much attention since the 1980s for its reduced friction and wear properties (Holmberg & Mathews, 1994). DLC coatings are of different types and can be produced using different methods. A review on the different areas of DLC films such as deposition, classifications and properties will be done on the subsequent subsections.

2.10.1 DLC Films: Deposition, Structure, Classification and Structural Properties

There are several methods to deposit DLC coatings which are primarily classified as chemical vapour deposition (CVD) and physical vapour deposition (PVD). The a-C:H coatings can be deposited using the CVD methods, such as d.c. plasma and radio frequency (r.f.) plasma assisted chemical vapour deposition, and few of the PVD methods, like sputter deposition, ion-plating techniques and ion-beam techniques. The PVD methods such as magnetron sputtering, mass selected ion-beam (MSIB), filtered cathodic arc vacuum (FCVA) are generally used to deposit hydrogen-free a-C and ta-C coatings (Makowski, et al, 2017; Neuville & Matthews, 1997; J Robertson, 1999). The properties of coatings can vary with the deposition techniques because the input parameters (ion energy, precursor gases, temperature, pressure, etc.) are different for different techniques (Hainsworth & Uhure, 2013). DLC films can be of nano-scale smoothness with very high hardness, even smoother than the diamond films. A wide range of materials can be coated with DLC films as the deposition can be done at low temperature (<100°C).
Carbon is thought as an unique, abundant and fascinating chemical element in the nature, because it can exist in all three different structures: sp$^3$, sp$^2$ and sp$^1$ (J. Robertson, 2002) and can form varieties of structures with the different fractions of sp$^3$ and sp$^2$ bonding in both crystalline and non-crystalline form (J. Robertson, 2002). Diamond and graphite are the examples of crystalline form of carbon and diamond-like-carbon materials (DLC) are the non-crystalline form of carbon. DLC is defined as the metastable form of non-crystalline carbon (a-C) network which is a mixture of sp$^2$, sp$^3$ structures as well as the hydrogen, based on the type of DLC coating. It is assumed that in DLC films, the sp$^2$ bonded clusters are embedded in the sp$^3$ bonded disordered carbon and the ratio of sp$^3$ to sp$^2$ structures are controlled by the deposition techniques and deposition parameters such as bias voltage (J. Robertson, 1992).

The DLC films are classified into three groups based on sp$^3$/sp$^2$ structures and hydrogen contents (J. Robertson, 2002). Firstly, the non-hydrogenated tetrahedral carbide (ta-C) DLC film, which is consisted of a very high fraction of sp$^3$ bonding. Secondly, the hydrogenated tetrahedral (ta-C: H) DLC film which is same as previous DLC film but contain a small fraction of hydrogen in the structure. And thirdly, the hydrogenated amorphous carbon film (a-H: DLC), which is consisted of a low fraction of sp$^3$ bonding and a high fraction of hydrogen as compared to the previous two types of the DLC films. Generally, hydrogenated DLC coatings contain less than 50% sp$^3$ structure and up to 50% H while hydrogen-free DLC coatings can contain more than 85% sp$^3$ structures (Jeng, Islam, Wu, Erdemir, and Eryilmaz, 2017; Alfred Grill, 1999). A ternary diagram, which represents various types of DLC films with respect to sp$^3$, sp$^2$ structures as well as H contents was introduced by Jacob and Moller and is shown in Figure 2.7 (Ferrari, Donnet, & Erdemir, 2007; Jacob & Möller, 1993).
It is already mentioned that the structure and properties of DLC films largely depend on the deposition methods and deposition parameters (ion energy, deposition pressure, deposition temperature and the substrate material). Moreover, the properties of DLC films strongly depend on the \( \text{sp}^2 \) to \( \text{sp}^3 \) ratio and the hydrogen content (C Donnet et al., 1994), for instance, DLC films with high amount of \( \text{sp}^3 \) bonding are harder than those with low amount of \( \text{sp}^3 \) (or high fraction of \( \text{sp}^2 \)). It is well known that diamond is the hardest known material with highest density and highest thermal conductivity of any materials ever discovered. Therefore, it would be more convenient to compare the properties of DLC films with diamond. Each type of DLC films has unique hardness value, density, thermal conductivity, friction and wear. For instances, majority of hydrogenated DLC (a-C:H) films show hardness value approximately 15% of diamond, because they are constituted of low fraction of \( \text{SP}^3 \) structures (e.g. 20-60% H and 20-50% \( \text{SP}^3 \)) (Helena Ronkainen, 2001), and ta-C DLC films show hardness value close to the diamond and this is due to their high amount of \( \text{SP}^3 \) (80-88%) structures (J Robertson, 1999). A major drawback for DLC coating is the high internal stresses such
as internal stress in a-C:H DLC coatings is about 4-6 GPa, which is about 10-12 GPa in ta-C DLC films (Helena Ronkainen, 2001). The high internal stresses can reduce the coating-substrate adhesion which can cause the early delamination of coating. The adhesion is a compound property which depends on the substrate, coating and deposition method as well as parameters. The internal stresses of DLC films can be reduced by the incorporation of N, Si and Metal (Alfred Grill, 1999). In addition, the interlayer can be used to increase the coating-substrate adhesion. The chromium based interlayer is highly appreciated for steel substrate to increase the coating-substrate adhesion (A. Grill, 1997), because the chromium and steel show very close thermal expansion coefficient (11.8 x 10⁻⁶ and 12.5 x 10⁻⁶ °C, respectively) and high toughness ensuring low thermal stress and high thermal strength (Hainsworth & Uhure, 2013).

DLC material is thermodynamically metastable, but however, they can be thermally decomposed or graphitized if the temperature is too high along with the out-diffusion of hydrocarbons and/or hydrogen. In a-C:H DLC, if the temperature exceeds the threshold value, the graphite crystal start to form as a result of dehydrogenation, but the hardness remains almost unchanged up to 700 °C and this is attributed to the incomplete crystallization of the graphite grains at this temperature (Liu, Xu, & Zheng, 2013). The thermal stability of ta-C DLC is quite good even at 1000 °C, because ta-C DLC films do not comprise hydrogen largely and are predominantly bonded with sp³ bonds. Hence, the thermal stability decreases with the decrease of sp³ bonds such as a 40% sp³ bonded ta-C film starts to graphitize at 430 °C (Kalish, Lifshitz, Nugent, & Prawer, 1999).
Table 2.1: Comparison of the major properties of amorphous carbon with the diamond as reference material (J. Robertson, 2002)

<table>
<thead>
<tr>
<th>Carbon Material</th>
<th>SP³ (%)</th>
<th>H (%)</th>
<th>Density (g cm⁻³)</th>
<th>Band Gap (eV)</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>100</td>
<td>0</td>
<td>3.515</td>
<td>5.5</td>
<td>100</td>
</tr>
<tr>
<td>Glassy C</td>
<td>0</td>
<td>0</td>
<td>1.3-1.55</td>
<td>0.01</td>
<td>3</td>
</tr>
<tr>
<td>Evaporated C</td>
<td>0</td>
<td>0</td>
<td>1.9</td>
<td>0.4-0.7</td>
<td>3</td>
</tr>
<tr>
<td>Sputtered C</td>
<td>5</td>
<td>0</td>
<td>2.2</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Ta-C</td>
<td>80-88</td>
<td>0</td>
<td>3.1</td>
<td>2.5</td>
<td>80</td>
</tr>
<tr>
<td>a-C: H hard</td>
<td>40</td>
<td>30-40</td>
<td>1.6-2.2</td>
<td>1.1-1.7</td>
<td>10-20</td>
</tr>
<tr>
<td>a-C: H soft</td>
<td>60</td>
<td>40-50</td>
<td>1.2-1.6</td>
<td>1.7-4</td>
<td>&lt;10</td>
</tr>
<tr>
<td>ta-C:H</td>
<td>70</td>
<td>30</td>
<td>2.4</td>
<td>2.0-2.5</td>
<td>50</td>
</tr>
</tbody>
</table>

2.10.2 Tribological Properties of DLC Films

The friction and wear behavior of DLC films are highly influenced by the films’ intrinsic properties, operating environment and test parameters (Martí-González & Bertran, 2015). DLC films show very low friction compared to other films (e.g. TiN films) such as, in ambient condition against steel surfaces, the typical friction coefficient of TiN film is 0.5 but it is 0.2 for DLC film (H Ronkainen & Holmberg, 2008). DLC films exhibit a range of friction coefficient (0.01~0.5) depending on the type and test conditions, for instances, in vacuum, the COF of a-C:H DLC is between 0.007~0.02, but in normal atmosphere (20%<H<60%), the range is 0.1~0.4 (C. Donnet, 1998). Furthermore, COF of a-C:H DLC increases with the increase of humidity whereas ta-C DLC maintain low COF (Zhang, Xie, Huang, and Leng, 2017).

Several mechanisms have been proposed to explain the tribological properties of DLC films and some of them are as follows. M. N. Gardos (Gardos, 1994) ascribed the ultra-low friction of DLC films in inert environment to the superior surface finish and the presence of an ultra-thin polymer-like layer of weak van der Waals forces on the topmost coating surface. Author has also mentioned that the friction coefficient can be
ten times higher if the bond strength increases from 0.08 eV per bond (Vander walls bonding of hydrocarbon) to 0.21eV per bond (for hydrogen bonding in water molecules at C=O site). The structural change or graphitization of DLC films which occurs due to the high contact temperature also reduce the friction, but however, increases the wear (Jahanmir, Deckman, Ives, Feldman, & Farabaugh, 1989). Transfer layers have varying influence on tribological properties such as Memming et al. (Memming, Tolle, & Wierenga, 1986) observed that the transfer layers affected the friction in dry oxygen and dry nitrogen, whereas, Kim et al. (Kim, Fischer, & Gallois, 1991) found that transfer layers affected both friction and wear of a-C:H films. Sugimoto et al. (Sugimoto & Miyake, 1990) observed the transfer of hydrocarbons with a specific orientation to the ball surface, which reduced friction. Erdemir et al. (AFAXZR Erdemir, Nichols, Pan, Wei, & Wilbur, 1994) observed a carbon rich transfer layer on the pin surface when rubbed against a-C:H film which was found to convert into graphite at high temperature and reduced the friction.

2.11 Application of DLC coatings

Generally, the “pure” DLCs are used for relatively low contact pressure, for examples, knives used in textile industry to cut the fiber. And, the doped DLCs are used when the shear stresses are medium to very high, for example, ball-bearing races, journal bearings, compressor screws, gears used in aircraft landing-flap controls, diesel engine injection system, etc. (Matthews & Eskildsen, 1994). DLC films are largely used in the biomedical application such as load-bearing surface of artificial joints, orthopedic pins and screws (Dearnaley & Arps, 2005). Moreover, DLCs are used in hard-disk drive and magnetic recording media as well (Casiraghi, Robertson, & Ferrari, 2007).
2.12 Summary

As both price and demand of lubricants are increasing, vegetable oils are in the front line of industry’s choice to solve these issues. In addition, ZDDP is always the first choice as additive if modification of lubrication composition is considered in order to reduce the wear. It is well known that ZDDP’s performance is excellent with steel, however, this is study is primarily to improve the tribological properties through modifying the contacting surface. And, the surface modification will be done by applying the Diamond-like carbon coating. Therefore, the performance ZDDP with DLC coating is quite vague and researchers are not sure about it. The main reason of the varying results the chemical “inactiveness” of DLC coatings. Therefore, it is crucial for researchers and engineers working in the coating and lubricant industries to develop a deeper understanding of the effect of ZDDP on the tribological properties of DLC coatings.
CHAPTER 3: MATERIALS AND METHODOLOGY

3.1 Introduction

This chapter begins with showing a flowchart of research methodology, see Figure 3.1. This chapter also introduces the materials (AISI 440C steel and ta-C DLC coating, base oil and zinc dithiophosphate (ZDDP)) used in this study, and defines methodologies for the determination of surface roughness, hardness, young modulus, friction coefficient, wear volume, lambda values, fatty acid composition of base oil, unsaturation of base oil, viscosity and density. The methodology for the deposition of DLC coating and for the tribology tests are explained as well.

Figure 3.1: A flowchart of research methodology.
3.2 Materials

**AISI 440 C:** AISI 440 C stainless steel balls of 12.7 mm diameter were used as the substrate material. AISI 440 C steel is highly used in bearing and hydraulic components (Dalibon, Charadia, Cabo, Trava-Airoldi, & Brühl, 2013; Zeng et al., 2000), where mechanical interaction of surfaces is very common. The elemental compositions (Wt %) of the AISI 440 C stainless steel was as follows: S-0.028, P-0.034, Mn-0.72, Si- 0.81, C-0.97, Cr-17.6 and Fe-79.84.

**Ta-C DLC coating:** In this study, the AISI 440C stainless steel ball was coated with the ta-C DLC films of 1 µm thickness from the “My Tech Seimitsu Sdn. Bhd. (Malaysia)” using Filtered Cathodic Vacuum Arc (FCVA) technique. A typical schematic diagram of FCVA technique is shown in Figure 3.2. Before inserting into the chamber, all balls were cleaned through rinsing in acetone bath. The deposition was done at 80 °C temperature, 75 A arc current and 1×10⁻⁵ Torr chamber pressure. The coating can fail early if the adhesion between coating and substrate is not sufficient (Xiao, Shi, Luo, & Liao, 2014). In this study, a Cr based interlayer was provided underneath the DLC film to increase the adhesion between DLC coating and steel.

![Figure 3.2](image)

**Figure 3.2:** A typical schematic diagram of FCVA deposition technique (Wang, Lau, Lee, Yu, Tay, Zhang, Tse, and Hng, 2003).
Base oil (BO) and anti-wear (AW) additives: The base oil used in this study was the commercially available canola oil. The motivation to work with vegetable oil is its merit as boundary lubricants (N. J. Fox & Stachowiak, 2007) and the high amount of polar and un-saturated molecules that are important for the friction and wear (M. Kalin & Vižintin, 2006). In this study, the base oil was additivated with 1% of secondary types of Zinc dialkyldithiophosphates (ZDDP), which is known as anti-wear additive. The chemical structure of secondary types of ZDDP is shown in Figure 3.3, where carbon chain forms bonding with oxygen atom. The tribofilm formation rate and the wear resisting capability of the secondary type of ZDDP are higher than the primary ZDDP, especially in DLC/DLC contact (Okubo et al., 2016).

![Secondary types of ZDDP](image)

Figure 3.3: Secondary types of ZDDP (Naveira Suarez, 2011).

3.3 Surface Analysis

This section will introduce the techniques used to analysis the materials for this study. The sub-sections will present the test equipment with the test parameters.

3.3.1 FESEM-EDX Analysis

Field Emission Scanning Electron Microscope (FESEM) works with electron instead of light to scan the surface, providing images of very high resolution. In the current
study, FESEM analyses were done at 2000x magnifications and 10 kV accelerating voltages. A schematic diagram and photo of FESEM is shown in Figure 3.4.

![Schematic diagram and photo of FESEM](image)

**Figure 3.4:** Schematic diagram (left) and photo (right) of FESEM.

Electron dispersive X-ray (EDX) spectroscopy was used to measure the chemical constituents of the test samples. EDX is a non-destructive technique provides the data through analyzing x-ray patterns deflected from a specified area. In this study, the EDX investigations were done at 2000x magnifications and 5 KV.

### 3.3.2 Mechanical Properties

The mechanical properties (hardness and elastic modulus) were measured using a HYSITRON UBI-1 nano-indentation tester equipped with a three sided Berkovich diamond tip. The schematic diagram and photo can be found in Figure 3.5. The nano-hardness measurement of DLC coating was done on the cross section of coating. The experimental parameters used in nano-indentation testing were as follows- Peak load, 10 mN; loading rate, 0.5 nN/s; loading time, 20 s, holding time, 5 s and unloading time, 20s, and finally, the hardness and elastic modulus was obtained from loading-unloading
curve following Oliver and Pharr method, details can be found here (ABOUGHARAM, 2008).

![Figure 3.5: Schematic diagram and photo of Nano-indenter.](image)

### 3.3.3 Raman Analysis

Raman spectroscopy is used to analysis the bonding in a material. The schematic diagram and photo of Raman spectrometer is shown in Figure 3.6. In this study, Raman analysis was done to observe whether there were any structural changes or graphitization on the DLC surface which is generally caused by friction induced temperature during the tribology tests. The input parameters during Raman analysis were- diode laser-514 nm, output power-10% in conjunction with 50x objective lens. The output power was set at 10%, because this power range can give the peak from the outermost surfaces without the influence of substrate on the measurements (Vengudusamy, Mufti, Lamb, Green, & Spikes, 2011). Moreover, the spectra were collected within 1000-2000 cm\(^{-1}\) band.
3.3.4 Surface Roughness

In addition, the surface roughness, which largely influences the coatings durability and the tribological results, was measured using Mitutoyo Surftest SJ-201 profilometer.

3.4 Lubricant Characterization

The equipment and the test parameters used for the analysis lubricant properties will be introduced in this section.

3.4.1 Viscosity and Density Measurement

Viscosity is a single most important factor of the lubricant which largely control friction and wear of a contact. In this study, the viscosity and density of lubricants were measured at 40 °C using SVM 3000-automatic viscometer, manufactured by Anton Paar, UK, see Figure 3.7. The D445 standard method was followed with the accuracy of ± 0.35% of the measured value for viscosity and 0.0005 g/cm³ for density.
3.4.2 Measurement of Fatty Acid Composition of Base Oil

It is widely known that vegetable oils are natural products originated from different plants. They contain ester compounds extracted from glycerol which has fatty acid chains of 14 to 20 carbon atoms. In addition, they also have high degrees of unsaturation or carbon-carbon multiple bond (Botinestean, Hadaruga, Hadaruga, & Jianu, 2012). In this study, the fatty acid composition of canola oil was measured using a gas chromatography-mass spectrometry (GC-MS). The schematic diagram of GC-MS can be found in Figure 3.8. The experiments were done using the RTX-5 (30m × 0.25mm × 0.25μm) column. The gas flow rate was chosen as follows-carrier gas-Helium, 1 ml/min (constant), injection volume-1μl, injection mode-split (split ratio-1:100). The temperature settings was as follows- chamber temperature was 250 °C and oven temperature was held at 50 °C for 2 min, then 10 °C per minutes to 240 °C and finally held at 240 °C for 7 minutes.
3.4.3 FT-IR Analysis

FTIR spectral analysis of base oil and ZDDP-added base oil was performed in a Perkin-Elmer Spectrum 400 FTIR analyzer. A MIR detector was equipped with FTIR and a standard KBr beam splitter and a DTGS detector were coupled with the equipment as well. Spectra were collected in the range of 4000 cm\(^{-1}\) to 450 cm\(^{-1}\) and 4 cm\(^{-1}\) resolution. Prior to start the experiments, the crystal was cleaned with toluene and then approximately 0.4 ml of oil was poured on the crystal. The schematic diagram basic mechanism of the FTIR spectroscopy is shown in Figure 3.4.
3.5 Friction Calculation

The tribometer generally provides friction torque (T) data and later, they are converted into friction coefficient (μ). The Equation (3.1) was used to calculate friction coefficient for four ball tribometer (Fazal, Haseeb, & Masjuki, 2013). Moreover, a schematic diagram is drawn (see Fig. 3.5) showing the position of applied load (W) and the distance between rotational axis and the center of contact.

Friction coefficient, \( \mu = \frac{T\sqrt{6}}{3Wr} \) (3.1)

Where, T, W and r (3.67) are the friction torque in kg.mm, the applied load in kg and the shortest distance between rotational axis and the center of contact in mm, see Figure 3.5.

![Figure 3.10: Schematics for the position of r and W in four ball arrangement.](image)

3.6 Wear Volume Calculation

Spherical cap (green portion) shown in Figure 3.6 can be considered as the wear volume of ball. In Fig. 3.6, h (mm) is the height of worn segment, a (mm) is the scar radius and R (mm) is the ball radius. The equation for wear loss (mm³) is derived below.

Here, \( \frac{V_{sector}}{V_{sphere}} = \frac{A_{cap}}{A_{sphere}} \), Or, \( V_{sector} = \frac{A_{cap}V_{sphere}}{A_{sphere}} \), Or, \( V_{sector} = \frac{2\pi rh + \frac{4}{3}\pi r^3}{4\pi r^2} \).
Or, \( V_{sector} = \frac{2}{3} \pi r^2 h \)

And, the volume of cone, \( V_{cone} = \frac{1}{3} \pi a^2 (r - h) \)

Where, \( a^2 = R^2 - (R - h)^2 = 2Rh - h^2 \)

Now, the volume of cap, \( V_{cap} = V_{sector} - V_{cone} = \frac{2}{3} \pi r^2 h - \frac{1}{3} \pi a^2 (r - h) \)

Finally, \( V_{cap} = \frac{1}{6} \pi h (3c^2 + h^2) \) \[ \text{where}, rh = \frac{a^2 + h^2}{2} \]

Since the wear loss (V) is same as the volume of cap (\( V_{cap} \)), therefore,

\[ V = \frac{1}{6} \pi h [3a^2 + h^2] \] (3.2)

**Figure 3.11**: Schematic diagram of a sphere showing the worn segment (green portion).

### 3.7 Determination of Lubricant Condition

The lubrication regime has a greater effect on friction and wear and the Tallian parameter “lambda (\( \lambda \))” value is generally used to determine the lubrication regime (Haque, Morina, Neville, Kapadia, & Arrowsmith, 2007; Mitjan Kalin, Velkavrh, &
Vižintin, 2009; M. Kalin et al., 2006). The lambda ($\lambda$) is defined as the ratio of the minimum oil film thickness and the equivalent surface roughness, see Equation (3.3) for mathematical formula of lambda (Mitjan Kalin et al., 2009).

$$\lambda = \frac{h_0}{\sqrt{R_{qA}^2 + R_{qB}^2}}$$  \hspace{1cm} (3.3)

Where, $h_0$ is the Minimum oil-film thickness ($\mu$m), measured using Dowson and Hamrock’s equation, see Equation (3.4) (Furtuna, 2011; Haque et al., 2007), $R_{qA}$ and $R_{qB}$ are the surface roughness of upper and lower contacting sphere in $\mu$m respectively. Dowson and Hamrock’s equation of oil film thickness $h_0$:

$$h_0 = 3.67 \times R' \times U_\omega^{0.68} \times G_\omega^{0.49} \times W_\omega^{-0.73} (1 - e^{-0.68k})$$  \hspace{1cm} (3.4)

Where $U_\omega = \frac{U \eta_o}{E'R'}$, $G_\omega = \alpha E'$ and $W_\omega = \frac{W}{E'R^2}$ are the non-dimensional speed parameter, material parameter and load parameter. And, $R'$, $E'$, $\eta_o$, $\alpha$, W, U and K are the equivalent radius, equivalent elastic modulus, viscosity, viscosity-pressure coefficient, applied load, entrainment speed and elliptical parameter respectively. The contacting geometry of two spheres when they tough each other is shown in Figure 3.7.

![Figure 3.12: Geometry of a contact between two spheres (Furtuna, 2011).](image-url)
Equivalent radius \((R')\) (Furtuna, 2011):

\[
\frac{1}{R'} = \frac{1}{R_x} + \frac{1}{R_y} = \frac{1}{R_A} + \frac{1}{R_B} + \frac{1}{R_A} + \frac{1}{R_B} = 2 \left( \frac{1}{R_A} + \frac{1}{R_B} \right)
\]

\((3.5)\)

Where, \(R_A\) and \(R_B\) are the radii of upper and lower contacting spheres, see Figure 3.7, and \(R_A = R_B = 6.35\) mm.

Equivalent elastic modulus \((E')\) (Furtuna, 2011; Hamrock, Schmid, & Jacobson, 2004):

\[
\frac{1}{E'} = \frac{1}{2} \left[ \frac{1-\sigma_A^2}{E_A} + \frac{1-\sigma_B^2}{E_B} \right]
\]

\((3.6)\)

Where, \(\sigma_A\) and \(\sigma_B\) are the Poisson’s ratios and \(E_A\) and \(E_B\) are Young’s modulus of upper sphere and lower sphere of the contact respectively.

Viscosity-pressure coefficient \((\alpha)\) (Biresaw & Bantchev, 2013):

\[
\alpha = (0.1657 + 0.2332 \log \nu_0) \times m_0
\]

\((3.7)\)

Where, \(\nu_0\) is the kinematic viscosity at the corresponding temperature and ambient pressure in cSt and \(m_0 = 5\) m where \(m\) is the slope between two temperatures \((37.8\ ^\circ\text{C} \text{ and } 98.9\ ^\circ\text{C})\) in the viscosity–temperature graph but in this study, slope was measured between \(40\ ^\circ\text{C}\ \text{and}\ 100\ ^\circ\text{C}\). The value of \(m\) was obtained by solving Equation (3.8).

\[
\log \log (\nu_0 + c) = A + m \log T
\]

\((3.8)\)

In Equation (3.8), \(c\) is a constant with a value between 0.7 and 0.8 cSt, \(A\) is another constant which was cancelled when the Equation (3.8) was solved at any two different temperatures (\(T\ in ^\circ\text{C}\)). Finally, \(m_0\) was obtained from \(m_0 = 5\) m and this was 2.73.

Typically, based on lambda value, the lubrication regimes are divided into three parts: \(\lambda \geq 3\) for hydrodynamic or the elastohydrodynamic regime, \(3 \geq \lambda \geq 1\) for mixed lubrication, and \(\lambda \leq 1\) for the boundary lubrication regime.
3.8 Friction and Wear Tests

The tribology tests were carried out in a four ball tribo-machine modeled in accordance with the standard IP-239/85. A typical schematic diagram of the four ball arrangement is shown in Figure 3.8. Prior to each test, all the key components of the four ball tribometer (cup, clamp ring and holders) as well as the sample balls were rinsed in acetone for 10 minutes and then dried to remove the residual particles from the surface. In a four ball tribo-system, three balls are clamped in a lower stationary cup and the fourth ball is fixed in the upper rotating chuck. In case of Steel/DLC contacts, the three coated balls were clamped in the lower stationary cup and the upper one was the uncoated steel ball. The room temperature was 30 °C and the parameters used in the tribology tests are given in Table 3.1. The lubricant was poured into the cup in such a way that the ball to ball contact was immersed. The four ball tribo-meter was interfaced with a computer to record the friction torque (T), and the wear scar diameter (WSD) was measured by an optical microscope (OM) before removing from the cup. It is worth mentioning that the tribo-machine cannot give friction coefficient; rather, the friction torque is to be converted into friction coefficient. The calculations used to convert the friction torque into friction coefficient and wear scar diameter into wear volume are shown above. The tallian parameter “lambda (λ)” was calculated to know the lubrication condition, see section 3.6. The lambda value was less than unity in all cases (see Table 3.1) which assured that the system was working under boundary condition (Mitjan Kalin et al., 2009).
Figure 3.13: Schematic diagram of a four ball tribo-meter.

Table 3.1: Parameters used in tribology tests and the lubrication condition

<table>
<thead>
<tr>
<th>Types of Contact</th>
<th>Load (N)</th>
<th>Temperature (°C)</th>
<th>Time (s)</th>
<th>Velocity (m/s)</th>
<th>Lambda (λ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>BO</td>
</tr>
<tr>
<td>Steel/Steel</td>
<td>100</td>
<td>30</td>
<td>3600</td>
<td>0.46</td>
<td>0.27</td>
</tr>
<tr>
<td>DLC/DLC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.39</td>
</tr>
<tr>
<td>Steel/DLC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.32</td>
</tr>
</tbody>
</table>
CHAPTER 4: RESULT AND DISCUSSION

4.1 Introduction

This chapter will present all the experimental results and their discussions. The chapter begins with showing material characterizations results which is followed by the friction and wear results as well as surface characterization. The chapter is ended up with the discussing the results.

4.2 Surface Analysis

4.2.1 FESEM Images of Steel Surface and DLC Coating

Figure 4.1 shows the FESEM images of AISI 440C steel ball and DLC coating. Some lighter colored bumps were found on the DLC surface.

![FESEM Images of Steel Surface and DLC Coating](image)

Figure 4.1: FESEM images of (a) AISI 440C steel and (b) ta-C DLC surface.

4.2.2 Mechanical Properties and Surface Roughness

The mechanical properties such as hardness and modulus of elasticity, and the surface roughness of the test samples were measured before starting tribology tests. The results are given in the Table 4.1. The hardness of ta-C DLC was few times of steel and
the roughness DLC coated surface was less than steel surface, which has absolutely positive influence on the tribological results.

**Table 4.1**: Physical properties of AISI 440 C steel ball and ta-C DLC coating

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>AISI 440 C steel ball</th>
<th>Ta-C DLC coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness GPa</td>
<td>~ 7.316</td>
<td>~ 64</td>
</tr>
<tr>
<td>Elastic Modulus (GPa)</td>
<td>~ 200</td>
<td>~ 509</td>
</tr>
<tr>
<td>Roughness, Ra (nm)</td>
<td>~ 40</td>
<td>~ 25</td>
</tr>
</tbody>
</table>

4.3 Lubricant Analysis

4.3.1 Viscosity and Density of Lubricants

The straight use of vegetable oils as lubricants entails the adjustment of viscosity and density. The kinematic viscosity and density of both base oils and additivated oils obtained in this study are given in the Table 4.2. The kinematic viscosity means the resistance of liquid to flow and is defined as the ratio of dynamic viscosity and density. Lubricants viscosity largely influences the lubrication system, particularly if the operating temperature is very low, the change in viscosity affects the fluidity of the lubricants, and thereby influence friction and wear results (Albertson, Staley, McDonald, & Pryor, 2010). Moreover, viscosity can avoid the collision and rubbing between contacting surfaces (Ting & Chen, 2011).

**Table 4.2**: Physical properties of lubricant composition

<table>
<thead>
<tr>
<th>Lubricant Composition</th>
<th>Kinematic Viscosity at 40 °C (mm²/s)</th>
<th>Density (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BO</td>
<td>35.606</td>
<td>0.9031</td>
</tr>
<tr>
<td>BO + AW</td>
<td>35.702</td>
<td>0.9059</td>
</tr>
</tbody>
</table>
4.3.2 Fatty Acid Composition

Fatty acids are the long hydrocarbon chains containing carboxyl group (-COOH) at one end, which is mainly the reactive portion of the molecule. Generally fatty acids are classified as the saturated and un-saturated. Saturated fatty acids are those which contain a single bond between two adjacent carbon atoms, and un-saturated fatty acids are those which contain more than single bond between two adjacent carbon atoms. The fatty acid composition of canola oil measured by the gas chromatography-mass spectrometry (GC-MS) given in Table 4.3. The results showed that canola oil is highly un-saturated oil which is congruent with the previous literature. It is important to note that the fatty acids are very important for the tribological properties, particularly un-saturated fatty acids which mainly reduce the friction and wear (Simič & Kalin, 2013, M. Kalin et al., 2006).

<table>
<thead>
<tr>
<th>Common name</th>
<th>Saturated</th>
<th>Unsaturated</th>
<th>Arachidic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lipid Number</td>
<td>Palmitic acid</td>
<td>Stearic acid</td>
<td>Oleic acid</td>
</tr>
<tr>
<td>Wt (%)</td>
<td>16:0</td>
<td>18:0</td>
<td>18:1</td>
</tr>
</tbody>
</table>

4.3.3 FT-IR Analysis

The FTIR spectra of the base oil and ZDDP-added base oil are shown in Figure 4.2. The characteristic peaks of FTIR spectrum and their descriptions are given in Table 4.4. It is widely known that vegetable oils are the ester compound (C=O) which exhibit a peak at 1743 cm$^{-1}$ in FTIR spectrum. In this study, a peak at 1743 cm$^{-1}$ was observed which confirmed that the oil was an ester compound. Another characteristic of vegetable oils is the carbon-carbon double bond (C=C) or unsaturation. A peak was
observed at 1651 cm\(^{-1}\) in the FTIR spectrum of this study, which represents the unsaturation of oils. It is important to note that the smaller peak represents the higher unsaturation level of the oil (Ullah, Bustam, & Man, 2014). A peak is seen at 984 cm\(^{-1}\) in case of additivated base oil, and according to a previous study (Toms & Powell, 1997), this peak indicates the presence of ZDDP (P-O-C) in the base oil.

![FTIR spectra](image)

**Figure 4.2**: FTIR spectra of the base oil and additivated base oil.

<table>
<thead>
<tr>
<th>Absorption bands (cm(^{-1}))</th>
<th>Functional group</th>
<th>Mode of vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>3007.45</td>
<td>=CH</td>
<td>C-H stretching vibration</td>
</tr>
<tr>
<td>2923.23</td>
<td>&gt;CH(_2)</td>
<td>Symmetric and asymmetric stretching</td>
</tr>
<tr>
<td>2853.81</td>
<td>&gt;CH(_2)</td>
<td>Methylene sym stretch</td>
</tr>
<tr>
<td>1743.05</td>
<td>C=O (ester)</td>
<td>Ester structure</td>
</tr>
<tr>
<td>1651</td>
<td>C=C</td>
<td>Unsaturation of oil</td>
</tr>
<tr>
<td>984</td>
<td>P-O-C</td>
<td>ZDDP</td>
</tr>
</tbody>
</table>

**Table 4.4**: Peaks of FT-IR spectra for base oil and additivated base oil

### 4.4 Friction Results

The tribological behavior was observed in Steel/Steel, Steel/DLC and DLC/DLC contacts in the presence of additivated and non-additivated base oil. In this study, self-
mated steel was studied as the reference material combination, and for the coating’s performance, the steel ball coated with tetrahedral diamond-like carbon (ta-C DLC)

Figure 4.3: Friction coefficient as function of time observed in (a) Steel/Steel, (b) Steel/DLC and (c) DLC/DLC contacts under BO and BO+AW additives.
material was studied in Steel/DLC and DLC/DLC contacts. Figure 4.3 presents the friction coefficient of all three contacts under both lubricating oils as a function of time. Moreover, the average friction coefficient for all three contacts under both oils is shown in Figure 4.4. The average friction coefficient observed under base oil was 0.062 in Steel/Steel, 0.059 in Steel/DLC and 0.048 in DLC/DLC contact, and the COF in the corresponding contacts under additivated oil was 0.066, 0.067 and 0.058 respectively. As seen in Figure 4.4, in the test with base oil, the COF was reduced when DLC coating was introduced in the contacts, it is therefore can be assume that coating had noticeable impact on the friction behavior. Friction coefficient in all contacts was increased when lubricated with additivated oil, which suggests anti-wear additive played a bit negative role on friction. From Figure 4.3, initially the friction coefficient was low in all three contacts under both oils, but after approximately 350-400 s, a rapid increase of the friction coefficient was found. However, the friction coefficient became stable with some fluctuations until the end of experiment, see Figure 4.3. The phenomenon of this drastic increased of friction coefficient will be illustrated in the discussion section.

![Figure 4.4: Steady state friction coefficient observed in Steel/Steel, Steel/DLC and DLC/DLC contacts under BO and BO+AW additives.](image)
4.5 Wear Results

Figure 4.5 shows the wear loss of all three contacts (Steel/Steel, Steel/DLC and DLC/DLC) for both base oil (BO) and base oil additivated with anti-wear agents (BO+AW) lubricated case. In the test with base oil, the wear loss was $5.57 \times 10^{-4}$ mm$^3$ in Steel/Steel contact, $9.81 \times 10^{-4}$ mm$^3$ in Steel/DLC contact and $6.02 \times 10^{-4}$ mm$^3$ in DLC/DLC contact, and when test was conducted with additivated oil, the wear loss in the corresponding contacts was $1.16 \times 10^{-4}$ mm$^3$, $3.27 \times 10^{-4}$ mm$^3$ and $2.36 \times 10^{-4}$ mm$^3$ respectively. Therefore, lowest wear loss was in Steel/Steel contact whereas highest was observed in Steel/DLC contact. However, the wear in DLC/DLC contact under base oil was a bit higher but comparable with Steel/Steel contact, such as, DLC/DLC contact showed 8.11% higher wear than Steel/Steel contact whereas this result was 76.46% in Steel/DLC contact. The wear in all contacts was reduced largely when tested with the additivated base oil as compared to the wear under base oil lubricated case. The highest wear reduction observed in Steel/Steel contact (approx. 79%) which was approximately

![Figure 4.5: Wear loss of ta-C DLC in DLC/DLC and Steel/DLC contacts for BO and BO+AW additives.](image-url)
66% in Steel/DLC contact and 60% in DLC/DLC contact. The trend of wear result under additivated oil is an indication of the reaction between metal and anti-wear additive. Despite exhibiting higher wear reduction under additivated oil, the wear in Steel/DLC contact was much higher than DLC/DLC contact. Hence, it is clear that the performance of additive relies on the materials of contact and both surface materials and oils are important for the wear properties of a contact.

4.6 FESEM-EDX Results

Figure 4.6 shows the FESEM images of worn surfaces observed in Steel/Steel contact for both base oil and additivated oil lubricated case. The feature of worn surfaces was completely different between two oils such as the deformation of wear debris and a sign of adhesion was observed under base oil (see Figure 4.6a) whereas the surfaces was covered with white layer in case of additivated oil (see Figure 4.6b). In addition, grooves were produced on the wear track in the direction of motion when tested with base oil, which was not found when tests were done in the presence of additive containing oils. Moreover, no transverse scratches were found on the rubbed surface under base oil which was present in case of additivated oil.

Figures 4.7 and 4.8 show the wear track of DLC surface and steel surface in Steel/DLC contacts for both base oil and additivated base oil lubricated case, respectively. In Steel/DLC contacts, the worn DLC surface was covered with many islands/flakes of adhered debris particles when tested with base oil (see Figure 4.7a). The mutually transferred particles were fused together by the high friction induced heating (known as welding) and might have formed those islands/flakes. Although DLC surfaces in Steel/DLC contacts under base oil showed highest wear (highest irrespective of contacts and oils), surprisingly, no mechanical damage and transverse cracks were
observed (see Figure 4.7a). However, a sign of adhesion and tribo-chemical reaction as well as the agglomeration of debris particles were found on the rubbed DLC surfaces. On the other hand, the feature of worn DLC surface in Steel/DLC contact was changed significantly when lubricated with additivated base oil such as the presence of fractures, loose particles, cracks in the direction of motion and subsequent pitting, see Figure 4.7b. In this study, the steel counter surfaces in Steel/DLC contact for both oils were investigated with FESEM for better understanding of wear mechanism. Images of worn steel surfaces in Steel/DLC contact for base oil lubricated case are shown in Figure 4.8a and b, and for additivated oil lubricated case are shown in Figure 4.8c and d. In addition, the images were collected at two magnifications such as 100x (see Figures 4.8a and 4.8c) and at 2000x (see Figures 4.8b and 4.8d), and at 10 KV accelerating voltages. The width of scar produced on the fourth ball was 597.78 μm under base oil and 453.08 μm under base oil containing additives. The agglomeration of debris particles were observed on the counter steel surface in Steel/DLC contact under base oil, see Figure 4.8b. The counter steel surface under additivated oil was covered with white phosphorous layer and looks like rough which can give an insight of why the DLC coated surface was fractured under additivated oil, see Figure 4.8d.

Figure 4.9 represents the FESEM micrographs of the worn DLC surfaces in DLC/DLC contacts for both BO and BO+AW additives. In DLC/DLC contacts, the ta-C DLC coated surfaces were not adequately protected when tested with base oil and a sign of breaking of coating was observed, see Figure 4.9a. However, no major sign of adhesion and the formation of island were observed and the surface outside of broken part looks like shiny and very smooth. In comparison with BO, the BO+AW additives largely prevented the mechanical damage and wearing-through of DLC coating in DLC/DLC contact, see Figure 4.9b. In addition, some pits were present on the rubbed
DLC surface when tested with the additivated base oil. It is important to note that no transverse scratches were found on the rubbed surfaces in DLC/DLC contact under any of two lubricated case. In summary, it is clear that the additives and counter surface had a qualitative effect on the DLC surface in all contacts.

![Figure 4.6](image1.png)

**Figure 4.6**: FESEM images of wear track in Steel/Steel contact when lubricated with (a) BO and (b) BO+AW.

![Figure 4.7](image2.png)

**Figure 4.7**: FESEM images of wear track of ta-C DLC in Steel/DLC contacts when lubricated with (a) BO and (b) BO+AW.
Figure 4.8: FESEM images of steel counterpart in Steel/DLC contact when lubricated with BO (a & b) and BO+AW (c & d).
Figure 4.9: FESEM images of wear track of ta-C DLC in DLC/DLC contacts when lubricated with (a) BO and (b) BO+AW.

EDX analysis was done to observe the elements present on the rubbed DLC surfaces in all three contacts (Steel/Steel, Steel/DLC and DLC/DLC) for both the base oil and additivated base oil. The EDX analysis was done for the as-deposited surface as the reference surface and the results are listed in Table 4.5. From Table 4.5, the test with BO caused less presence of Carbon and high presence of Oxygen, Chromium and Iron regardless of contacts, and these results were vice versa in experiments with BO + AW additives. In the current study, the high presence of Oxygen and Iron under base oil would form the iron-oxide hard particles. The EDX measurements confirmed the presence of additive decomposed element (S, P and Zn) on the shiny region of rubbed DLC surfaces in both contacts when lubricated with additivated oils (see Table 4.5) and similar observation is reported in (Ng & Kumar Sinha, 2014; Okubo et al., 2016), where it is also reported that the phosphorous rich tribofilms are generally wear preventive.
Table 4.5: Elemental compositions obtained from EDX analysis

<table>
<thead>
<tr>
<th>Tested surface</th>
<th>Lubricant composition</th>
<th>Elemental composition in atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited</td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Steel/Steel</td>
<td>BO</td>
<td>98.78</td>
</tr>
<tr>
<td></td>
<td>BO+AW</td>
<td>12.35</td>
</tr>
<tr>
<td>DLC surface in Steel/DLC</td>
<td>BO</td>
<td>34.15</td>
</tr>
<tr>
<td></td>
<td>BO+AW</td>
<td>53.75</td>
</tr>
<tr>
<td>Steel surface in Steel/DLC</td>
<td>BO</td>
<td>23.33</td>
</tr>
<tr>
<td></td>
<td>BO+AW</td>
<td>8.10</td>
</tr>
<tr>
<td>DLC/DLC</td>
<td>BO</td>
<td>48.80</td>
</tr>
<tr>
<td></td>
<td>BO+AW</td>
<td>64.35</td>
</tr>
</tbody>
</table>

4.7 Raman Analysis

The high working temperature and/or friction induced heating can cause the structural change of DLC coatings which is also called graphitization of DLC coatings (Al Mahmud et al., 2014). Raman analysis was done to know whether there was any graphitization of DLC coating or not. The as-deposited DLC surface and rubbed DLC surfaces of both contacts (DLC/DLC and Steel/DLC) for base oil lubricated case were investigated. Raman spectrum of DLC coatings show a peak around 1360 cm\(^{-1}\), known as D peak, due to the breathing mode of \(\text{sp}^2\) atoms in rings only, and a peak around 1560 cm\(^{-1}\), known as G peak, as a result of bond stretching of \(\text{sp}^3\) atoms in both chains and rings (Ferrari & Robertson, 2001). The Raman spectrum of rubbed DLC surfaces in both contacts was compared with Raman spectrum of as-deposited DLC coating within 1000-2000 cm\(^{-1}\), see Figure 4.10. The graphitization is generally confirmed from the increase in the peak ratio \((I_d/I_g)\) between as-deposited surface and rubbed surfaces. In this study, the change in the peak ratios \((I_d/I_g)\) in both contacts was small, see Figure 4.10, which indicates the possibility of nano-scale graphitization. It is important to note that the Raman analysis for the additivated oil was not done following the observation
of a previous study (M. Kalin, Roman, & Vižintin, 2007; R. Zahid et al., 2015) that anti-wear additive generally inhibit the graphitization, and due to the high friction coefficient under additivated oil, which indicates that if there was any graphitization under additivated oil, the friction result should be reverse of the observed result.

Figure 4.10: Raman spectra in (a) DLC/DLC and (b) Steel/DLC contacts under BO.

4.8 Surface Roughness

In this study, the roughness of all three contacts (Steel/Steel, Steel/DLC and DLC/DLC) under both base oil and additivated base are shown in Figure 4.11.
Moreover, the roughness of unworn steel and DLC surfaces are also shown in the Figure 4.11. The surface roughness in this study was as follows: unworn steel surface- 40nm, unworn DLC surface-25 nm, worn steel surface in Steel/Steel contact-85nm for BO and 92 nm for BO+AW, DLC surface in Steel/Steel contact-64 for BO and 82 nm for BO+AW, and in DLC/DLC contacts- 55 nm for BO and 74 nm for BO+AW additive. It is clear that the surface roughness was increased in all contacts under additivated base oil compared to that of base oil lubricated case. The roughest roughness was observed in Steel/Steel contact and lowest was in DLC/DLC contact. And, roughness in Steel/DLC contact was in between of other two contacts. Our roughness results are congruent to the previous studies (Suarez, Grahn, Pasaribu, & Larsson, 2010; LJ Taylor & Spikes, 2003; Tomala, Naveira-Suarez, Gebeshuber, & Pasaribu, 2009) where it is reported that the rubbing of DLC with the AW additive can increase the surface roughness.

![Figure 4.11](image)

**Figure 4.11**: The roughness of unworn steel and DLC, and worn surfaces in Steel/Steel as well as worn DLC surface in Steel/DLC and DLC/DLC contacts for BO and BO + AW additive.
4.9 Discussion

This study is based on the influence of counter surfaces as well as anti-wear additives on the tribological behavior of DLC coatings. Here, the tetrahedral diamond like carbon (ta-C DLC) coating was tested in self-mated contact and against steel counterpart in the presence of additivated and non-additivated base oil. Moreover, the Steel/Steel contact was studied as the reference tribo-pair and compared with other tribo-pairs.

It is shown in Figure 4.5 that among all three contacts, the wear was lowest in Steel/Steel contact under both base oils and additivated oils. It is widely known that vegetable oils due to its polar groups and unsaturated molecules reduce friction and wear of steel surface. The polar molecules adsorb with the metal surface and form a triolayer which protects the surface from being worn out (N. J. Fox & Stachowiak, 2007; Hsien, 2015; M. Kalin et al., 2006). A previous study (N.J. Fox, Tyrer, & Stachowiak, 2004) has reported that among all unsaturated fatty acids, the oleic acid mainly reduces wear of the metal surface. It is observed in this study with GCMS that canola oil contain high amount of oleic acid, and therefore, it can be said that our result is in agreement with the previous study. When tribology tests were conducted in the presence of ZDDP-added base oil, the wear of steel surface was reduced largely, see Figure 4.5. Previous studies (Zhang & Spikes, 2016) have reported that ZDDP reduce wear of steel surface through producing a zinc phosphate triolayer. A white tribo-layer was formed on the worn steel surface, see Figure 4.6b, and this was dominated by ZDDP decomposed elements (Table 4.5). Hence, the observation of this study was in agreement with the previous studies. It is important to note that ZDDP can reduce wear by both physical and chemical adsorption (Lin & So, 2004). As seen in Figure 4.5, the wear of ta-C DLC was much lower in self-mated contact (DLC/DLC) than against steel counterpart (Steel/DLC) under both additivated and non-additivated base oils. In this
study, the wear of DLC surface was highest in Steel/DLC contact when lubricated with base oil. It seems the several times harder DLC coating was easily worn out when rubbed against steel surface. In the contacts where one surface is coated with hard materials, the debris particles, formed during tribology tests, can penetrate into the uncoated surface, and later those debris particles begin to rub against the coated surfaces and accelerates the wear of coated surface (Ali Erdemir, 2004). Moreover, few studies (Narulkar, Bukkapatnam, Raff, & Komanduri, 2009; Shimada et al., 2004) have reported that the carbon show strong affinity for ferrous to form covalent bond. It is assumed in this study that due to the thermo-chemical interaction of DLC and steel surface, the carbon atoms from DLC surface diffused into the ferrous surface, and thereby accelerated the wear of DLC surface. The formation of islands/flakes was observed on the rubbed DLC surface in Steel/DLC contact, see Figure 4.7a. The friction induced heating could fuse the loose wear particles and lead the formation of those islands/flakes (Masjuki & Maleque, 1997; Mutyala, Singh, Evans, & Doll, 2016). The tribo-chemical wear and adhesive wear seem to be the leading wear mechanism in Steel/DLC contacts when lubricated with base oil, see Figure 4.7a. On the other hand, despite strong affinity of carbon for carbon atoms to form covalent bond, the lower wear of ta-C DLC in DLC/DLC contact compared to Steel/DLC contact might be due to graphitization effect, which was slightly higher in self-mated DLC than steel/DLC contact, and the surface contamination by adsorbed oils which generally suppress the covalent bonding formation between carbon atoms (Abdullah Tasdemir et al., 2013). Moreover, the lower contribution of adhesion by the counter surface in DLC/DLC contact compared to Steel/DLC contact might keep wear low in self-mated contact. It is worth mentioning that no major sign of adhesion was observed in DLC/DLC contact, see Figure 4.9a. In addition, there was no transverse scratch in DLC/DLC contact which might be due to the rubbing of two surfaces of equal and extremely high hardness. The
breaking of coating in self-mated contact under base oil suggests that the high contact stresses were produced at some points, and the smooth mirror like surface outside of broken part indicates the wear was the polishing mechanical types of wear, see Figure 4.9a.

It has already been mentioned in the Wear result section that Wear were reduced in all contacts when tested with additivated oils compared to when tested with base oil, and highest wear reduction was obtained in Steel/Steel contact. The lowest wear in Steel/Steel contact under ZDDP has already been established in many previous researches, it is therefore can be said that wear of this study was in agreement with the previous research. The percent wear reduction in Steel/Steel, Steel/DLC and DLC/DLC contact was 79%, 66% and 60% respectively. The wear reduction in Steel/DLC contact due to ZDDP can be attributed to the metal-additive relation similar to Steel/Steel contact as one surface was steel, but it is difficult to decide for the case of DLC/DLC contact, since both surfaces are considered as chemically “inert”. ZDDP can adsorb physically and chemically on the steel surface and produce zinc phosphate dominated tribo-layer on the steel surface (Lin & So, 2004; Nicholls, Do, Norton, Kasrai, & Bancroft, 2005; Zhang & Spikes, 2016). It can clearly be seen on the FESEM images of steel surface in Steel/DLC contact (see Figure 4.8 c and d) that the surface was covered with white tribo-layer which was led by additive derived elements, see EDX results in Table 4.5. Therefore, it is assumed in this study that the wear reduction in Steel/DLC contact was done by the ZDDP derived tribo-layer formed on the steel counterpart that prevented the iron-carbon thermo-chemical reaction through keeping the contacting surfaces apart from each other. Moreover, the rubbed DLC surface in Steel/DLC contact was fractured, see Figure 4.7b, and this result suggests that the tribo-layer formed on the steel counterpart might be of brittle nature. It can clearly be seen that the rubbed steel
surface in Steel/DLC contact looks like rough and brittle, see Figure 4.8d. In addition, some loose particles were found on the rubbed DLC surfaces in Steel/DLC contact, but however, no sign of smear of them was observed. The wear DLC/DLC contact was lower than Steel/DLC contact under additivated oil, even though both surfaces are considered as chemically “inert”. It is studied previously that the ZDDP can adsorb physically with DLC surface (Lin & So, 2004), hence, it is assumed that the physical adsorption of ZDDP passivated the DLC surface, and thereby, generated a repulsive interaction between interacting surfaces because of anti-bonding behavior and prevented from being worn out (Abdullah Tasdemir et al., 2013). Thus, addition of additive to the base oil prevented the wear and breaking of DLC coating in self-mated contacts. No adhesive wear was observed in DLC/DLC contact under ZDDP-added oil and it is assumed that the ZDDP decomposed elements might have penetrated into the asperities of the sliding surfaces in an irregular intervals and prevented the adhesive wear in DLC/DLC contact (YONG, 2014) has reported.

The damage of DLC surface in both Steel/DLC and DLC/DLC contact in base oil case can be attributed to the iron-oxide hard particles since the presence of iron and oxygen was very high under base oil (Okubo et al., 2016). The surface damage and the presence of iron and oxygen were low under additivated base oil compared to base oil lubricated case. A previous study (Martin, Onodera, Minfray, Dassenoy, & Miyamoto, 2012) observed in a Molecular Dynamics study that the anti-wear additives prevent the formation of iron-oxide abrasive particles as well as surface damage. Moreover, the breaking and/or removal of coating might be related with the wear behavior since both of them were reduced when lubricated with additivated oil. Similar observation can be found in (M Kalin et al., 2004), where authors have reported that the coating spallation is related to the hardness and the tribological properties, rather than the coating-
substrate adhesion. The role of additive in reducing wear can also be understood from the high presence of phosphorous comparative to other additive decomposed elements, because phosphorus rich tribo-layer is generally wear protective (Okubo et al., 2016).

Figure 4.4 shows the comparison of the coefficient of friction (COF) in Steel/Steel, Steel/DLC and DLC/DLC contacts between base oil and additivated oil. In this study, the COF under base oil was highest in Steel/Steel contact and the inclusion of ta-C DLC coated surface in the contact reduced friction coefficient such as the COF in Steel/DLC contact was lower than Steel/Steel contact and the lowest COF was observed in DLC/DLC contact. The base oil used in this study contained high amount of polar groups and un-saturated molecules and it is well known that the oils due to their polar groups and unsaturated molecules adsorbs with the sliding surfaces and form a thin layer, and thereby reduce friction (N. J. Fox & Stachowiak, 2007; M. Kalin et al., 2006). The lowest friction coefficient in DLC/DLC contact suggests that any components of the base oil performed better with ta-C DLC coating than steel. A previous study (M. Kalin et al., 2006) has reported that the polar groups and unsaturated molecules are more important for the tribological properties of “nonreactive” DLC coating than reactive steel surface. Another study (Bouchet et al., 2017) has reported that the oleic acid perform extremely well with ta-C DLC in self-mated contact compared to Steel/Steel contact. The canola oil used in this study contained high amount of oleic acid, hence, it can be concluded that among all three contacts, the ta-C DLC in self-mated contact showed lowest friction coefficient due to the high amount of oleic acid in base oil. The low friction and high wear of ta-C DLC in DLC/DLC contact compared to Steel/Steel contact under base oil indicates that the shear strength produced on the DLC surface by the oil molecules was lower than on steel surface, which was in agreement with a previous study (M. Kalin et al., 2006). Moreover, the Raman analysis of DLC
surface was done in Steel/DLC and DLC/DLC contact to observe whether
graphitization occurred or not during tribology tests. It was observed in this study that a
nano-scale graphitization occurred in both contacts, which was high in the DLC/DLC
contact than in Steel/DLC contact, see Figure 4.10, and for this reason, the friction
coefficient in DLC/DLC contact might be lower than Steel/DLC contact. In the test with
additivated oil, the friction coefficient was increased in all three contacts as compared to
test with base oil. A previous study has (M. Kalin & Vižintin, 2006) reported that the
shear strength produced by adsorbed additive molecules are higher than the shear
strength produced by base oil molecules and this phenomenon can be the reason of
increased friction coefficient under additivated oil. On the other hand, the roughness of
rubbed surface was higher in all contacts under ZDDP-added oil as compared to the
base oil lubricated case, see Figure 4.11, which was a cause of increased friction
coefficient under ZDDP-added oil (Bec et al., 1999; Menezes & Kailas, 2008; L Taylor,
Dratva, & Spikes, 2000). Some factors that could cause friction coefficient lowest in
DLC/DLC contact among all three contacts are high hardness and low adhesion of ta-C
DLC (M. Kalin & Vižintin, 2006). Figure 4.3 shows that initially the friction coefficient
was low in all three contacts and friction coefficient was increased suddenly around
300~400s irrespective of contacts and oils, and again became steady. Few studies
(Hwang, Kim, & Lee, 1999; Zmitrowicz, 2006) have reported that the formation,
agglomeration of wear particles and detach of them from the sliding surface has direct
effect on friction and wear behavior of the contact. Those papers have also stated that
the formation of wear particles can increase friction coefficient suddenly. After drastic
increase, the friction coefficient became steady and this was due to the continuous
particle agglomeration and break off (Hwang et al., 1999). This paper has also reported
that if the number of newly formed particles is equal to the number of particles leaving
the contacts, the steadiness of friction coefficient can be continued. In summary, taking
the substantial decrease of wear into consideration, the small increase of friction can be an acceptable “compromise” for ta-C DLC coating against anti-wear additive used in this study.
CHAPTER 5: CONCLUSION AND FUTURE WORK

5.1 Conclusions

This study is based on the experimental investigation of tribological properties of ta-C DLC coatings. The tests were conducted in Steel/Steel, Steel/DLC and DLC/DLC contact under base oil with or without additives at boundary condition. The findings of this study are summarized below.

- All contacts (Steel/Steel, Steel/DLC and DLC/DLC) showed lower coefficient of friction under base oil compared to that under additivated oil.

- The COF under base oil was lowest in DLC/DLC and highest in Steel/Steel contacts. The base oil contained high amount of oleic acid which generally perform better with ta-C DLC than steel, so this might be a reason of lowest COF in DLC/DLC contact. DLC’s intrinsic properties as well as the higher graphitization in DLC/DLC contact could also be the cause of why COF in DLC/DLC was lower than Steel/DLC contact. The increased shear strength as well as increased surface roughness under additivated oils might be the main cause of higher COF in all contact compared to base oil.

- Wear in all contacts were reduced when lubricated with the additivated oil compared to base oil. The wear reduction was high in metal containing contact such as percent wear reduction due to additives in Steel/Steel, Steel/DLC and DLC/DLC contact was 79%, 66% and 60% respectively.

- In case of additivated base oil, the phosphorous rich tribolayer was observed that could be the cause of reduced of wear. The assumption carried value because both phosphorous and wear reduction was high in Steel/DLC compared to DLC/DLC.

- The tribochemical reaction between carbon and iron was caused high wear of DLC surface in Steel/DLC contact and the graphitization prevented the carbon-carbon affinity and thereby wear in DLC/DLC contact. The wear debris was agglomerated in
Steel/DLC under base oil and the surface under additivated oil looked like rough. The damage of coating in DLC/DLC was prevented when tested with additivated oil. Finally it can be concluded that the tribological results depends on both material and lubricant combinations.

5.2 Future work

Future work in the field of DLC coating and biodegradable oils are vast and ongoing as the industries are desperately working to minimize energy and material consumptions and to enhance machine durability. Here, following points are suggested for future work.

- Perform tribological studies by changing humidity which can provide data on how oxygen affects the tribological properties of DLC coating.
- Examine the tests at different temperature which is important to known BL regime in the presence of different lubricant composition to know the optimized coating-lubricant combination.
- Study can also be performed in contacts coated with DLCs other than ta-C DLC, for instance, metal doped DLCs.
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