

FRICTION AND WEAR ANALYSIS OF PALM KERNEL METHYL ESTER
CONTAINING A POLYMERIC VISCOSITY INDEX IMPROVER

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DEDICATION

This thesis is dedicated to my beloved parent,
Norlidah binti Awang,
Dandan bin Abdullah,
Siblings,
And all my friends.

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“In the name of Allah the Most Compassionate, the Most Merciful”

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ABSTRACT

The search for renewable resources and the development of bio-lubricants as a substitute for mineral oils are being considered as a top priority in the fuel and energy fields. Bio-lubricants derived from vegetable oils are an attractive alternative to conventional petroleum-based lubricants due to their renewability, biodegradability, high lubricity and high flash point. Nevertheless, some types of vegetable oils have a few issues with regard to their low viscosity that limit their potential to be used as bio-lubricants in automotive applications. Thus, the present work featured a specific study on the application of ethylene-vinyl acetate (EVA) copolymer as a viscosity index improver (VII) additive inside vegetable oils. The lubrication performance of palm kernel methyl ester (PKME) with the added EVA copolymer was experimentally evaluated using a four-ball tribotester and modified pin-on-disc tester. Tests were performed with 2%, 3% and 4% concentrations of EVA copolymer at various loads, temperatures and sliding speeds. The results obtained were compared to the commercial mineral engine oil, SAE 40, for reference purposes. The present research revealed that the addition of 4% EVA copolymer managed to enhance the viscosity index of PKME by up to 61% of its original value. Based on the four-ball test, it was found that the PKME formulated with 4% EVA copolymer produced slightly better friction-reducing properties and smoother worn surfaces than SAE 40. Meanwhile, the results of the modified pin-on-disc test showed that the application of EVA copolymer successfully minimized the coefficient of friction (COF) of PKME and also enabled it to give a better performance than SAE 40. Thus, the reduction of frictional force by using this formulated bio-lubricant will contribute to the efficiency of internal combustion engine in the future. However, the anti-wear performance of PKME added with EVA copolymer is slightly lower than SAE 40. Therefore, further improvisation method should be taken in order to solve this issue. Finally, it is suggested that the EVA copolymer shows good potential as a VII for enhancing the tribological performance of vegetable oils.

ABSTRAK

Usaha untuk meneroka sumber yang boleh diperbaharui dan pembangunan minyak pelincir bio untuk menggantikan minyak mineral kini menjadi keutamaan dalam bidang tenaga dan bahan api. Minyak pelincir bio yang dihasilkan daripada minyak sayuran adalah alternatif yang menarik untuk menggantikan minyak pelincir konvensional berasaskan petroleum disebabkan oleh sifat boleh diperbaharuinya, boleh terbiodegradasi, dengan keupayaan pelinciran yang tinggi dan takat meledak yang tinggi. Walaubagaimanapun, beberapa jenis minyak sayuran mempunyai sedikit permasalahan dengan tahap kelikatan mereka yang rendah yang membataskan potensi mereka untuk diaplikasi dalam industri automotif. Kajian ini akan memaparkan analisis khusus aplikasi ethylene-vinyl acetate (EVA) kopolimer sebagai aditif penaik indeks kelikatan di dalam minyak sayuran. Prestasi pelinciran minyak isirong sawit metil ester (PKME) yang telah ditambah dengan EVA kopolimer telah dinilai menggunakan ujian empat-bola tribo dan ujian *pin-on-disc* yang telah dimodifikasi. Ujian telah dijalankan ke atas kepekatan EVA kopolimer 2%, 3% dan 4% pada beban, suhu dan halaju yang berbeza. Keputusan yang diperolehi telah dibandingkan dengan minyak enjin mineral komersial, SAE 40 untuk tujuan rujukan. Kajian ini menunjukkan bahawa penambahan sebanyak 4% EVA kopolimer berhasil untuk menaiktaraf indeks kelikatan minyak isirong sawit metil ester (PKME) sebanyak 61% daripada nilai asalnya. Berdasarkan ujian empat-bola tribo, dapat dilihat bahawa PKME yang diformulasikan dengan 4% EVA kopolimer menghasilkan sifat pengurangan-geseran yang rendah dan permukaan haus yang lebih licin daripada SAE 40. Sementara itu, keputusan daripada ujian *pin-on-disc* menunjukkan bahawa aplikasi EVA kopolimer telah berjaya meminimalkan nilai pekali geseran untuk PKME dan memberikan prestasi yang lebih baik dari SAE 40. Pengurangan daya geseran dengan penggunaan minyak pelincir bio ini akan menyumbang kepada tahap efisien enjin pembakaran dalaman di masa hadapan. Walaubagaimanapun, prestasi anti-haus untuk PKME diformulasikan dengan EVA kopolimer masih lagi rendah berbanding SAE 40. Oleh itu, usaha penambahbaikan lanjut seharusnya dijalankan untuk menyelesaikan isu ini. EVA kopolimer dicadangkan sebagai aditif penaik indeks kelikatan bagi tujuan peningkatan prestasi minyak sayuran.

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LIST OF ABBREVIATIONS

AISI	-	American Iron and Steel Institute
ASTM	-	American Society for Testing and Materials
AW	-	Anti-Wear
CO	-	Castor Oil
COF	-	Coefficient of Friction
EC	-	Ethyl Cellulose
EHD	-	Elastohydrodynamic
EP	-	Extreme Pressure
EVA	-	Ethylene-Vinyl Acetate
FAME	-	Fatty Acid Methyl Ester
FFA	-	Free Fatty Acid
FFB	-	Fresh Fruit Brunch
FFL	-	Fully Formulated Lubricant
FTIR	-	Fourier Transform Infrared Spectroscopy
HFRR	-	High Frequency Reciprocating Test Rig
HOSO	-	High Oleic Sunflower Oil
ISL	-	Initial Seizure Load
LNSL	-	Last Non-Seizure Load
NMR	-	Nuclear Magnetic Resonance Spectroscopy
OFR	-	Oscillatory Flow Reactor
PFAD	-	Palm Fatty Acid Distillate
PK	-	Palm Kernel
PKME	-	Palm Kernel Methyl Ester
PO	-	Paraffin Oil
POME	-	Palm Oil Methyl Ester
PMA	-	Poly (alkyl) methacrylate
PME	-	Palm Methyl Ester
PS	-	Palm Stearin
RBD	-	Refined, bleached and deodorised
SAE	-	Society of Automotive Engineers
SBS	-	Styrene-Butadiene-Styrene

SO	-	Sunflower Oil
SYO	-	Soybean Oil
TMP	-	Tri-methylolpropane
VI	-	Viscosity Index
VII	-	Viscosity Index Improver
WL	-	Weld Load
WSD	-	Wear Scar Diameter
ZDDP	-	Zinc-dialkyldithiophosphates

LIST OF SYMBOLS

μ	-	Coefficient of Friction
D_h	-	Hertz diameter of the contact area
F	-	Force
g	-	Gravity = 9.81 m/s
h	-	Fluid film thickness
H	-	Kinematic viscosity at 40°C of an oil of 100 viscosity index having the same kinematic viscosity at 100°C as the oil whose viscosity index is to be calculated mm ² /s (cSt).
N	-	Applied Normal Load
P	-	Static Applied Load
Ra	-	Surface Roughness
Rv	-	Deep Valley
U	-	Kinematic viscosity at 40°C of the oil whose viscosity index is to be calculated mm ² /s (cSt).
VI	-	Viscosity Index
Y	-	kinematic viscosity at 100°C of the oil whose kinematic viscosity is to be calculated, mm ² /s (cSt).
Yi	-	Profile Deviation

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CHAPTER 1

INTRODUCTION

1.1 Background of study

In recent years, energy conservation has become a very important issue that requires attention. The loss of energy in any mechanical system is mainly due to friction, which causes the system to be less effective and consumes costs for maintenance at short intervals. This problem can be reduced by the use of a proper lubrication process. However, the most common source of lubricants is petroleum-based oil because of its well-known properties and performance. In fact, about 38 million metric tons of lubricants have been used globally in the last decade, with the majority of these being from petroleum-based lubricants (Syahir et al., 2017). This situation poses a constant threat to the environment due to the inherent toxicity and non-biodegradable nature of petroleum-based oils.

In response to this issue, there is mounting pressure to reduce or eliminate the usage of petroleum-based oils as they pollute the environment and cause health problems in industrial workers. Recently, there has been an increasing interest to develop vegetable oils as an alternative lubricant with environmental-friendly characteristics. The main reasons why vegetable oils are being considered as a new type of bio-lubricant resource are their biodegradability, generally lower toxicity and renewability. Thus, they can be used in a sensitive environment and are able to prevent pollution because of their environmental benefits. In addition, they also have good lubricity, a high flash point, lower volatility and good skin compatibility (Mobarak et al., 2014).

Vegetable oil, especially palm oil, is one of the good candidates that can be developed to replace petroleum-based oil as a new type of bio-lubricant oil. As is known, the automotive industry is a major consumer of lubricants. Bio-lubricants with

a low pour point are in demand because they can perform well even at low temperatures and provide excellent lubrication during cold starts (De Carvalho et al., 2010). Thus, systematic researches and studies have to be carried out in order to develop bio-lubricants that can fulfil automotive standards of performance for lubricants.

The aim of this study was to solve the current issues concerning palm kernel oil, including stability at low temperatures and low viscosity characteristic. Thus, a chemical modification technique was selected to derive a bio-lubricant with a lower pour point by using an established experimental setup. Meanwhile, a major part of this research was focused on discussing about the application of ethylene-vinyl acetate (EVA) copolymer as a viscosity index improver (VII) additive inside palm kernel oil. In general, VII have been used in lubricant industry to increase the kinematic viscosity and viscosity index of the base lubricant oils. The improvement in their kinematic viscosity and viscosity index of the lubricant oil up to an optimum level will generate a sufficiently thick film for reducing friction and wear. EVA copolymer was selected for use in this study because it has been proven from a previous research that this substance is able to increase the viscosity of vegetable oil (Quinchia et al., 2010; Quinchia et al., 2014). Next, the tribological performance of this formulated bio-lubricant was evaluated using a four-ball tribotester and modified pin-on-disc tester.

1.2 Problem Statement

Nowadays, many industries are experiencing significant growth worldwide, and this will lead to a continuous increase in the demand for petroleum-based lubricants in the future (Nagendramma and Kaul, 2012). This phenomenon will have a negative impact on the environment because petroleum-based lubricants are non-biodegradable and toxic.

Palm oil is the most widely consumed vegetable oil on the planet due to its versatility, where it can be used for both food and non-food products. It can be processed into many products such as cosmetics, shampoo and laundry detergent. Palm

olein is widely used in the food industry as a cooking oil. However, it has been reported that there is still an excess supply of palm oil in the form of palm kernel and palm stearin because it has yet to be utilized to its full potential (Jayadas et al., 2007). The bright future of palm oil will not be disturbed as the latest food-producing industries are using various palm oil products.

Several other palm oil products for non-food applications include palm kernel (PK), palm stearin (PS) and palm fatty acid distillate (PFAD). All of them usually exist in solid form below room temperature due to their high pour point. Thus, direct applications of these types of palm oil will not be possible due to the fluidity issue for the lubrication of important parts. The issue of the high pour points of PK, PS and PFAD can be solved using the available chemical modification techniques, especially transesterification. The aim of transesterification is to convert the free fatty acid content of palm oil together with alcohol to produce fatty acid ester and glycerol (McNutt, 2016).

Recently, transesterification process of vegetable oil was carried out in order to derive methyl ester for the production of bio-diesel. The transesterification of methyl ester will reduce the pour point by removing the free fatty acid from the oil content and breaking the crystalline structure. Besides, bio-diesel resulted from this process will have low viscosity characteristics and helps to solve the clogging issue inside fuel injectors of diesel engines (Ali et al., 2016).

However, low viscosity characteristic of methyl ester is not desirable in the automotive lubricant industry because it is unsuitable to be used directly as an engine oil (Zulkifli et al., 2014). Usually, the minimum value for the viscosity of commercialized mineral engine oil is around 20 cSt under 100 °C. However, the value of viscosity for the vegetable oil which facing this problem is much lower than that. Low viscosity issue will makes it difficult for the methyl ester to generate a sufficiently thick film to protect the cylinder liner surfaces and lead to severe wear. The addition of viscosity index improver (VII) is among the common applied method to overcome this issue. This substance will increase the viscosity of the lubricant and should be able to resist the thinning effects due to the increment of temperature. Recently, EVA copolymer are being tested as VII inside several types of vegetable oil by the previous

researchers. Based on the finding, this kind of polymer able to enhance the viscosity of vegetable oils significantly and can contribute to the friction-reducing properties as well. In this study, EVA copolymer was tested as VII inside palm kernel methyl ester in order to prepare a bio-lubricant which possess good viscosity characteristics and decent lubricity performances.

1.3 Objectives of Study

The objectives of this study are as follows:

- i. To study the effects of polymeric viscosity index improver (VII) additive, ethylene-vinyl acetate copolymer on the viscosity index increment of palm kernel methyl ester.
- ii. To establish the tribological performance of palm kernel methyl ester formulated with different percentages of VII additive using the four-ball tribotester under normal loading and extreme pressure condition.
- iii. To analyse the lubricity of the lubricant samples in terms of coefficient of friction, surface roughness and wear condition of the piston ring using a modified pin-on-disc tribotester.

1.4 Scope and Limitations of Study

The scope and limitations of this study are as follows:

- i. Refined, bleached and deodorised (RBD) palm kernel oil was chosen in this study due to its availability and cost.
- ii. Ethylene-vinyl acetate copolymer with 25% of vinyl acetate content was used as the VII additive inside the palm kernel methyl ester at various concentrations of 2%, 3% and 4% of weight percent.
- iii. Commercial mineral engine oil (SAE40) was used as the reference lubricant for comparison purposes.

- iv. The four-ball test was conducted according to ASTM D4172 with different sets of temperatures including 0 °C, 30 °C, 75 °C and 90 °C. Then, an extreme
- v. The modified version of the pin-on-disc test was conducted according to ASTM G99 using a real piston ring and curve rotating disc. The applied loads were varied at 1 kg, 3 kg and 5 kg under a constant sliding speed of 1.5 ms⁻¹. Subsequently, the sliding speeds were varied at 1.5 ms⁻¹, 2 ms⁻¹ and 2.5 ms⁻¹ under a constant applied load of 1 kg.

1.5 Significance of the Study

The development of palm oil as a new source of bio-lubricant is one of the most significant contributions of this research. As is known, the volume of palm oil production in Malaysia is one of the highest among the producing countries. It surely makes a huge contribution to the Malaysian economy in terms of annual exports. By considering the great potential of palm oil, Malaysia should take this opportunity to be a market leader in the bio-lubricant industry. Besides, Malaysia has to show its commitment and play an active role in utilising palm oil as a source of renewable energy in order to reduce greenhouse gas emission and ultimately, global warming.

However, before palm oil can be commercialized as a bio-lubricant, systematic researches and development procedures have to be executed in order to determine the actual lubricity behaviour of this vegetable oil in order to improve its performance. Thus, the findings of this study may contribute to the development of palm oil to be used extensively in many engineering applications, especially in the automotive industry. This new type of bio-lubricant is believed to be not only environmentally friendly, but is also expected to be cost-effective as it is available in abundance in Malaysia.

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APPENDIX B

List of Publications

Journal with Impact Factor

1. **Dandan, M. A.**, & Samion, S. (2019). Tribological Analysis of Palm Kernel Methyl Ester Containing Polymeric Viscosity Improver. *Green Materials*, 1-9. <https://doi.org/10.1680/jgrma.18.00067>. (Q3, IF:1.344)
2. **Dandan, M. A.**, Samion, S., Azman, N. F., Zawawi, F. M., Hamid, M. K. A., & Musa, M. N. (2019). Performance of polymeric viscosity improver as bio-lubricant additives. *International Journal of Structural Integrity* (Q3,ISI)..

Indexed Journal

1. **Dandan, M. A.**, Aiman Wan Yahaya, W. M., Samion, S., & Musa, M. N. (2018). A comprehensive review on palm oil and the challenges using vegetable oil as lubricant base-stock. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences*, 52(2), 182-197. (Indexed by SCOPUS)
2. **Dandan, M. A.**, Yahaya, W. M. A. W., & Samion, S. (2018). The effect of fluidity of palm kernel oil with pour point depressant on coefficient of friction using fourball tribotester. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences*, 50(2), 97-107. (Indexed by SCOPUS).
3. The Effect of the Different Percentage of Pour Point Depressant (PPD) On the Tribological Properties of Palm Kernel Oil. *Tribology in Industry* (Indexed by SCOPUS).