TRIBOLOGICAL PROPERTIES OF PALM OIL-BASED GREASE WITH NANO PARTICLE ADDITIVE

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TRIBOLOGICAL PROPERTIES OF PALM OIL-BASED GREASE WITH NANO PARTICLE ADDITIVE

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DECLARATION

I hereby declare that this work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree.

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LIST OF SYMBOLS/ ABBREVIATIONS

μ_d	dynamic viscosity of lubricant grease
H	kinematic viscosity at 40 °C of a reference oil of VI 100 with the same kinematic viscosity as the palm oil-based bio- lubricant grease at 100 °C
L	kinematic viscosity at 40 °C of a reference oil of VI 0 with the same kinematic viscosity as the palm oil-based bio- lubricant grease at 100 °C
r	distance from the contact surface centre on the lower balls to the axis of rotation
T	frictional torque
U	kinematic viscosity of the palm oil-based bio- lubricant grease at 40°C
W	applied normal load
Y	kinematic viscosity of the palm oil-based bio- lubricant grease at 100°C
μ	coefficient of friction
ν	kinematic viscosity of lubricant grease
ρ	density of lubricant grease

BMG	biodegradable mineral grease
COF	coefficient of friction
EHL	elastohydrodynamic lubrication
FGG	food grade grease
FTP	flash temperature parameter
PFA	Palm Formulation A
PFB	Palm Formulation B
VI	viscosity index
WSD	wear scar diameter

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ABSTRAK

Kesan penggunaan meluas minyak mineral dan minyak sintetik sebagai minyak pelincir komersial yang membahayakan alam sekitar telah menimbulkan kebimbangan dalam kalangan masayarakat. Justeru, pembangunan lestari untuk menghasilkan pelincir bio berasaskan minyak sayuran adalah penting bagi menggalakkan penggunaan minyak pelincir terbiodegradasikan sebagai pengganti minyak pelincir komersial. Pemekat dan nanopartikel telah diusulkan sebagai tambahan yang mampu meningkatkan sifat tribologi pelincir berasaskan minyak sayuran. Dalam kajian ini, sifat tribologi gris berasaskan minyak sawit yang diformulasikan dengan minyak sawit olein, lithium stearat dan serbuk nano kuprum telah dinilai secara eksperimental menggunakan penguji tribo empat bola. Pelincir gris gred makanan dan gris mineral komersial juga telah diuji untuk perbandingan. Ujian tribologi telah dijalankan pada suhu 75℃ dan kelajuan 1200rpm dengan beban normal 40kg selama 1 jam mengikut ASTM D2266. Set ujian tambahan pada suhu 100℃ juga dijalankan untuk mengkaji kesan suhu terhadap sifat pelincir. Sifat-sifat fizikal pelincir termasuk kelikatan, indeks kelikatan dan parameter suhu kilat serta sifat-sifat tribologi termasuk tork geseran, pekali geseran, diameter parut haus, ciri- ciri permukaan haus dan kekasaran permukaan telah dikaji. Hasil kajian menunjukkan bahawa gris berasaskan minyak sawit yang diformulasikan memberikan sifat tribologi yang lebih baik dari segi indeks kelikatan yang lebih tinggi serta tork geseran, pekali geseran, kesan pengoksidaan dan kekasaran permukaan yang lebih rendah berbanding gris gred makanan dan mineral. Namun begitu, gris yang dihasilkan berasaskan minyak sawit menunjukkan sifat yang kurang baik dari segi diameter parut haus dan parameter suhu kilat. Berdasarkan hasil kajian, ciri- ciri tribologi minyak pelincir bio gris berasaskan minyak sawit adalah setanding dan kompetitif dengan minyak pelincir komersial.

TRIBOLOGICAL PROPERTIES OF PALM OIL-BASED GREASE WITH NANO PARTICLE ADDITIVE

ABSTRACT

The harmful environmental effect of the widespread use of mineral oil and synthetic oil as commercial lubricant greases has been raising concerns in the community. Therefore, the sustainable development of vegetable oil-based bio-lubricants is important to promote the use of biodegradable greases to replace commercial greases. A proposal was made that thickeners and nanoparticles as additives have the capability to improve the tribological properties of the vegetable oil- based lubricants. In this study, the tribological properties of palm oil-based greases which were formulated with refined palm olein, lithium stearate soap and copper (Cu) nanopowder were evaluated experimentally using a four ball tribotester. Commercially available food grade grease and biodegradable mineral grease were also tested for comparison. The tribological wear tests were conducted at 75℃ temperature and 1200rpm speed under a normal load of 40kg for 1 hour as per ASTM D2266. An additional set of test at 100℃ was carried out to study the effect of temperature on the lubricant properties. The physical properties of the lubricant including viscosity, viscosity index and flash temperature parameter and the tribological properties including frictional torque, friction coefficient, wear scar diameter, surface wear characteristics, and surface roughness were investigated. These findings showed that the formulated palm oil-based grease exhibited finer tribological properties in terms of higher viscosity index and lower frictional torque, friction coefficient, oxidation effect and surface roughness as compared with food grade grease and biodegradable mineral grease. However, the formulated palm oil-grease exhibited less desired properties in terms of wear scar diameter and flash temperature parameter. From the findings, it can be inferred that the tribological characteristics of the palm oil-based bio-lubricants greases are comparable and competitive with the commercial greases.

CHAPTER 1 : INTRODUCTION

1.1 Research Background

Lubrication is defined as a complex process where a substance called lubricant is put between more than one interacting surfaces which are in relative motion to one another (Salih et al., 2013). The lubricants play a vital role in minimizing friction and wear by maintaining a thin coat of lubrication between these interacting surfaces in order to hinder direct contact. The prevention of direct contact suppresses the friction and wear between the surfaces (Sharma and Sachan, 2019). Besides, lubricants serve to distribute heat and transport foreign particles. As such, lubricants play a huge role in all industrial applications such as the automobile sector, food processing sector, cable car sustenance and many more (Hassan et al., 2016). In general, there are four kinds of lubricants namely oil, grease, penetrating lubricants and dry lubricants with the first two being the most common lubricants. Oil is a thin liquid which exists in different viscosity and can be added with additives to impede oxidizing and corrosion whereas grease is obtained by blending oil, thickener and additional additives. Grease has similar lubricating properties as oil but it has a texture and stickiness which helps it adhere to surfaces effectively such as on gears, bearings, linkages and chains.

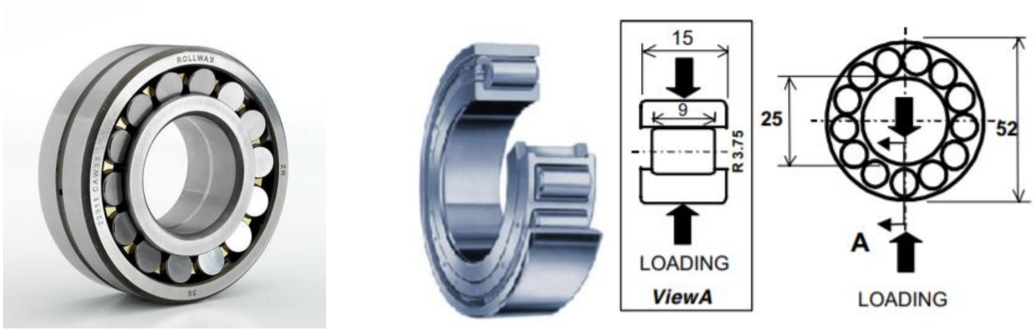

Figure 1.1 Roller bearings (Serrato et al., 2007)

Figure 1.1 shows the roller bearings in which lubricant grease is commonly used on. Roller bearings are precision bearings like balls or rollers which carry loads in various applications with relatively small resistance. They are sturdy in the toughest condition and sustain a lengthy service time. The industries use grease as lubricants for bearings due to its easy handling and protective sealing capabilities for the system. The intent of lubricating roller bearings is to lessen the friction and abrasions which are resulted from direct metal-to-metal contact and also transfer heat produced by friction. In roller bearings, there is rolling friction between the surfaces in contact which results in elastohydrodynamic lubrication (EHL) when lubricant is used. It also functions to extend the durability of bearings by preventing harmful corrosion and contamination of the rolling elements by foreign objects.

Mineral oil-based lubricants such as petroleum and also synthetic lubricants are the main source of industrial lubricants, especially for the engines and mechanics industry. However, the usage of mineral oil-based lubricants and synthetic lubricants has brought environmental concern due to them not being readily biodegradable and toxic (Aiman & Syahrullail, 2017). Mineral oil-based lubricants and synthetic lubricants can cause environmental pollution by means of open burning, dispersing of the lubricants and their pollutants to the air, drinking water and sea. Not only that, there is a limit to the sources of mineral oil and they will run out in the forthcoming.

As the use of lubricants become more widespread in various industries, there has been a rising environmental concern regarding a large amount of non-biodegradable lubricants being used. In fact, statistics have shown that an estimated of 12 million tonnes and more of lubricant waste is discharged into the environment annually (Hassan et al., 2016). Due to the increasing awareness of environmental pollution caused by non-biodegradable lubricants, more tribological studies are being conducted to develop biodegradable plant oil-based lubricant as a replacement or substitute to the conventional lubricants that are available commercially. Bio- lubricants are lubricants that are both rapidly decomposable and atoxic to human beings or other living things especially in marine environments. Plant oil-based lubricant formulations have been studied as a possible source of bio-lubricants as they are biodegradable, renewable and have superb lubricity. Generally, plant oil-based lubricants have outstanding properties for the application of lubrication like high viscosity index, high lubricity, lower volatility, low toxicity and high bio- degradability. Over the past decades, studies were conducted on vegetable oils such as canola oil, soybean oil, palm oil, almond oil and cactus oil. The use of vegetable oil is not unfamiliar where in India, coconuts were used by the industries in lubrication of two-stroke engine (Govindapillai et al., 2009).

Among these, palm oil is one of the plant-based oil that has been tested widely in the lubrication sector over the years to determine its characteristics and potential to be used as a possible lubricant due to their benefits over the conventional lubricants which are environmentally friendly, economical, renewable and easily accessible. Not to mention that Malaysia is the world's second-highest producer of palm oil, making it a suitable substitute for mineral oil in our country. Over the past years, there have been researches that studied the tribological properties of palm oils of different groups where 100% pure palm oil is studied as a test lubricant (Masjuki et al., 1999), palm oil is used as additives, palm oil is used together with additive (Chew & Bhatia, 2009) and where palm oil emulsion is used. According to past researches on the performance of palm oil lubricants, palm oil has the potential to be a good lubricant due to its low friction coefficient.

Despite its widespread application in various researches, the research of palm oil is still limited when it comes to formulation with additives and thickeners. The use of palm oil in grease production is rarely reported and the wear and friction performance is unknown. The main purpose of this project is to evaluate the tribological properties; such as anti-wear, friction and viscosity index of a newly formulated palm oil-based lubricant with added nanoparticles and thickeners in comparison with commercial grease which is currently available in order to assess its potential as a sustainable bio-lubricant.

1.2 Problem Statement

Mineral oil and synthetic oil has been widely used as lubricants in various industries due to their lubricating properties. However, the currently available mineral oil-based and synthetic oil-based grease produce toxic wastes which are harmful to the industrial labour, environment and community. The sustainable development of the conventional mineral oil-based grease and synthetic oil-based grease which are commercially available in the market have been disputed by the community due to their adverse environmental effect. Over the years, there has been growing research to encourage the use of vegetable oil-based lubricants such as palm oil to replace mineral oil-based lubricants due to their properties of being non-toxic and biodegradable. However, the lubricating properties of palm oil-based lubricants when mixed with nanoparticles additives and thickeners is still not well-researched in this area. Therefore, research should be conducted with the aim of producing an environmentally friendly, biodegradable and sustainable natural source of palm oil-based grease with performance comparable with the currently available commercial conventional lubricant grease.

1.3 Project Objectives

In this project, the objectives to be achieved are:

- To develop a biodegradable palm oil- based grease lubricant which is comparable with commercially available lubricant greases in terms of lubricity.
- To evaluate the viscosity of the developed biodegradable palm oil-based grease at different operating temperature.
- To investigate the tribological behaviour of the biodegradable palm oil-based grease.

1.4 Scope of Work

In this project, the scope is on experimental work which requires basic knowledge in tribology. Firstly, the bio- lubricant grease will be prepared using palm oil as the base lubricant, nanoparticles additives and thickener. A few experimental tests will then be carried out to study the physical characteristics such as viscosity, viscosity index and flash temperature parameter, and the tribological performance such as friction and wear behaviour of the formulated palm oil-based bio- lubricant grease. The result is then compared with available commercial greases such as food grade grease and biodegradable mineral oil grease.

1.5 Thesis Outline

- **Chapter 1 (Introduction)**, explains the background study of the project, the objectives that need to be achieved, the problem statement of the project and the thesis outline.
- **Chapter 2 (Literature Review)**, focuses on the good attributes and anti-wear properties of vegetable oil-based bio-lubricants in past researches, the use of palm oil as bio-lubricants, the formulation and preparation of greases and tribological testing methods of lubricants.

- **Chapter 3 (Research Methodology)**, shows the preparation of bio- lubricant grease, viscosity test of bio- lubricant grease, tribological testing of lubricant grease and surface wear characterization using SEM EDX and IFM analysis
- **Chapter 4 (Results and Discussion)**, presents the physicochemical properties of the test lubricant greases, tribological testing outcome of friction evaluation, wear scar and flash temperature parameter as well as worn surface characteristics.
- **Chapter 5 (Conclusion and Future Work)**, summarizes the outcomes of the project and the recommendation of the possible future work.

CHAPTER 2 : LITERATURE REVIEW

2.1 Overview

In this chapter, six topics will be presented which includes:

- The use of bio-lubricants
- Vegetable oil as bio-lubricants vs traditional commercial bio-lubricants
- Palm oil as bio-lubricants
- Formulation and preparation of lubricant grease
- Tribological testing of lubricant grease

2.2 Bio- lubricant

Due to the environmental advantages of bio-lubricants, they are expected to replace an estimated 90% of petroleum-based lubricants (Reeves, 2013). The word "bio- lubricant" for lubricants that are originated from bio-based crude materials like animal fats, plant oils and eco-friendly hydrocarbons are bio-degradable and non-harmful to living things in which impacts are less damaging. These lubricants consist of plant oils, animal fats or both which are chemically modified through processes such as transesterification, epoxidation, and esterification reactions. Researches have turned to chemical modifications of these oils in order to enhance the oxidation and thermal stability to increase their ability to operate within a wide range of operating conditions.

2.3 Vegetable Oil as Bio- lubricants Vs. Traditional Commercial Lubricant

Research on biodegradable lubricants is rising as one of the dominant focus in lubrication where the use of vegetable-based oils has been reputable as lubricant components (Rudnick, 2013). Vegetable oils, in particular, such as canola, castor, rapeseed, sunflower, sweet almond, cactus and palm oil is a promising candidate for biodegradable lubricants. The effectiveness of vegetable oils as a component of bio-lubricants is attributed to their chemical composition. Generally, vegetable oils are made up of triglycerides, which are formed from glycerol molecules long-chain fatty acids and hydroxyl groups joined together with ester linkage. Triglycerides are sometimes referred to as triacylglycerol. This structure results in appealing qualities of a lubricant as the polar properties and fatty acids give a high resistance lubricant film which interacts strongly with metal surfaces by strong adherence. The ability of the fatty acids to stick to metal surfaces is due to closely packed inherited polar carboxyl which is efficacious in wear and friction reduction through metal-to-metal contact minimization (Grushcow, J, Smith, 2005). Figure 2.1 shows a coating of protective film which is formed by fatty acids molecules. Besides that, there is stable viscosity of the oil attributed to the strong intramolecular interactions which are resistant to temperature changes (Fox & Stachowiak, 2007).

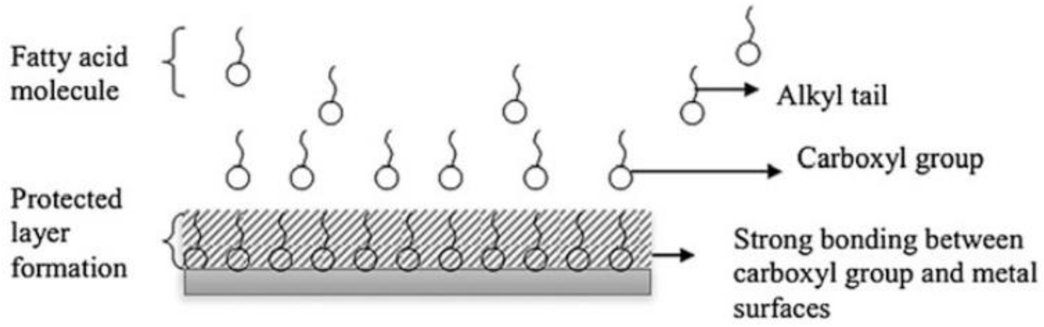

Figure 2.1 Formation of protective film by vegetable-based oil on metallic surfaces (Zulkifli, 2014)

Many kinds of research have shown that bio-based lubricants composed of vegetable oils are decomposable and cheaper than traditional commercial mineral oil and synthetic oil. Vegetable oil-based bio-lubricants even showed quite acceptable performance as lubricants relating to viscosity, friction coefficient and wear performance and has the potential to be utilized in engineering and industrial applications. Generally, vegetable oils have better lubricity, high viscosity index, high flash point, low evaporative loss and good metal adherence in comparison with petroleum-based lubricants (T. M. Panchal et al., 2017). Past researches have claimed that vegetable oil-based lubricants have better lubricating properties in comparison to mineral oil and synthetic oil as vegetable oil-based lubricants have lower viscosity, higher viscosity index, lower friction coefficient, less wear, higher flash temperature parameter and less waste (Aiman et al., 2017; Aiman & Syahrullail, 2017; Delgado-Tobón et al., 2018; Jabal et al., 2019; Masjuki et al., 1999; Zulkifli et al., 2013). These properties will be discussed further in the following sub-sections 2.3.2, 2.3.3, 2.3.4, 2.3.5 and 2.3.6.

2.3.1 Factors for Vegetable Oil Selection

Besides suitable physicochemical properties, there are also several major factors in selecting the appropriate vegetable oil as the bio- lubricant base oil as listed by Rudnick below (Rudnick, 2013):

- Oil production of the vegetable-based oil resources should be sufficient.
- There should be more monounsaturated fatty acid compared to polyunsaturated fatty acids in the chemical structure of the vegetable oil.
- The vegetable oil should have a steady trading price in the market.

2.3.2 Viscosity and Viscosity Index

The viscosity of a lubricant is regarded as part of the major parameter when it comes to a specific application in which the lubricant is used. Viscosity is a measure of how much internal resistance is applied by a fluid against the flow and it is a property of the fluid. It influences the liquid thickness and the wear rate of the surface on which the liquid is being rubbed (Jabal et al., 2019). The viscosity of a lubricant is reliant on the chemical structure of the vegetable oil which is the carbon chain length and degree of unsaturation that influences the parameter. As the length of the hydrocarbon increases, the viscosity of the lubricant increases as well.

Another property related to viscosity is the viscosity index (VI) which denotes the effect of temperate changes on the viscosity. A low viscosity index means a great viscosity change relative to temperature. On contrary, a high viscosity index implies a small viscosity change over a wide spectrum of temperature. An ideal lubricant would have high viscosity index. This is because, at low temperature, excessive thickening can be avoided while preventing excessive thinning at high temperature (Zulkifli et al., 2013). The viscosity index should be high enough to retain the lubricating layer thickness, and low enough to ensure the flow of oil through relevant parts. The viscosity index of an unknown lubricant can be calculated according to the standard American Society for Testing and Materials ASTM D2270 based on the unknown lubricant's kinematic viscosity at 40 ℃ and 100 ℃ as well as the information from two reference oils (Wheeler, 1998).

Research conducted by Masjuki et al., Aiman et al. and Zulkifli et al. showed that the vegetable oil-based lubricants being tested possessed lower viscosity when compared to mineral oil-based lubricants (Aiman & Syahrullail, 2017; Jabal et al., 2019; Masjuki et al., 1999; Zulkifli et al., 2013). On contrary, the vegetable oil-based lubricants had a higher viscosity index in comparison to mineral oil-based lubricants. This property is attributed to the existence of triglycerides in the vegetable oil-based lubricants which maintain strong intermolecular interaction with the rise in temperature. The hydrogen bonds within the triglyceride molecules contribute to a higher viscosity index (Masjuki et al., 1999).

2.3.3 Coefficient of Friction

Research by Jabal et al., Aiman et al. and Arnoldo et al. showed that the friction coefficient obtained was lower when vegetable oil-based lubricants were used in comparison to the traditional mineral oil (Aiman et al., 2017; Aiman & Syahrullail, 2017; Delgado-Tobón et al., 2018; Jabal et al., 2019). These results can be explained by the polar nature of vegetable oils, which is more suited to metal surfaces, resulting in better lubricity than non-polar mineral oils which is composed of aliphatic hydrocarbons. Throughout the lubricating process, a monolayer film is formed when the polar heads of the fatty acid chains in vegetable oils adsorbs to the metal surface. This prevents direct metal-to-metal contact and lessens the friction coefficient between the surfaces (Nosonovsky & Bhushan, 2012).

2.3.4 Wear Characteristics

Wear can be defined as the removal of material from a solid surface or undesired displacement. Figure 2.2 shows the resultant surface wear that can be observed on the steel balls when they are subjected to anti-wear testing using a four ball tribotester machine. Wear often occurs when there is a relative force or sliding between two surfaces under load which results in gradual loss of the material. Wear can be characterized into four types; namely adhesive, abrasive, corrosive and surface fatigue. A wear characteristic is commonly determined by the wear scar diameter, where a larger wear scar diameter suggests that the wear is more serious (Hassan et al., 2016).

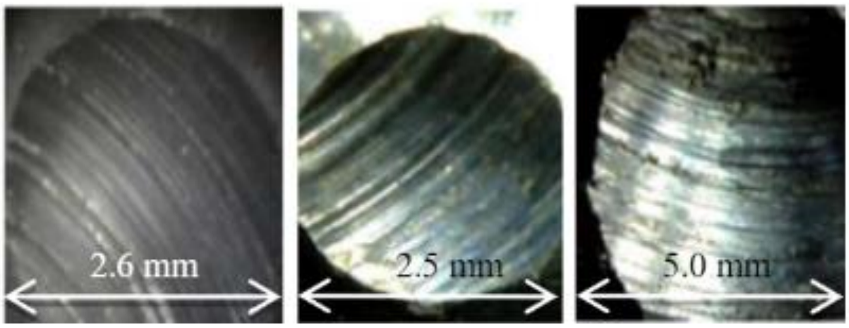

Figure 2.2 Surface wear on the steel balls subjected to anti-wear testing (Delgado-Tobón et al., 2018)

In Masjuki et al., Jabal et al. and Aiman et al. works, when vegetable oil-based lubricants were used, the wear scar diameter measured was lower in comparison to when traditional mineral oil was used (Aiman & Syahrullail, 2017; Delgado-Tobón et al., 2018; Jabal et al., 2019; Masjuki et al., 1999). This can be explained by the presence of unsaturated fatty acids layer in vegetable oils which usually have a thicker molecular layer. When combined with the bare metallic surface, a thick metallic soap layer is created by adsorption which enhances lubricating features and anti-wear performance.

2.3.5 Flash Temperature Parameter

Flash temperature parameter (FTP) is a value which is used to express the critical temperatures where the lubricants will fail to work in specific operating conditions. The value of FTP is a measure of the possibility of a lubricant film breaking down or degenerating when in action. A higher value of FTP shows that the lubricant has a higher lubricity performance because it means there is a lower possibility of lubricant breakdown or degeneration (Hassan et al., 2016). Thus, a high value of FTP is desirable as it indicates good lubricating performance.

There have been past researches where a high flash temperature parameter is obtained when vegetable oil-based lubricant is used as compared to mineral oil-based lubricant. In a work by Syahrullail et al., RBD palm olein gave a higher value of FTP at a range of 40 to 90 as compared to paraffinic mineral oil with FTP range of 15 to 25 at high pressure and high load (Syahrullail et al., 2013). A research conducted by Jabal et al. showed results where higher values of FTP were obtained when sunflower oil is used in comparison with mineral oil at different loads (Jabal et al., 2019). In other words, these researches have shown that the use of vegetable oil as lubricants reduces the possibility of lubricant thin film breaking down which increases lubricating performance.

2.3.6 Waste

Kumar et al.'s work evaluated the biodegradability of the Jatropha oil where the biodegradability and toxicity of the lubricant are taken into consideration. The findings showed the degradation of the base oil before the recommended incubation of 28 days by calculating the rate of conversion of the base oil to CO_2 under exposure to microorganisms under controlled aerobic aquatic conditions. This indicated a high biodegradability. Besides, the growth curve of the bacterial cell NS/8 signified that the base oil samples had no toxic effect, meaning that the base oil was found to be non-toxic (Nagendramma & Kumar, 2015).

2.4 Palm Oil as Bio- lubricants

With reference to the mentioned criteria for the selection of vegetable oil in section 2.3.1, palm oil has the largest potential while dealing with the issue of Malaysia's domestic energy safety and legal requirements regarding the environment. Out of the total world oil production, palm oil contributes the largest portion at approximately 36 % with Malaysia being one of the biggest palm oil-producing countries together with Indonesia, Thailand, Columbia and Nigeria (Gulzar, 2018).

Palm oil consists of 50–70% palmitic acid, $C_{15}H_{31}COOH$, which is a class of glycerine. Palm oil is primarily composed of triglycerides with small amounts of partial glycerides, free fatty acids and non-glyceride substances. There have been past researches using palm oil which yield positive results, particularly high viscosity index, low friction coefficient and low wear characteristics attributed to the presence of fatty acids films.

However, there were two pieces of research where the experiments resulted in less desirable results. Masjuki et al. (Masjuki et al., 1999) found that the friction coefficient was higher when palm oil was used as compared to mineral oil-based commercial lubricant. Aiman et al. findings stated that a higher wear scar diameter was observed when palm kernel was used, in comparison with mineral oil (Aiman et al., 2017). This behaviour was likely due to the corrosive wear which rooted from the palmitic and fatty acids composition of palm oil. The fatty acid is the product of the hydrogenation process that takes place during the experiment and it contributes to the corrosive effect. Another plausible reason is due to the lower boundary effect or the breakdown of boundary lubrication due to the low viscosity value of palm oil (Aiman & Syahrullail, 2017). Boundary lubrication occurs when two interacting surfaces are close together that the surface interactions between monomolecular or multi-molecular films of lubricants and the solid asperities dominate the contact as illustrated in Figure 2.3. The failure in boundary lubrication is caused by adhesive and chemical or corrosive wear. According to Zhang C. (2014), the bulk flow properties of the lubricant such as viscosity plays a part in the friction and wear behaviour (Zhang, 2014).

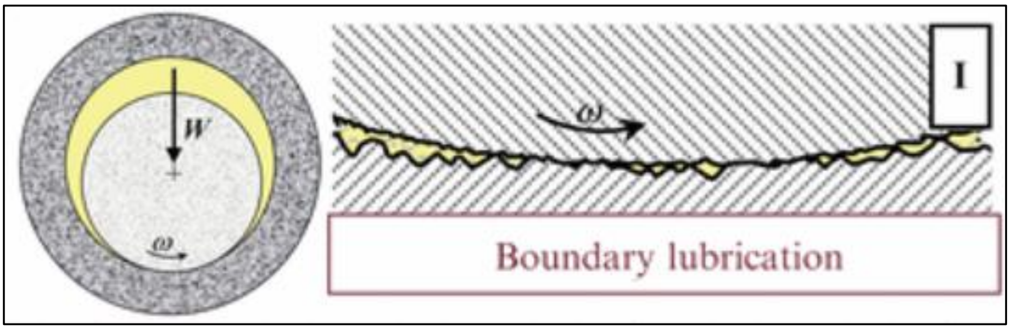

Figure 2.3 Boundary lubrication between two interacting surfaces (Dobrica & Fillon, 2013)

2.5 Formulation of Grease

A lubricant should be able to retain efficient lubrication for a prolonged time before it is worn out. In order to fulfil these expectations and improve the tribological characteristics of the lubricants, many researchers have added additives and thickeners to the base vegetable oil to produce a multipurpose lubricant grease with desirable performance. The term multipurpose lubricating grease can be defined as a colloidal dispersion of base oil, thickener and additives. The base oil performs the actual lubrication. The thickener gives suitable rheological and tribological behaviour to the grease. Additives enhance properties such as oxidation, lubricity, wear or friction (Nagendramma & Kumar, 2015). Modifications of vegetable oils through the addition of additives and thickeners improve the properties related to viscosity, adherence to the metal surfaces, stability, and more which impacts its tribological qualities.

2.5.1 Base Oils

Base oil functions as the foundation of the lubricant grease before it is mixed together with additives and thickener. The base oil can be either mineral oil, synthetic oil or vegetable oil with a typical composition of 70 – 95 % (Daud, 2010).

2.5.2 Thickeners

According to the National Lubricating Grease Institute (NLGI) Guide, the thickener is defined as solid particles that are relatively evenly spread and diffused in liquid lubricant in order to create the stable structure of lubricating grease. The solid particles can be fibres which are common in metallic soaps thickeners or plates and spheres which is used in non-soap thickeners (Turner et al., 2020). Lubricant greases have advantages over liquid lubricants which flows easily and solid lubricants. This is because liquid lubricants need a reservoir to hold their volume, making them easy to leak. Lubricating greases, on the other hand, can maintain their body structure without needing a reservoir. This is where thickeners come into play. The consistency of greases is due to a gel-forming network where the thickening agent is dispersed in the base lubricant. As mentioned earlier, while the base oil carries out the actual lubrication, the thickener functions to gives grease its characteristic consistency which maintains the oil in place. Thus, the base lubricant provides the lubricating properties to the grease whereas the thickener holds the matrix together as a gelling agent (T. M. Panchal et al., 2017).

The primary type of soap thickeners which is usually used in multipurpose grease is metallic soaps such as lithium, sodium, calcium and aluminium which are prepared through the neutralization of purified fatty acids (Daud, 2010). Among these, lithium 12-hydroxy stearate greases are the most extensively used soap greases due to the efficiency of lithium soap as thickeners. Greases which are added with lithium soap have good lubricity, shear stability, thermal resistance and low oil separation. Lithium lubricating greases are frequently used in bearings in automotive and industrial applications.

The good attributes of lithium-12-hydroxy stearate as a thickener, which is more commonly known as lithium soap can be seen from past researches of Nagendramma et al. and Panchal et al. (Nagendramma & Kumar, 2015; T. Panchal et al., 2015; T. M.

Panchal et al., 2017). A research conducted by Panchal et al. found that the Karanja oil ester-based lithium grease showed desired anti-wear properties when subjected to extreme pressure in terms of reduction of wear scar and coefficient of friction when compared with mineral oil (T. Panchal et al., 2015). In a work by Kumar et al., the comparative study of bio-lubricant grease (Jatropha vegetable oil added with lithium oleate and stearate soap as well as additives) and multipurpose commercial grease showed that the parameters of wear scar diameter obtained with the bio- lubricant grease with added thickeners were better than that of commercial grease (Nagendramma & Kumar, 2015).

2.5.3 Additives

According to the National Lubricating Grease Institute (NLGI) Guide, an additive is a substance, either an organic or inorganic compound that is mixed in lubricant to alter its properties. Additives usually have a typical composition of 0.1 – 15 % of the lubricating grease which differs based on the type of additives and their application. The most widespread of additive types used are anti-corrosion, anti-wear (AW) or extreme pressure (EP), anti-oxidant and viscosity index improver.

2.5.3(a) Anti-wear and Friction Modifiers Additives

In roller bearing applications where there are two metallic surfaces making contact and moving in relative to one another, anti-wear additives and friction modifiers are crucial to hinder wear and tear. Wear and friction improvers compose of chemical additives that can be split into three types, namely adsorption or boundary additives, anti-wear additives and extreme pressure additives (Gulzar, 2018).

The function of adsorption or boundary additives is to lessen the asperity contact caused by unevenness of surfaces. AW additives are added into lubricant greases in order to hinder wear loss and friction between lubricated surfaces by keeping the surfaces separated under moderate to great loads. AW additives create an adsorbed layer on the metallic surfaces which prevents the surfaces from having contact with one another. EP additives are used for applications with higher loads in order to provide extra load carrying capacity under boundary lubrication circumstances. They react chemically with the metallic surfaces under great load and increased temperature conditions to form a lubricating film which is chemically bonded (Turner et al., 2020).

2.5.3(b) Nanoparticles as Additives

Nanoparticle-based lubricant additives are referred to as functional particles which are smaller than 200 nm in size in minimum one dimension that is added to the base oil to improve lubricating oil performances. Nanoparticles are a fairly new class of additives in the development history of lubricant additives (Wang, Q. Jane; Chung, 2013). Despite being new in the field of lubricant tribology, nanoparticles have more advantages as compared to traditional additives in terms of high suspension density, action mechanisms and high strength of boundary films, making them suitable as an anti-wear additive, extreme-pressure additive, friction additive and more (M. Liu; X. Li; S. Wang, Y. Sun, 2002). There are many classifications of nanoparticle additives such as metal, metal compound, rare earth compound, carbon material, polymer and structural material.

It has been reported in research papers in recent years that the addition of nanoadditives to base lubricants is effective in reducing wear and friction in mechanical systems. Various nanoparticles have been studied to be used as lubricant grease additives such as copper (Cu) (Guzman Borda et al., 2018), iron (Fe), cobalt (Co) (Padgurskas et al., 2013), zinc dialkyldithiophosphate (ZDDP) (Nagendramma & Kumar, 2015; T. Panchal et al., 2015) and titanium dioxide (TiO_2) (Ilie & Covaliu, 2016). Padgurskas et al. (2013) studied tribological properties of lubricant additives based on Fe, Cu and Co nanoparticles that were added individually and also combined in pairs to mineral oil base lubricant. This research showed that the Cu nano- additives reduced the friction and wear significantly as compared to the combination with other nanoparticles and also the mineral oil base lubricant itself (Padgurskas et al., 2013). A research conducted by Borda et al. also showed that the addition of copper nanoparticles as additives into mineral oil resulted in a reduction of the friction coefficient and improvement of the anti-wear characteristics, making copper nanoparticle an appropriate friction modifier and anti-wear agent (Guzman Borda et al., 2018). Similarly, other researches using zinc dialkyldithiophosphate as an additive with Jatropha vegetable oil showed promising results as well.

Researches attributed the promising tribological properties of the nanoparticles additives to their shape and deposition on contact surfaces which forms a thin film that impedes metal-to-metal contact. The spherical shape of most nanoparticles additives produces a ball-bearing effect which changes the friction characteristic from sliding to a combination of sliding and rolling at the contact area, thus reducing friction (Wu et al., 2007). The ball bearing effect is illustrated in Figure 2.4. The added nanoparticles reduce friction and wear through lubrication mechanisms such as are the rolling effect, colloidal effect, small-size effect, third body effect and protective film effect. Other than reducing friction, lubricant grease with additives is also capable of increasing the load-carrying capacity of the lubricating fluid.

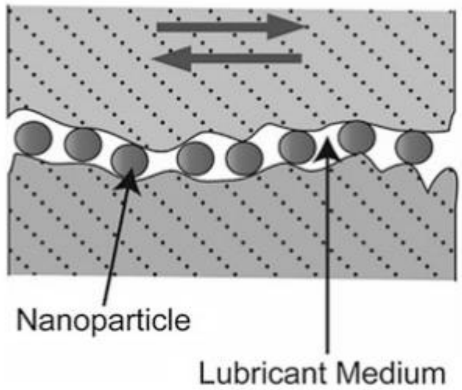

Figure 2.4 Illustration of ball bearing effect by nanoparticle additive based lubricant at contact area (Kheireddin, 2013)

There are several methods to incorporate the nanoparticles into the base oil for stable dispersion stability of the nanolubricants. Methods used in past researches include magnetic stirring (Sui et al., 2015), ultrasonic probe (Alves et al., 2013), ultrasonic bath (Asrul et al., 2013), chemical agitation (Laad & Kumar, 2018), ultrasonic shaker agitation (M. V. Thottackkad et al., 2012) and more.

2.6 Preparation of Grease

Most of the lubricants in researches are specially formulated to assess the tribological performance of the differently formulated greases. In Kumar et al. (2015) work, eight different formulations of multipurpose grease consisting of Jatropha vegetable residual oil, lithium soap and multifunctional additive were synthesized using a hot plate, an adjustable-speed stirrer and a grease kettle as set up. The authors first prepared the lithium oleate and stearate soaps separately which serves as a thickener. The base oil, thickener and additives were added into the grease kettle in the composition of 90%–96%, 3%–5.5% and 1%–5% respectively. The mixture was then heated to 90–130 °C and stirred for 4–9 hours. In Abdulbari et al. (2018) research, the authors started stirring the contents under slow agitation of 200 rpm before increasing the mixing speed to around 1000 – 1500 rpm in order to assist and speed up the blending and homogenization of the lubricant components (Abdulbari & Zuhan, 2018). After the heating was stopped, the stirring was continued until the contents were cooled down to room temperature. The formulated grease was then moved to a clean dry beaker and covered with aluminium foil. The grease was left overnight in order to check for its dispersion stability. If the grease is separated into layers, it is disposed of. Otherwise, the grease can be kept for further evaluation of performance behaviour (Nagendramma & Kumar, 2015). The dispersion stability analysis method will be discussed in section 2.6.1.

2.6.1 Dispersion Stability Analysis

For an effective lubricating performance of the formulated grease, a stable dispersion of nanoparticles additives in its base oil is desired. This property can be determined through a dispersion stability analysis. According to Maheswaran et. al. and Sadeghinezhad et. al., dispersion stability is defined as how stable the suspension of nanoparticles are in the base oil without settling down or deposition of the particles due to downward force (Maheswaran & Sunil, 2016; Sadeghinezhad et al., 2016). Various methods have been created to analyse the stability of nanolubricants and multipurpose lubricant greases such as sedimentation method, spectral absorbency method and zeta potential analysis. Among these, the sedimentation method which is also known as the "observation stability test" is the simplest and most cost-effective (Gulzar et al., 2017). Sedimentation can be understood as an action where the nanoparticles which are entrained in the base lubricant settles down as sediment at the bottom. For this evaluation, the sedimentation is usually visually analysed by taking photographs of the samples in a test tube for observation purposes. A stable lubricant grease should have nanoparticles that remain suspended for a long period of time with minimum sedimentation (Azman & Samion, 2019). One limitation of this method that it is time-consuming although the test durations differ for different nanoparticles and lubricants mixtures. Figure 2.5 shows the photograph taken to observe the sedimentation of nanoparticles dispersed in paraffin oil.

Figure 2.5 Photograph taken to observe the sedimentation of nanoparticles added in paraffin oil (Peng et al., 2010)

2.7 Tribological Testing of Lubricants

In order to study the lubricating performance of lubricants in the context of friction and wear mechanisms, tribological test or tribotest are carried out. One common class of the tribotest is the model test where the critical tribological load of a component in the real application is simulated in a laboratory under controlled and variable testing settings (Torbacke & Kassfeldt, 2014). There is numerous geometric arrangement under this model test class such as the pin-on-disk tribotest, reciprocating tribotest, ball- on-flat tribotest and four ball tribotest as shown in Figure 2.6.

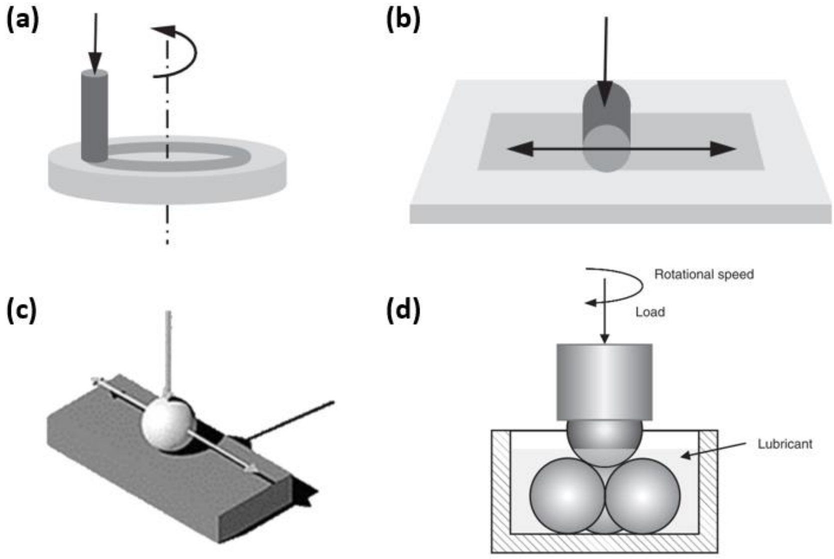

Figure 2.6 A variety of geometric configuration of tribology model test (a) pin-on- disk (b) reciprocating (c) ball-on- flat (d) four ball

2.7.1 Four Ball Tribotester

A four ball tribotester is a fundamental apparatus in the lubricant industry and research to evaluate the tribological properties of lubricating oil and grease. It is utilized for the study of friction and wear behaviour of lubricants under different test conditions. Figure 2.7 and Figure 2.8 shows the picture and the schematic diagram of the equipment respectively. The primary parts of this equipment are the ball pot cum oil cup, collet, ring, rotating spindle, torque arm, heating plate and thermocouple. This equipment uses four identical steel balls; where three balls at the bottom are stationary and are immersed in the test lubricant along with a top ball which is fixed above them. Thus, the three bottom stationary balls make a three-point contact with the top ball (Sharma & Sachan, 2019). The four ball tribotester is connected to a data acquisition system where friction coefficient values are recorded directly from the four ball tribotester. The wear scar diameter is measured using an optical microscope to characterize the worn surfaces of the stationary balls.

Figure 2.7 A four ball tribotester (Jabal et al., 2019)

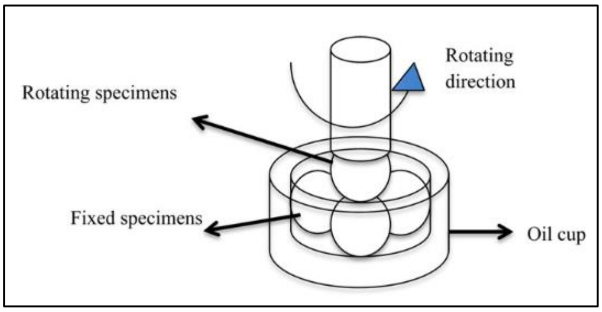

Figure 2.8 Schematic diagram of a four ball tribotester (Zulkifli et al., 2013)

The four ball tribotester can run various type of standards such as the wear preventive (WP) test of ASTM D4172 standard and ASTM D2266 standard for lubricating fluids and lubricating greases respectively. Under these standards, the test conditions are 40 ± 2 kg normal load, operating temperature of 75 ± 2°C, rotational speed of 1200 ± 60 rpm and operation time of 60 ± 1 min. (Standards, 2011)

2.8 Summary

a) Plant oil-based lubricants are environmentally friendly and also exhibits good tribological performance, with some even exceeding the performance of commercial mineral oil and synthetic oil.

b) Palm oil-based lubricants have been a popular option in tribological researches over the years due to their biodegradability and promising lubricity.

c) Thickeners are used as a binding agent in order to improve lubricating performance. One common thickener used in research papers is lithium soap.

d) Additives are used to reduce friction wear in the contact surface during lubrication. Based on the researches, copper nanoparticles yield the most promising results among all the alternatives.

CHAPTER 3 : RESEARCH METHODOLOGY

3.1 Overview

In this chapter, the preparation of newly formulated bio- lubricant grease, viscosity test of the newly formulated bio- lubricant grease, tribological testing, and surface wear characterization using scanning electron microscope with energy dispersive x-ray analyzer (SEM EDX) analysis and infinite focus microscope (IFM) analysis is presented. Figure 3.1 shows the overall flowchart of this study.

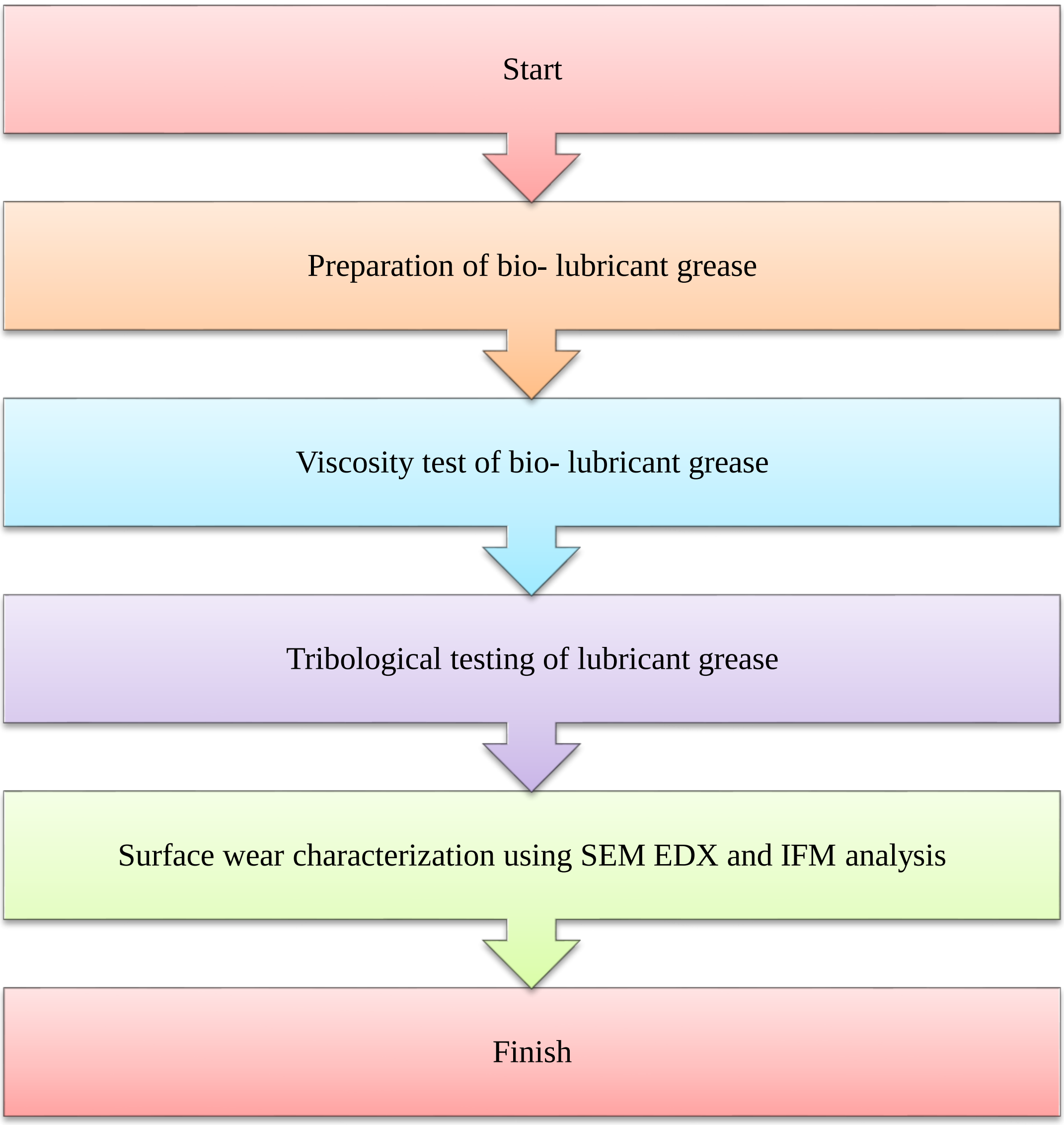

Figure 3.1 Overall flowchart of the project

3.2 Preparation of Bio- lubricant Grease

For this study, a newly formulated palm oil-based bio- lubricant grease of two different compositions is synthesized.

3.2.1 Materials

The bio- lubricant grease consists of refined palm olein as base oil, lithium stearate as a thickener, and copper nanopowder as additive as shown in Figure 3.2. Palm olein is the liquid fraction which is acquired from the fractionation of palm oil after crystallization at a controlled temperature. In this self-formulated lubricant grease, the refined palm olein which is purchased at a local market acts as the foundation of the lubricant grease and performs the actual lubrication. As a thickener, the lithium stearate or more commonly known as lithium soap gives a desired consistency to the lubricant grease by forming a gel network by dispersing in the base lubricant. Copper nanopowder which was commercially obtained from Alfa Aesar is added as an additive to enhance anti-wear and anti-oxidation properties. Table 3.1 outlines the properties of the copper nanopowder.

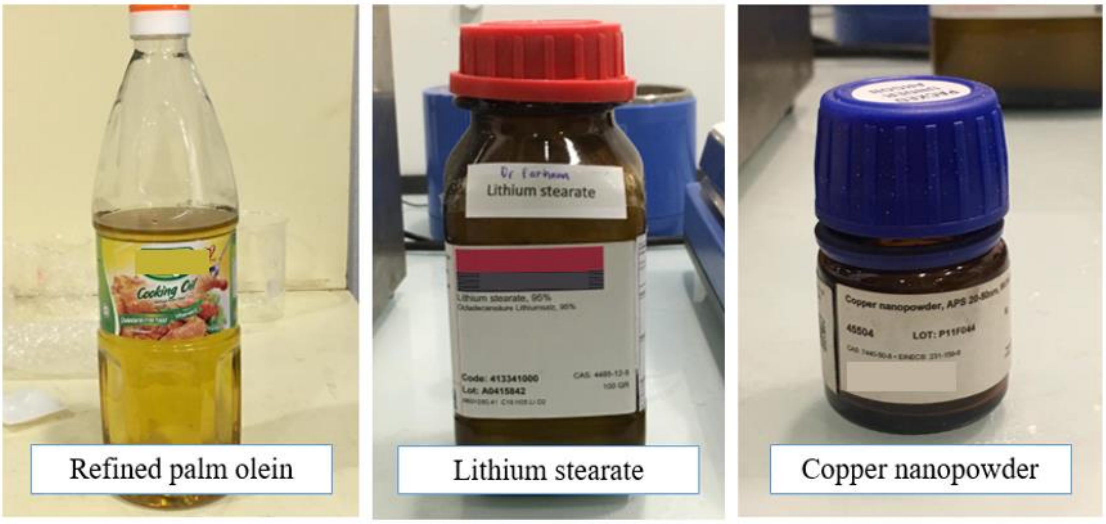

Figure 3.2 Materials used in synthesis of palm oil based bio- lubricant grease

Table 3.1 Properties of copper nanopowder

Nanoparticles	Physical Form	Morphology	Purity (%)	Size
Copper	Powder	Spherical	99.9	50 nm

3.2.2 Apparatus

The experimental setup consists of a magnetic stirrer as the heating and agitation source, an adjustable speed overhead stirrer and a beaker as shown in Figure 3.3.

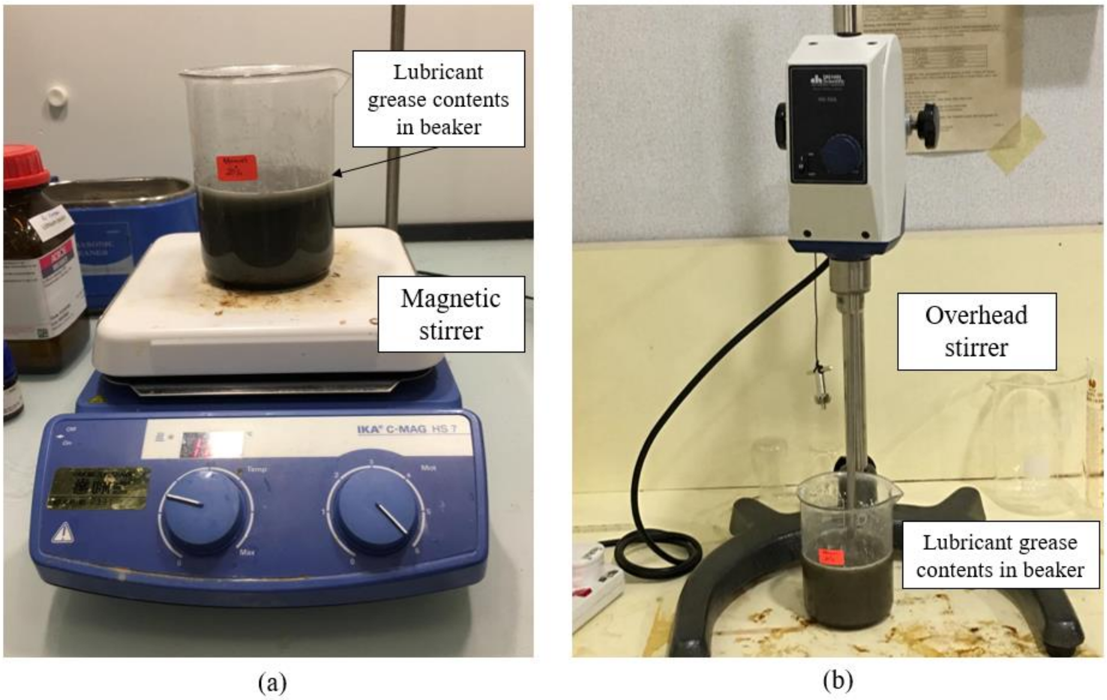

Figure 3.3 Experimental setup during (a) heating and (b) cooling of lubricant grease

3.2.3 Synthesis of Grease

The refined palm olein base oil, lithium stearate soap and copper nanopowder are added into a beaker at two different sets of compositions as outlined in Table 3.2. The beaker containing the lubricant grease content is then placed on the magnetic stirrer as shown in Figure 3.3(a). The contents in the beaker are heated using the hotplate as the heat source to a temperature of 90 to 130℃ while stirring for 5 hours. The stirring is started under slow agitation at mixing speed of 750 rpm (speed setting number 3) before it is increased to mixing speed of 1500 rpm (speed setting number 6) in order to assist and speed up the mixing and homogenization of the components. After the heating is stopped, the stirring is continued using the overhead stirrer until the contents are cooled to room temperature as shown in Figure 3.3(b). The prepared grease is then transferred into a clean dry beaker and is covered with a plastic cling film. The formulated grease is left overnight to check for its stability.

Table 3.2 Composition of formulated palm oil-based bio- lubricant grease

Content	Composition (w/w)	
	Formulation A	Formulation B
Refined palm olein	93.5	90.5
Lithium stearate soap	5	8.1
Copper nanopowder	1.5	1.4

3.3 Physical Properties Test of Palm Oil-Based Bio- lubricant Grease

After synthesizing the palm oil-based bio- lubricant greases, tests are done to determine their density, viscosity and viscosity index since these values cannot be obtained through the datasheet.

3.3.1 Density

A simple experiment is conducted to obtain the density of the palm oil-based bio- lubricant greases of both formulations. First, an empty graduated beaker is weighed to obtain its mass. Palm Formulation A is poured into the graduated beaker to the 40 ml level. The mass of the graduated cylinder with the 40 ml content is then weighed again. With this, the mass of 40 ml Palm Formulation A, m can be obtained by subtraction. This procedure is repeated for Palm Formulation B.

By assuming that the volume, V used for each lubricant grease is 40 ml = 40 cm, the density of the lubricant, ρ can be calculated using equation (1):

$$Density, \rho\ (g/cm^3) = \frac{mass, m\ (g)}{volume, V\ (cm^3)} \qquad (1)$$