TRIBOLOGICAL STUDY OF POLYOL ESTER-BASED BIOLUBRICANTS AND THE EFFECT OF MOLYBDENUM SULPHIDE AS LUBRICANT ADDITIVES

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

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Field of Study: Energy (Tribology)

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TRIBOLOGICAL STUDY OF POLYOL ESTER-BASED BIOLUBRICANTS AND THE EFFECT OF MOLYBDENUM SULPHIDE AS LUBRICANT ADDITIVES

ABSTRACT

The possible scarcity of oil and gas resources in the future (whether in quantity or areas of availability) is a major concern throughout the world. For this reason, governments all over the world are working on reducing their dependence on imported energy resources. Alternative energy resources such as bioethanol, biodiesel and biomass have gained prominence over the years in order to substitute petroleum-derived products. Biolubricants have also gained importance as alternatives to conventional petroleum-based lubricants in various applications, especially in the automotive industry. Biolubricants (also known as bio-based lubricants) are appealing alternatives for mineral-based lubricants because of their biodegradability and good lubricity. Owing to the advantages of biolubricants, the study was conducted to investigate the physicochemical properties and wear preventive characteristics of polyol ester-based biolubricants, namely, neopentyl glycol (NPG), trimethylolpropane (TMP), and pentaerythritol (PE) ester-based biolubricants. In addition, different concentrations of surface-capped molybdenum sulphide (known as friction modifier additive) were blended into the polyol ester-based biolubricants to study the effect of additive on the friction and wear properties. A four-ball wear tester is used to investigate the tribological properties (coefficient of friction and wear scar diameter) of the biolubricants in accordance with ASTM standard test methods, and the results are compared with those for paraffin oil and commercial lubricant. In general, the tribological performance of biolubricants is comparable to that for paraffin oil, and therefore, these polyol ester-based biolubricants are potential alternatives to replace mineral-based lubricants. Besides that, the addition of molybdenum sulphide improves the friction and wear properties of the polyol ester-based biolubricants.

Keywords: bio-based lubricants; polyol ester; tribological properties; lubricant additive.

KAJIAN TRIBOLOGI.BIOPELINCIR BERASASKAN ESTER POLYOL DAN KESAN MOLIBDENUM SULFIDA SEBAGAI BAHAN TAMBAHAN PELINCIR

ABSTRAK

Kebarangkalian kekurangan sumber minyak dan gas pada masa akan datang (sama ada kuantiti atau bidang ketersediaan) adalah satu kebimbangan utama di seluruh dunia. Atas sebab ini, kerajaan di seluruh dunia sedang berusaha untuk mengurangkan pergantungan mereka kepada sumber tenaga yang diimport. Sumber tenaga alternatif seperti bioetanol, biodiesel dan biojisim telah menjadi terkenal dalam beberapa tahun ini dalam usaha untuk menggantikan produk yang berasal daripada petroleum. Biopelincir juga telah mendapat perhatian sebagai alternatif kepada minyak pelincir konvensional berasaskan petroleum dalam pelbagai aplikasi, terutamanya dalam industri automotif. Biopelincir (juga dikenali sebagai pelincir berasaskan bio) adalah alternatif yang menarik untuk pelincir berasaskan mineral kerana keterbiodegradasikan (*biodegradability*) mereka dan pelinciran yang baik. Disebabkan kelebihan yang terdapat pada biopelincir, kajian ini telah dijalankan untuk mengkaji sifat-sifat fizikokimia dan ciri-ciri pencegahan hausan biopelincir berasaskan ester *polyol*, iaitu biopelincir berasaskan ester *neopentyl glycol* (NPG), *trimethylolpropane* (TMP), dan *pentaerythritol* (PE). Di samping itu, molibdenum sulfida (dikenali sebagai bahan tambahan pengubahsuai geseran) telah dicampur ke dalam biopelincir berasakan ester *polyol* dengan kepekatan yang berbeza untuk mengkaji kesan bahan tambahan ke atas sifat-sifat geseran dan hausan. Penguji hausan empat bola digunakan untuk menyiasat sifat-sifat tribologi (pekali geseran dan diameter parut hausan) biopelincir mengikut kaedah ujian piawaian ASTM, dan hasilnya dibandingkan dengan minyak parafin dan pelincir komersial. Secara umum, prestasi tribologi biopelincir adalah setanding dengan minyak paraffin, dan oleh itu, biopelincir berasaskan ester *polyol* ini adalah alternatif yang berpotensi untuk menggantikan pelincir berasaskan mineral. Selain itu, penambahan molibdenum sulfida meningkatkan sifat-sifat geseran dan hausan biopelincir berasaskan ester *polyol*.

Kata kunci: pelincir berasaskan bio; ester *polyol*; sifat-sifat tribologi; bahan tambahan pelincir.

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LIST OF SYMBOLS AND ABBREVIATIONS

CoF : Coefficient of friction

CL : Commercial lubricant

EDS : Energy-dispersive X-ray spectroscopy

EP : Extreme pressure

FAME : Fatty acid methyl ester

ISL : Initial seizure load

NPG : Neopentyl glycol

PE : Pentaerythritol

SEM : Scanning electron microscope

SCMS : Surface-capped molybdenum sulphide

TMP : Trimethylolpropane

VI : Viscosity index

WL : Weld load

WSD : Wear scar diameter

CHAPTER 1: INTRODUCTION

1.1 Overview

Energy plays an essential role in the lives of humankind in order to perform daily activities as well as boost the nation's economic growth. In one review conducted by BP Statistical Review of World Energy, the total consumption of world primary energy in 2017 was 13511.2 million tonnes of oil equivalent (mtoe), with Malaysia consumed 99.6 mtoe of primary energy (Review, 2018). Oil maintained its status as world's dominant fuel at 34% of share in 2017, as shown in Figure 1.1.

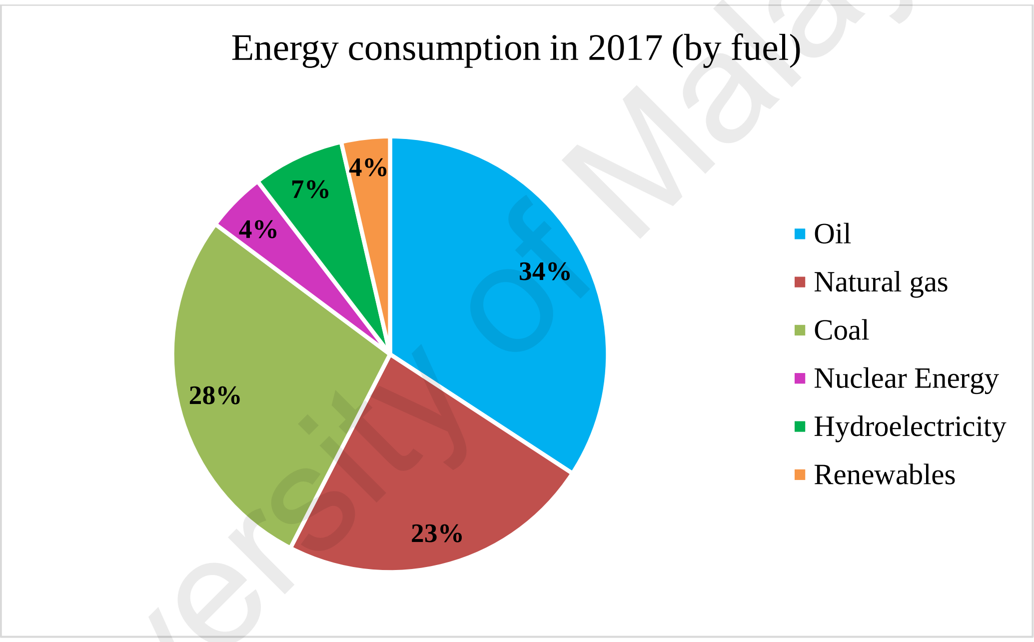

Figure 1.1: Consumption of world primary energy in 2017 by fuel (Total consumption: 13511.2 mtoe)

Fossil fuels play a major role in fulfilling global energy demands for many years and to date, fossil fuel-based crude oils are used as the raw materials to produce fuels and lubricants. The ever-increasing demand of energy sources is alarming because the depletion of fossil fuels will have a serious impact on people's lives (Fantazzini et al., 2011). Along with the growing concern on the detrimental impact of fossil fuels on the environment, it has led researchers to explore alternative sources of energy for lubricant.

In 2014, the global lubricant market was reported to be 36.36 million tonnes and the volume was predicted to increase to 43.87 million tonnes by 2022 (Research, 2016). There are many factors that affect the lubricant market. The ever-increasing demands for lubricant for use in the automotive (lightweight passenger cars and heavy-duty commercial vehicles), industrial machinery (industrialization), and construction industries are believed to boost the growth of the lubricant market over the period. Besides that, the development of biolubricants through research and development (R&D) affect the global lubricants industry demand.

According to a report published by Industry Experts, the global consumption of biolubricants in 2013 and 2014 are estimated at 1.3 and 1.4 million pounds, respectively. The volume is expected to reach 1.9 million pounds by 2020 (Experts, 2014). Meanwhile, in another report, the biolubricants market was analysed based on type, application, end-use industry, and region (MarketsandMarkets, 2016). It was reported that in 2015, Europe was spearheading the biolubricants market, which may be due to their environmental concerns. However, North America is predicted to dominate the biolubricants market by 2021. The Vessel General Permit enforced by the United States Environmental Protection Agency is expected to affect the usage of biolubricants use in North America during the period.

Even though Malaysia is one of the major suppliers of plant-based oils, especially palm oil, the use of plant-based oils as lubricants is not yet established (Ching, 2015). This may be due to the higher cost of producing plant oil-based lubricants compared with petroleum-derived lubricants as well as lack of environmental awareness and government regulations. However, the Government of Malaysia has begun to encourage companies to convert plant-based oils into useful products such as base stocks and lubricants by giving grants and tax breaks. Under the Economic Transformation Programme (National Key

Economic Area: Palm Oil & Rubber sector, Entry Point Project 6 or EPP 6), the Government of Malaysia aims to develop palm oil-derived products of higher value (PEMANDU, 2015). For example, the EPP has obtained an investment worth RM416.2 million from the Emery Oleochemicals Group to develop and produce palm-based biolubricants.

1.2 Background

The use of vegetable oils for lubrication purposes has been in practice throughout history. However, this idea was scrapped due to the discovery of petroleum and the availability of low-cost oils in the 20th century in order to support the industrial expansion. In recent years, there is a new interest in producing lubricants from vegetable oils due to growing concern over the environmental impact of fossil fuels.

Biolubricants are promising alternatives to mineral oils since they retain the technical specifications of conventional lubricants. Biolubricants are ester-based biodegradable lubricants, mostly derived from edible and non-edible vegetable oils. Natural esters are triglycerides of vegetable oils. Many studies have been carried out to investigate the potential and production of vegetable oil-based lubricants (Gawrilow, 2004; Ghazi et al., 2009; Lazzeri et al., 2006). In addition, biolubricants can be oleochemical esters of fatty acids, such as diesters, polyol esters and complex esters.

In its natural form, however, vegetable oils have disadvantages; poor low-temperature properties and poor oxidation stability. Researchers have proposed ways to overcome these limitations such as chemical modification *via* transesterification, esterification, epoxidation and hydrogenation (Pinto et al., 2013; Leslie R Rudnick, 2010; Tayde et al., 2011; Robiah Yunus et al., 2004a; Robiah Yunus et al., 2005).

1.3 Problem statement

Natural oils such as vegetable oils have become favourable feedstocks for lubricants, notably because of their biodegradability and low toxicity. One of the crucial parameters that need to be considered for lubrication is the tribological properties of the lubricant. However, the use of bio-based lubricants is limited due to their incompatibility with several applications. In order to use such lubricants in existing engine application, lubricant additive technology is needed to display a comparable performance to that of conventional mineral-based lubricants. As a well-known friction modifier, molybdenum sulphide is widely presented as an additive in mineral oils. However, very few have reported the combination of molybdenum sulphide and biolubricants.

Therefore, it is very imperative to explore and gain a better understanding on the friction and wear characteristics of biolubricants, specifically polyol ester-based biolubricants. In addition, the effects of molybdenum sulphide on the tribological properties of biolubricants have not been investigated extensively and thus, it is worthy of investigation for research contributions. This research focuses on the potential of polyol ester-based biolubricants as an alternative source of lubricating oil. Moreover, this study involves the tribological performance of polyol ester-based biolubricants with the addition of molybdenum sulphide.

1.4 Objectives of the research

The objectives of the study are as follows:

1. To study the physicochemical and tribological properties of polyol ester-based biolubricants, namely, neopentyl glycol (NPG), trimethylolpropane (TMP), pentaerythritol (PE) ester-based biolubricants,
2. To analyse the effects of surface-capped molybdenum sulphide addition on the friction and wear behaviours of polyol ester-based biolubricants,

3. To investigate the effect of temperature on the tribological properties of surface-capped molybdenum sulphide added polyol ester-based biolubricants.

1.5 Scope of research

This study focused on exploring the tribological performance of polyol ester-based biolubricants that are synthesized from oleic acid *via* esterification. This study is also focused on investigating the tribological properties of surface-capped molybdenum sulphide as a lubricant additive. The additive was prepared using the solvothermal method and lauric acid was used as the capping agent. The surface-capped molybdenum sulphide was added into the biolubricants at different concentrations, ranging from 0.025 to 0.100 wt%. A four-ball wear tester was used for the tribological tests. The tribological properties of the biolubricants were evaluated based on the coefficient of friction (CoF) and wear scar diameter (WSD). The friction and wear behaviours of these biolubricants were compared with those for paraffin oil (base oil) and commercial lubricant (fully formulated engine oil).

1.6 Outline of the dissertation

This dissertation consists of five chapters and organised in the following order:

Chapter 1: This chapter gives a brief overview and background of the research pertaining to energy, global lubricant market and consumption, and biolubricants. The problem statement, research objectives, and scope of the research are also presented in this chapter.

Chapter 2: This chapter is focused on the literature review of the biolubricants, their physicochemical properties, modification of biolubricants, and lubrication characteristics. The roles of additives in lubricants are also presented in this chapter.

Chapter 3: This chapter gives a detailed description of the materials and experimental procedures used to achieve the research objectives.

Chapter 4: The experimental results obtained in this study are presented in the form of tables and figures. The results are discussed and analysed critically based on the current findings and previous published studies.

Chapter 5: The conclusions drawn based on the key findings are presented in this chapter. Recommendations for future work are also presented in this chapter.

CHAPTER 2: LITERATURE REVIEW

The literature review is focuses on the concept of tribology, lubricants and biolubricants, physicochemical properties of biolubricants, the modification of vegetable oils and their tribological characteristics and the use of additives in lubricants.

2.1 Brief concept of tribology

Tribology is the science of the interactions between two surfaces in relative motion. Tribology includes the study of friction, lubrication, and wear, and it has become the foundation to select the suitable lubricant for a particular application.

Friction is the resisting force tangential to the interface between two bodies when, under the action of an external force, one body moves or tends to move relative to the other. The coefficient of friction, μ, is used to characterize friction. It is the dimensionless ratio of the friction, F, to the force, N, pressing the two bodies together, as given in Equation 2.1.

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

Meanwhile, wear is a damage to a solid surface, generally involving progressive loss of material, due to the relative motion between that surface and a contacting substance or substances. There are a few common types of wear: abrasive, adhesive, corrosive, and fatigue wear. Although friction and wear are related, there is no general correlation between the coefficient of friction and wear rates (Bayer, 2002). However, changes in the coefficient of friction with time or sliding distance often are associated with changes in wear behaviour. For example, a reduction in the coefficient of friction with continued sliding might indicate the formation of a stable transfer film.

The reduction of friction and wear between contacting surfaces by application of a lubricant is called lubrication Generally, a lubricant reduces both friction and wear, but this is not necessarily the case with all tribosystems. Lubricant may cause an increase in wear while lowering friction or may lower the wear while increasing friction. The three broad categories of lubrication are dry, boundary, and fluid lubrication (Bayer, 2002). Dry lubrication is lubrication provided by solids, which frequently provide good lubrication when they are easily sheared, form tribofilms, or form weak bonds. Meanwhile, fluid and boundary lubrication are general types of lubrication provided by fluids (oils and greases).

Stribeck curve, as shown in Figure 2.1, is often used to describe the relationship between coefficient of friction and so-called Hersey number, a dimensionless lubricant parameter, where η is the oil viscosity, N is the speed of the surfaces, and P is the normal load of the tribological contact. There are three lubrication regimes, depending on the thickness of the lubricating film between the moving parts: boundary, mixed, and hydrodynamic. Table 2.1 describes the lubrication regime.

$$\text{Hersey number} = \frac{\eta N}{P} \qquad (2.2)$$

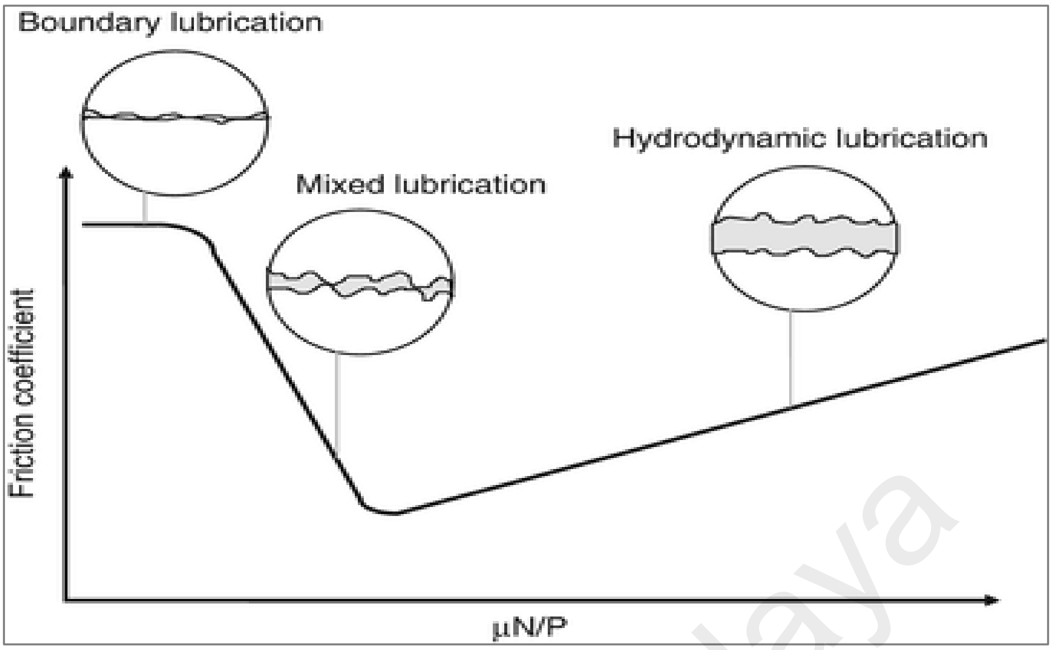

Figure 2.1: A schematic of Stribeck curve (Y. Wang & Wang, 2013)

Table 2.1: Brief description of lubrication regime based on Stribeck curve

Lubrication regime	**Description**
Boundary	- Low Hersey number - Friction coefficient is high - Very thin fluid film, formed on and between the contacting surfaces - Friction surfaces are in contact at micro asperities
Mixed	- High Hersey number - Friction coefficient decreases to a minimum value - Thin fluid film - Some asperity contact
Hydrodynamic	- Higher Hersey number - Friction coefficient is linearly ascending due to fluid film lubrication (friction is related to viscous dragging forces in the oil film) - The contacting surfaces is completely separated by hydrodynamic film (no asperity contact)

2.2 Introduction to bio-based lubricants

Lubricants are essential for almost all aspects of modern machinery. As the name implies, lubricants are substances used to lubricate surfaces that are in mutual contact in order to facilitate the movement of components as well as reduce friction and wear. Lubricants are used for various purposes, as shown in Figure 2.2. Choosing the suitable lubricant that fits the purpose of the application helps extend the lifespan of machinery and its components as well as increase their efficiency and reliability. It has been reported that more than 50% of the lubricants used throughout the world are the contributors of environmental pollution due to total-loss lubrication, spillage and evaporation (L.R. Rudnick, 2013). For this reason, there is an urgent need to produce biodegradable lubricants from renewable and sustainable sources. In general, a good lubricant should have high viscosity index (VI), high flash point, low pour point, good corrosion resistance and high oxidation stability, as shown in Figure 2.3.

Lubrication

- By introducing a lubricating film between moving parts, it minimizes the contact and lowers the force needed to move one against the other. Thereby, it is reducing wear and saving energy.

Transfer power

- Lubricant is used as a power transfer medium in some applications, for example, in hydraulic system and automatic transmission's torque converter. Hydraulic fluids constitute a big portion of all lubricants produced in the world.

Cooling

- Lubricant has good thermal conductivity. It will act as a heat sink and dissipates the heat away from the critical moving parts of equipment. Therefore, it will decrease the possibility of machine component deformation and wear. The heat generated is either from friction between surfaces or conduction and radiation, due to close proximity of the parts to a combustion source.

Cleaning

- Lubricant removes potential harmful products such as dirt, wear debris, carbon and sludge. Lubricant circulation systems have the advantage of carrying away internally generated debris and external contaminants that get introduced into the system to a filter where they can be eliminated. Therefore, it will help smooth operation of the equipment.

Figure 2.2: Functions of lubricants

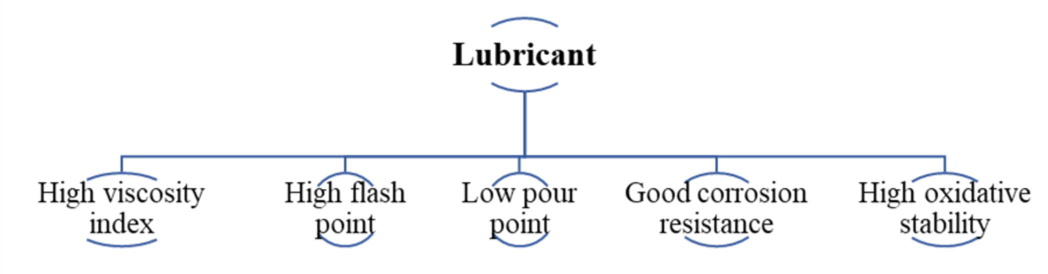

Figure 2.3: Properties of a good lubricant

Lubricants are usually categorized based on the type of base oil. The first category consists of mineral lubricants (also known as conventional lubricants), which are derived from mineral-based oils (refined petroleum). The second category comprises synthetic lubricants, which are artificially produced from chemical compounds through specific chemical processes. Some of the synthetic base stocks are polyalphaolefin (PAO), polyalkyleneglycol (PAG), and esters. The third category is bio-based lubricants or biolubricants.

In general, biolubricants can be defined as products with low toxicity and excellent biodegradability. Biolubricants are not necessarily derived from vegetable-based oils but they are usually derived from these oils. Biolubricants may also be synthetic esters, which are partially derived from renewable sources or produce from various natural sources such as solid fats, waste materials and tallow. The main component of vegetable oils is triacylglycerols (98%) as well as a variety of fatty acid molecules attached to a single glycerol structure. The minor components of vegetable oils are diglycerols (0.5%), free fatty acids (0.1%), sterols (0.3%), and tocopherols (0.1%) (L.R. Rudnick, 2013). The triglyceride structure consists of three hydroxyl groups esterified with carboxyl groups of fatty acids, as shown in Figure 2.4.

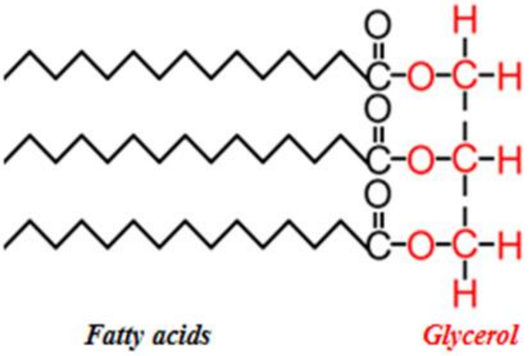

Figure 2.4: Triglyceride structure

The triglyceride structure gives these esters a high viscosity (and thus, high VI) because of their high molecular weight. The triglyceride structure is also responsible for the structural stability of the esters over a reasonable operating temperature range (de Almeida et al., 2002; Erhan & Asadauskas, 2000; Fox & Stachowiak, 2007; Salih et al., 2013). In general, fatty acids can be classified as saturated, mono-, di- and tri-unsaturated fatty acids. Excessive amounts of long-chain saturated fatty acids lead to poor low-temperature behaviour whereas excessive amounts of certain polyunsaturated fatty acids lead to unfavourable oxidation behaviour as well as resignation at high temperatures (Erhan et al., 2006; Fox & Stachowiak, 2007; H.-S. Hwang & Erhan, 2001; Salih et al., 2013). The flash point of the lubricant is also higher due to the very low vapour pressure and volatility. This reduces potential fire hazards of the lubricant while in use (Adhvaryu & Erhan, 2002; Kodali, 2002; Srivastava & Prasad, 2000). It shall be noted that long-chain monounsaturated fatty acids also deteriorate the low-temperature behaviour of the lubricant.

2.2.1 Vegetable oils as lubricant base stocks

Vegetable oils can be generally classified as edible and non-edible oils, as shown in Figure 2.5. The vegetable oils used to produce biolubricants may differ from one country to another due to climatic and geographical factors. For example, rapeseed and sunflower oils are often used in Europe whereas soybean oils are mainly used in the United States of America. In contrast, the main feedstocks of biolubricants in Asia are palm and coconut oils. However, nowadays, it is more desirable to use non-edible oils to produce biolubricants since these oils are derived from waste crops (Atabani et al., 2013) and this eliminates the use of food crops for lubricant production. However, the use of non-edible oils for biolubricants is only favourable if there is sufficient land area for both edible and non-edible crops. Economic factors may also be a factor that influence farmers to switch from producing food crops to biofuel crops even if the latter is non-edible. This scenario will create an imbalanced market since food prices increase if food production decreases (Paul Kenney & Erichsen, 1983).

Vegetable oils

Edible oils

- Sunflower oil
- Rapeseed oil
- Canola oil
- Soybean oil
- Palm oil
- Coconut oil
- Olive oil
- Castor oil

Non-edible oils

- Jatropha oil
- Callophyllum inophyllum oil
- Neem oil
- Karanja oil

Figure 2.5: Classification of vegetable oils

2.3 Physicochemical properties of biolubricants

Studies on the physicochemical properties of lubricants are important in order to understand and evaluate the performance of lubricants. These physicochemical properties include viscosity, viscosity index, flash point, pour point, oxidation stability, total acid number (TAN), total base number (TBN), volatility, and corrosiveness of lubricants. The properties of vegetable oils are closely associated with the structural parameters of the fluid particles. In general, vegetable oils possess low toxicity, high biodegradability, high lubricity, high flash point, and good VI, as well as low friction and wear characteristics compared to mineral oils. Even though vegetable oils have many advantages compared to mineral oils, these oils also have a few disadvantages such as low pour point and poor oxidation stability.

2.3.1 Viscosity and viscosity index

Viscosity is a measure of a substance's resistance to flow and it corresponds to the informal concept of 'thickness'. High viscosity means that the substance has high resistance to flow and *vice versa* (Mobarak et al., 2014). Viscosity plays a vital role in influencing the ability of the lubricant to reduce friction and wear (Salimon et al., 2010). A very high viscosity increases the oil temperature and drag whereas a very low viscosity increases the metal-to-metal contact friction between the moving parts. Epoxidized soybean oil has high viscosity compared with commercial lubricants and therefore, it is suitable for high-temperature applications (Ting & Chen, 2011).

Meanwhile, VI is a measure of the change in the viscosity of the substance in response to changes in temperature. A high VI indicates a small variation in the viscosity with respect to changes in temperature and *vice versa*. A high VI is an essential characteristic of a good lubricant since it indicates that the lubricant can be used over a wide range of temperature by maintaining the thickness of the oil film. In contrast, a low VI indicates that the viscosity of the lubricant is less stable at high temperature and hence, the film thickness of the oil tends to be thinner and becomes less viscous at elevated temperatures. Vegetable oil-based lubricants generally have higher VI than mineral oils (Asadauskas et al., 1997; Sripada et al., 2013).

2.3.2 Flash point

The flash point refers to the lowest temperature at which lubricant must be heated before it vaporizes. Lubricants will ignite (not burn) when they are mixed with air. This property is useful to determine the volatility of a lubricant. Lubricants should have high flash point to ensure safe operation and minimum volatilisation at the maximum operating temperature (Salimon et al., 2010).

2.3.3 Pour point

Pour point is the lowest temperature at which a liquid is designed to flow. In general, lubricants with low pour points are desirable since these lubricants provide good lubrication at extremely low temperatures (Benchaita & Lockwood, 1993) as well as during cold starts (Mobarak et al., 2014). If the pour point is not sufficiently low, the lack of lubricant flow lead to excessive friction, wear and heat in the system, which will lead to equipment damage or failure. Low-temperature performance is the main constraint when it comes to using vegetable oils as lubricants. Several studies have been carried out over the years to determine the low-temperature properties of vegetable oils and these studies revealed that most vegetable oils will become cloudy as well as precipitate and solidify at -10°C upon long-term exposure to cold temperatures, resulting in poor flow and pumpability (Asadauskas & Erhan, 1999; Kassfeldt & Dave, 1997; Quinchia et al., 2012; Rhee et al., 1995). This is due to the fact that vegetable oils tend to form macro-crystalline structures at low temperatures through uniform stacking of the 'bend' triglyceride backbone. These structures restrict the ease of flow in the system through the loss of kinetic energy of the individual molecules during self-stacking (Erhan et al., 2006).

2.3.4 Oxidation stability

Oxidation is a chemical reaction that occurs when the lubricant combines with oxygen. Oxidation stability indicates the ability of the lubricant to withstand oxidation. High oxidation stability is an important criterion for lubricants since a low oxidation stability causes the lubricant to oxidize rapidly if it is untreated. Consequently, the lubricant thickens and polymerizes into a plastic-like consistency. Numerous studies have been carried out to investigate the oxidation stability of vegetable oils (Erhan et al., 2006; Frega et al., 1999; Kodali, 2002). The oxidation stability of vegetable oils is generally lower than that for synthetic esters because of the higher degree of unsaturation in vegetable oils (L.R. Rudnick, 2013). The main factor that affects the oxidation of vegetable oils is the presence of unsaturated fatty acids particularly polyunsaturated compounds such as linoleic and linolenic acids (X. Wu et al., 2000).

2.4 Modification of vegetable oils

The low-temperature fluidity and chemical stability (oxidation and thermal stabilities) of vegetable oils are due to their fatty-acid structure (Wagner et al., 2001), as shown in Figure 2.6. The unsaturated structural ‘double bond’ elements in the fatty acid component and the β-CH group of the alcohol components results in oxidation and thermal instability since the double bonds in the alkenyl chains are reactive and readily react with oxygen in the air (Wagner et al., 2001). The β-hydrogen atom in glycerol removes easily from the molecular structure, cleaving the esters into acid and olefin. However, it shall be noted that some unsaturation is necessary in order to maintain the low-temperature properties of the lubricant.

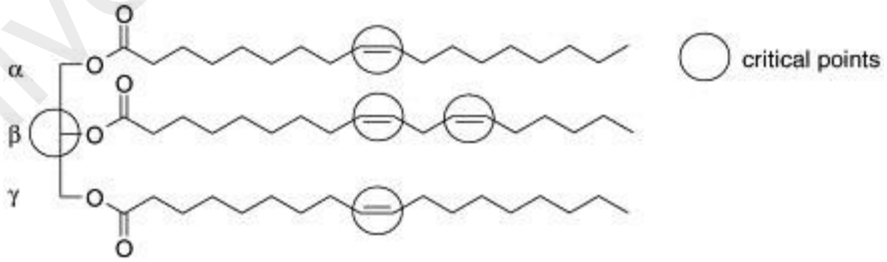

Figure 2.6: Structure of the fatty acid, in which the critical points are the β-CH group and unsaturated fatty acid residues

Much effort has been made to improve the low-temperature properties and oxidation stability of vegetable oils, which include transesterification of polyol and methyl ester from vegetable sources (Hamid et al., 2012; Uosukainen et al., 1998; Robiah Yunus et al., 2004b; R. Yunus et al., 2003; Robiah Yunus et al., 2002), esterification of polyol and fatty acids (Arbain & Salimon, 2011a, 2011b; Padmaja et al., 2012), selective hydrogenation of polyunsaturated C=C bonds of fatty acid chains (Bouriazos et al., 2010; Echeverria & Andres, 1990; Pinto et al., 2013) and conversion of C=C bonds into oxirane rings via epoxidation (Tayde et al., 2011; X. Wu et al., 2000). There are several advantages of modifying vegetable oils chemically which include stability of the lubricant over a wide temperature range as well as excellent wear and friction characteristics (Adhvaryu et al., 2004).

2.4.1 Polyol ester as alternative lubricant

Polyol esters are synthesized by the reaction of polyhydric alcohol (polyol) with various fatty acids. Owing to their exceptional characteristics, polyol esters are considered to be great alternatives for lubrication. The characteristics of polyol esters include excellent lubricity, high biodegradability, great additive solvency and good thermal stability (M. M. Wu et al., 2017), owing to the high degree of polarity of polyol esters. Polyol esters are typically the ideal lubricants for applications where ecological impact is crucial.

Polyol esters are produced by transesterification reaction between fatty acid methyl ester (FAME) and polyol in the presence of an acid or base catalyst. Figure 2.7 shows the synthesis of palm oil methyl ester-based PE ester via transesterification. Besides that, esterification of polyol with fatty acids of vegetable oils (with acid as catalyst) can also be used to produce polyol esters. As shown in Figure 2.8, TMP ester was produced by esterification. In both transesterification and esterification reactions, the glycerol is replaced with polyol which does not contain β-hydrogen atoms, namely neopentyl glycol (NPG), trimethylolpropane (TMP), and pentaerythritol (PE) (Ghazi et al., 2009; Sripada et al., 2013). The key findings of previous studies related to the production and physicochemical properties of polyol esters are summarised in Table 2.2.

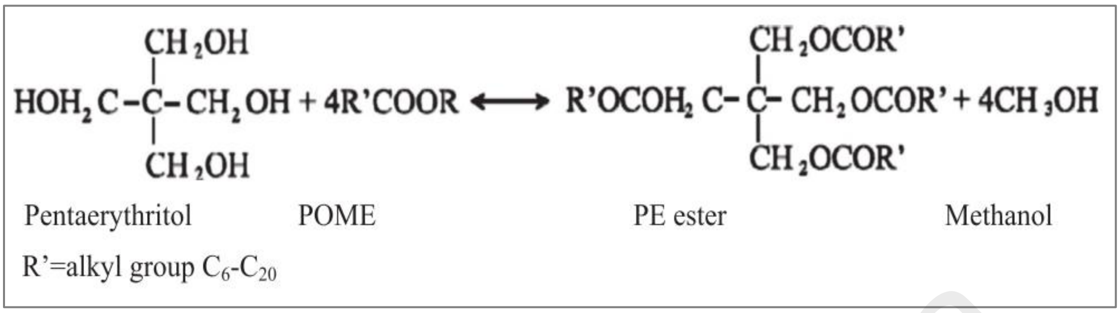

Figure 2.7: Transesterification of fatty acid methyl ester with PE polyol (Zulkifli et al., 2016)

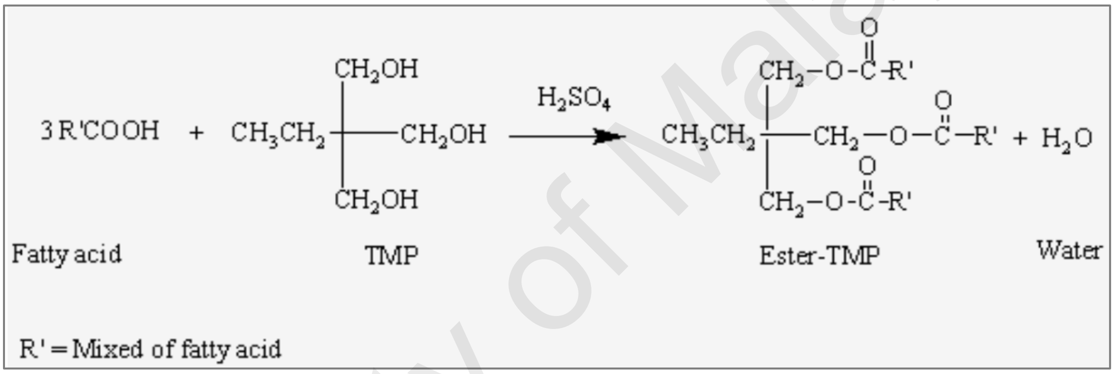

Figure 2.8: Esterification of fatty acid with TMP polyol (Arbain & Salimon, 2011b)

Table 2.2: Summary of key findings of previous studies related to the production and properties of polyol esters

Polyol ester	**Catalyst**	**Kinematic viscosity (mm^2/s)**		**Viscosity index**	**Pour point (°C)**	**Flash point (°C)**	**TAN (mgKOH/g)**	**Oxidation stability**	**Copper corrosion**	**Reference**
		40°C	**100°C**							
NPG-di-undecenoate	Stannous chloride	11.2	3.2	162	-33	254	0.05	264 °C[1]	1a	(Padmaja et al., 2012)
TMP-tri-undecenoate		23.8	5.3	165	-36	286	0.05	336 °C[1]	1a	
PE-tetra-undecenoate		36.1	7.3	172	+3	296	0.1	390 °C[1]	1a	
TMP oleate	Sulfuric acid	80.80	15.32	200	-59	289	-	189 °C[1]	-	(Mahmud et al., 2015)
PE oleate		52.22	16.33	309	42	300	-	177 °C[1]	-	
PE tetraoleate	Ion exchange resin (Form: -SO_3H)	63.08	12	190	-24	272	0.5	-	1	(Nagendramma, 2011)
PKOME[2]-based TMP	Sodium methoxide	49.7	9.8	187	-1	304	0.3	-	1b	(R. Yunus et al., 2003)

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[1] Thermogravimetric analysis

[2] Palm kernel oil methyl ester

Table 2.2 continued

Polyol ester	Catalyst	Kinematic viscosity (mm^2/s)		Viscosity index	Pour point (°C)	Flash point (°C)	TAN (mgKOH/g)	Oxidation stability	Copper corrosion	Reference
		40°C	100°C							
RSO[3]-based NPG	Para toluene sulfonic acid (p-TSA)	23.1	5.9	222	-15	266	0.123	15 min[4]	1a	(Kamalakar et al., 2013)
RSO[3]-based TMP		38.4	8.6	212	-6	299	0.229	12 min[4]	1a	
RSO[3]-based PE		62.6	12.6	206	-3	308	0.311	10 min[4]	1a	
Olive oil-based NPG	Calcium methoxide	15.32	4.31	209.8	-15.5	--	0.40	-	-	(Gryglewicz et al., 2003)
Olive oil-based TMP		36.00	8.32	218.3	-13.0		0.55	-	-	

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[3] Rubber seed oil

[4] Rotating bomb oxidation test

2.5 Tribological characteristics of biolubricants

Examining the effects of tribological system parameters on the chemistry of the lubricant can help one to identify the lubrication requirements for a given application. It is known that vegetable oils provide good lubrication through their ester functionality (Steren, 1989). The polar head of the fatty acid chain attaches to the metal surface through a chemical process, resulting in the formation of a monolayer film, as shown in Figure 2.9. The non-polar end of the fatty acid chain sticks away from the metal surface, which reduces the coefficient of friction (Adhvaryu & Erhan, 2002; Jayadas et al., 2007; Masjuki & Maleque, 1997; Masjuki et al., 1999). A number of studies pertaining to the tribological properties of various vegetable oils are summarized in Table 2.3.

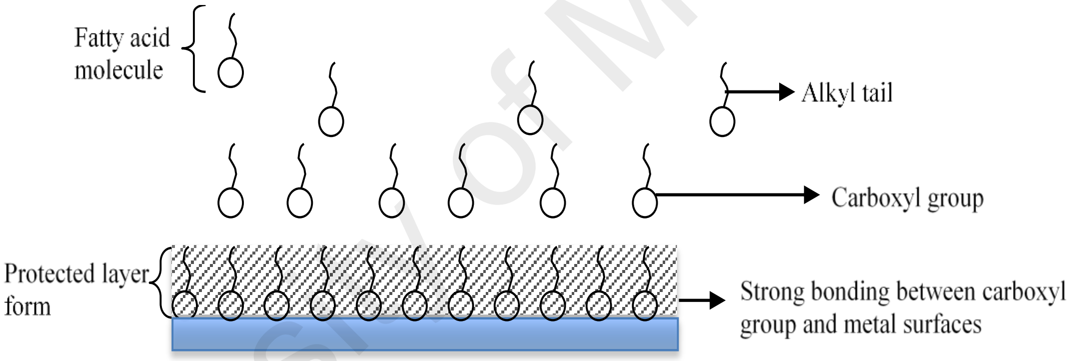


Figure 2.9: Polarity of fatty acid molecule

Table 2.3: Tribological properties of vegetable oil-based lubricants

Vegetable oils	**Test specifications**	**Operating conditions**	**Findings**	**Reference**
Jatropha oil	Four-ball wear test Ball (AISI E-52100 steel): 12.7 mm diameter, 64 HRC	ASTM D4172 Duration: 60 minutes; Rotational speed: 1200 rpm; Load: 40 kg; Temperature: 75°C	Jatropha oil has high unsaturated hydrocarbons (C18:1). It is known that the polar head of the fatty acid tends to attach itself to the metal surface. It is believed that the polar head of the fatty acids in the *Jatropha* oil reacts with the steel surface and forms soapy layer which helps protect the surface against wear.	(Lubis et al., 2011)
Palm oil-based ester	Four-ball wear test	IP 239 Duration: 30 minutes; Rotational speed: 1200 rpm; Load: 40 kg; Temperature: 50, 60, 70, 80, 90, 100 °C	The CoF increases with increasing temperature for NPG. However, the CoF decreases with increasing temperature for PE and formulated PE, which indicates that the PE gives better protection to the surfaces at high temperatures due to its thermal stability. In addition, the scar produced increases with increasing temperature. This is due to the fatty acids present in the ester, which can accelerate the formation of scar due to its corrosive nature. The acidic compound causes instability of the oil, which increases the wear rate.	(Aziz et al., 2016)

Table 2.3 continued

Vegetable oils	**Test specifications**	**Operating conditions**	**Findings**	**Reference**
Calophyllum inophyllum (CI)-based TMP ester	Four-ball tribotester Ball (Carbon-chromium steel SKF): 12.7 mm diameter, 62 HRC	Duration: 60 minutes; Rotational speed: 1200 rpm; Load: 40 kg; Temperature: 50, 60, 70, 80, 90, 100°C	The CoF for the CI TMP ester is lowest compared to that for paraffin oil and CL. The CoF decreases with an increase in temperature. The presence of long-chain fatty acids in the CI TMP ester improves the boundary lubrication properties and the film is effective even at high temperatures. The WSD is lower for the CI TMP compared to that for paraffin oil but the WSD is larger than that for CL since it contains additives which give protection to the ball surface	(Habibullah et al., 2015)
Coconut oil	Four-ball tester	ASTM D4172-94 and ASTM D2783	Even though the CoF is lower for coconut oil than that for SAE 20W50 oil, the WSD is larger. The reaction between the oil and the metal surface during sliding results in continuous removal of the soap film formed on the metal surface. The soap film has low shear strength and therefore, the CoF is low. The CoF and WSD improved significantly upon the addition of 2 wt% of AW/EP additive. The weld point also increases as this additive concentration.	(Jayadas et al., 2007)

2.6 Additives in lubricating oil

The limitations of vegetable oils such as poor thermo-oxidative stability and cold flow behaviour may also be enhanced by adding additives. Manufacturers of various vegetable oils can use the same base stock for each formulation and choose different additives in order to fulfil the requirements of a specific application. Additives may constitute up to 10% (by weight) for some oils. The presence of additives helps improving the properties of lubricants and biolubricants in terms of corrosion inhibition as well as friction and wear characteristics. In general, esters with biodegradable additives are superior to pure oils or vegetable oil blends in terms of their wear resistance (Balamurugan et al., 2010). The common additives used in lubricant are shown in Figure 2.10.

Figure 2.10: Lubricant additives

2.6.1 Dispersion stability of nanoparticles

Due to Brownian motion, the dispersion of nanometre-sized particles is stable when these particles are added into base oils (Y. Hwang et al., 2008). However, problems with the dispersion stability problems may arise because nanoparticles tend to agglomerate, forming aggregates. Due to gravity, the agglomeration of nanoparticles results in sedimentation and which reduces the lubrication performance of oils. There are various methods that can be used to disperse nanoparticles in base oils, including agitation by magnetic stirring (J. H. Wang et al., 2016), sonication by using an ultrasonic bath (Asrul et al., 2013; Cizaire et al., 2002; Kun Hong Hu et al., 2011; Jatti & Singh, 2015; Xie et al., 2016) or ultrasonic probe/homogenizer (Abdullah et al., 2016; Alves et al., 2013; Mosleh et al., 2009; V. Srinivas et al., 2017; Tontini et al., 2016; Viesca et al., 2011).

The use of surfactants as dispersing agents is known to enhance the dispersion of nanoparticles, which is a simple and economical technique. This technique reduces the surface tension between the nanoparticles and base oil. Various surfactants have been used to enhance the dispersion of nanoparticles such as oleic acid (Abdullah et al., 2016; Asrul et al., 2013; Gulzar et al., 2015), polyisobutylene (V. Srinivas et al., 2017) and sodium dodecyl sulphate (SDS) (J. H. Wang et al., 2016). Alternatively, surface modification can be used to enhance the dispersion of nanoparticles by using capping agents such as oleic acid (Song et al., 2012). The surface of nanoparticles is encapsulated by this agent, which reduces the surface energy and prevents agglomeration. The surface-capped nanoparticles have been proven to have excellent lubrication performances compared to uncoated particles. This is because surface modification prevents material transfer among the nanoparticles and cold-welding between shearing surfaces (Akbulut, 2012).

2.6.2 Lubrication additive mechanism

The mechanism of lubricant additives is important in order to understand the interaction between particles and contact surfaces. A few mechanisms have been reported by researchers, including the mending effect, ball bearing effect, and film formation, as shown in Table 2.4.

Table 2.4: Mechanisms of lubricant additives reported in previous studies

Mechanism	**Description**	**Researchers**
Mending effect	The additives are believed to deposit on the contact area and fill in the scars of the worn surfaces, which compensates the loss of mass. The deposition of additives on the surface significantly improve the tribological properties of the lubricant	(Alves et al., 2013; Jatti & Singh, 2015; Song et al., 2012; V. Srinivas et al., 2017; Viesca et al., 2011)
Ball bearing effect	The spherical particles will likely act as ball bearings, which roll into the rubbing surfaces. The particles change the friction mechanism between the frictional pairs from sliding friction to rolling friction, which reduces the contact area.	(Abdullah et al., 2014; Asrul et al., 2013; Cizaire et al., 2002)
Protective film formation	A protective film is formed due to the reaction between the friction surfaces, base oil, and additives in a mechanism known as tribo-sintering. The tribofilm is highly influenced by the test conditions (temperature and pressure). This film protects the surface, which reduces friction and wear.	(Abdullah et al., 2016; Alves et al., 2013; Kun Hong Hu et al., 2011)

2.6.3 Molybdenum sulphide as a lubricant additive

Molybdenum sulphide is widely known as a friction modifier lubricant additive, which reduces the coefficient of friction between contacting surfaces (Parenago et al., 2002). This sulphur-containing molybdenum inorganic compound is categorized as a dichalcogenide. This compound is naturally obtained from molybdenite ores by flotation process. Many synthetic approaches have been developed to produce molybdenum sulphide such as hydrothermal reaction, precursor decomposition, solution reaction, surfactant-assisted reaction and sulphide sulphidation (Roslan, 2017).

Molybdenum atoms are situated between layers of sulphur atoms. The weak van der Waals interactions between the sulphide sheets result in low coefficient of friction for the compound (V Srinivas et al., 2014; Xie et al., 2016). This additive is commonly used as a lubricant additive in most of 2-stroke and 4-stroke engine oils and the oils are proven to retain their lubricity in most cases (V Srinivas et al., 2014). Various forms of molybdenum sulphide have been used by researchers such as microparticles, nanoparticles, nanotubes, nanosheets, and fullerene-like structures (IF-MoS_2) (Bakunin et al., 2006; Charoo & Wani, 2016; K. H. Hu et al., 2009; X. G. Hu et al., 2005; Kogovšek et al., 2013). Table 2.5

Table 2.5: Properties of molybdenum sulphide (Gulzar et al., 2015)

Properties	**Value**
Molecular weight (g/mol)	160.07
Density (g/cm^3)	5.06
Melting point (°C)	2375
Hardness (Moh)	1.0
Appearance	Black/lead-grey solid

Several studies have shown the capability of molybdenum sulphide to reduce the coefficient of friction of various surfaces such as the boundary-lubrication of steel-steel contacts (K. H. Hu et al., 2009), magnesium alloy-steel contacts (Xie et al., 2016), titanium-steel pairs (Mosleh et al., 2009), and diamond-like carbon coating (Kogovšek et al., 2013). The key studies related to the application of molybdenum sulphide in lubricant are summarised in Table 2.6.

Gulzar et al. (2015) observed that the dispersibility of 1 wt% molybdenum sulphide in chemically modified palm oil (TMP ester) is stable over 70 h, with and without the addition of oleic acid as surfactant. However, this additive is not suitable for long stationary applications due to sedimentation after 14 days. In a different study, there is a significant variation in the average size of molybdenum sulphide particles (1 wt%) dispersed in commercial engine oil indicating that the particles tend to agglomerate and begin to sediment over a period of 10 days (V. Srinivas et al., 2017). However, the dispersibility of molybdenum sulphide in engine oil is stable at lower concentrations within the same period.

Table 2.6: Key findings of previous studies related to the addition of molybdenum sulphide in lubricants

Lubricant	**Test specifications**	**Operating conditions**	**Findings**	**Reference**
600 N gear oil (contains 2-3% of sulphur)	Four-ball wear test	According to ASTM D2783	Base oil dispersed with 0.05 wt% MoS_2 improves the load wear index and higher weld load compared to 0.1 wt%. which probably due to overcrowding of nanoparticles. The reduction in friction is possibly caused by the deposition of nanoparticles on the surfaces.	(V Srinivas et al., 2014)
SAE 20W-40 engine oil	Four-ball wear test	According to ASTM D4172	Almost 20% reduction in the WSD for lubricant with addition of 1.0 wt% IF-MoS_2 due to the spherical morphology of nanoparticles.	(Charoo & Wani, 2016)
	Universal tribometer (piston ring and cylinder liner tribo-pair)	Sliding velocity: 20 and 30 mm/s; Load: 100, 150 and 200 N; Duration: 15 minutes; Stroke length: 2 mm	The CoF is proportional to normal load; the bigger the load, the higher the CoF. Meanwhile, the wear loss of cylinder liner is reduced by 30-65% with the application of IF-MoS_2 as additive in lubricant and it shows that the nanoparticles exist at the surface.	

Table 2.6 continued

Lubricant	**Test specifications**	**Operating conditions**	**Findings**	**Reference**
Naphthenic oil	Universal tribometer (pin-on-disc geometry)	Load: 7.1 N; Frequency: 2 Hz; Amplitude: 10 mm; Duration: 1 hour	An impressive 86% reduction in the CoF with the addition of 1 wt% of flower-like MoS_2 in the base oil. The well-dispersed nanoparticles develop a stable tribofilm to protect the contact surfaces.	(Tontini et al., 2016)
Polyalphaolefin (PAO)	Four-ball test	Load: 392 N, Rotating speed: 1450 rpm; Duration: 30 minutes; Temperature: Room temperature	The CoF and WSD for PAO with addition of 0.5 wt% MoS_2 is smaller compared to PAO alone and the value is stable throughout the test due to the tribofilm formed.	(J. H. Wang et al., 2016)
	Ball-on-disk	Load: 2 N; Sliding speed: 0.037 m/s; Duration: 8 minutes; Temperature: 22, 200, 350, 450 and 600 °C in air	Below 350 °C, the tribological characteristics improves with the addition of 0.5 wt% MoS_2 in PAO. Plus, the width of worn groove on the disc is thinner (250 μm) compared to PAO alone.	

Table 2.6 continued

Lubricant	**Test specifications**	**Operating conditions**	**Findings**	**Reference**
Commercial engine oil (EOT5#)	Reciprocating ball-on-flat tribometer	Load: 3 N; Sliding speed: 0.08 m/s; Duration: 30 minutes	The higher the concentration of MoS_2, the lower the CoF, with 31.25% reduction shown by the addition of 1.0 wt% MoS_2 in the engine oil. Its nano-sized feature permits the additive to enter the contact surfaces and avoid direct contact. Besides that, the wear volume also decreases compared to base lubricant. Protective films are established due to tribochemistry reaction between the nanoparticles and rubbing surfaces.	(Xie et al., 2016)
SAE 20W-40 motor oil	Four-ball tester	According to ASTM D4172	Improvement in wear scar is shown by lower weight fractions. With the addition of 0.25 wt% and 0.5 wt% MoS_2 in base oil, the WSD decreases from 401.18 µm to 390.22 and 375.22 µm, respectively. Plus, the molybdenum element is reported to deposit on the surface based on EDS results.	(V. Srinivas et al., 2017)

2.7 Summary

The ever-increasing demand for energy, depletion of fossil fuels, as well as the increase in global awareness regarding the environmental impact of fossil fuels has led to much research and development in search of renewable and sustainable sources of energy. Unlike conventional petroleum-derived lubricants, biolubricants are clean lubricants having the chemical structure of a fatty acid. To date, many vegetable oils from edible and non-edible sources have been used to produce biolubricants; however, those derived from non-edible sources are more attractive since they do not rely on edible feedstocks, which are more suited for food production. Climate and geographical factors both play a critical role in determining whether vegetable oils should be used to produce biolubricants.

Vegetable oils offer a number of advantages over conventional mineral oils since these oils are highly biodegradable and environmentally safe. Even though the thermo-oxidative stability of vegetable oils can be a problem, this issue can be overcome by modifying the vegetable oils chemically *via* transesterification, esterification, epoxidation or selective hydrogenation. Vegetable oils have potential as lubricants due to their ester functionality and the main factors that affect their tribological properties are the length of the carbon chains, the type of fatty acids, and polarity. The properties of biolubricants can also be improved by the addition of additives, depending on the specific requirements of the application.

With significant improvements of vegetable oils by chemical modification or incorporation of additives, biolubricants appear to be promising alternatives to replace petroleum-derived lubricants in the future. Even though a large number of studies have been carried out over the years regarding the application of vegetable oils as biolubricants, more research is needed to gain a deeper understanding on the lubrication mechanisms of these lubricants, their blends and their compatibility with a variety of additives. Therefore, this study was carried out to investigate the tribological properties of polyol esters as biolubricants, as well as the effect of molybdenum sulphide addition on the friction and wear behaviours of biolubricants. The key studies related to types of oils and additives used for biolubricants are summarised in Table 2.7.

Table 2.7: Summary of previous studies based on type of base oils and additives

		Without additive	**MoS$_2$**	**CuO**	**Graphene**	**Additives package**
Mineral-based oil	**Paraffin oil**	(Habibullah et al., 2015) (Zulkifli et al., 2014)	(Zhang et al., 2015) (K. H. Hu et al., 2009)	(Asrul et al., 2013)		
	Commercial lubricant	(Aziz et al., 2016)	(V. Srinivas et al., 2017)	(Jatti & Singh, 2015)		
Synthetic -based oil	**PAO**	(Jiang et al., 2015)			(Azman et al., 2016)	
Bio-based oil	**NPG ester**	(Jiang et al., 2015) (Aziz et al., 2016)				
	TMP ester	(Habibullah et al., 2015) (Zulkifli et al., 2014) (Zulkifli et al., 2016)	(Gulzar et al., 2015)	(Gulzar et al., 2015)	(Azman et al., 2016)	
	PE ester	(Jiang et al., 2015) (Aziz et al., 2016) (Zulkifli et al., 2016)	(Roslan et al., 2017)			(Aziz et al., 2016)
	Palm oil		(Zhang et al., 2015)			
	Rice bran oil	(Rani et al., 2015)				
	Sunflower oil	(Rani et al., 2015)				

CHAPTER 3: METHODOLOGY

3.1 Introduction

The flow chart of the research methodology adopted in this study is shown in Figure 3.1. Firstly, the polyol ester-based biolubricants were selected and compared with paraffin oil and commercial lubricant. Secondly, molybdenum sulphide additive was produced *via* solvothermal route. The additive was added into the polyol ester-based biolubricants at different concentrations and the physicochemical properties of the biolubricants were measured. Following this, the four-ball wear tester was used to study the friction and wear properties of the polyol ester-based biolubricants with and without the addition of molybdenum sulphide, in accordance with the ASTM standard test method. The coefficient of friction was calculated, and the stationary balls were collected after the tribological tests for wear scar measurement and surface analysis.

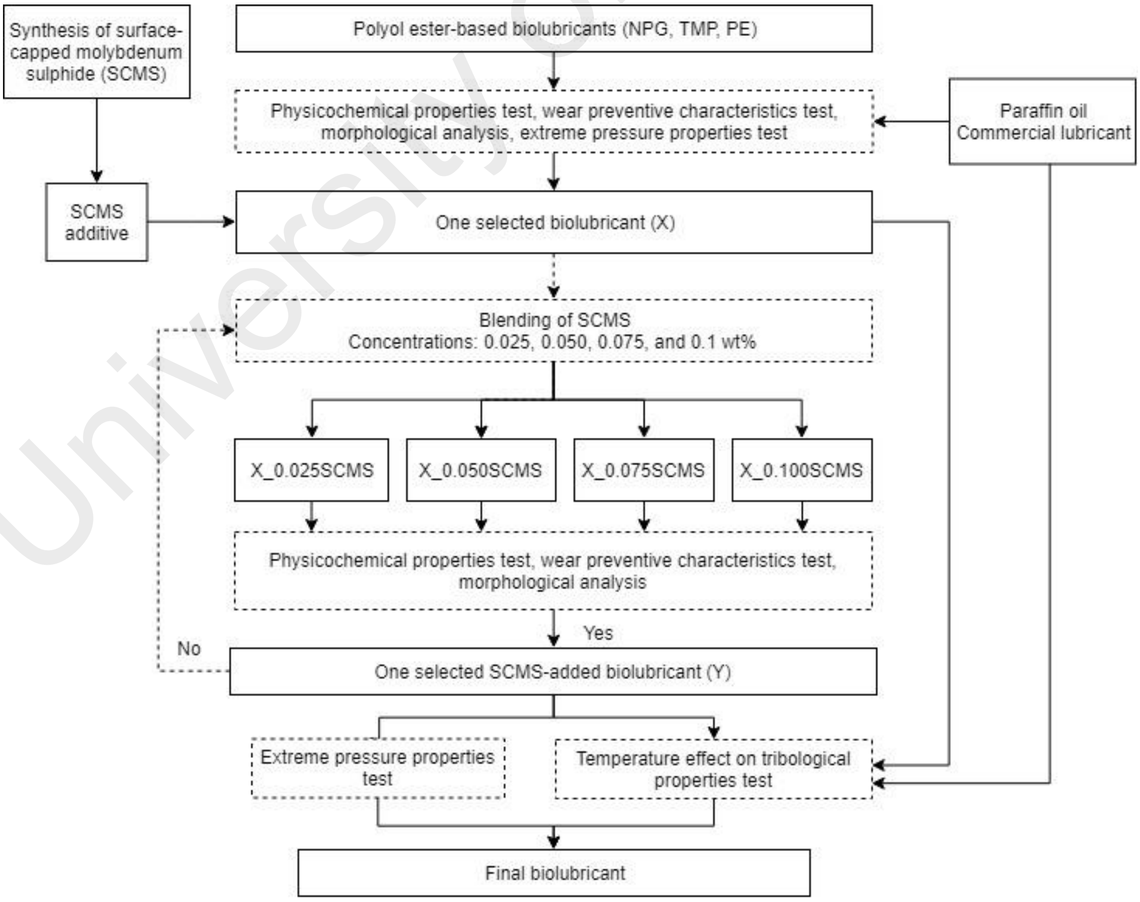


Figure 3.1: Flow chart of the research methodology

3.2 Synthesis of surface-capped molybdenum sulphide

The surface-capped molybdenum sulphide was synthesised using the solvothermal approach, where lauric acid was used as the capping agent (Roslan et al., 2017). Lauric acid has the ability to interact with the molybdenum sulphide particles due to their hydrocarbon chains and functional groups. Figure 3.2 shows the morphology of the surface-capped molybdenum sulphide (SCMS) (Roslan et al., 2017). The average size of SCMS particles is 64 nm.

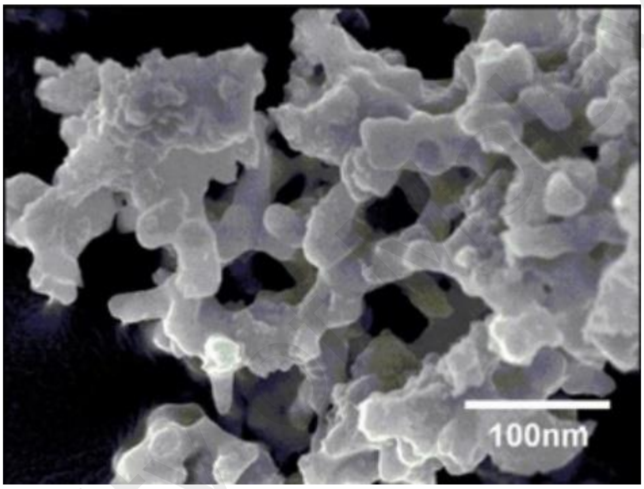


Figure 3.2: FESEM image of surface-capped molybdenum sulphide

The first step involves preparing the molybdenum(II) acetate. Hence, 5 g of hexacarbonylmolybdenum ($Mo(CO)_6$) was added into a two-neck round-bottom flask (500 mL) containing 100 mL of glacial acetic acid. Following this, 50 mL of acetic anhydride was poured into a pressure-equalising dropping funnel and then attached to the middle neck of the flask. A nitrogen gas inlet was fitted through the other neck of the flask and the opening port of the dropping funnel was closed using a septum cap. The flask was immersed in an ice-water bath, which was placed on top of the plate of the magnetic stirrer. Next, acetic anhydride was added into the mixture and the mixture was stirred continuously. After the process was complete, the flask was taken out from the ice-water bath and left to cool to room temperature.

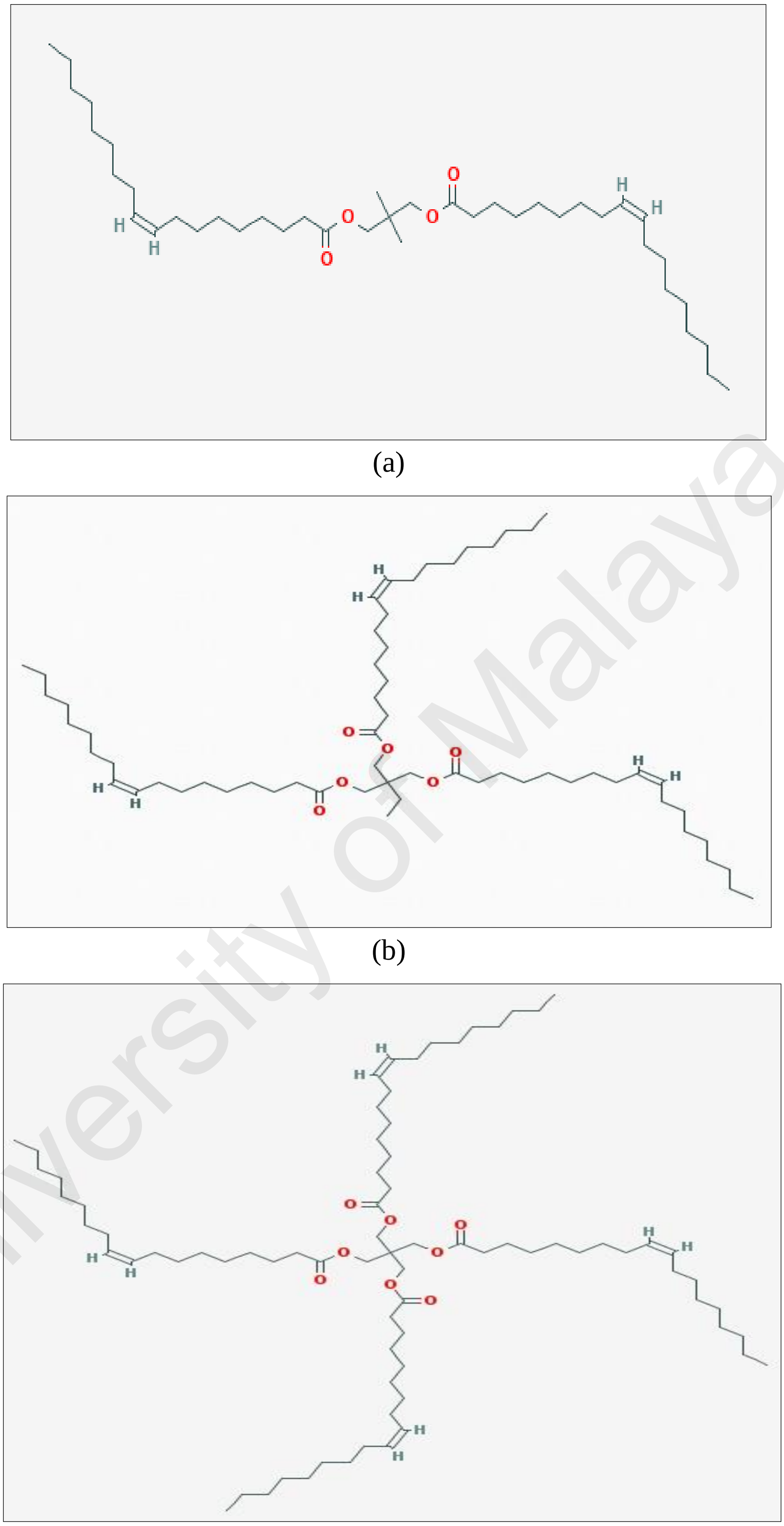
Next, the pressure-equalising dropping funnel was replaced with a condenser and the flask was placed on the heating and stirring mantle. The flask was fitted with a nitrogen gas inlet through the other neck of the flask with silicone oil bubbler to monitor the rate of N_2 flow through the apparatus. The solution was refluxed at 180 °C and a bright yellowish crystal of molybdenum (II) acetate appeared in the solution after 20 h. The solution was left to cool to room temperature and the N_2 gas was then turned off. The bright yellow product was isolated using suction filtration technique and washed with approximately 10 mL of cold ethanol. The product was dried in a laboratory oven at 60 °C for 2 h.

The second step involves synthesising the surface-capped molybdenum sulphide. Mo-O complexes were prepared through solvothermal reaction between molybdenum(II) acetate and lauric acid, and $C_{12}H_{24}O_2$ (alkyl substituent of fatty acid) in hexane medium. Hence, 0.5 g of freshly prepared molybdenum(II) acetate, 0.5 g of thioacetamide, and 2 g of lauric acid were dissolved in 60 mL of n-hexane under sonication and the mixture was then transferred into a Teflon-lined stainless steel autoclave. The autoclave was closed tightly and heated to 140 °C for 3 h and then left to cool to room temperature. The precipitates produced were centrifuged and washed several times with n-hexane and finished with ethanol. The final fine dark product formed was dried in the laboratory oven for 3 h at 50 °C.

3.3 Preparation of lubricant samples

3.3.1 Selection of lubricants

Paraffin oil and commercial lubricant (CL) were used in this study for comparison purposes. Paraffin oil is a colourless and odourless mineral oil. It is a light mixture of non-vegetable alkanes, varying from C15 to C20. The CL is a fully formulated lubricant that is commercially available in the market and it is essentially a combination of a base stock and additive package. The CL used in this study is SAE 40. Three types of polyol ester-based biolubricants were chosen for this study: (1) neopentyl glycol dioleate (NPG ester), (2) trimethylolpropane trioleate (TMP ester), and (3) pentaerythritol tetraoleate (PE ester). The structures of the polyol esters used in this study are shown in Figure 3.3. These polyol esters were purchased from Shandong Ruijie Chemical Industry Co., Ltd., Qingdao, China. Oleic acid, which is a fatty acid present in most vegetable oils, was used to synthesize the polyol ester-based biolubricants *via* esterification. The polyols used were neopentyl glycol, trimethylolpropane and pentaerythritol.



(a)

(b)

(c)

Figure 3.3: Structures of the polyol ester-based biolubricants used in this study; (a) neopentyl glycol dioleate, (b) trimethylolpropane trioleate, and (c) pentaerythritol tetraoleate (PubChem, 2006)

3.3.2 Composition of the lubricants

In the second part of this study, the SCMS was blended with one of the polyol ester-based biolubricants (i.e. PE ester, based on the first part of the experiment) at four concentrations: 0.025, 0.050, 0.075, and 0.1 wt%. The compositions of the lubricants used in this study are shown in Table 3.1. To ensure the dispersion of the additives, the nanoparticles were mixed thoroughly with the biolubricants using a magnetic stirrer and the nanoparticles were dispersed evenly by sonication for 1 h with 2-s pulse at 50 Hz frequency.

Table 3.1: Compositions of the lubricants used in this study

	Lubricant sample code	**Composition by weight percent (wt%)**					
		Paraffin oil	**Commercial lubricant (CL)**	**NPG ester**	**TMP ester**	**PE ester**	**SCMS**
Part 1	Paraffin	100	-	-	-	-	-
	CL	-	100	-	-	-	-
	NPG	-	-	100	-	-	-
	TMP	-	-	-	100	-	-
	PE	-	-	-	-	100	-
Part 2	PE_0.025SCMS	-	-	-	-	99.975	0.025
	PE_0.050SCMS	-	-	-	-	99.950	0.050
	PE_0.075SCMS	-	-	-	-	99.925	0.075
	PE_0.100SCMS	-	-	-	-	99.900	0.100

3.4 Measurement of the physicochemical properties of the lubricant samples

In this study, the density at 15 °C and kinematic viscosities at 40 and 100 °C of the samples were determined according to the ASTM D445 standard test method. The VI was determined based on the kinematic viscosities at 40 and 100 °C in accordance with the ASTM D2270 standard test method. The kinematic viscosities of the samples were measured using Stabinger SVM^{TM} 3000 viscometer (Anton Paar, UK). The repeatability of the viscosity was 0.1%. The viscometer was calibrated using the calibration fluids provided by the manufacturer at least once in every 6 months to ensure reliability of the viscosity measurements. The flash point of the base oils was checked in accordance with the ASTM D93 standard test method using Pensky-Martens closed-cup flash point apparatus (Model: PM4, Petrotest, Germany).

3.5 Friction and wear testing

A four-ball wear tester (Model: TR 30H, DUCOM, India) was used in this study to investigate the friction and wear properties of the lubricant samples. As the name implies, the four-ball wear tester consists of three stationary balls in a ball pot and the fourth ball is attached to the rotating spindle. Standard AISI 52100 chrome steel balls were used in the tests, each having a diameter of 12.7 mm and a hardness of 64-66 Rc (Rockwell hardness). Prior to each test, the steel balls, oil cup, and clamping parts were cleaned thoroughly with toluene and wiped using clean tissues. Approximately 10 mL of lubricant sample was used for each wear and friction test. The test was repeated three times for each sample in order to determine the experimental uncertainties.

Figure 3.4 shows the diagram of the four-ball wear tester. The load was applied by spinning ball, which presses into the centre of the triangular formation of the three stationary balls. The wear scar diameter (WSD) was used to assess the wear generated on the stationary balls and was measured using a calibrated optical microscope.

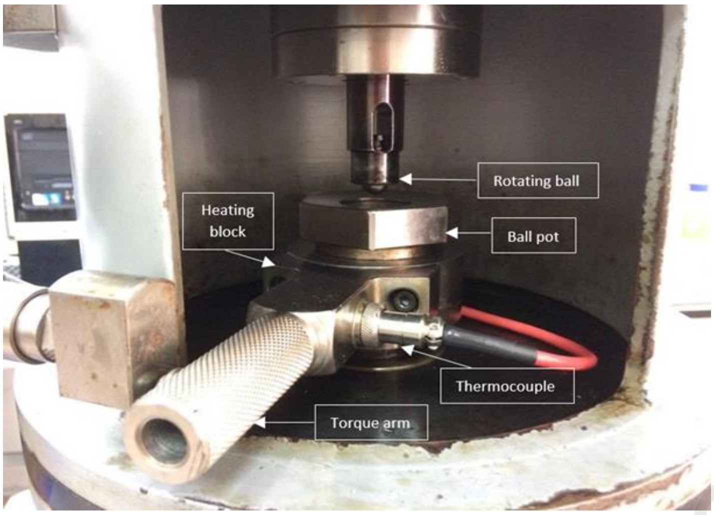


Figure 3.4: Four-ball wear tester

3.5.1 Coefficient of friction

The CoF was used to evaluate the friction characteristics of the polyol ester-based biolubricants. The CoF is a dimensionless parameter, which is defined as the ratio of the friction force between two bodies to the normal force that presses these bodies together. The frictional forces were monitored in real-time by recording the shaft torque continuously. The CoF plays an important role in determining the transmission efficiency. According to the IP-239 standard, the CoF is given by (Ing et al., 2012):

$$\mu = \frac{T\sqrt{6}}{3Wr} \qquad (3.1)$$

where μ is the CoF, T is the frictional force (Nm), W is the applied load (N), and r is the distance from the centre of the contact surface of the lower balls to the axis of rotation. In this study, r is 3.67 mm.

3.5.2 Measurement of the wear preventive characteristics

The wear preventive characteristics of the lubricant samples were determined following the procedure stipulated in the ASTM D4172 standard test method. This is a preliminary evaluation of the anti-wear properties of the lubricants in sliding contact.

Each test was conducted for 60 min at 75 °C with an applied load of 40 kg. The rotational speed of the spindle was 1200 rpm. Seizure and welding do not typically occur in this condition.

3.5.3 Measurement of the extreme pressure properties

Extreme pressure tests were carried out to determine the initial seizure load (ISL), weld load (WL), CoF and WSD of the steel balls lubricated with the polyol ester-based biolubricants. The applied load was increased by 20 kg every 10 s until the balls were welded at a rotational speed of 1770 rpm. The tests were conducted at room temperature. Figure 3.5 shows the wear-load line, ABCD.

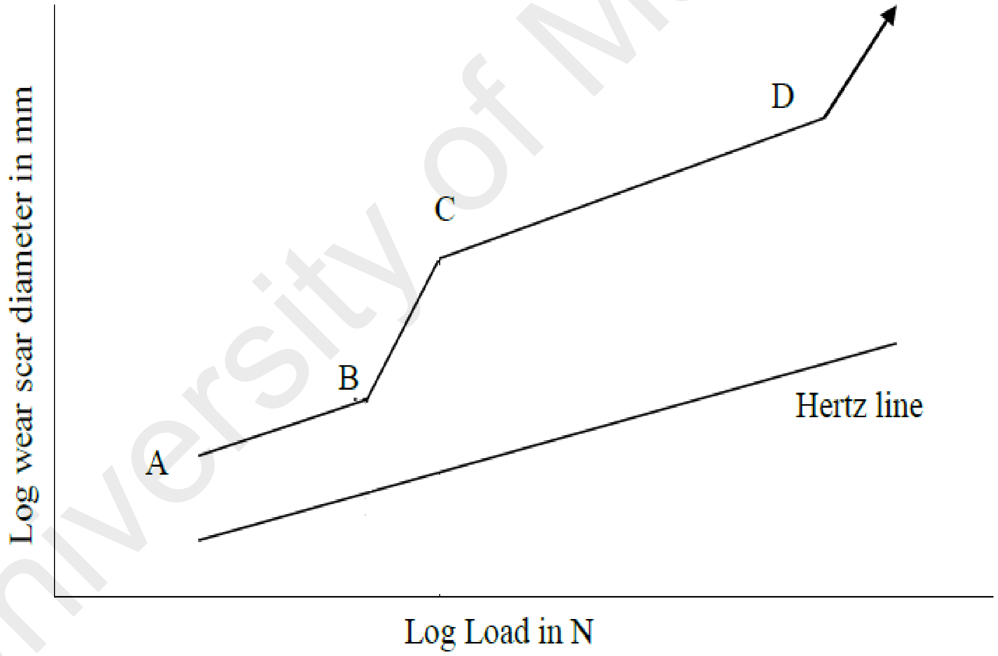


Figure 3.5: Weld load graph with Hertz line

The Hertz line is a straight line obtained by plotting the calculated Hertz scar diameter against the applied load. The Hertz scar diameter indicates the diameter of an indentation caused by the deformation of the balls. The Hertz scar diameter can be determined using the following equation, where D_h is the Hertz diameter of the contact area and P is the applied load ("ASTM D2783-03," 2014).

$$D_h = 8.73 \times 10^{-2}\sqrt[3]{P} \qquad (3.2)$$

The ISL implies the load at which the wear-load line deviates from the Hertz line and therefore, it indicates a sudden increase in the WSD at the applied load. The WL is the load at which the lubricant fails completely and the spinning ball welds to the three stationary balls, indicating that the extreme pressure of the lubricant-force has been exceeded.

3.5.4 Measurement of the temperature effect on tribological properties

The four-ball wear tester was used to investigate the effect of temperature on the tribological properties of the polyol ester-based biolubricants. The test was performed at various temperatures (50, 60, 70, 80, 90 and 100 °C) for 60 min with an applied load of 40 kg at 1200 rpm. This method was also used by Aziz et al. (2016) and Zulkifli et al. (2014). The temperature of the sample chamber was controllable by a heater attached to the ball pot and the resulted temperature was measured by thermocouple, as shown in Figure 3.4.

3.6 Morphological analysis of steel balls

3.6.1 Optical microscope

The wear scars generated on the stationary steel balls were examined under an optical microscope, as shown in Figure 3.6. The WSD was used to assess the lubricity of the polyol ester-based biolubricants. The optical microscope was connected to the four-ball tester and the scars were measured using a digital image acquisition system.

Figure 3.6: Optical microscope

3.6.2 Scanning electron microscope

Scanning electron microscope (SEM) was used to examine the morphologies of the wear scars (Model: Phenom ProX, Phenom-World, Netherlands), as shown in Figure 3.7. SEM uses a focused beam of electrons instead of light to project an image of the specimen and obtain information about its composition. The main advantage of SEM over optical microscope is its large field-depth, which allows a large amount of sample to be focused at a time. In addition, SEM produces high-resolution images, which enable one to examine closely spaced features at high magnifications. The specimen preparation is simple because most SEMs only require the specimen to be conductive. In this study, the samples were fixed onto a metal stub using electrically-conductive double tape before being connected to the specimen holder.

Figure 3.7: Scanning electron microscope

Energy-dispersive X-ray spectroscopy (EDS) is an analytical technique used for elemental analysis or chemical characterization of a sample. EDS is dependent on the interaction between the X-ray excitations and the sample. EDS is based on the principle that each element has a unique atomic structure, resulting in a unique set of peaks in its X-ray emission spectrum. EDS provides quantitative analysis of the elemental distribution in a surface. In this study, the energy-dispersive X-ray spectrometer was attached to the SEM.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Introduction

The experimental results are presented in three main sections (Section 4.1-Section 4.3) based on the objectives of this research. Section 4.1 is focused on the physicochemical and tribological properties of polyol ester-based biolubricants while Section 4.2 is focused on the friction and wear behaviours of the SCMS-added polyol ester-based biolubricants. Finally, the effect of temperature on the tribological characteristics of the lubricant samples are presented in Section 4.3.

4.2 Physicochemical and tribological properties of polyol ester-based biolubricants

4.2.1 Physicochemical properties

Kinematic viscosity is one of the important properties of lubricants since it provides information on the resistance of the lubricant to flow under the influence of gravity. In general, lubricants should have a kinematic viscosity that is sufficiently high in order to form a thicker lubricating film, which will provide better surface protection. The kinematic viscosities at 40 and 100 °C for the paraffin oil, CL, and ester-based biolubricants investigated in this study are presented in Table 4.1 It can be seen that the paraffin oil and polyol ester-based biolubricants have lower kinematic viscosities at both 40 and 100 °C than CL, where the kinematic viscosities at 40 and 100 °C are 125.83 and 13.32 mm^2/s, respectively. This result conforms well with those of Aziz et al. (2016) and Zulkifli et al. (2013) who found that the kinematic viscosity is higher for CL compared to polyol ester-based biolubricants due to the presence of additives in the lubricant formulation. The kinematic viscosities at 40 °C for the PE, TMP, and NPG ester-based lubricants are 58.46, 45.82 and 23.33 mm^2/s, respectively, which are significantly higher than that for paraffin oil (12.78 mm^2/s). The more the number of acyl groups, the higher the viscosity of the polyol ester-based biolubricants (Gryglewicz et al., 2003; Kamalakar et al., 2013).

VI is a parameter that indicates the effect of temperature on the viscosity of lubricants. In general, the most desirable lubricant is one that can sustain a steady viscosity over a wide range of temperatures. A high VI indicates that there is less variation in the viscosity of the lubricant due to changes in the temperature, which indicates that the oil is stable. The VI is determined based on the kinematic viscosities at 40 and 100°C. In this study, the VIs for the PE, TMP, and NPG ester-based lubricants are found to be 185, 186, and 212, respectively, as shown in Table 4.1. However, the CL has the lowest VI, with a value of 100.

It can also be seen from Table 4.1 that the CL has the lowest flash point, with a value of 256 °C. In contrast, the flash point is higher for the NPG ester-based lubricant (270 °C) as well as TMP and PE ester-based lubricants (300 °C). These values indicate that the polyol ester-based biolubricants have a lower tendency to evaporate, which is indeed one of the main requirements of lubricating oils. A higher flash point is essential in order to reduce safety hazards during handling, storage, and transportation and it is often associated with the volatility of additives present in the lubricants.

Table 4.1: Physicochemical properties of paraffin oil, CL, and polyol ester-based biolubricants

Lubricant sample	Density at 15°C (g/cm^3)	Kinematic viscosity (mm^2/s)		VI	Flash point (°C)
		40°C	100°C		
Paraffin	0.8371	12.78	3.17	112	180
CL	0.8933	125.83	13.32	100	256
NPG	0.9078	23.33	5.83	212	270
TMP	0.9190	45.82	9.13	186	300
PE	0.9289	58.46	11.06	185	300

4.2.2 Wear preventive characteristics

The average CoF values for paraffin oil, CL, and polyol ester-based biolubricants are shown in Figure 4.1. It can be observed that the CoFs are lower for the NPG, TMP and PE ester-based lubricants compared to those for paraffin oil and CL. In general, vegetable oils and fatty acid esters provide better lubricity due to the ester functionality. The CoF values are almost similar for the TMP and PE ester-based lubricants whereas the CoF is slightly lower for NPG ester-based lubricant. The CoFs for the NPG, TMP, and PE ester-based lubricants are lower than that for paraffin oil by 20, 13, and 11%. In general, a higher CoF is associated with lower oil viscosity (Sharma et al., 2009). However, the high CoF for the CL indicates that a high kinematic viscosity does not necessarily lead to good friction-reducing properties. These results are comparable to those of Aziz et al. (2016) who found that the friction due to fluid drag on the moving surfaces in the mixed film lubrication regime may have led to the higher CoF values. The micro-asperities between the surfaces overcome the effect caused by the oil viscosity on the tribological properties, which in turn, increases the CoF.

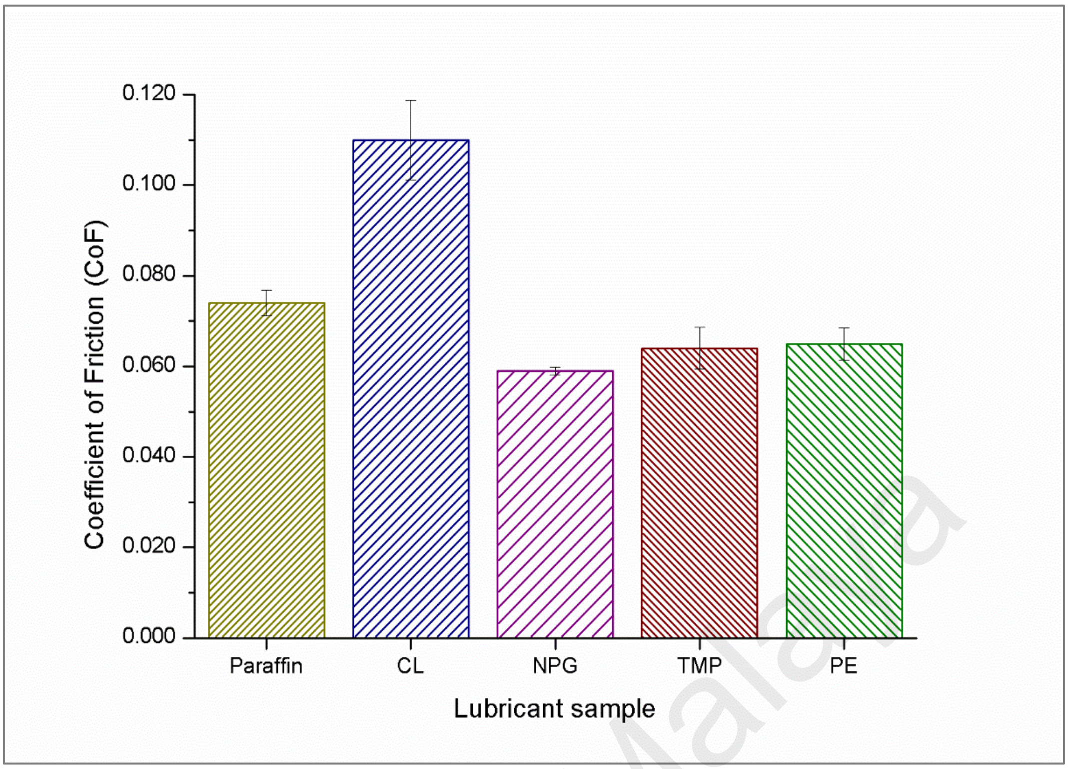


Figure 4.1: CoFs for paraffin oil, CL, and polyol ester-based biolubricants (Test conditions: Load = 40 kg; Duration = 1 h; Temperature = 75°C; Rotational speed = 1200 rpm)

The WSDs of the standard AISI 52100 steel balls lubricated with paraffin oil, CL, and polyol ester-based biolubricants are shown in Figure 4.2. It is evident that the WSD is the lowest for the CL. The WSDs are significantly smaller for NPG, TMP, and PE ester-based lubricants compared with that for paraffin oil, though the values are still higher than that for CL. The WSDs are reduced by 17.4, 18.2, and 20.3% for the NPG, TMP and PE ester-based lubricants, respectively, relative to that for paraffin oil. The presence of fatty acids in the polyol esters may lead to oil degradation (Kodali, 2002) and stimulate the formation of wear scar owing to their corrosive nature. The oil structure may be unstable due to the presence of acidic compounds, which leads to a higher wear rate, as observed by Aziz et al. (2016).

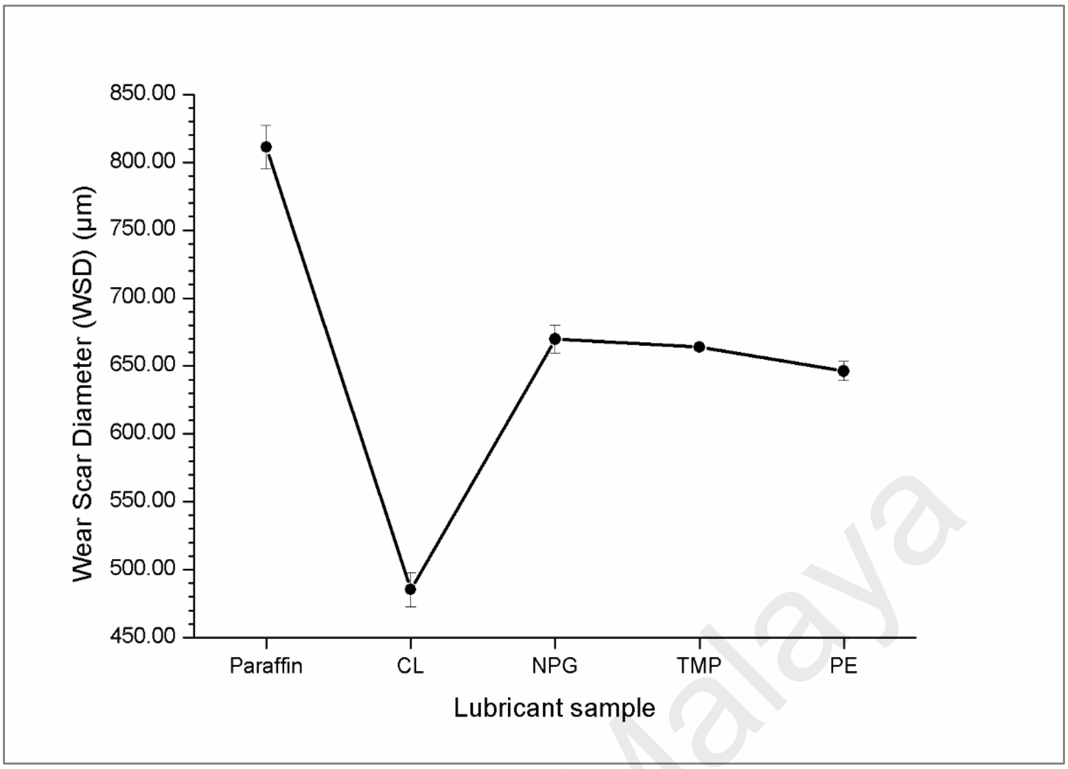


Figure 4.2: Wear scar diameter of standard AISI 52100 steel balls lubricated with paraffin oil, CL, and polyol ester-based biolubricants (Test conditions: Load = 40 kg; Duration = 1 h; Temperature = 75°C; Rotational speed = 1200 rpm)

The fatty acid chains as well as polarity and ester functionality are the factors that influence the friction and wear prevention characteristics of polyol ester-based biolubricants. The existence of long-chain fatty acids in the ester-based lubricants contributes to the lower CoF values. These fatty acid components create layers on the rubbing surfaces and improves surface protection. The ester functionality of the fatty acids assists the compounds to adhere to the metal surface, which reduces friction. The active group of the compounds begins functioning at the metal-to-metal contact, forming an anti-friction film (Madankar et al., 2013). The esters have high affinity towards the metal surface, which can be attributed to their polar functional groups, which creates a protective layer over the surface (Lawal et al., 2013).

The polyol ester-based biolubricants have lower CoFs but larger WSDs compared to CL. The wear process can be typically divided into two periods: (1) 'running-in' period and (2) steady-state period. During the 'running-in' period, the CoFs are higher for polyol ester-based biolubricants compared to that for CL, as shown in Figure 4.3. The film layer formed on the contact surfaces begins to break down and the friction torque increases, which increases the size of the wear scar. The asperities are flattened out in this stage. The ‘running-in’ period is followed by the steady-state period, where the CoFs of the polyol ester-based biolubricants decrease gradually due to the smoother contact surfaces (Waara et al., 2004).

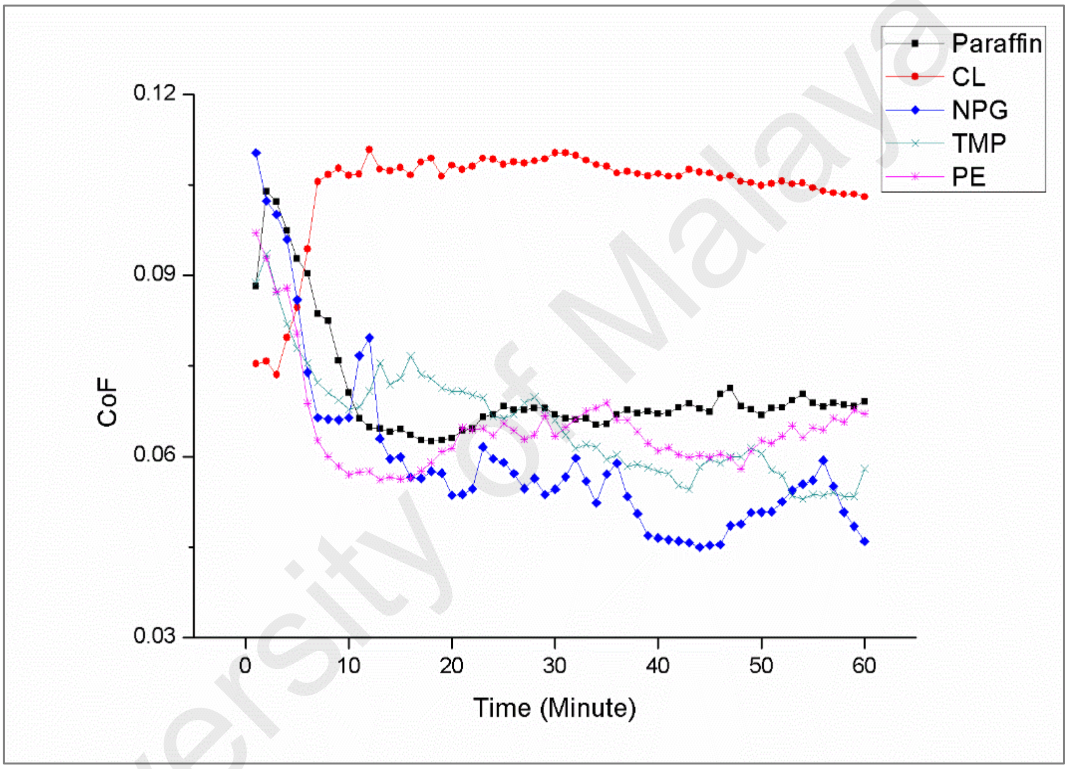


Figure 4.3: Variation of the CoF with time for different lubricant samples (Test conditions: Load = 40 kg; Duration = 1 h; Temperature = 75°C; Rotational speed = 1200 rpm)

In general, the PE ester-based lubricant results in the highest CoF but the lowest WSD among the polyol ester-based biolubricants investigated in this study. It is observed in a previous study that the tribological properties of the lubricant improve with an increase in the number of carboxylate ester groups (Pettersson, 2003). The increase in the number of carboxylate ester groups results in a stronger bond between the molecules, which increases the resistance of the lubricant to shear forces. Since PE has four groups of carboxylate ester, the CoF of the PE ester-based lubricant during the ‘running-in’ period is smaller compared to that for NPG ester-based lubricant, which has two groups of carboxylate ester. This is due to the stronger molecular bond in the PE ester-based lubricant, which results in better friction resistance and smaller worn scar. The results obtained in this study are consistent with the findings of Adhvaryu et al. (2006) and Pettersson (2003) who observed that the WSD decreases with an increase in the number of carboxylate ester groups. However, some researchers noted that the actual number of acyl groups that can be esterified has a minor effect on the friction-reducing and wear prevention characteristics of lubricants (Havet et al., 2001; Kamalakar et al., 2013).

Table 4.2 shows the SEM images and EDS spectra of the wear scar formed on the AISI 52100 steel balls lubricated with paraffin oil, CL, and polyol ester-based biolubricants. It is apparent from the results that the wear scar is largest for the paraffin oil compared with other samples, as shown in Table 4.2 (a). Indeed, the paraffin oil does not lead to the formation of a lubricating film, which results in direct surface contact between the steel balls (Zulkifli et al., 2016). As a result, there is adhesion of micro-asperities and plastic deformation on the surface. It can be observed from Table 4.2 (b) that the wear scar is smaller for the CL, without any critical scuffing on the surface. The image reveals the presence of mild wear on the surface of the steel balls. In addition, the presence of elements such as phosphorus (P), sulphur (S), zinc (Zn), and calcium (Ca) in the EDS spectrum indicates that the additives present in the CL provide good protection of the surface of the stationary steel balls during the four-ball wear test, resulting in the lowest WSD, as shown in Figure 4.2.

It can be observed from Table 4.2 (c) that the wear scar appears rougher with irregular edges for the steel balls lubricated with NPG ester-based lubricant. It is evident that there is severe wear on the surface, judging from the presence of grooves. However, there are fewer grooves for the steel balls lubricated with TMP ester-based lubricant, as shown in

Table 4.2 (d). However, it is apparent that there is severe wear on the surface of the steel balls, indicated by the presence of scratches and pits within the wear scar. More importantly, adhesive wear occurs at the edges of the wear scar. The dark region on the surface may represent the corrosive product of the sample (Haseeb et al., 2010). Table 4.2 (e) shows more regular edges compared with Table 4.2 (c), with grooves on the wear scar for the steel balls lubricated with PE ester-based lubricant. There is severe wear on the surface, particularly within the dark region located near the centre of the wear scar. In addition, delamination occurs at the bottom-right region of the wear scar, indicating that there is material removal within this region.

Table 4.2: SEM images of the wear scar and EDS spectra of the worn surface lubricated with: (a) paraffin oil, (b) CL, (c) NPG, (d) TMP, and (e) PE ester-based lubricant at a constant load of 40 kg

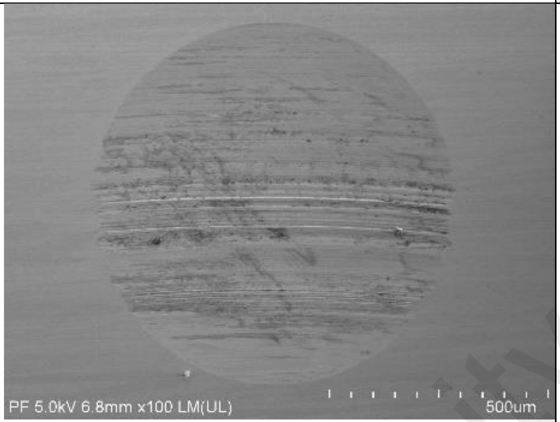
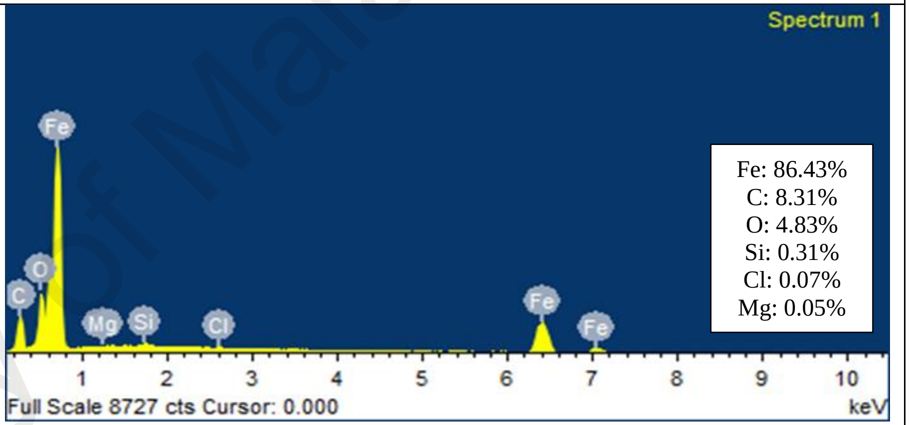
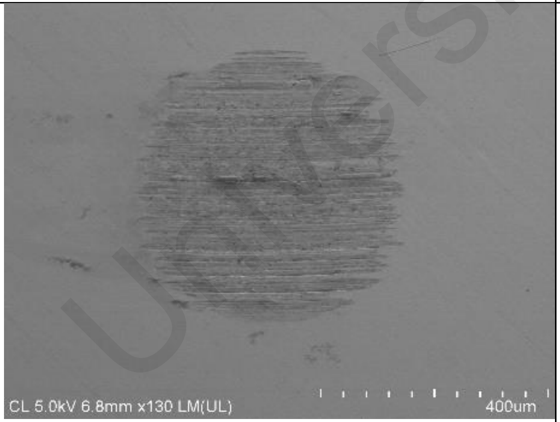
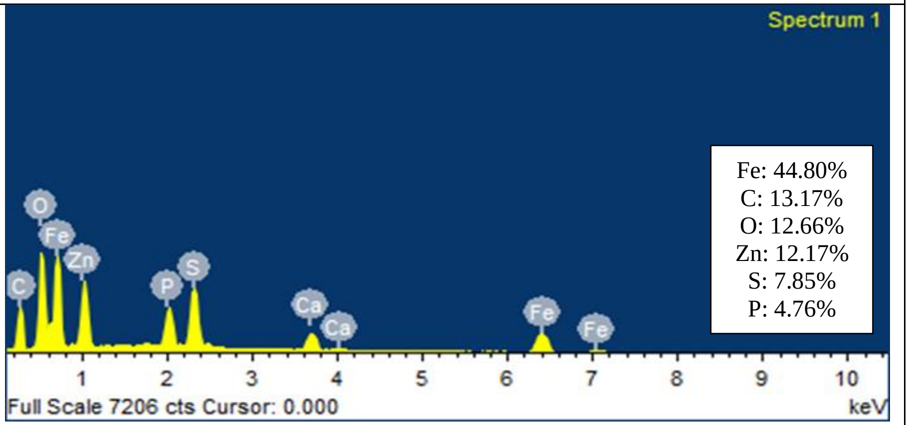
Lubricant sample	**SEM image**	**EDS spectra (y-axis: Number of counts; x-axis: Energy)**
(a) Paraffin		 Fe: 86.43% C: 8.31% O: 4.83% Si: 0.31% Cl: 0.07% Mg: 0.05%
(b) CL		 Fe: 44.80% C: 13.17% O: 12.66% Zn: 12.17% S: 7.85% P: 4.76%

Table 4.2 continued

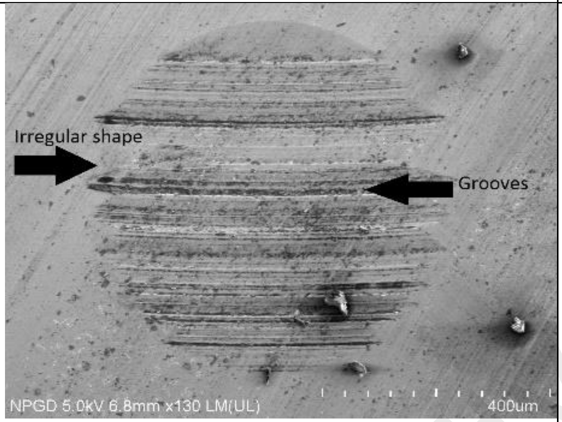
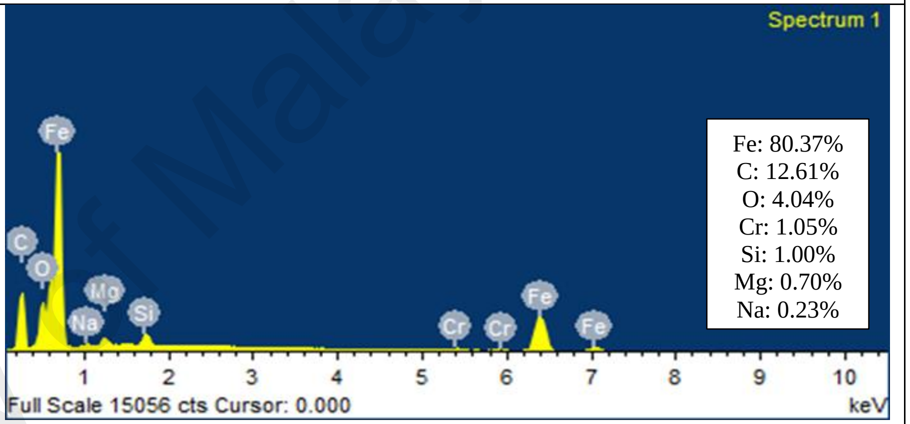
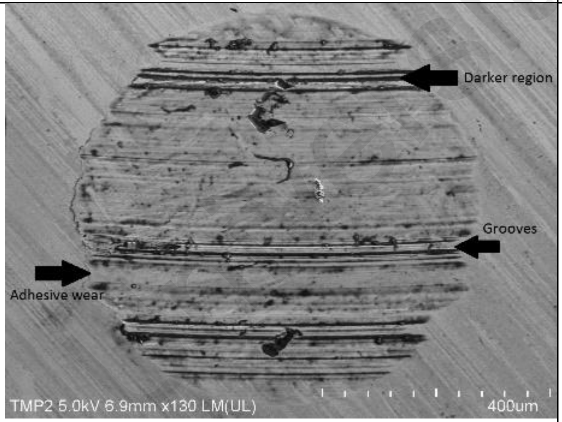
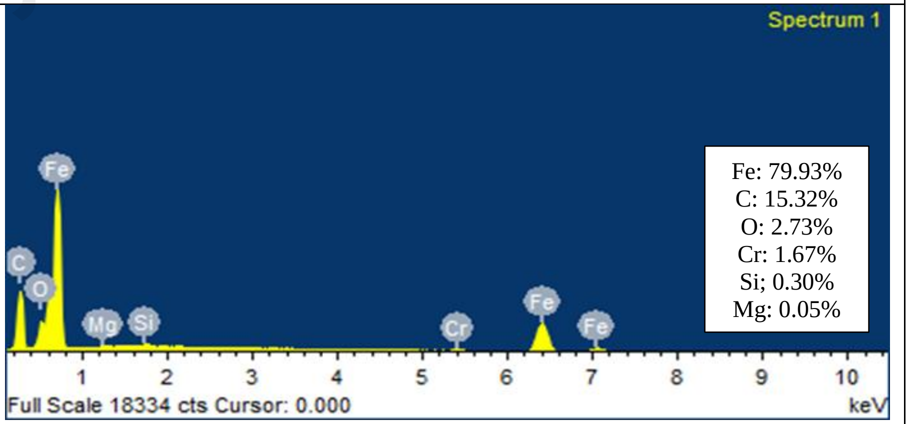
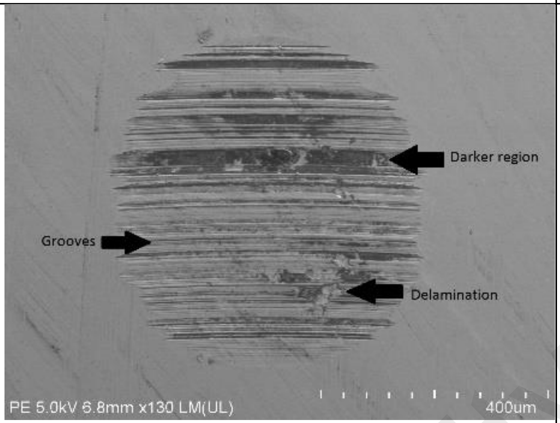
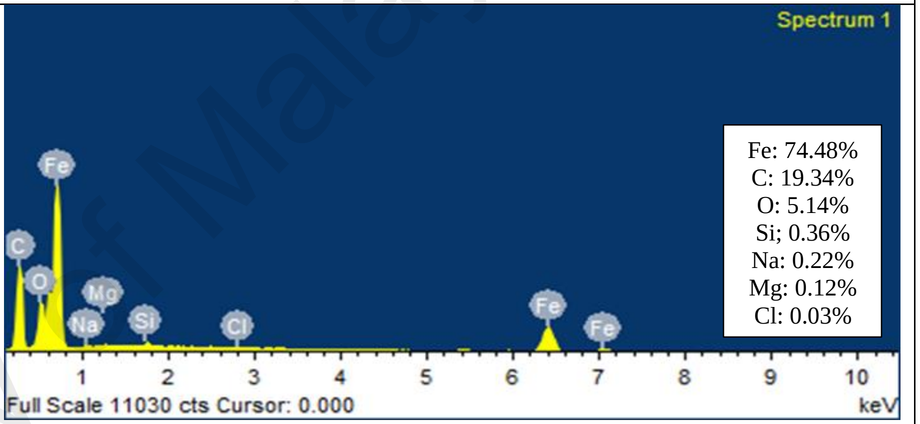
Lubricant sample	SEM image	EDS spectra
(c) NPG		
(d) TMP		

Table 4.2 continued

Lubricant sample	SEM image	EDS spectra
(e) PE		

4.2.3 Extreme pressure characteristics

The initial seizure loads (ISL), weld loads (WL), CoFs, and WSDs for the paraffin oil, CL, and polyol ester-based biolubricants at an applied load of 100 kg are presented in Table 4.3. In general, the CL has the best performance in extreme pressure condition since it has the highest ISL (100 kg) and WL (180 kg), as well as the lowest CoF (0.071) and WSD (0.5095 mm). This implies that the presence of additives (particularly, extreme pressure additive) improves the extreme pressure behaviour of the CL. The ISLs, WLs, CoFs and WSDs of the polyol ester-based biolubricants are comparable to those for paraffin oil; however, it is evident that these lubricants outperform paraffin oil under extreme pressure condition. The results obtained in this study conform well with those of Zulkifli et al. (2013), who found that the ISL for palm oil-based TMP ester biolubricants was 40 kg. Furthermore, they found that the addition of TMP ester in the fully formulated lubricant improves the extreme pressure characteristics of the lubricant.

Table 4.3: ISLs, WLs, CoFs, and WSDs for the paraffin oil, CL, and polyol ester-based biolubricants (Test conditions: Duration = 10 s; Temperature = Room temperature; Rotational speed = 1770 rpm)

Lubricant sample	**ISL (kg)**	**WL (kg)**	**CoF at 100 kg**	**WSD at 100 kg (mm)**
Paraffin	40	140	0.600	3.62
CL	100	180	0.071	0.51
NPG	40	160	0.243	2.54
TMP	40	160	0.227	2.68
PE	60	160	0.184	2.39

Figure 4.4 shows the variation of the CoF as a function of time for the paraffin oil, where the applied load is varied at 40, 60, 80 and 100 kg. It is apparent that the CoF is lowest at an applied load of 40 kg, with an almost constant trend. This is due to the

formation of a thin lubricating film over the surface of the steel balls, which is able to withstand the applied load. As the load is increased further, there is a dramatic increase in the CoF due to the breakdown of the thin lubricating film. The CoF continues to increase until the steel balls are welded together. This is due to the high pressure and temperature during the test, which leads to evaporation of the lubricating film, resulting in welding of the steel balls.

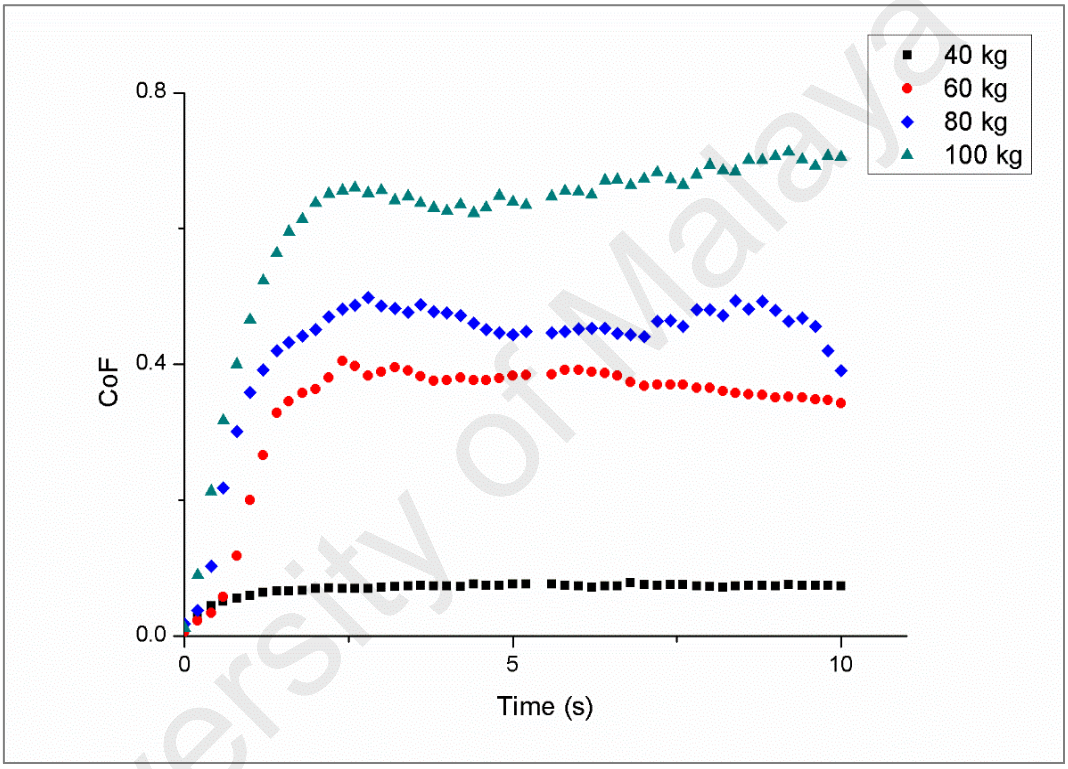


Figure 4.4: Variation of the CoF as a function of time at various loads for the paraffin oil

Figure 4.5 shows the variation of the CoF as a function of time for the CL, where the applied load is also varied at 40, 60, 80 and 100 kg. It is apparent from the results that there is no ISL for this lubricant up to an applied load of 100 kg, which indicates that the CL has superior extreme pressure characteristics compared to paraffin oil. It is believed that the extreme pressure additive present in the CL contributes towards the lower CoF values.

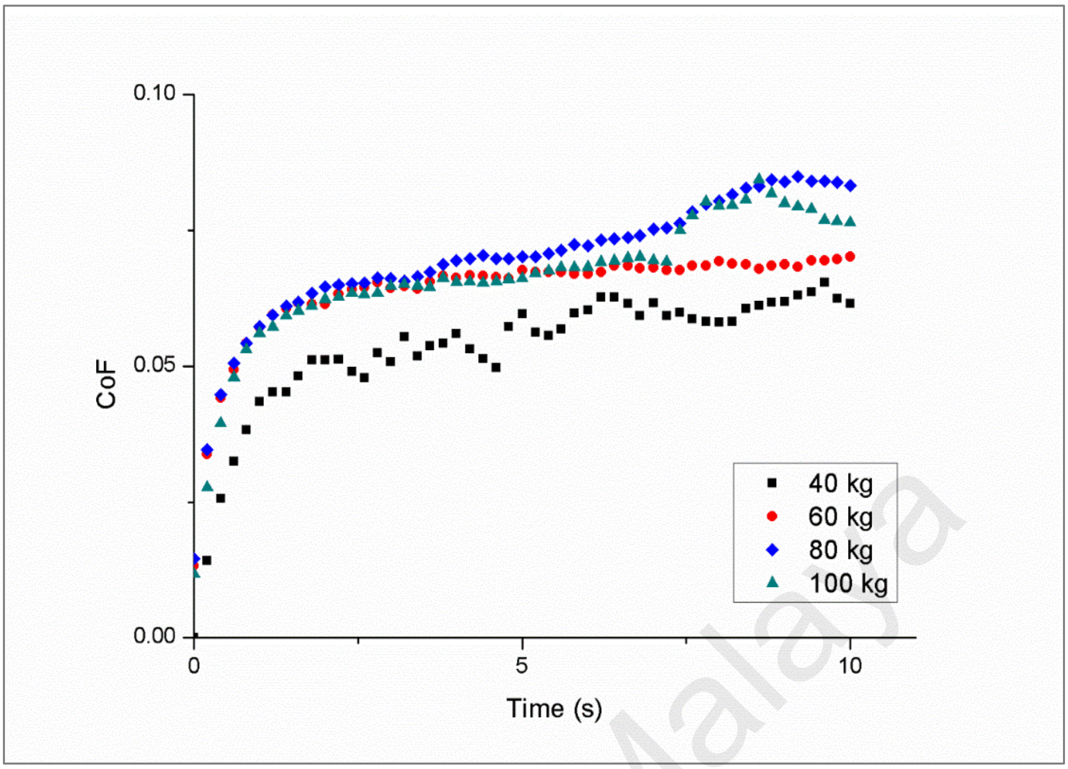


Figure 4.5: Variation of the CoF as a function of time at various loads for the CL

Figure 4.6 and Figure 4.7 show the variations of CoF as a function of time for NPG and TMP ester-based lubricant, respectively. It can be observed that the trend for these biolubricants is characteristically different from that for paraffin oil. It can be observed from both of these figures that the CoF increases up to a maximum value with an increase in time, followed by a decrease beyond this maximum point, particularly at an applied load of 80 and 100 kg. In contrast, there is no distinctive maximum point observed for the paraffin oil. However, the variation of the CoF is similar for paraffin oil and NPG and TMP ester-based lubricants at an applied load of 40 kg. Upon close inspection of these plots, it is evident that the CoF values are lower for the NPG and TMP ester-based lubricants.

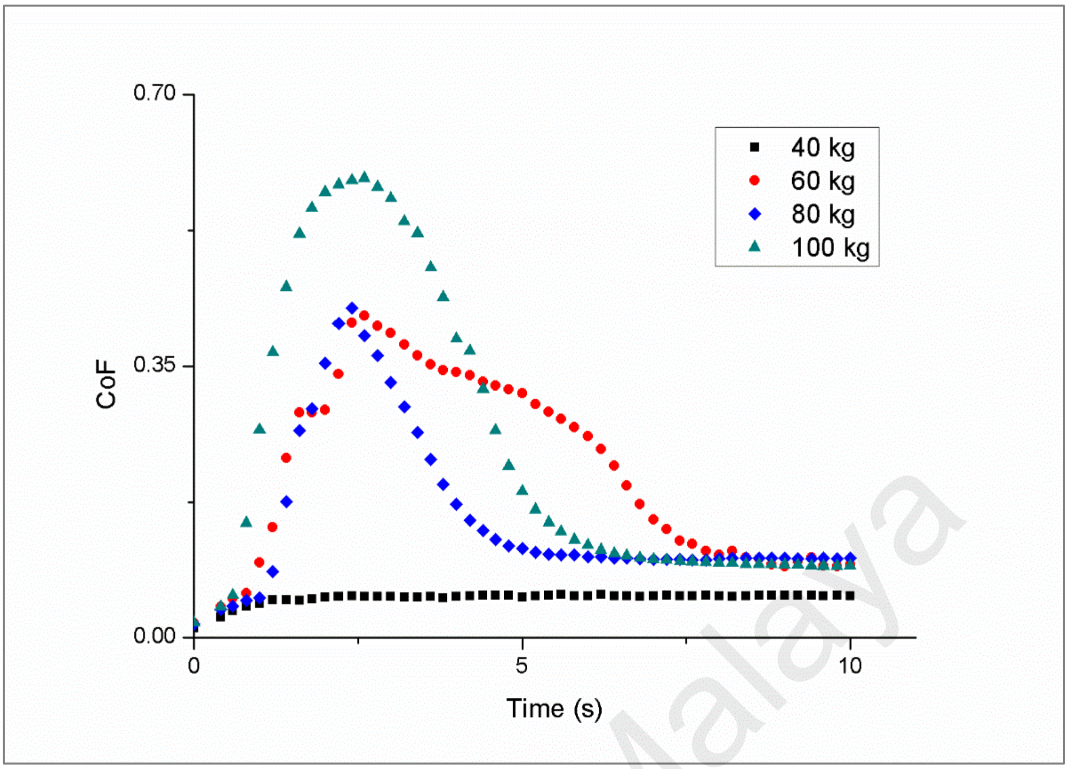


Figure 4.6: Variation of the CoF as a function of time at various loads for the NPG ester-based lubricant

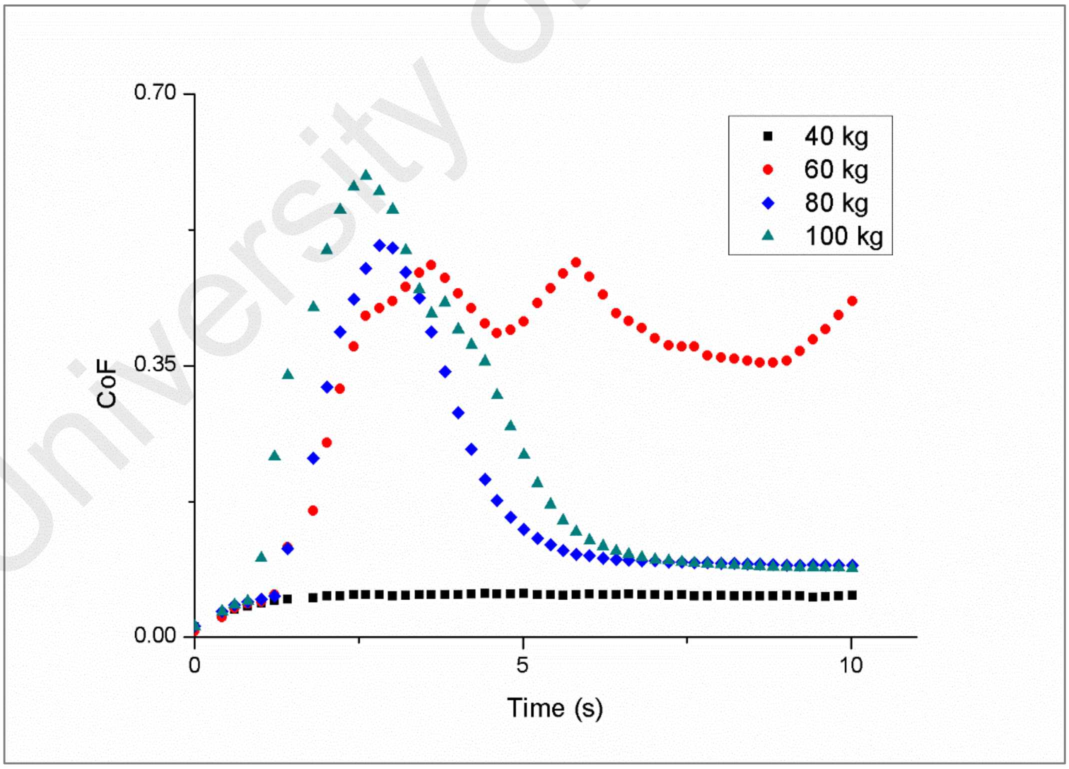


Figure 4.7: Variation of the CoF as a function of time at various loads for the TMP ester-based lubricant

It can be observed from Figure 4.6 that there is a pronounced increase in the CoF with an increase in time up to ~2.5 s, followed by a gradual decrease thereafter at an applied load of 60 kg. This is likely due to the ‘running-in’ effect, in which the lubricating film thickness is very thin such that contact begins at the peak of the asperities. This increases the CoF and wear (Zulkifli et al., 2016). However, the ‘running-in’ effect eventually reaches a steady-state condition, where the contact surfaces become smoother and the wear rate is low and stable. Based on the results, it can be deduced that the NPG and TMP ester-based lubricants have better extreme pressure characteristics compared with paraffin oil. However, the extreme pressure characteristics of these biolubricants are still inferior compared with those for CL.

Figure 4.8 shows the variation of the CoF as a function of time for the PE ester-based lubricant, where the applied load is varied at 40, 60, 80 and 100 kg. It is apparent from the results that the trend for the PE ester-based lubricant is similar to that for other polyol ester-based biolubricants since the CoF increases up to a maximum value with an increase in time, followed by a decrease beyond the maximum point. This trend occurs only for an applied load of 80 and 100 kg. Interestingly, the CoF values are significantly lower at an applied load of 40 and 60 kg. At these loads, the trend of the CoF is almost invariant with respect to time, and more importantly, the CoF values are nearly coincident. The results indicate that the lubricating film formed over the surface of the steel balls is able to withstand an applied load up to 60 kg. However, the ‘running in’ effect occurs when the applied load is increased to 80 kg. In general, the PE ester-based lubricant has the best extreme pressure characteristics among the polyol ester-based biolubricants investigated in this study.

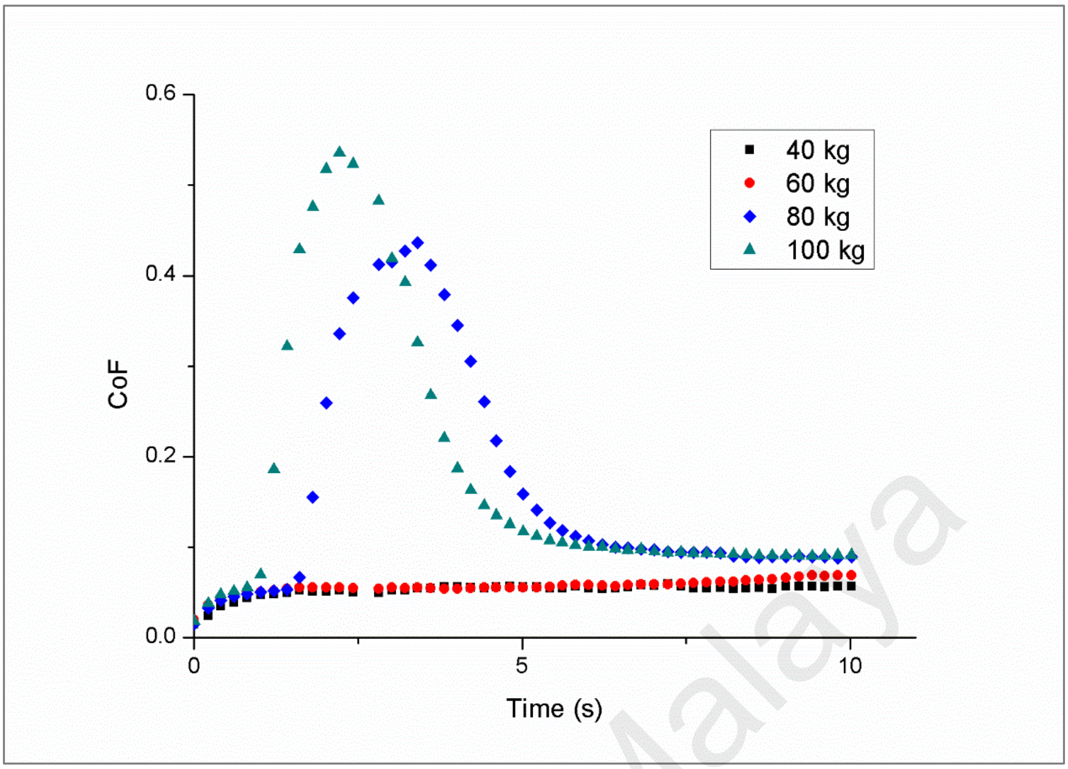


Figure 4.8: Variation of the CoF as a function of time at various loads for the PE ester-based lubricant

The correlations between the WSD and applied load for the paraffin oil, CL, and polyol ester-based lubricants investigated in this study are shown in Figure 4.9. It can be seen that there is no significant difference in the WSD between the paraffin oil and NPG ester-based lubricants at lower loads. However, as the load is increased further, there is a pronounced increase in the WSD for the paraffin oil compared to NPG and PE ester-based lubricants. The paraffin oil is only able to withstand loads up to 120 kg, and the steel balls eventually weld together at 140 kg. The variations of WSD are similar for the NPG and TMP ester-based lubricants, where both of these lubricants can sustain an applied load up to 140 kg, and the steel balls eventually weld together at 160 kg. The most interesting finding of this study is that the WSD is lowest for the PE ester-based lubricant among all polyol ester-based lubricants investigated in this study. This may be due to the higher number of carboxylate ester groups in PE ester-based lubricant, which improves the extreme pressure properties of the lubricant. There is a gradual increase in the WSD up to an applied load 60 kg, followed by an abrupt increase beyond this point until the steel balls weld together at 140 kg. In general, the WSD is lowest for the CL within the range of applied loads considered in this study, indicating that the thin lubricating film established over the surface is able to withstand higher loads compared with other lubricants. In addition, the CL has the highest ISL and WL.

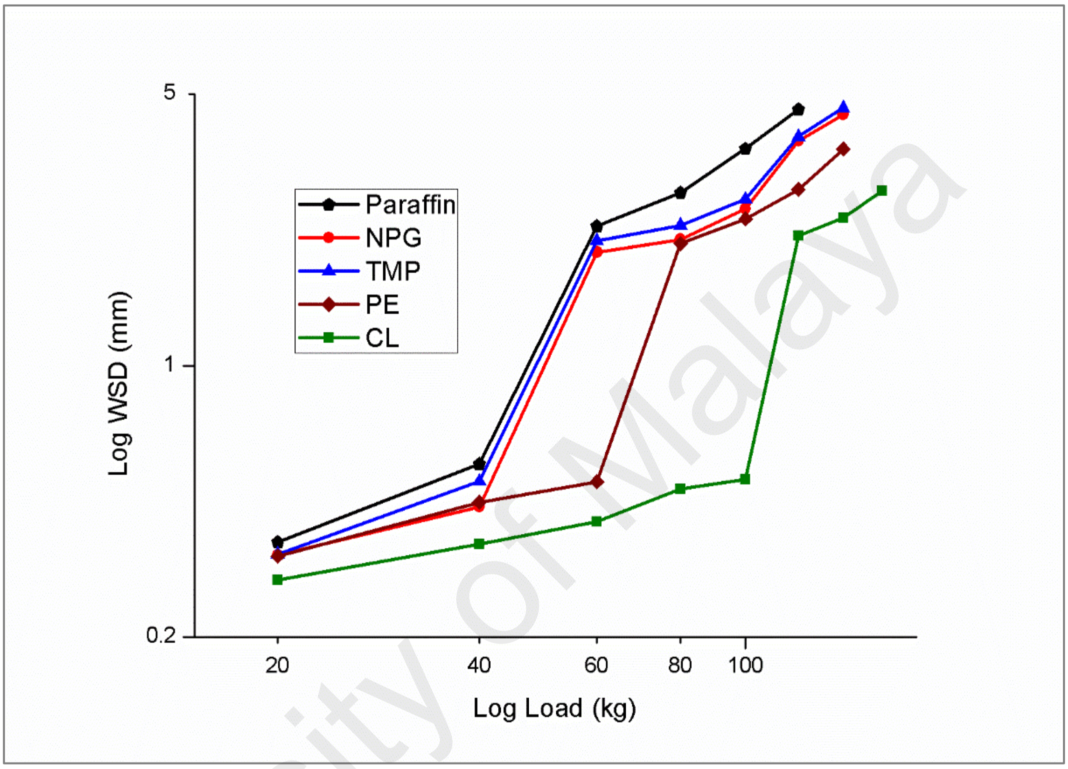


Figure 4.9: Correlations between the WSD and applied load for the lubricants (Test conditions: Duration = 10 s; Temperature = Room temperature; Rotational speed = 1770 rpm)

4.3 Friction and wear behaviours of the SCMS-added polyol ester-based biolubricants

Based on the tribological performance and surface analysis, it can be deduced that the PE ester-based lubricant has better wear prevention and surface characteristics compared with the other lubricants investigated in this work. Hence, this biolubricant is chosen for further investigation, which is to analyse the effect of SCMS addition on the friction and wear behaviours of polyol ester-based biolubricants.

4.3.1 Effect of SCMS addition on the physicochemical properties of PE ester

The physicochemical properties of PE ester-based lubricant before and after the addition of SCMS at different concentrations are presented in Table 4.4. The density of the PE ester-based lubricant at 15 °C is 0.9289 g/cm^3. The density is slightly higher after the addition of SCMS, where the values ranges from 0.9297 to 0.9299 g/cm^3. There is no significant difference in the densities of the PE ester-based lubricants, indicating that the addition of SCMS does not influence the density of the base oil.

Table 4.4: Physicochemical properties of PE ester-based lubricant with the addition of molybdenum sulphide

Lubricant sample	Density at 15°C (g/cm^3)	Kinematic viscosity (mm^2/)		VI
		40°C	100°C	
PE	0.9289	58.46	11.06	185
PE_0.025SCMS	0.9297	64.32	12.02	187
PE_0.050SCMS	0.9298	63.39	11.95	188
PE_0.075SCMS	0.9299	64.52	12.09	188
PE_0.100SCMS	0.9298	64.18	12.06	188

The kinematic viscosities at 40 and 100 °C of the PE ester-based lubricant after the addition of SCMS at four concentrations (0.025, 0.05, 0.075, and 0.1 wt%) are shown in Table 4.4. Upon the addition of SCMS, the PE ester-based lubricant exhibits higher kinematic viscosities at 40 and 100 °C. The kinematic viscosities of the PE ester-based lubricant without additive at 40 and 100 °C are 58.46 and 11.06 mm^2/s, respectively. Meanwhile, the viscosities of the SCMS-added PE ester-based lubricants at 40 and 100 °C range from 63.39 to 64.52 mm^2/s and from 11.95 to 12.09 mm^2/s, respectively.

The VIs of the PE ester-based lubricant after the addition of SCMS at four different concentrations are also shown in Table 4.4. It can be seen that there is a slight difference in the VI before and after the addition of SCMS. The VI is 185 for the PE ester-based lubricant whereas the VIs of the SCMS-added PE ester-based lubricants range from 187 to 188. The addition of the SCMS additive into the PE ester-based biolubricant may reduce the effect of temperature on the viscosity and helps the lubricant to maintain its viscosity when there are changes in temperature.

4.3.2 Effect of SCMS addition on the tribological properties of PE ester-based lubricant

Figure 4.10 shows the average CoFs of the steel balls lubricated with SCSM-added PE ester-based lubricant for four different concentrations of SCMS. The results were obtained from the four-ball wear tester. It can be observed that the CoF is reduced upon the addition of SCMS additive in the PE ester-based lubricant. The CoF is significantly reduced when the SCMS concentration is increased up to 0.075 wt%. A higher CoF is obtained when the SCMS concentration is further increased to 0.1 wt%. The highest improvement in friction behaviour is obtained when 0.075 wt% of SCMS is added into the PE ester-based lubricant, where the CoF is reduced by 20% compared to that for the pure PE ester-based lubricant. Hence, the CoF for steel-to-steel contact in the four-ball configuration can be reduced by adding SCMS into the PE ester-based lubricant.

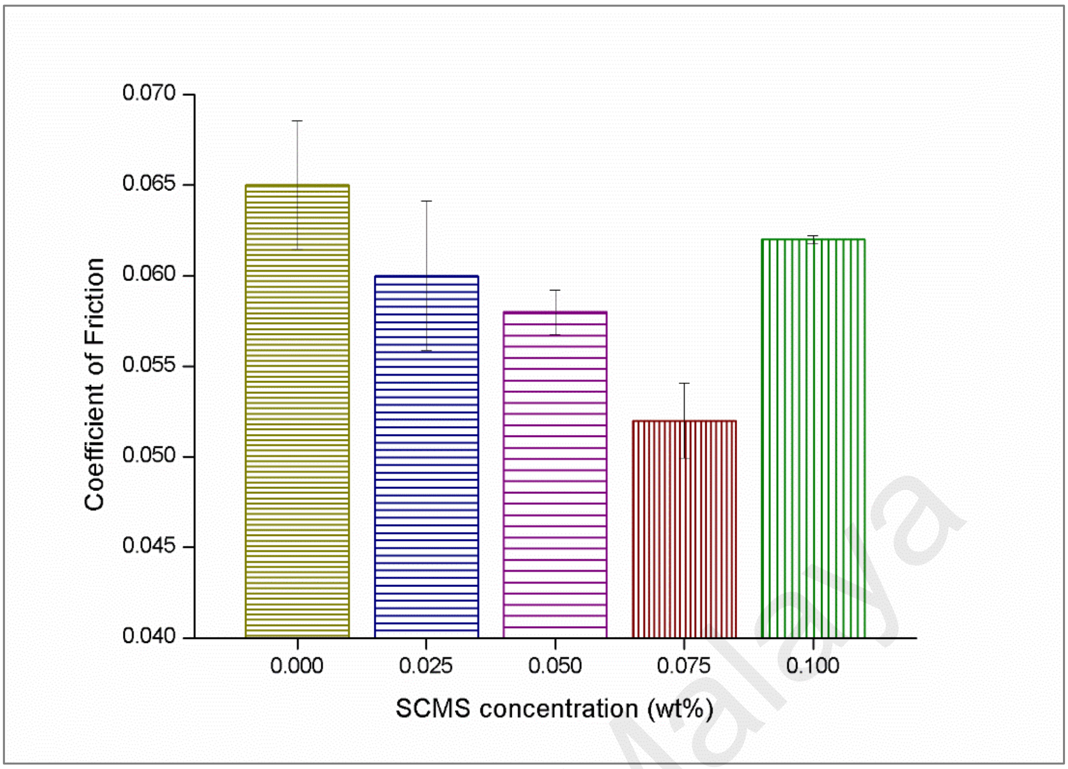


Figure 4.10: CoFs of PE ester-based lubricant with different SCMS concentrations (Test conditions: Load = 40 kg; Duration = 1 h; Temperature = 75°C; Rotational speed = 1200 rpm)

The wear scars on the steel balls were also measured and the results are shown in Figure 4.11. It can be seen that the addition of SCMS from 0.025 to 0.075 wt% reduces the WSD on the steel balls compared to that for pure PE ester-based lubricant. The addition of 0.075 wt% of SCMS into the PE ester-based lubricant results in the smallest WSD, where the WSD is reduced by only 1.4% compared to that for pure PE ester-based biolubricant. However, the WSD increases by 3% when the SCMS concentration is increased to 0.1 wt%.

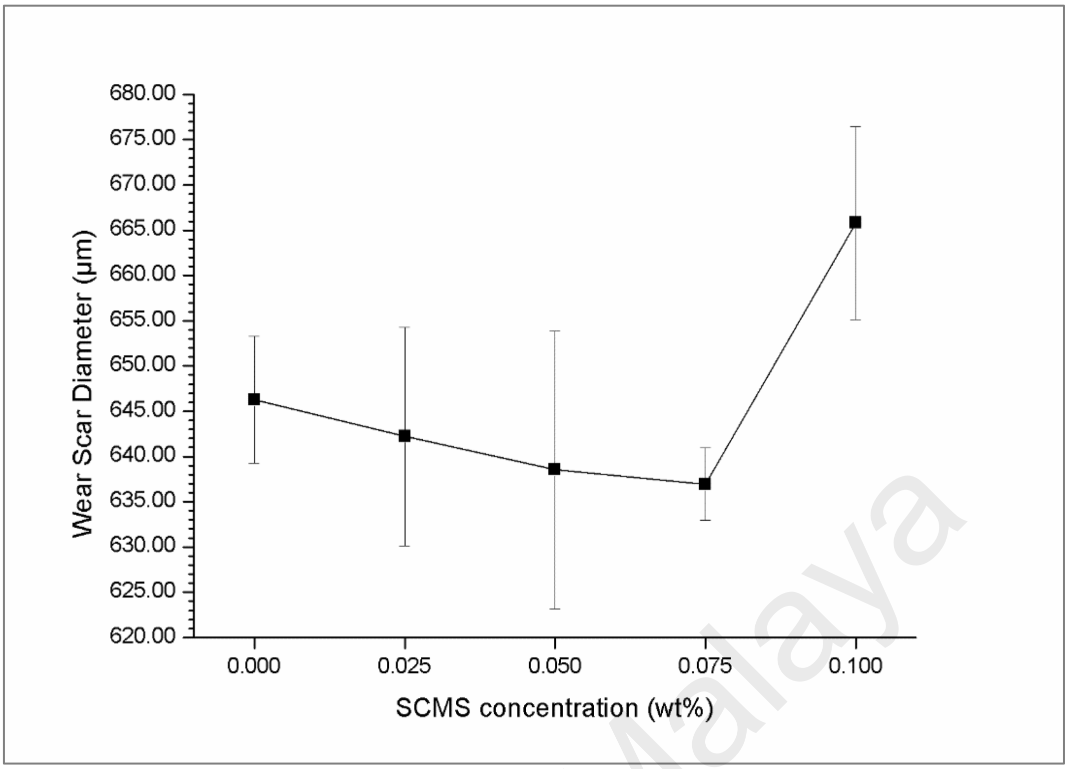


Figure 4.11: WSDs of PE ester-based lubricant with different SCMS concentrations (Test conditions: Load = 40 kg; Duration = 1 h; Temperature = 75°C; Rotational speed = 1200 rpm)

Figure 4.12 shows the variation of CoF as a function of time of the SCMS-added PE ester-based lubricants. In general, the trends for all samples are similar to that for pure PE ester-based lubricant, as shown in Figure 4.3. The CoF increases to a maximum value at the beginning of the test, which is due to the ‘running-in’ effect. The CoF then decreases gradually with an increase in time because of the smoother metal surfaces. For the PE ester-based lubricant added with 0.1 wt% of SCMS, the CoF is highest at the beginning of the test compared to that for other concentrations. However, the CoF decreases towards the end of the test such that the value is significantly lower compared to the other SCMS-added PE ester-based lubricants. Thus, the addition of 0.1 wt% of SCMS may have caused the high CoF and WSD for the lubricant sample.

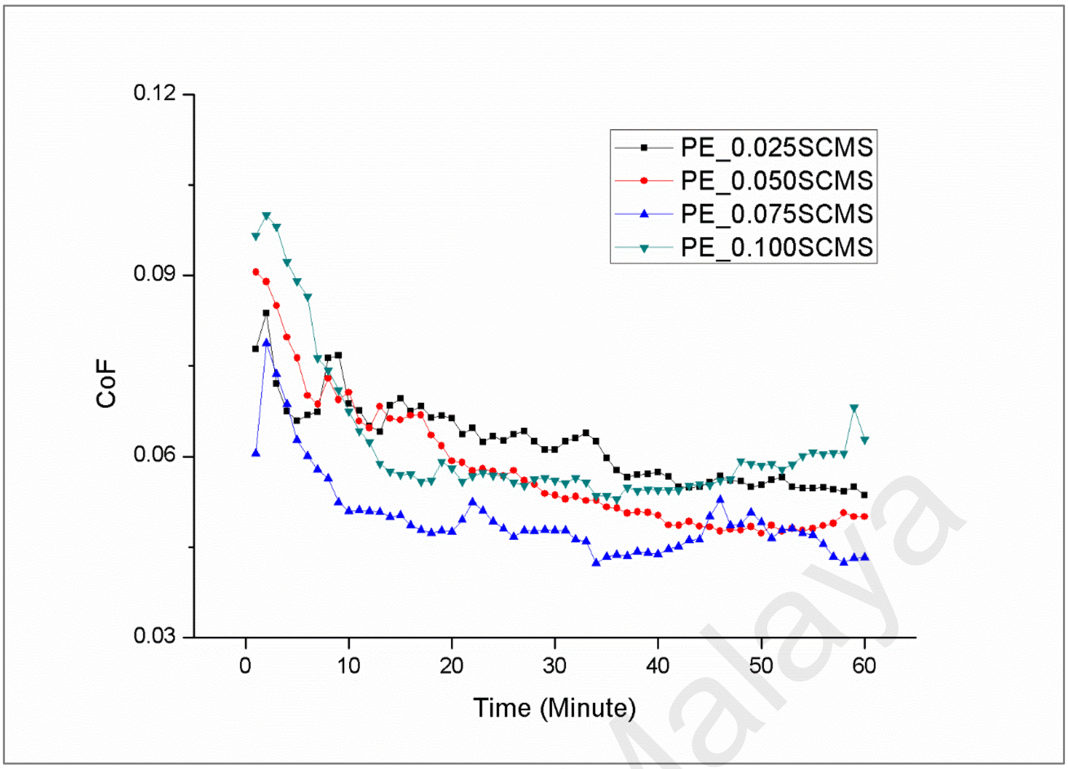


Figure 4.12: Variation of CoF with time for the SCMS-added PE ester-based lubricants (Test conditions: Load = 40 kg; Duration = 1 h; Temperature = 75°C; Rotational speed = 1200 rpm)

4.3.3 Surface analysis

Table 4.5 shows the SEM images of the wear scar on the steel balls lubricated with different lubricant samples, along with the EDS spectra. Different features can be observed on the balls lubricated with lubricants with and without the SCMS additive. It can be seen from Table 4.5 (a) that the surface of the wear scar appears rougher, with larger grooves formed on the steel balls lubricated with the pure PE ester-based lubricant. In contrast, the surface of the wear scar appears smoother for the steel balls lubricated with the PE ester-based lubricant was added with 0.025, 0.05, 0.075, and 0.1 wt% of SCMS, as shown in Table 4.5 (b)-(e). The grooves on the worn surfaces are also narrower compared to that in Table 4.5 (a). This indicates that the SCMS additive can improve the condition of worn surface of the steel balls. The additives in the lubricant may be deposited on the worn surfaces, which reduce the asperity-to-asperity contact and protect the surface of the steel balls.

The presence of additives on the worn surfaces was confirmed by the EDS analysis. The weight percentages of the elements and the EDS spectra of the worn surfaces are also shown in Table 4.5. The EDS spectra show the presence of molybdenum and sulphur for the steel balls lubricated with the SCMS-added PE ester-based lubricants. Even though the signal intensities of Mo and S are weaker compared to that for Fe, the intensities still prove the existence of SCMS additive on the worn surfaces. Based on the results, molybdenum and sulphur elements are present on the worn surfaces of the steel balls, which provide protection to the surfaces.

Based on the friction and wear behaviour of the lubricant samples as well as the results of the surface analysis, it can be deduced that there are some possible mechanisms that lead to the reduction in friction and wear of the steel balls due to the addition of SCMS in the lubricants. During the friction and wear tests, the SCMS additive is able to enter the space between the steel balls and the additive likely imbeds the grooves and scars formed on the worn surfaces. The SCMS additive has self-repairing or mending effect, which leads to good tribological properties. Hence, the improvement in the friction and wear characteristics is attributed to the deposition of SCMS additive on the surfaces. In contrast, the poor friction and wear properties obtained from the addition of 0.1 wt% of SCMS may be due to the disturbance caused by excessive amounts of additive after the grooves are sufficiently filled (Kun Hong Hu et al., 2011).

Table 4.5: SEM images of the worn surface and EDS spectra of steel balls lubricated with: (a) pure PE ester-based lubricant and SCMS-added PE ester-based lubricants at concentration: (b) 0.025 wt%, (c) 0.050 wt%, (d) 0.075 wt%, and (e) 0.100 wt%

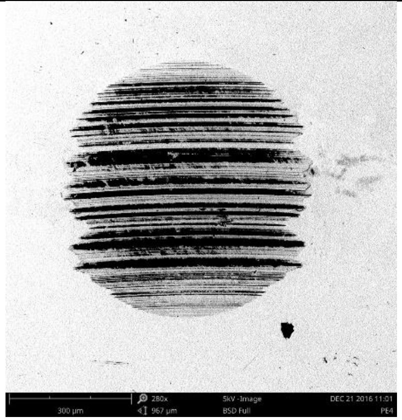
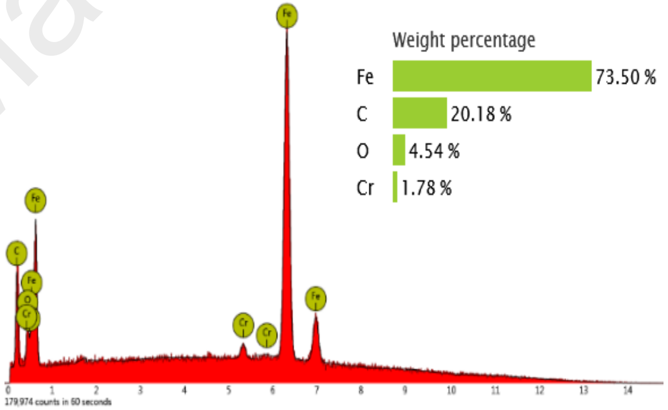
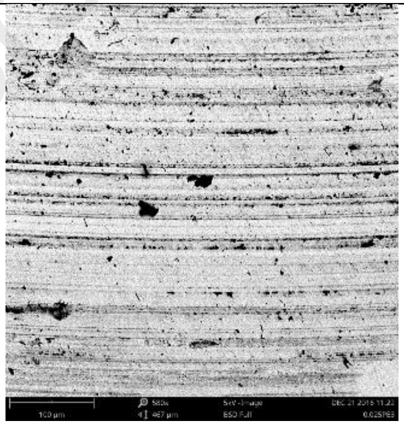
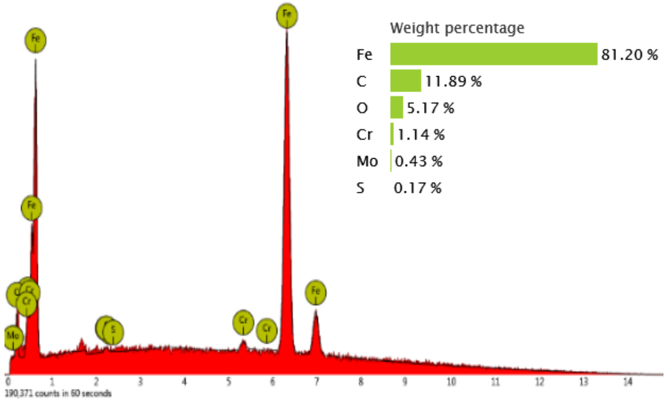
Lubricant sample	**SEM image (magnification: 280x)**	**SEM image (magnification: 580x)**	**EDS spectra (y-axis: Number of counts; x-axis: Energy)**
a) PE			
b) PE_0.025SCMS			

Table 4.5 continued

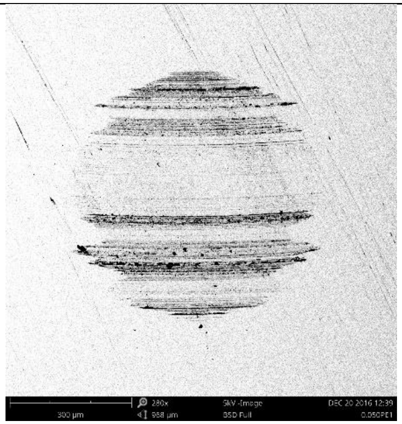
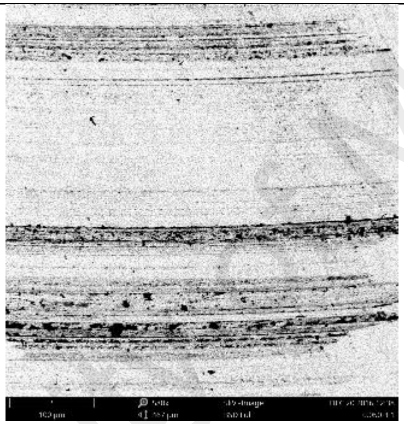
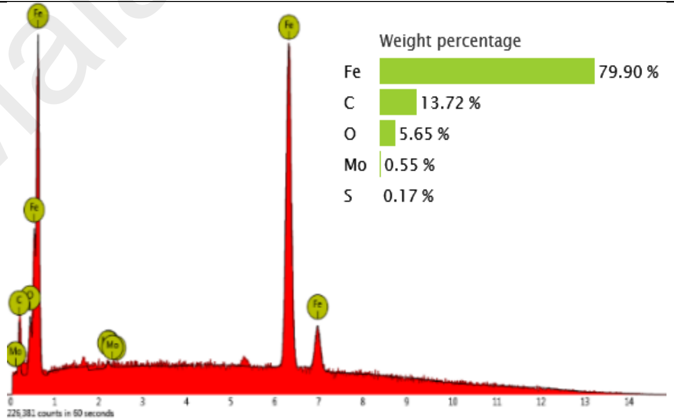
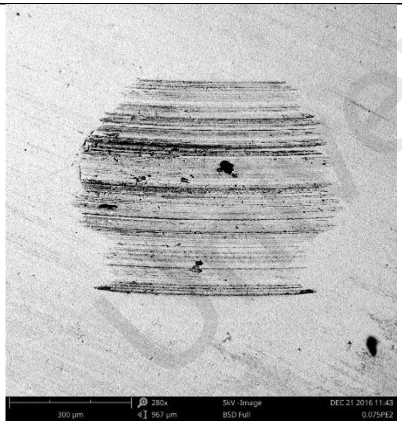
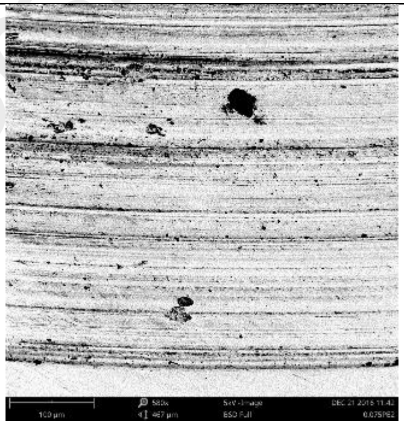
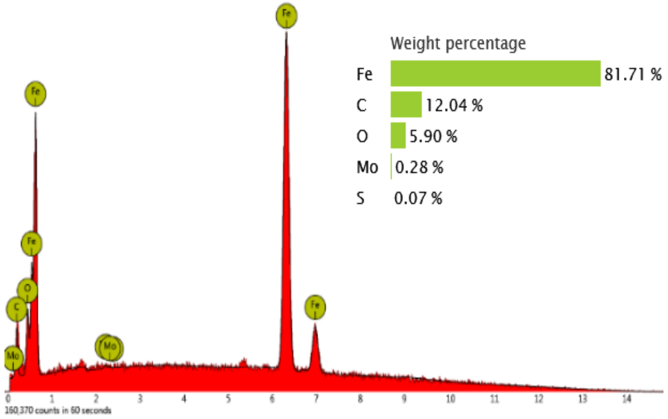
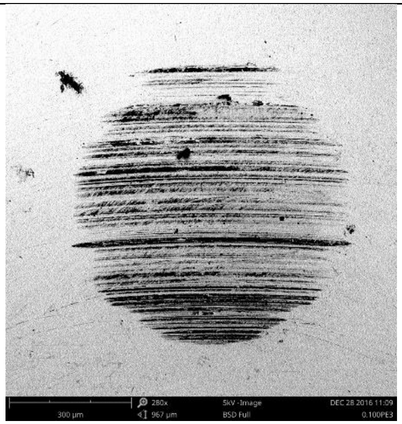
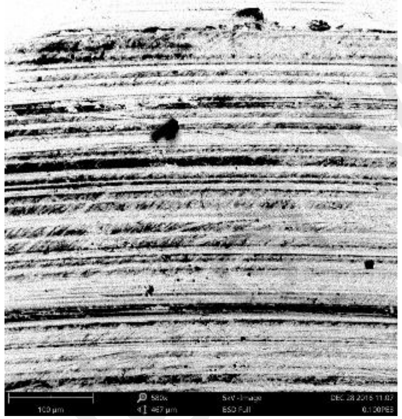
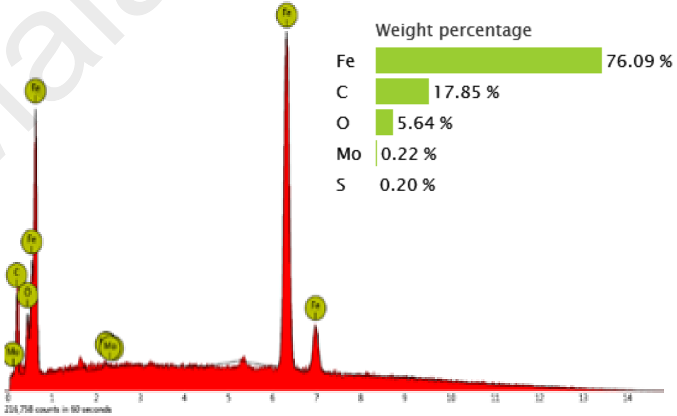
Lubricant sample	SEM image (magnification: 280x)	SEM image (magnification: 580x)	EDS spectra
c) PE_0.050SCMS			
d) PE_0.075SCMS			

Table 4.5 continued

Lubricant sample	**SEM image (magnification: 280x)**	**SEM image (magnification: 580x)**	**EDS spectra**
e) PE_0.100SCMS			

4.3.4 Extreme pressure characteristics

The ISL, WL, CoF and WSD of the PE ester-based lubricant added with 0.075 wt% of SCMS additive at an applied load of 100 kg are presented in Table 4.6. The ISL and WL of the SCMS-added PE ester-based lubricant are 60 and 160 kg, respectively. Even though the ISL and WL are similar to those for the to the pure PE ester-based lubricant, the addition of 0.075 wt% of SCMS in the PE ester-based lubricant results in lower CoF and WSD values at an applied load at 100 kg compared to those for the pure PE ester-based lubricant (Table 4.3). The CoF and WSD reduced by 10.9 and 13%, respectively.

Table 4.6: ISL, WL, CoF, and WSD of the SCMS-added PE ester-based lubricant (SCMS concentration: 0.075 wt%)(Test conditions: Duration = 10 s; Temperature = Room temperature; Rotational speed = 1770 rpm)

Lubricant sample	ISL (kg)	WL (kg)	CoF at 100 kg	WSD at 100 kg (mm)
PE_0.075SCMS	60	160	0.164	2.08

Figure 4.13 shows the variation of the CoF as a function of time for the PE ester-based lubricant containing 0.075 wt% of SCMS additive. The applied load is varied at 40, 60, 80, and 100 kg. In general, the trends are identical to that for the pure PE ester-based lubricant (Figure 4.8). The CoFs are relatively lower at an applied load of 40 and 60 kg compared to those at an applied load of 80 and 100 kg, where the CoFs increase to the maximum values as time increases, followed by a decrease beyond the maximum values. However, the CoFs decrease after the addition of SCMS additive in PE ester-based lubricant. At an applied load of 100 kg, the maximum CoF of the SCMS-added PE ester-based lubricant is 0.46 (Figure 4.13) whereas the maximum CoF of the pure PE ester-based lubricant is at 0.54 (Figure 4.8).

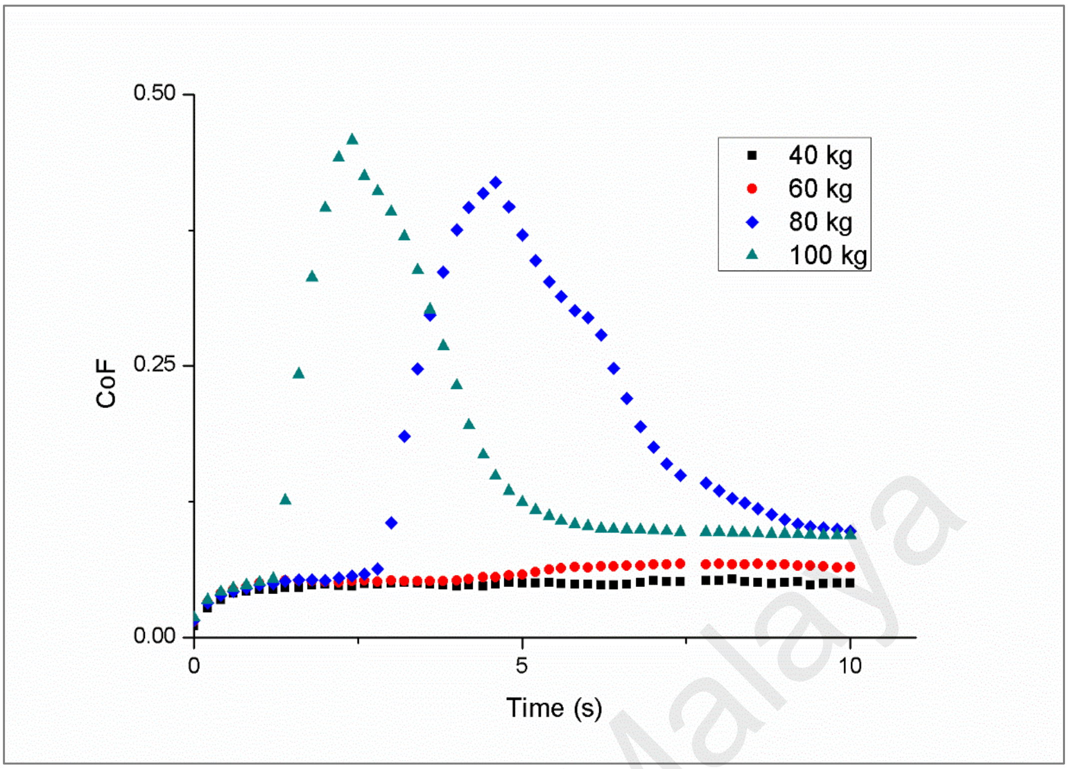


Figure 4.13: Variation of the CoF as a function of time at various loads for the SCMS-added PE ester-based lubricant (Test conditions: Duration = 10 s; Temperature = Room temperature; Rotational speed = 1770 rpm)

Figure 4.14 shows the correlation between the WSD and applied load for the PE ester-based lubricant containing 0.075 wt% SCMS additive. It can be seen that the WSD is smaller for the SCMS-added PE ester-based lubricant compared to that for the pure PE ester-based lubricant. There is no significant difference in the WSD at lower loads, but the WSD reduces for the SCSM-added PE ester-based lubricant as the load increases. This indicates that the SCMS additive enhances the extreme pressure performance of the polyol ester-based biolubricant by reducing friction and wear, especially at higher loads. Indeed, such improvement in the extreme pressure performance upon the addition of molybdenum sulphide in various base oils were reported by other researchers (Gulzar et al., 2015; V Srinivas et al., 2014; V. Srinivas et al., 2017).

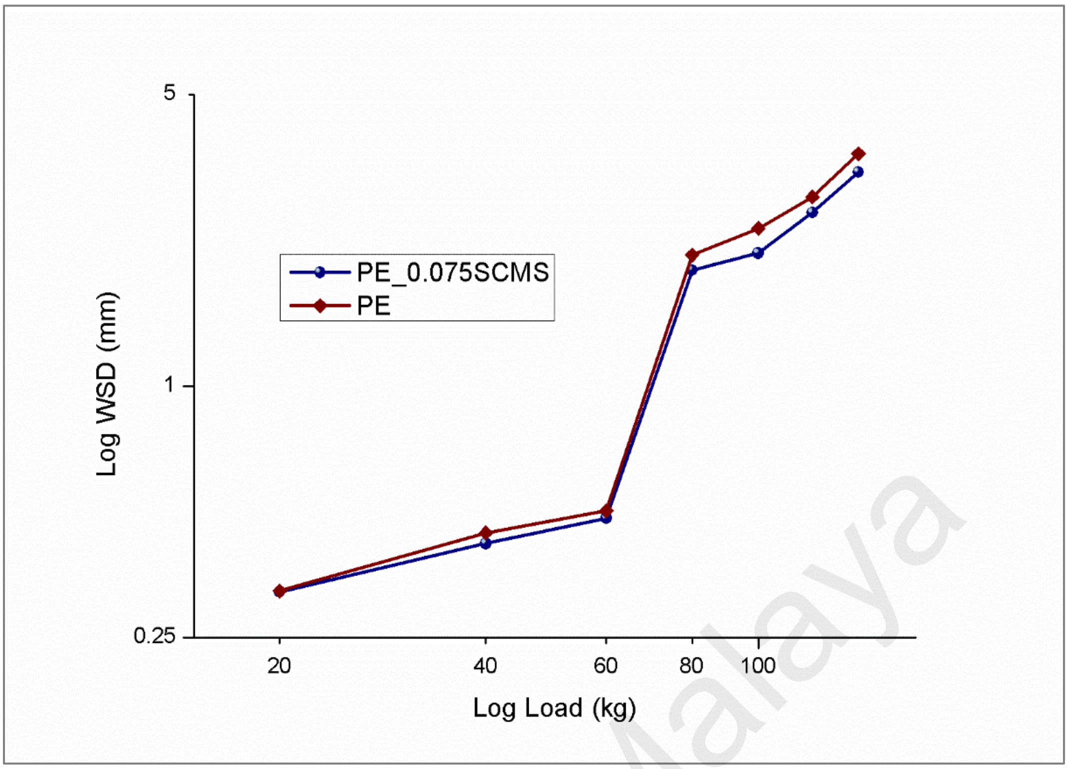


Figure 4.14: Correlation between the WSD and applied load for the SCMS-added PE ester-based lubricant (Test conditions: Duration = 10 s; Temperature = Room temperature; Rotational speed = 1770 rpm)

4.4 Temperature effect on the tribological properties of lubricants

4.4.1 Coefficient of friction and wear scar diameter

Figure 4.15 shows the CoFs for the paraffin oil, CL, pure PE ester-based lubricant, and SCMS-added PE ester-based lubricant at different temperatures. It can be seen that CL has the highest CoF and the CoF increases as the temperature increases. This is likely due to the decrease in the viscosity over a wide range of temperatures. As the viscosity decreases, the oil layer becomes thinner between the metal-to-metal surface and thus, the CoF increases (Singh et al., 2017). Paraffin oil also shows the same trend as the CL, where the CoF increases with an increase in the oil temperature. Meanwhile, the CoFs are lower for the PE ester-based lubricant and the trend differs from that for paraffin oil and CL. It can be observed that the CoF decreases as the oil temperature increases. The fatty acid chains in the polyol ester-based biolubricant reduces friction by forming fatty acid layers on the contact surfaces. It can be seen that the CoF is the lowest for the PE ester-based lubricant containing 0.075 wt% of SCMS additive. It can be deduced that the CoF can be further decreased by adding SCMS into the PE ester-based lubricant. In addition, the trend is similar to that for the pure PE ester-based lubricant since the CoF decreases with an increase in temperature.

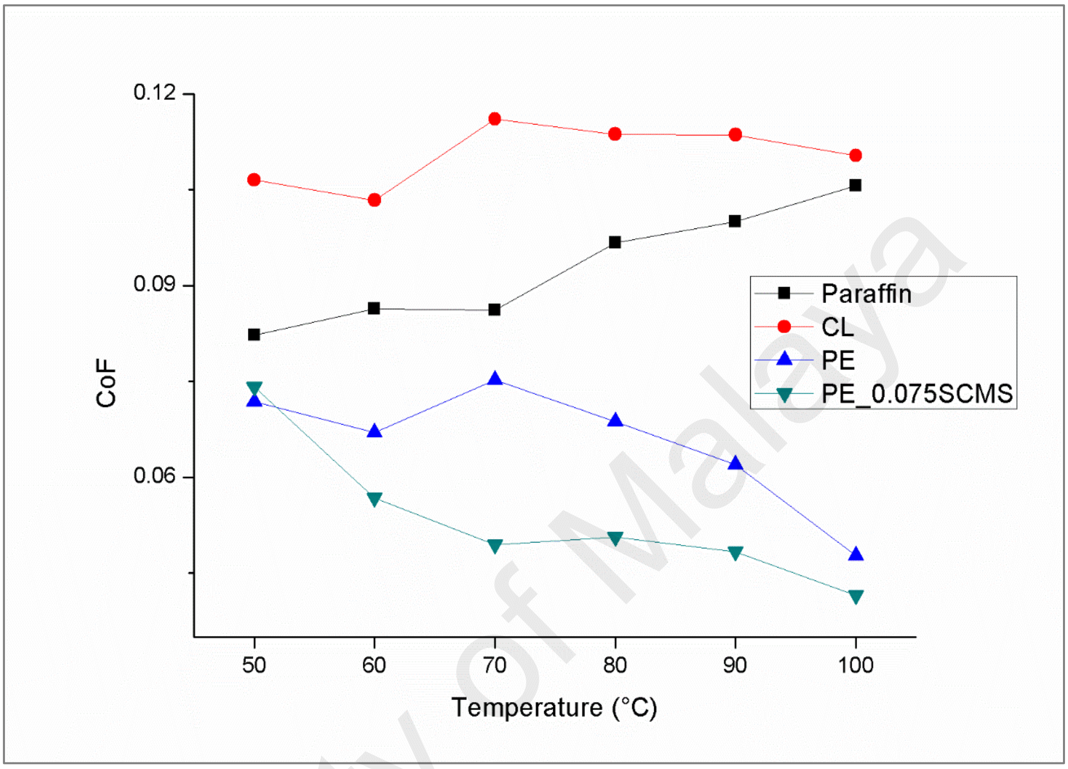


Figure 4.15: Effect of temperature on the CoF for the paraffin oil, CL, pure PE ester-based lubricant, and SCMS-added PE ester-based lubricant (Test conditions: Load = 40 kg; Duration = 1 h; Rotational speed = 1200 rpm)

Figure 4.16 shows the effect of temperature on the WSD for the paraffin oil, CL, pure PE ester-based lubricant, and SCMS-added PE ester-based lubricant. It can be seen that the CL has the smallest WSD and WSD is most stable at different temperatures. In contrast, paraffin oil has the largest WSD and the scar formed on the metal surface increases as the temperature increases. The PE ester-based lubricant has smaller WSD compared with that for paraffin oil; however, the size of the wear scar is still larger than that for CL. Based on the results, the WSD decreases as the oil temperature increases. The same trend is observed for the SCMS-added PE ester-based lubricant. The addition of 0.075 wt% of SCMS into PE ester-based lubricant reduces the size of the wear scar formed on the steel balls. Indeed, the WSD is smaller for the SCMS-added PE ester-based lubricant compared to that for the pure PE ester-based lubricant.

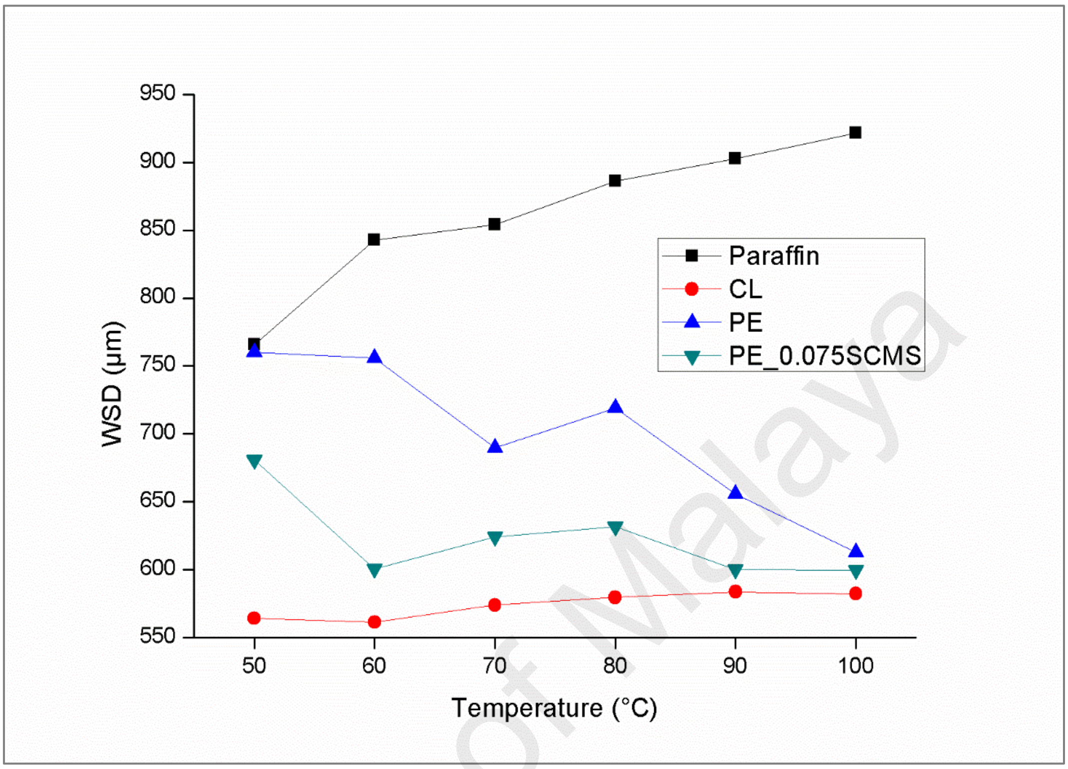


Figure 4.16: Effect of temperature on the WSD for the paraffin oil, CL, pure PE ester-based lubricant, and SCMS-added PE ester-based lubricant (Test conditions: Load = 40 kg; Duration = 1 h; Temperature = 75°C; Rotational speed = 1200 rpm)

Figure 4.17 shows the variation of CoF as a function of time at different temperatures for the paraffin oil. At 50 °C, the CoF is quite stable with an almost constant trend. However, as the temperature increases, there is a sudden increase in the CoF at the beginning of the test, followed by a decrease after the maximum value. The variation of CoF as a function of time for the CL is shown in Figure 4.18. The trends of the CoF are similar at all tested temperatures, where the CoF gradually increases and then eventually stabilizes over time. The CL forms a lubricating film at the beginning of the test, which protects the contact surfaces against wear caused by the high temperature. The wear prevention characteristics of the CL are due to the presence of high-performance additives in the CL such as zinc, sulphur, phosphorus and calcium elements, which is proven by EDS analysis.

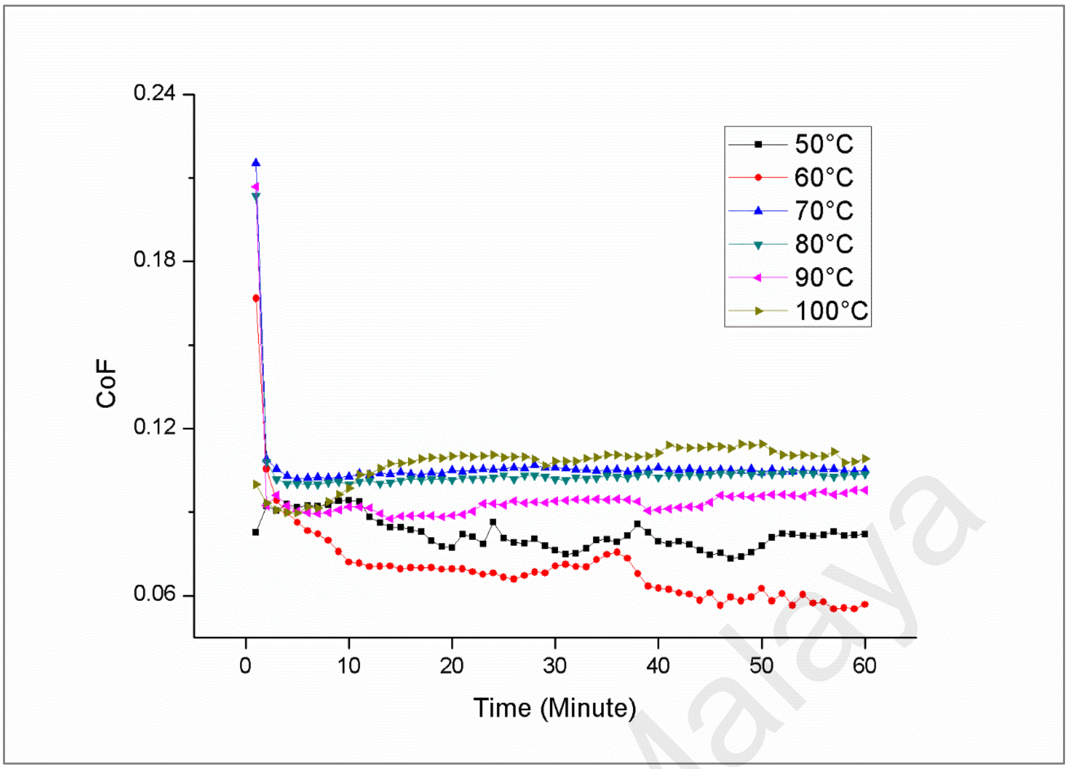


Figure 4.17: Variation of the CoF as a function of time at various temperatures for the paraffin oil

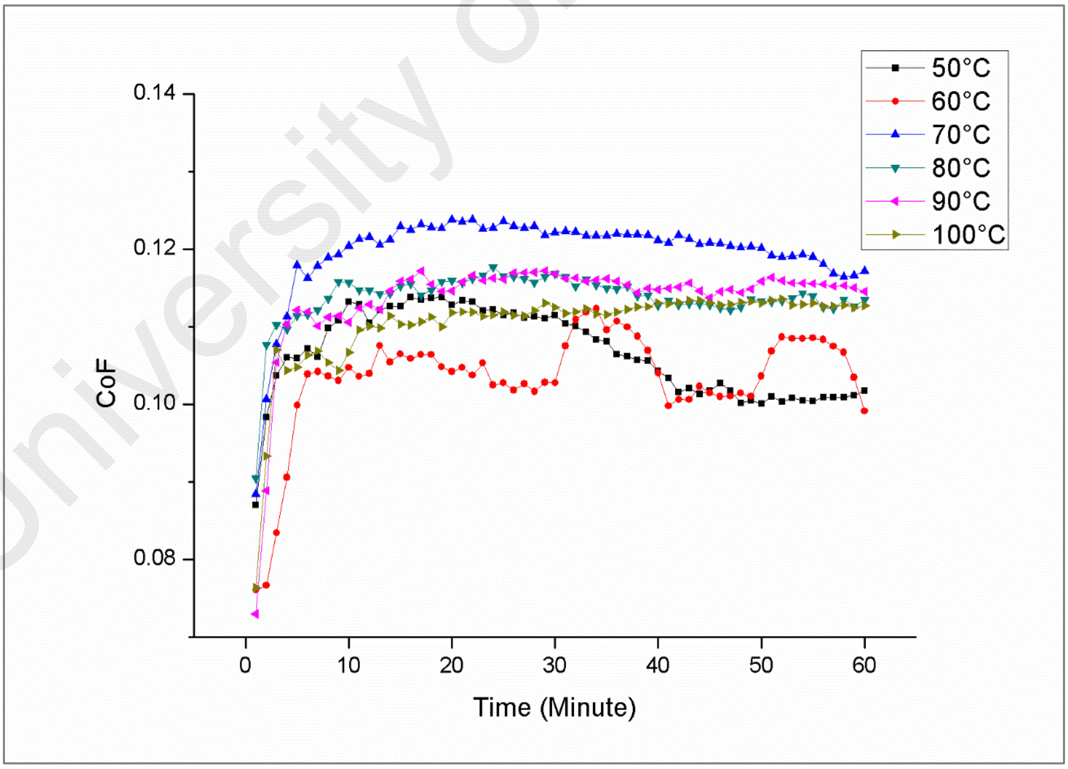


Figure 4.18: Variation of the CoF as a function of time at various temperatures for the CL

Figure 4.19 shows the variation of CoF as a function of time for the pure PE ester-based lubricant. It is apparent that there are fluctuations in the CoF compared to those for paraffin oil and CL at all oil temperatures. This instability may be due to the failure of the lubricating film in protecting the surfaces of the steel balls as well as asperities on the surfaces. Figure 4.20 shows the variation of the CoF as a function of time for the PE ester-based lubricant containing 0.075 wt% of SCMS additive at various tested temperatures. The trend of the SCMS-added PE ester-based lubricant is almost similar to that for the pure PE ester-based lubricant. However, it can be observed that the CoF is more stable with the addition of SCMS additive in the polyol ester-based biolubricant. This may be due to the chemical layer formed by the sulphides, which protects the contacting surfaces by entering the asperities and reducing the friction.

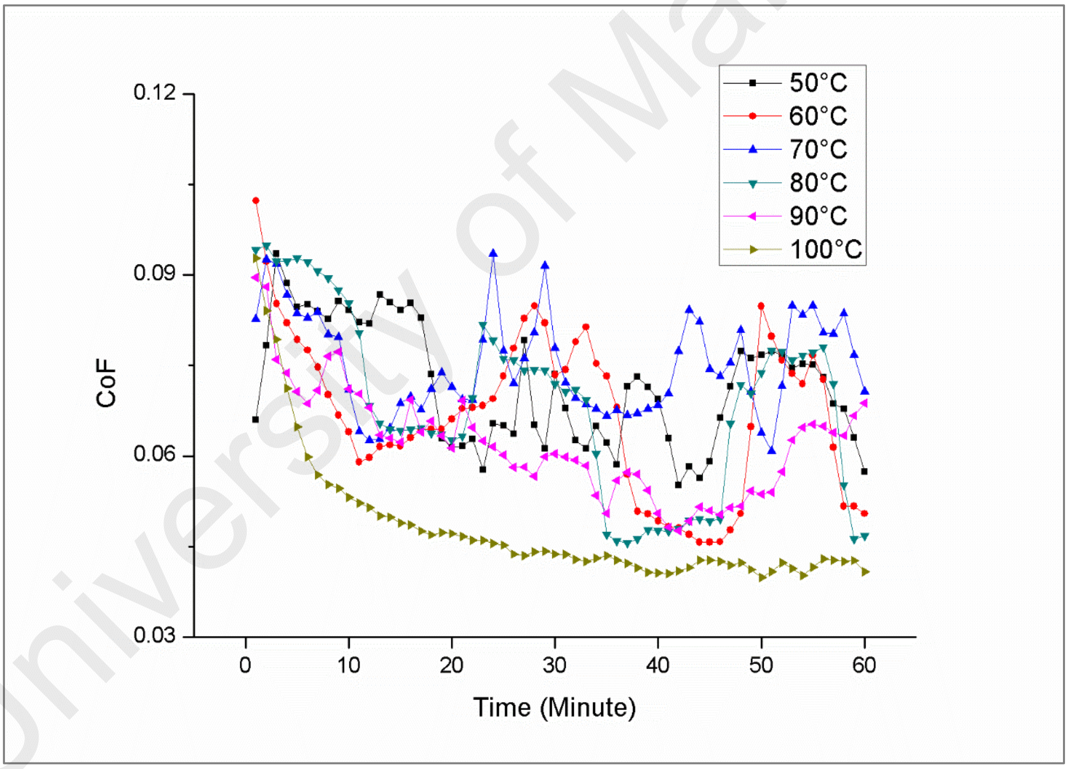


Figure 4.19: Variation of the CoF as a function of time at various temperatures for the PE ester-based lubricant

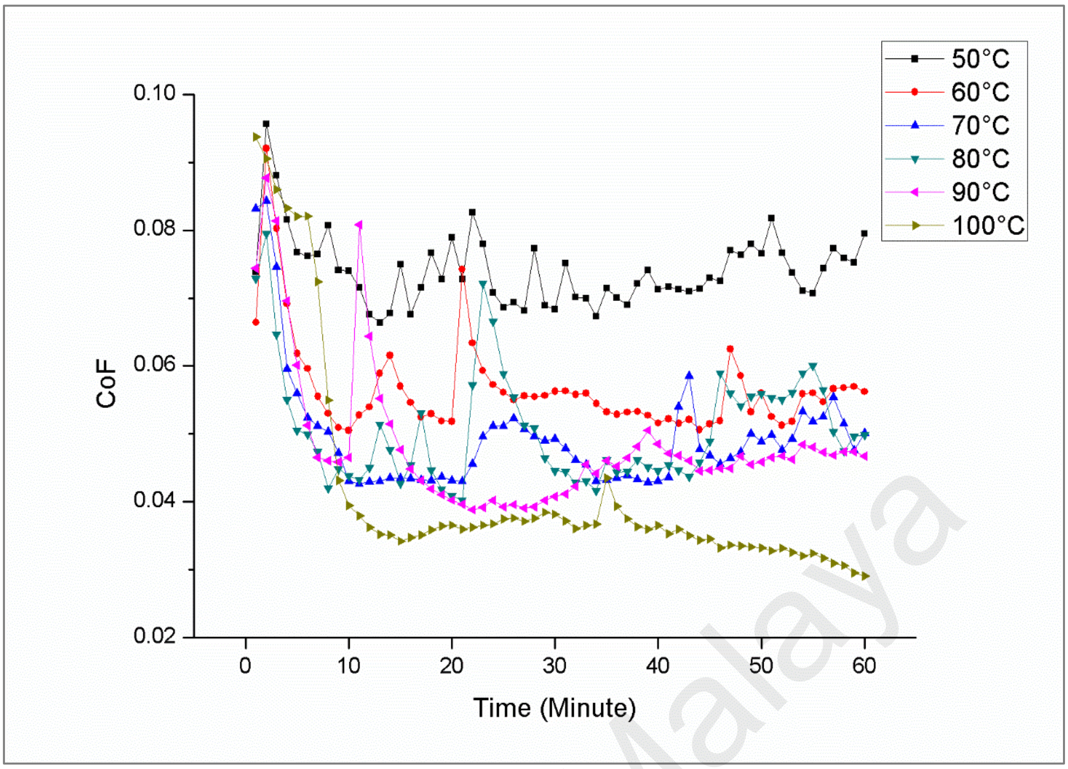


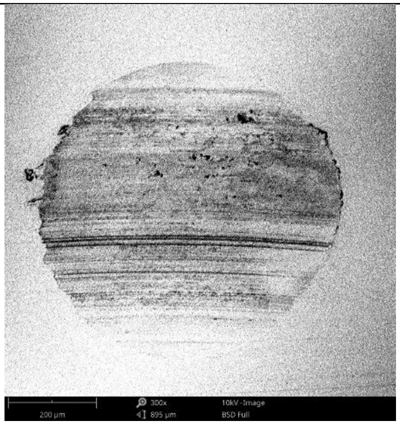
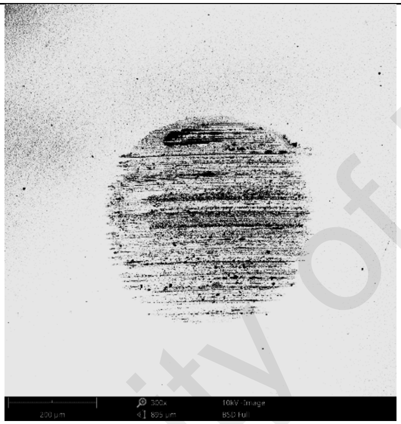
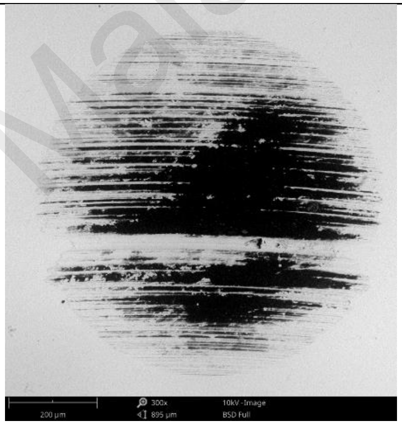
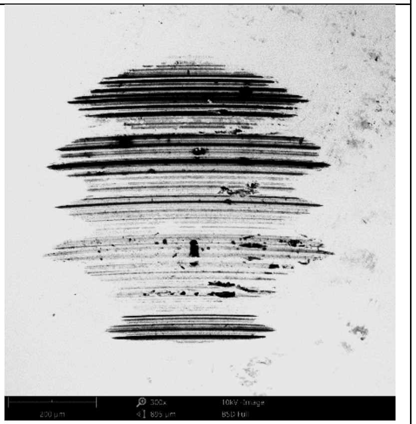
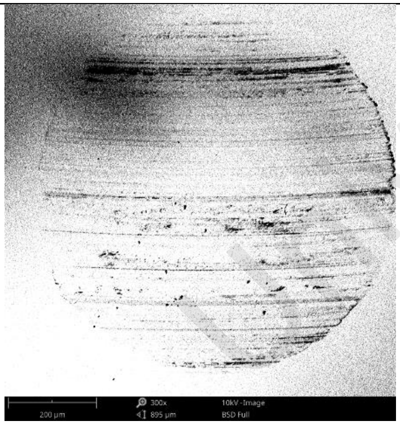
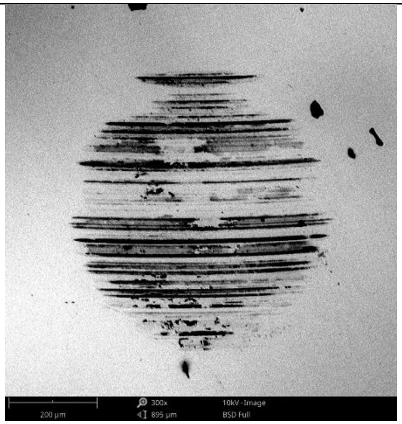
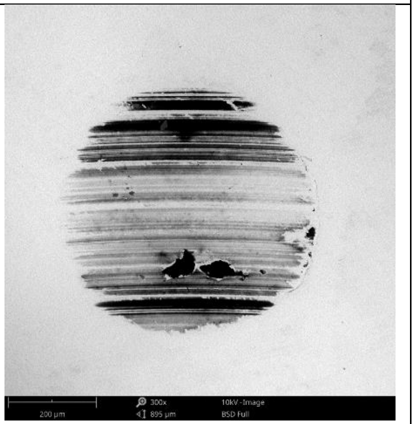
Figure 4.20: Variation of the CoF as a function of time at various temperatures for the SCMS-added PE ester-based lubricant

4.4.2 Surface analysis

Table 4.7 shows the SEM images of the wear scar formed on the steel balls lubricated with various oil samples at 50 and 100°C. The wear scar is largest for the paraffin oil, as shown in Table 4.7 (a). It can be seen that the worn surface is smoother compared to the polyol ester-based biolubricant, which conforms to the results of Zulkifli et al. (2014). It can be observed from Table 4.7 (b) that the wear scar is smallest for the steel balls lubricated with CL at both 50 and 100 °C. The presence of various additives in the lubricant formulation contributes to the surface protection even at elevated temperatures. At high temperature (100 °C), there are more scratches on the worn surface lubricated with CL. For steel balls lubricated with the pure PE ester-based lubricant, there are irregular edges observed on the wear scar, as shown in Table 4.7 (c). The severe wear at the centre of the worn surfaces may be due to the failure of the lubricant to provide sufficient lubrication at the high-pressure contact area (Zulkifli et al., 2014). The worn surface appears rougher, judging from the wide and deep grooves formed on the scar.

Meanwhile, the wear is rather mild for the steel balls lubricated with PE ester-based lubricant containing 0.075 wt% of SCMS, as shown in Table 4.7 (d). There are fewer scratches on the worn surface in the sliding directions compared to the surface lubricated with the pure PE ester-based lubricant. In addition, the darker regions on the worn surfaces in for Table 4.7 (c) and Table 4.7 (d) represent the corrosive product, which is due to oxidation of the PE ester-based lubricant.

Table 4.7: SEM images of the worn surface at 50 and 100 °C for steel balls lubricated with (a) paraffin oil, (b) CL, (c) pure PE ester-based lubricant, and (d) PE ester-based lubricant with 0.075 wt% of SCMS additive

Lubricant sample	a) Paraffin	b) CL	c) PE	d) PE_0.075SCMS
SEM image at 50°C				
SEM image at 100°C				

4.5 Summary

The key findings of this research are summarized in this section. Based on the results presented in Section 4.1, the kinematic viscosities and VIs of polyol ester-based biolubricants are higher compared to those for paraffin oil. In general, the kinematic viscosities increase with an increase in the number of acyl groups (PE > TMP > NPG). The polyol ester-based biolubricants have lower CoFs compared to paraffin oil and CL due to their ester functionality. The CoFs are reduced by 20, 13, and 11% for the NPG, TMP, and PE ester-based lubricants, relative to that for paraffin oil. Meanwhile, the WSDs are significantly smaller for the polyol ester-based biolubricants compared with that for paraffin oil. The WSDs reduce by 20.3, 18.2, and 17.4% for the PE, TMP, and NPG ester-based lubricants, respectively. The SEM images revealed that there are irregular edges in the wear scars for the steel balls lubricated with polyol ester-based lubricants. The wear scar of the steel balls lubricated with the PE ester-based lubricant has fewer grooves compared to those lubricated with the NPG and TMP ester-based lubricants. Based on the results of the extreme pressure tests, it can be deduced that the PE ester-based lubricant has the best performance compared to other polyol ester-based lubricants. The ISL and WL for the PE ester-based lubricant are 60 and 160 kg, respectively, and the WSD is the lowest at all applied loads.

Based on the results presented in Section 4.2, there is no significant change in the density of PE ester-based lubricant after the addition of SCMS at four different concentrations (0.025, 0.05, 0.075, and 0.1 wt%). Meanwhile, the addition of SCMS into the PE ester-based lubricant results in slightly higher kinematic viscosities. There is also a small increment in the VI (up to 188) upon the addition of SCMS additive. In terms of the tribological performance, the addition of SCMS additive reduces the CoF and WSD of the PE ester-based lubricant. The CoF is lowest when 0.075 wt% of SCMS is added into the PE ester-based lubricant, where the CoF is reduced by 20% compared to that for the pure PE ester-based lubricant. In addition, the WSD is successfully reduced by 1.4% upon the addition of 0.075 wt% of SCMS in the PE ester-based lubricant. Based on the SEM images, the surfaces of the steel balls lubricated with the SCMS-added PE ester-based lubricant are smoother and the grooves are narrower compared to those lubricated with pure PE ester-based lubricant. The presence of molybdenum and sulphur in PE ester-based lubricant is proven by the EDS analysis. The elements are attached on the surfaces of the steel balls, which give protection to the worn surfaces. The additives are likely to enter the space between steel balls and attach to the worn surfaces. The tribological performance is improved due to the deposition of SCMS additive on the steel ball surfaces. In terms of the extreme pressure properties, the addition of 0.075 wt% of SCMS reduces the CoF and WSD at an applied load of 100 kg by 10.9 and 13%, respectively, compared to those for a pure PE ester-based lubricant. The ISL and WL are 60 and 160 kg, respectively.

The effect of temperature on the tribological properties of the lubricant samples is discussed in Section 4.3. The CoFs increase with an increase in temperature for the paraffin oil and CL. In contrast, the CoF decreases as the temperature increases for the PE ester-based lubricant. The lowest CoF obtained when 0.075 wt% of SCMS is added into the PE ester-based lubricant. In addition, the WSD is smaller for the PE ester-based lubricant shows compared to that for the paraffin oil and the WSD is further reduced with the addition of 0.075 wt% of SCMS. The WSD also decreases as the oil temperature increases. However, the WSD is smallest and most stable at all tested temperatures for the CL due to the various additives in the lubricant formulation.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The following conclusions can be drawn based on the objectives given in Chapter 1. Based on objective 1, the physicochemical properties of the polyol ester-based biolubricants are superior to those for paraffin oil. These biolubricants improve the wear prevention characteristics and extreme pressure properties in terms of the CoF and WSD. For objective 2, the addition of SCMS improves the friction and wear behaviours of PE ester-based lubricant. The highest improvement is obtained when 0.075 wt% of SCMS is added into the PE ester-based lubricant. Finally, for objective 3, the CoF and WSD of PE ester-based lubricant are smaller compared to paraffin oil. The tribological properties of the PE ester-based lubricant are further improved upon the addition of SCMS.

5.2 Recommendations for future work

In general, the objectives of this research are achieved. However, there is still a need to explore the properties of biolubricants such as biodegradability, toxicity, oxidative and thermal stability. Besides that, it is imperative to conduct further investigation on lubricant additives and their dispersibility in order to develop fully formulated biolubricants. Moreover, investigation on the effect of other lubricant additives on the tribological performance of biolubricants is needed in order to develop fullt formulated biolubricants. Experimental study on tribological properties using different geometric configurations (i.e. pin-on-plat, pin-on-disc, piston ring-on-cylinder liner) is highly recommended. Finally, the use palm oil-based biolubricants is crucial to support local palm industry.

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LIST OF PUBLICATIONS AND PAPERS PRESENTED

i. Journal article

Zainal, N.A., Zulkifli, N. W. M., Gulzar, M., & Masjuki, H. H. (2018). A review on the chemistry, production, and technological potential of bio-based lubricants. Renewable and Sustainable Energy Reviews, 82(Part 1), 80-102.

ii. Paper presented

Zainal, N. A., Zulkifli, N. W. M., & Masjuki, H. H. (2017, 5-6 April). Tribological behaviours of polyol ester-based environment-friendly lubricant. Paper presented at the International Technical Postgraduate Conference, Kuala Lumpur, Malaysia