

***COMPARISON OF BIO-OIL AND SYNTHETIC LUBRICANTS
TRIBOLOGICAL CHARACTERS***

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COMPARISON OF BIO-OIL AND SYNTHETIC LUBRICANTS TRIBOLOGICAL CHARACTERS

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UNIVERSITI SAINS MALAYSIA

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DECLARATION

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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STATEMENT 1

This thesis is the result of my own investigation, except where otherwise stated. Other sources are acknowledged by giving explicit references.

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LIST OF ABBREVIATIONS

AISI	American Iron and Steel Institute
ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
AW	Anti-wear
COF	Coefficient of Friction
EDX	Electron dispersive analysis of X-rays
EP	Extreme Pressure
FM	Friction Modifier
OA	Orthogonal Array
SEM	Scanning Electron Microscope
TAG	Triacylglycerols
WSD	Wear Scar Diameter

ABSTRAK

Pelincir semula jadi telah dibangunkan sebagai alternatif kepada pelincir berasaskan minyak mineral kerana kebimbangan alam sekitar dan bekalan petroleum yang semakin berkurangan. Minyak sayuran (minyak sawit merah, minyak kacang soya, minyak kelapa dan minyak bunga matahari) telah dikaji sebagai pelincir semula jadi dan campurannya dengan bahan tambahan anti haus untuk menentukan potensi penggunaannya dalam enjin kereta. Penguji empat bola dan pin pada cakera digunakan untuk menjalankan eksperimen di bawah piawaian ASTM. Atas sebab penanda aras, prestasi dibandingkan dengan minyak enjin komersial.

Pengurangan dalam geseran dan haus adalah diabaikan apabila menggunakan nisbah minyak sayuran dan minyak mineral yang sama. Peningkatan yang ketara dalam geseran dan haus dilihat dengan penambahan 1% berat nanozarah Titanium Dioksida kepada minyak sayuran. Menggunakan penambahan ini, pekali geseran minyak sayuran adalah setanding dengan minyak enjin komersial. Ejen anti haus dan pengubah suai geseran semuanya dilakukan oleh Titanium Dioksida dalam minyak sayuran.

Dari segi rintangan haus dan kestabilan oksidatif, kelemahan minyak sayuran tulen ditentukan lebih besar berbanding geseran apabila semua data dipertimbangkan. Kesan ini dinyatakan apabila digabungkan dengan minyak mineral, apabila prestasi tribologi mereka didominasi. Walau bagaimanapun, menggunakan bahan tambahan Titanium Dioksida anti haus komersial, minyak sayuran menunjukkan janji sebagai pelincir alternatif untuk sistem enjin kereta, walaupun pada hakikatnya masih terdapat ruang untuk penambahbaikan.

ABSTRACT

Bio-lubricants have been developed as an alternative to mineral oil-based lubricants because of environmental concerns and the diminishing supply of petroleum. Vegetable oils (red palm oil, soybean oil, coconut oil and sunflower oil) were studied as bio-lubricants and their mixes with anti-wear additives in order to determine their potential usage in car engines. A four-ball tester and pin-on-disc were used to conduct the experiments under ASTM standard. For benchmarking reasons, the performance was compared to that of commercial engine oil.

The reduction in friction and wear was negligible when using an equal ratio of vegetable oil and mineral oil. A considerable improvement in friction and wear was seen with the addition of 1% wt of Titanium Dioxide nanoparticles to vegetable oils. Using this addition, the friction coefficient of vegetable oils was comparable to that of a commercial engine oil. Anti-wear agent and friction modifier are all performed by Titanium Dioxide in vegetable oils.

In terms of wear-resistance and oxidative stability, the disadvantage of pure vegetable oils is determined to be greater compared to friction when all the data are considered. This effect was pronounced when combined with mineral oils, when their tribological performance predominated. However, using the commercial anti-wear Titanium Dioxide additive, the vegetable oils showed promise as an alternative lubricant for automobile engine systems, despite the fact that there is still considerable room for improvement.

CHAPTER 1

INTRODUCTION

1.1 Overview

Different sorts of lubricants are accessible all around the world, including mineral oils, manufactured oils, re-refined oils, and vegetable oils. Many of the lubricants which are accessible in the market depend on mineral oil got from petroleum oil which are not adaptable to the environment since, in such a case that its harmfulness and non-biodegradability. The unknown oil reserve and the expanding utilization, which made worry to utilize petroleum-based lubricants subsequently, to track down alternative lubricants to satisfy the future need is a significant issue.

Subsequently, vegetable oil can be assumed an important part to substitute the petroleum lubricant as it has various benefit over base oil like sustainability, harmless to the ecosystem, biodegradability, less poisonousness, etc. The vegetable oil-based lubricant is the best replacement for petroleum based synthetic lubricants. Vegetable oils are mainly triglycerides which contain three hydroxyl groups and long chain unsaturated free fatty acids attached at the hydroxyl group by ester linkages acids, favours triglycerides crystallization (Shahabuddin et al., 2013).

Since vegetable oils has poor low temperature behaviour, oxidation and thermal stability, a chemical modification is the best way to improve the thermo-oxidative stability of vegetable oil. There was a researcher who have found that the additives in lubricating oil play an important role in the reduction of the friction and wear behaviour of two mating surfaces. A few previous reports confirming that the effect of nanoparticle dispersed in lubricating oil showed a better friction reduction and wear resistance between two rubbing surfaces (Baskar et al., 2015). Furthermore, the addition of nanoparticles increases the viscosity of base lubricant.

However, only several research conducted on the effect of bio-lubricant and synthetic lubricant added nanoparticle (Masripan et al., 2020)(Singh et al.,2020). Therefore, this research has been conducted to study the comparison of bio-lubricant and synthetic lubricants tribological characters using Four-ball tester and pin-on-disc tester.

1.2 Project Background

The right lubricant composition can aid in lowering heat loss and friction. The mineral-based lubricant has been utilised in commerce for many years. People are now beginning to understand the damaging consequences that mineral-based lubricants have on the environment. Due to the harmful effects, many researchers are beginning to explore for alternatives to replace numerous petroleum-based products. Numerous studies are being done to improve the performance of bio-based lubricant so that it might take the place of mineral-based lubricant use (Mobarak et al., 2014)(Soltani et al., 2020). Bio-based lubricants with significant additives exceed petroleum-based lubricants in terms of efficiency. Vegetable oil-based bio-based lubricants, according to researchers, have great tribological qualities and are more environmentally friendly (Rajaganapathy et al., 2020). However, the main disadvantage of this oil is that pure vegetable-based lubricants have limited oxidative stability, which causes them to oxidise quickly as the temperature changes. To improve the oil's tribological properties, additives are added to the base oil.

It is a relatively new concept to use nanoparticles as lubricants and oil additives. These solid material-containing small-particle oil additives are difficult to employ and have only recently been acknowledged as practical. Since oil additives are less sensitive to temperature and have fewer tribo-chemical interactions than conventional additives, using them as nano-lubricants has various benefits.

Different anti-friction and anti-wear mechanisms using the nanoparticle additives have been explained in previous papers (Musial et al., 2020; Zulkifli et al., 2013). Studies using nanoparticles as oil lubricant additives have shown that they deposit on friction surfaces, improve the tribological characteristics of the base oil, and exhibit effective friction and wear reduction characteristics even at low concentrations. Due to their effective antioxidant properties, low toxicity, pleasant odour, and non-volatility, titanium dioxide (TiO₂) nanoparticles as a lubricant additive have received a lot of interest in research. The novel technique should be useful for the TiO₂ nanoparticles used as additives in engine oil, gear oil, and other industrial lubricants. It was first utilised to manufacture a lubricant containing TiO₂ nanoparticles. The tribological characteristics of TiO₂ nanoparticles in base oil as a lubricating addition were also investigated at the same time. Thus, utilising a four-ball tribometer and a pin-on-disc tribometer, the work discusses the friction-reducing and anti-wear behaviour of TiO₂ nanoparticle suspensions in base oil under mixed lubrication (Ilie & Covaliu, 2016).

1.3 Problem Statement

Lubricant is essential to give the machine a longer life span, to tolerate higher temperatures and pressures, and to improve energy efficiency. Mineral-based and synthetic-based lubricants have been widely used in the automotive and industrial sectors for many years, and consumers have come to trust their functionality and efficiency. Due to the ecological imbalance, bio-based lubricants have replaced mineral-based lubricants. So far, the qualities of bio-based lubricants have been positive. However, there is still more that can be done to improve the tribological behavior of bio-based lubricants, particularly in terms of anti-wear and friction-reducing agents. In this present work, supposedly bio-lubricant would give a better tribological

performance rather than synthetic lubricant and we are to suggest by adding a small amount of TiO_2 to all bio-lubricant so that it could improve the performance of current composites based on modern trend. Hence, the main objective is to investigate the tribological characteristics of modified bio-lubricants with additive of TiO_2 nanoparticles and making comparison to raw bio-lubricants and synthetic lubricant in the market.

1.4 Objectives

The objectives of this project are:

1. To investigate the tribological characteristics of addition TiO_2 as additive to bio lubricant
2. To compare the tribological behavior between natural and synthetic lubricants in terms of anti-wear and friction-reducing agents

1.5 Scope of Work

The scope of work is the activities and laboratory work that will be conducted to achieve objectives. The bio-lubricant used were red palm oil, coconut oil, sunflower oil and soybean oil. For the synthetic lubricant, motor engine oil was used. In experimental testing, Four Ball Tribo-machines and Pin-on-Disc Test will be used to evaluate the performance of bio and synthetic lubricant, then analyze by Scanning Electron Microscopy and Energy Dispersive Spectroscopy analysis. Material fabrication, preparation and properties verifications are also will be done by researching previous journals to verify the pour point and the flash point of the base vegetable oil. Furthermore, CNC machine will be used for pin fabrication.

1.6 Thesis Outline

Generally, this thesis will be organized into 5 chapters. Chapter 1 (Introduction) is mainly focused on overview of this chapter, background of this project, project objectives and scope of work. Chapter 2 (Literature Review) is discussing about related journal that had been published by various authors. Chapter 3 (Methodology) contains procedures and steps taken while carrying out of this project, from fabrication of the specimens prior to testing until final analysis out of the specimens. Furthermore, Chapter 4 (Result and Discussion) will be discussed about results obtained from wear tests and based micro graphical captured images from SEM laboratory and EDX analysis. The last chapter is Chapter 5 (Conclusion) which conclude the project research and recommend future can be carried out.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

2.2 Lubricant

Lubrication has been useful to humans since ancient times. It was claimed that ancient Egyptians began using liquid to cool their wheel carts and discovered that it also reduced friction. Modern lubrication is getting increasingly advanced as a result of the creation of automobiles and jet engines, both of which are considered severe and widespread applications.

2.2.1 Engine lubricant

There are four common types of engine oil, including synthetic oil, synthetic blends, high mileage oil, and traditional oil. Oil engineers, scientists, and chemists manufacture synthetic motor oil in a laboratory using precisely controlled ingredients. When paired with a high-performance additive package, this yields an oil with the maximum level of lubrication and engine protection, typically providing higher protection at start-up, better cleansing properties, enhanced longevity, and better protection against heat build-up (Shahidan bin Daud & Kameil bin Abdul Hamid, 2015).

With between 18 and 34 carbon atoms per molecule, the petroleum hydrocarbon used to make the majority of engine lubricants is heavier and thicker. There are several main categories of additives, including ashless dispersants, zinc dialkyldithiophosphates, calcium sulphonates, calcium phenates, oxidation inhibitors, and anti-wear inhibitors (Chandp & Kumarp, 2017). These lubricant additives may provide a serious health danger to people, especially to the respiratory system and the body's skin, which may itch and develop eczema. Lubricant additives can be persistent in the environment

and do not easily biodegrade. Advances in manufacturing are limiting the amount of harmful by products released into the environment.

2.2.2 Bio-lubricant

Bio-lubricant is defined as a lubricant made from renewable, non-toxic raw materials, such as vegetable and animal oils, that is also environmentally friendly and safe for people and other living things. From plant seeds, vegetable oil can be extracted for the manufacturing of bio-lubricant, including edible and non-edible varieties. Castor oil, karanja, neem, rice bran, rapeseed, linseed, mahua, palm oil, sunflower oil, coconut oil, soybean oil, olive oil, and canola oil are some of the vegetable oils that can be utilised as bio-lubricants (Annisa & Widayat, 2018).

Vegetable oils are a viable and suitable alternative resource because they are non-toxic, biodegradable, and favourable to the environment. Most bio-lubricants are made of esters. Vegetable oil triglycerides called natural esters exist. Vegetable oil triglycerides have a stronger affinity for metal because they are more polar than petroleum-based oil triglycerides. Vegetable oils generally have more lubricity than mineral oils, high viscosity index, high flash point and low evaporative losses. Bio-lubricant oils are great alternatives to mineral oils because they possess certain natural technical properties and biodegradable (Masripan et al., 2020).

However, plant-based vegetable oils have a volatile character. It is affected by the amount of free acid in vegetable oil. Therefore, the amount of fatty acids in vegetable oil should be known. The fatty acid profile of typical vegetable oils found in Malaysia is shown in Table 2.1 (Annisa & Widayat, 2018).

Table 2.1 Fatty Acids in Composition of Vegetables Oils

Vegetable oils	Palmitic (16:0)	Stearic (18:0)	Oleic (18:1)	Linoleic (18:2)	Linolenic (18:3)
Sunflower oil	6.1	5.3	21.4	66.4	-
High oleic sunflower	3.5	4.4	80.3	10.4	-
Safflower oil	6.4	2.5	17.9	73.2	-
High oleic safflower oil	6.7	2.2	77.5	13.2	-
High linoleic safflower oil	6.7	2.6	14.6	75.2	-
Soybean oil	6.0	5.2	20.2	63.7	5.0
High oleic soybean oil	6.2	3.0	83.6	3.7	1.7
Corn oil	10.6	2.0	26.7	59.8	0.9
Cottonseed oil	18.0	2.0	41.0	38.0	1.0
Rapeseed oil	3.5	0.9	19.4	22.3	8.2
Canola oil	2.5	1	64.4	22.2	8.2
Peanut oil	10	3	50	30	-
Linseed oil	5	3	22	17	52
Olive oil	14	2	64	16	2
Coconut oil	9	2	7	1	-
Palm oil	42	5	41	10	-

2.3 Properties of Bio-lubricant

Specification of lubricant properties of vegetable oils is important to understand the effect of each property to the application of lubricant such as in engines, rotary machines and others. As different applications have their own specific ambient such as operating temperature, pressure, speed of transverse or rotation motion, etc. Following about this matter, lubricant properties like viscosity, thermos-oxidative stability and tribological behaviour are discussed.

2.3.1 Viscosity

Viscosity is the most important consideration when selecting a lubricant for any given application. Viscosity is the measurement of a fluid's thickness under specific conditions. Due to increased intermolecular friction, a lubricant with a greater viscosity is more viscous and tacky. The viscosity of an oil is affected by its chemical structure, such as the length of its carbon chains and degree of unsaturation. A longer chain of hydrocarbons increases viscosity.

Table 2.2 Physicochemical properties of vegetable oils and their respective lubricants

Lubricant	Viscosity 40 °C (cSt)	Viscosity 100 °C (cSt)	Viscosity Index	Pour Point (°C)	Flash Point (°C)
Castor oil	220.6	19.72	220	-27	250
Castor/TMP	20.94	4.47	127	-	-
Jatropha oil	35.4	7.9	205	-6	186
Jatropha/TMP	43.9	8.71	180	-6	325
Palm oil	52.4	10.2	186	-5	-
Palm/TMP	47.9	9.0	176	-2	355
Olive oil	39.62	8.24	190	-3	318
Olive/PE	63.08	12.00	190	-24	-
Rapeseed oil	45.60	10.07	180	-12	252
Rapeseed/alcohols	7.8–38.2	2.7–8.4	205–224	-31.3 to -18	-
Soybean oil	28.86	7.55	246	-9	325
Soybean/alcohols	10.3–432.7	3.0–34.4	45–195	-	-
Sunflower oil	40.05	8.65	206	-12	252
Sunflower/octanol	7.93	2.74	226	-3	-

2.3.2 Thermo-Oxidative Stability

The thermo-oxidative stability of bio-lubricants is reduced by the presence of unsaturated bonds. Nonetheless, it is possible to achieve a suitable relationship between the behaviour of the bonds at low temperature and their thermo-oxidative stability by using bio-lubricants with outstanding characteristics and a vegetable oil (sunflower, canola, or soybean) content of at least 80 percent. By chemically altering vegetable oil by saturation of the $-C=C-$ link, thermo-oxidative stability can also be enhanced,

resulting in bio-lubricants that can be utilised as hydraulic lubricants, transmission fluids, and engine or compressor lubricants. The thermo-oxidative stability and viscosity index can be enhanced by first saturating $-C=C-$ bonds (through epoxidation) and then branching them. Therefore, the viscosity can be modified by altering the length of the alkyl chain (Cecilia et al., 2020).

2.4 Lubricant Additives

In today's industrial oils and automobile lubricants, a wide range of lubricant additives are utilised. Tribological improvers include friction modifiers, anti-wear additives, and extreme pressure additives, which modify the rubbing surface chemically. Considerable effort has been expended to comprehend the action mechanism of these chemicals. It was discovered that instrumental surface analyses are effective techniques. Lubricants are multicomponent solutions containing a number of additives. Occasionally, the interactions of components influence the characteristics of lubricants. Synergism and/or antagonism of additives are still unpredictable despite the extensive knowledge of lubricant formulation in international industries. Consequently, a scientific strategy is strongly desired.

2.4.1 Nanoparticles as Additives

Industrial businesses have recently created and increased lubricant performance by using nanoparticles. By lubricating with lubricant mixed with the proposed nanoparticles, the topographical and morphological properties of the surfaces of the mechanical parts in contact with each other were to be improved. Therefore, the dispersion of nanoparticles in a base grease has improved tribological properties, such as friction and anti-wear, and is regarded as an environmentally beneficial process (Ali et al., 2022).

One of the most efficient ways to lower friction and wear, eliminate energy loss, reduce emissions, and protect the environment is by adding Nano-additives to lubricants. bringing attention to the fact that, in comparison to non-nano common additives, nanoparticle additives considerably reduce friction between the lubricated surfaces (Ghaednia et al., 2015).

Table 2.3 Nano-additives in lubricants materials to ameliorate tribological properties of friction and wear

Lubricant (Base on)	Nanoparticles Additives	Nanoparticle Role (Betterment of tribology properties)	Morphology technique
Phenol/Formaldehyde Resin-based	Carbon Nanotube	Friction, anti-wear, surface hardness	TEM
Soybean Oil MQL grinding tests	MoS ₂ nanoparticles	(COF decreased by more than 20%) (anti-wear result around 30%)	TEM
Mineral oil	Graphene Oxide Nano sheets (GO)	Friction	SEM
Engine oil (SAE10W)	Nano Hexagonal Boron Nitride (hBN)	14.4% improvement COF 65% improvement wear	SEM
Liquid Paraffin	CuO nanoparticle	Friction, anti-wear (COF = 0.185 and 0.123)	-
Water-Based Lubricant	Titanium dioxide nanoparticles (TiO ₂)	Friction	TEM + SEM + AFM
Oil-based lubricants	Nano lamellar WS ₂ and MoS ₂ (Nano lamellar tungsten and molybdenum)	Friction, anti-wear (μ_{min} = 0.024 and 0.064)	(SEM), X-ray (XRD) and (DTA)
Vegetable Based Oil	Graphite Nanoparticles	deposition film + Friction, anti-wear	FE-SEM, EDS
Sodium oleate (SOA)	CuO nanoparticle	reducing friction	SEM, EDS
Mineral-based oils (CMRO)	Multi-Walled Carbon Nano-Tubes (MWCNT)	lowest frictional force + High dispersion	-
Water lubricated Rubber	CuO, WS ₂ and TiO ₂	Anti-wear	-
Water-based lubricant	MoS ₂ Nanoparticles	reducing friction noise.	SEM, X-ray
Engine oil	layered double hydroxide (LDH) Nano platelets	COF (83%), wear (43.2%)	XRD, TEM
Lithium grease	Al ₂ O ₃ and TiO ₂ nanomaterials	COF, anti-wear	-
Water-based fluid	nanometer-silicon dioxide	COF (26-39)% wear (7%)	XRD, SEM
Mineral oil (MO 4E)	SiO ₂ nanoparticles	Friction, anti-wear	XPS, TEM, SEM
aluminium composites	Nano-Lubricant, Al ₂ O ₃	Coefficient of Performance (COP) (25%)	-
lubricating oil	nanoscaled silicon carbide	Friction, anti-wear, tensile strength	SEM
diamond like carbon (DLC) coating	Cerium oxide (CeO ₂) Zirconium dioxide (ZrO ₂)	improve the tribological properties + promote the dispersion of WS ₂ + anti-friction and anti-wear	TEM, SEM, (WSD)
Castor oil	(CuO) and (MoS ₂)	Decreases wear (77%) & friction (32%)	FE-SEM, Ex-situ optical micrographs
canola oil	graphene sheets	Decreases Friction,	SEM
Mixture of R290/R600	TiO ₂ Nano Fluid	COF (81.7-76.03) % Anti-wear(93.17-92.23)%	-
coarse rapeseed oil	nanoparticles ZnO	coefficient of friction (COF) and wear + smooth surface	EDX, SEM
engine oils	Nanodiamond and Nano graphite	COP improve wear reduction of the friction losses.	TEM SEM -
diesel oil	ZnO and MoS ₂	the fuel consumption was reduced by 21% at zero load Improve the pure oil's thermophysical properties. Reduces mass loss of pins by 93%	TEM, SEM, XRD
paroline oil	nano-copper particle	improvement of the tribological performance+ (COF = 0.12)	TEM
Calcium grease	Titanium dioxide and carbon nanotubes TiO ₂ /CNTs	wear (72.3%), COF(60%) viscosity (74.2%) shear (48.2%)	XRD, SEM, TEM

2.4.2 Titanium Dioxide as Nanoparticles Additives

As an oxide of a transitional metal belonging to the dicalcogenide family, titanium dioxide (TiO₂) is a friction modifier like molybdenum disulphide (MoS₂) and tungsten disulphide (WS₂), which reduce friction and wear in both solid and fluid friction (Cristea et al., 2018).

Nano bio-lubricants were produced from palm and brassica oil with 0.5 percent TiO₂ nanoparticles on a weight basis, based on the findings of this journal. The viscosity of nano bio-lubricants increases with weight % and decreases with temperature increase. Under the conditions of an ASTM standard pin on disc tribometer

experiment, the addition of TiO₂ demonstrated superior anti-friction and anti-wear properties. The nanoparticles operate as a protective layer and produce a thin film between the contact region, which aids in reducing the wear rate in the contact area (Rajaganapathy et al., 2020).

2.5 Material Handling Preparation

In this section, various preparation methodologies are discussed based on previously read literatures related to mixing of lubricants with nanoparticle compound.

2.5.1 Method of Preparation for Four-Ball Experiment

Four-ball testing machines are commonly used to evaluate the tribological qualities of lubricating oils, such as their wear-preventive properties, severe pressure resistance, and shear stability. Under regular operating conditions, the device can be used to measure coefficient of friction, anti-wear, and load carrying ability of lubricating oils. This machine consists of four balls, three of which are clamped together at the bottom and one at the top. The test ball is pressed against the three balls at the bottom of a ball pot containing the lubricating oil being evaluated. The top ball is spun at the desired speed while the three balls beneath it are forced against it. In general, these devices consist of rubbing test specimens subjected to varied, measured stresses. The testing machines vary in terms of speeds, specimen geometry, load ranges, temperature ranges, and test materials. The lubricating oils are chosen based on many operational conditions, such as temperature rise, operating load, normal working temperature, and extreme situations, among others. With the use of an image acquisition equipment, the diameter of the wear scars for the tested oils. With the aid of Windu com 2014 software, image acquisition and magnification are perform (Manikandan et al., 2019).

2.5.2 Method of Preparation for Pin on Disc Experiment

The pin on disc test is used to determine friction and wear rates and the wear resistance of materials. This method is utilised because to its relative simplicity and abundance of tribological contacts that may be accurately described by a single pin-on-disk motion, including dry contacts of bolt screws, rail wheels-to-rail contact, and lubricated contacts of biological implants.

Typically, the test permits testing of multiple motion modes, including unidirectional, fretting, and other complicated motion patterns. Under the provided load, the stationary pin is forced against the rotating disc. The pin can be of any shape; however, the most common shapes are spherical (ball or lens) or cylindrical due to the simplicity of alignment of such pins (as opposed to flat pins, which are susceptible to misalignment, which can result in non-uniform loading and theoretical analysis challenges). Throughout the test, friction, wear, and temperature are continuously measured. After a predetermined number of cycles, the test is terminated, and further data processing processes typically consist of surface topography analysis to assess wear volume and surface roughness evolution.

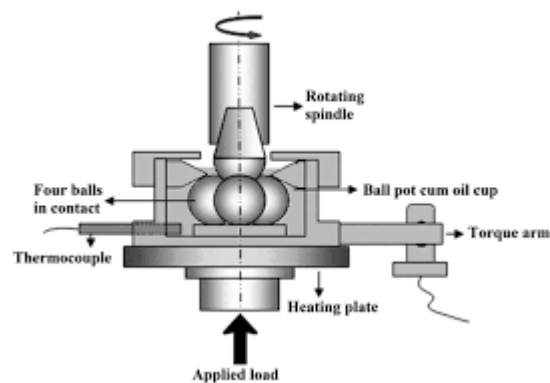


Figure 2.1 Schematic Diagram of Four-Ball Test (Baskar et al., 2015)

In this work, the tribometer comprised of a powered spindle and chuck for holding the rotating disc, a lever-arm device for holding the pin, and attachments for forcing the pin specimen against the rotating disc specimen with a regulated load. The disc's wear track was circular, and the tribometer included a friction force measurement mechanism for calculating the friction coefficient (Trivedi & Bhatt, 2017).

2.6 Summary

The literature review highlights the studies that shows the chemically modified vegetable oil with and without additives in general and specifically targeted for four-ball tribometer and pin-on-disc machine. Based on the findings, the attractive behaviour of nanoparticles such as friction and wear protection are much useful in lubrication purposes and suitable candidates as additives to improve tribological performance of a bio-lubricant.

Although there are many conventional base oils with nanoparticles that provide a solution to many problems associated with traditional lubricant that contain hazardous composition such as Sulphur and Phosphorus, a positive impact on environment can be achieved by implementing bio-based base stocks in lubrication composition with TiO₂ nanoparticles as additives. In previous discussion, vegetable oil promising characteristics as base stocks which will be replacing the conventional base oil that typically 80% of lubricant formulation. The research gap is the capability of vegetable oil as base stock as replacement for conventional base oil in typical lubricant with TiO₂ nanoparticles as additive formulation.

CHAPTER 3

METHODOLOGY

3.1 Overview

In this chapter, it contains three sections which are the first section is focused on specimens' preparations including pins and lubricants. The second section is wear test by using pin on disc tester and four ball tester. The third section is analysis after the experiment has been carried out. All experiment analysis is done using SEM imaging machine and energy dispersion x-ray machine.

3.2 Workflow Chart

In this project, specimens such as aluminium pins and synthesized vegetable oils with 1wt% of TiO₂, were prepared in workshop and laboratory, respectively as first part of the project. The parameters involved in Four-Ball wear and Pin-on-Disc experiments were done by following STM standards and Taguchi Orthogonal Array L9 Method (A L9). Upon completion of parameter settings, Four-Ball wear and Pin-on-Disc experiments were done in laboratory. The analysis of both experiments were done by using Scanning Electron Microscope machine, Four-Ball microscope machine and Scar-view software.

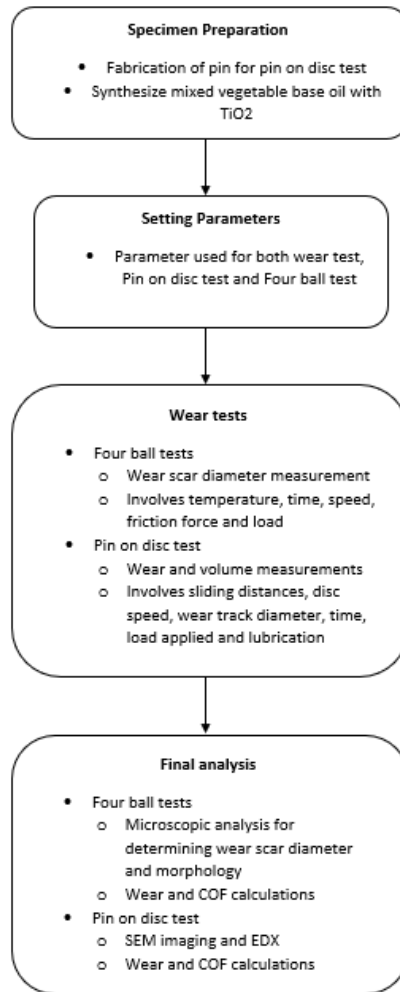


Figure 3.1 The process flow of project starting from sample preparation until final analysis of sample

3.3 Fabrication of pin for Pin on Disc Wear Test

The raw material of the pin is Aluminium. There are 54 pins that were fabricated from a two aluminium rods with diameter of 9 mm as shown in Figure 3.2. All pins are individually cut to 30 mm length by using CNC lathe machine as in Figure 3.3. Then, all pins are left with a notch for wear test.



Figure 3.2 Fabricated pins from aluminium rod



Figure 3.3 CNC machine for cutting the rod into pins

3.4 Lubrication Preparation

In this research project, there are five lubricants were tested in wear tests which are synthetic lubricant and vegetable oil base lubricant. Vegetable base oil will be paired with nanoparticle additive that is Titanium Dioxide (TiO_2).

3.4.1 Synthetic Lubricant

Synthetic lubricant SAE5W40 was used for wear tests. The synthetic lubricant was purchased at petrol station. Technical specification is listed in Appendices. This synthetic lubricant is used for automobile such as high-end cars.



Figure 3.4 Synthetic SAE5W40

3.4.2 Vegetable oils with TiO₂ Nanoparticles

Vegetable oils that were used as base oil are red palm oil, coconut oil, soybean oil and sunflower oil. Both of vegetable oil and nanoparticle, TiO₂, are obtained from online supplier and it is in powder form as in Figure 3.5. The process of synthesizing the bio-lubricant with TiO₂, nanoparticles were carried out by using one-step method. The one-step method is a step that directly combining both nanoparticle and base oil. Sonication and stirring were used to disperse the nanoparticle in the base oil.

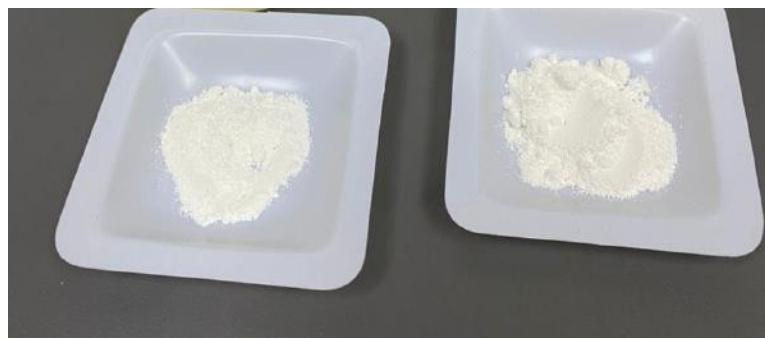


Figure 3.5 TiO_2 nanoparticles in powder form

In this research project, we used 1wt% concentration of TiO_2 , to bio-lubricant. First, 1.2 grams of TiO_2 , powder was weighted by using digital weight scale for 120ml of base oil. Second, the weighted powder is placed into a beaker followed by 118.8ml of base oil poured. Third, the beaker will undergo sonication process for about 30 minutes with interval of 10 minutes run and 5 minutes waiting time. This step was taken to ensure the physical characteristic of the base oil remain unchanged. Then, the mixed base oil with TiO_2 , is stirred by using magnetic stirring machine for 10 minutes. Figure 3.6 and Figure 3.7 are sonication process and stirring process for all selected vegetable oils.



Figure 3.6 Sonification process after combining red palm oil and TiO₂ powder



Figure 3.7 Stirring method after sonification process to disperse the nanoparticles evenly in mixed lubricant

3.5 Wear Test

In this section, wear tests are performed to analyse the performance of selected vegetable oil with nanoparticles and synthetic lubricant. The machines that will be used which are Four-ball machine and Pin-on-disc machine.

3.5.1 Four Ball Tribometer

The first wear test is conducted by using four-ball tribometer microscopic image acquisition. There are a total of four balls for each run of the selected lubricants. The balls are chromoly alloy steel AISI E52100, with diameter of 12.7 which is stated in ASTM D4172. The upper 1 ball will be in a rotating chuck while other three balls are held in place with specific torqued friction lever. The selected lubricants are poured after three balls are placed into the torqued friction lever. The upper ball is pressed on to the three balls with specific loads that are placed at the arm of the machine.



Figure 3.8 Four-ball tribometer machine

The parameters of the four-ball tribometer that can be manually adjusted are load, rotating speed, temperature of the lubricant and running time. All procedures and parameters of the experiment runs are according to standard ASTM D4172 and Taguchi OA L9. All lubricants with and without TiO₂ nanoparticles will be used in the experiment. The data from this experiment will be compared with the pin-on disc data to verify the trend of the data.

3.5.2 Pin-on-Disc Tribometer

In this research, the sliding wear tests were conducted by using friction and wear monitoring machine, DUCOM TR-20, such as stated in ASTM G99-95a. The cylindrical pin is dimensioned at 30 mm in length and 9 mm in diameter, tested against a disc that made of hardened ground steel. The pin is pressed on of the disc with the help of arm or lever and specific amount of load arm/lever. Figure 3.9 is Pin-on-Disc DUCOM TR-20 machine that is in School of Mechanical Engineering laboratory.



Figure 3.9 Pin on Disc machine

The parameters that can be adjusted and controlled are duration, rotation speed (rpm), load and wear track distance. All procedures and parameters that are used in this experiment are based on standard ASTM G99-95a and Taguchi OA L9. These tests will be conducted under lubrication condition at room temperature. The lubricants were dropped 0.5ml for every 5 minutes. All lubricants are tested with and without TiO₂ nanoparticles.

3.5.3 Weight and Volume Measurement

Wear results were reported as volume loss in cubic millimetres for the pin. The amount of wear was determined by weighing the pin specimen before and after the test. Then, the difference between initial and final weight was considered as weight loss as in **Equation 3.1**

$$\text{Weight loss, } \Delta m \text{ (g)} = \text{Initial weight} - \text{final weight} \quad (3.1)$$

Then, the material removal rate (wear rate) will be calculated by using,

$$\text{Material removal rate, } mrr = \frac{\text{weight loss}}{\text{sliding distance}} \quad (3.2)$$

3.6 Analysis of the experiment

After conducting all tests, the wear surfaces of the pin specimens are analysed by using SEM imaging machine. The SEM imaging machine uses electrons to indicate the morphology (texture) of the wear surfaces. It was done under three different of microscopic zoom which are 500,100,1.



Figure 3.10 SEM imaging machine with EDX analysis

As for four balls from four-ball tribometer wear tests, the wear scar diameter of the balls is measured by using the microscopic imaging acquisition. After each run, the lubricant is removed from the friction lever and the friction lever is placed under the microscopic imaging acquisition. With the help of the microscopic imaging acquisition software and a microscopic camera, we can manually locate the wear scar and measure its diameter.

Besides, EDX analysis also used in analyse the data which is to identify the elemental composition of sample. The abscissa of the EDX spectrum indicates the ionization energy and ordinate indicates the counts. Higher the counts of a particular element, higher will be its presence at that point or area of interest. For this project, EDX analysis is used to identify the percentage Titanium in vegetable base oil lubricants.